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Structural Studies of Coordination Compounds. A Joint NQR and X-Ray Investigation of Trialkylphosphine–Gallium Trichloride Adducts

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The temperature dependence of the ^{35}Cl NQR spectra of trimethyl- and triethylphosphine–gallium trichloride adducts and the crystal structure of the trimethyl compound at 297 and 223 K are reported. The NQR data, which indicate that the phosphines are very good donors toward $GaCl_3$, are interpreted by means of the Townes and Daily treatment, and a simple vibrational analysis by computer curve fitting is described. The tendency toward equivalence of the three chlorines in the vicinity of 420 K is tentatively explained by conformational changes and the onset of hindered molecular rotation. The crystal structure of $(CH_3)_3P\cdot GaCl_3$ shows that the space group is $P2_1/m$ with $a = 7.630$ (7) Å, $b = 10.465$ (9) Å, $c = 6.510$ (9) Å, $\beta = 113.86$ (9)° at 297 K, and $Z = 2$. The structure is solved by standard methods based on two sets of reflections collected at 297 and 223 K with final agreement indexes of 6.3 and 3.8%. An unusual feature is that the molecules adopt an eclipsed rather than staggered conformation. Comparison of the unit cell parameters with those of analogous compounds reveals an unusually short *b* axis and small cell volume resulting from the rearrangement to a more compact structure. It is proposed that, within the series considered, molecular size influences the conformation adopted and hence the possibility of an energetically favorable contraction; a critical *b*-axis length is postulated above which rearrangement is possible.

Introduction

While conducting a systematic investigation of addition compounds of the type $R_nD\cdot ACl_3$, with R = CH_3 or C_2H_5, D = O, S, N, P, or As, and A = B, Al, or Ga, we have generally observed different line multiplicities for the ^{35}Cl nuclear quadrupole resonance spectra of the ethyl and methyl compounds.[1] Three signals of equal intensity are normally found for the ethyl adducts while the spectra of the methyl complexes usually consist of two lines, having intensities corresponding to a 2:1 ratio of inequivalent chlorine sites, which strongly indicates that a molecular plane of symmetry is a feature common to the structures of the latter compounds.

Previous x-ray diffraction studies of members of the series have been confined to the trimethylamine and trimethylphosphine adducts of boron trichloride[2,3] and trimethylamine–aluminium trichloride.[4] No crystal structure of a gallium analogue has been reported although gas-phase electron diffraction measurements on related compounds are known.[5] Broad-line NMR and NQR variable temperature data for trimethylamine boron trichloride have been explained by Gilson and Hart in terms of hindered molecular rotation.[6] Apparently this is in conflict with the published x-ray structure,[2] in which the atomic positions are well defined; however, the difficulty may possibly be resolved if the difference in time scale of the experiments is considered and a suitable rotational transition rate postulated.

For these reasons we decided that a joint study of other compounds in the series, by NQR and x-ray diffraction at several temperatures, would be of interest. Since, to our knowledge, no other crystal structure of a coordination compound involving the gallium–phosphorus bond has been reported, trimethylphosphine–gallium trichloride was chosen to be the subject of this investigation.

Experimental Section

Preparation of Samples. The trialkylphosphines were obtained by the action of phosphorus tribromide on the appropriate Grignard reagent.[7] Both adducts were prepared by the dropwise addition of a slight excess of the ligand, dissolved in dichloromethane, to a well-agitated solution containing 10 g of commercial (99.99%) gallium trichloride in the same solvent at 250 K under a strictly controlled dry argon atmosphere in a general purpose vacuum-line apparatus. After returning to ambient temperature overnight, the reaction mixture was filtered by means of a glass sinter, integral to the apparatus, and all volatile material was removed by vacuum. The triethyl adduct, which is moderately soluble in dichloromethane, was purified by recrystallization at room temperature with a gentle current of dry argon providing controlled evaporation of the solvent; this method has proved successful in producing samples of compounds, sensitive to atmospheric reagents, with the high bulk crystallinity desirable for NQR spectroscopy. No satisfactory solvent for trimethylphosphine–gallium trichloride was found but the initial reaction product was of sufficient crystallinity to permit the NQR determinations to be made without further treatment. A small quantity of this material

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was sealed, under argon at a pressure of 5.10^{-3} Torr, in a Pyrex glass tube. Specimens for the x-ray measurements were obtained by sublimation of this sample at 470 K.

NQR samples were prepared by sealing approximately 10 g of each product in 20-mm diameter Pyrex ampules.

NQR Spectroscopy. All spectra were recorded with sideband suppression, using Zeeman modulation, on a Decca NQR spectrometer (7–90 MHz) for which special coils were made to accommodate the 20-mm diameter samples. A field effect transistor circuit[8] was used to provide increased recording time constants and filter slope[9] resulting in a valuable improvement in signal to noise ratio for the detection of relatively weak resonances. The initial, absolute calibration of the spectrometer marker system was performed with a Schlumberger FB 2603 frequency counter. Most of the measurements were carried out with the spectrometer probe immersed in constant temperature slush baths which were prepared by mixing pure organic solvents (isopentane, ether, chloroform, carbon tetrachloride, chlorobenzene, ...) with liquid nitrogen. The remaining data were obtained dynamically in the manner described by Smith and Tong.[10] Sample temperatures below 300 K were measured with a copper–constantan thermocouple and a Comark 1623 electronic thermometer using an external ice point reference; all temperatures are estimated to be accurate to ±1 K.

X-Ray Structure Determination and Refinement. A colorless single crystal of $(CH_3)_3P{\cdot}GaCl_3$ measuring approximately 0.19 × 0.41 × 0.06 mm was introduced, under a dry nitrogen atmosphere, into a Lindemann capillary tube which was then flame sealed. The preliminary x-ray study was conducted by photographic methods using a STOE "Reciprocal Lattice Explorer" camera and Zr-filtered Mo Kα radiation. The unit cell parameters were derived from three sets of photographic data. Systematic absences of $0k0$ were noted for odd k, indicating either the centrosymmetric space group $P2_1/m$ or the noncentrosymmetric group $P2_1$.

The specimen was then mounted on a CAD4 Enraf-Nonius PDP8/M computer-controlled single-crystal diffractometer and the unit cell parameters were refined by optimizing the settings for 25 reflections. The density of 1.75 (2) g cm^{-3}, determined by flotation, is in good agreement with the value calculated for two formula units in a unit cell volume of 475.4 (1.5) Å^3 at 297 K. The intensities of selected reflections ($I > 3\sigma(I)$) were corrected for Lorentz and polarization factors and absorption corrections were applied. Atomic scattering factors of Cromer and Waber[11] for the nonhydrogen atoms and those of Stewart, Davidson, and Simpson[12] for spherical hydrogen atoms were used. Real and imaginary dispersion corrections given by Cromer were used for gallium and phosphorus.[13]

The structure was resolved for two sets of data, first at 297 K and then at 223 K in order to facilitate the location of the hydrogen atoms. Variations in the unit cell parameters with temperature were followed by automatically refining the settings for the 25 chosen reflections.

The centric space group $P2_1/m$ was assumed on the basis of the following facts: (a) The structures of similar molecular compounds[2,3] belong to this space group. (b) The NQR results indicate that two of the chlorines are equivalent. This implies that they are related by a mirror plane which passes through the gallium and phosphorus atoms, one of the carbons, and the remaining chlorine. This space group is confirmed by the successful structure determination at two temperatures.

A three-dimensional Patterson function yielded the positions of the phosphorus, gallium, and chlorine atoms; the carbons were located by successive refinements and Fourier synthesis. The structure refinements were done using full-matrix least-squares techniques. Difference Fourier maps for the 223 K data enabled the positions of the hydrogen atoms to be determined. All nonhydrogen atoms were then allowed to refine with anisotropic thermal parameters and a fixed, isotropic thermal parameter of $B_H = B_{eqC} + 1$ Å^2 was assigned to the hydrogen atoms (B_{eqC} is the isotropic equivalent temperature factor of the carbon to which the hydrogen is bonded; $B_{eq} = {}^4/_3\sum_{i,j}(\vec{\mathbf{a}}_i{\cdot}\vec{\mathbf{a}}_j)\beta_{ij}$). A difference Fourier map (223 K data set) then showed no peaks greater than 0.4 e Å^{-3}. In addition to local programs, the following ones were used on the CICT CII IRIS 80 system: Zalkin's FOURIER, Ibers and Doedens's NUCLS, Busing, Martin, and Levy's ORFFE, and Johnson's ORTEP.

Results

Temperature Dependence of NQR Lines. The ^{35}Cl resonance frequencies are given at three standard temperatures in Table I while a graphical presentation of the complete experimental data is provided in Figures 1 and 2.

Table I. ^{35}Cl NQR Frequencies for Trimethylphosphine–Gallium Trichloride and Triethylphosphine–Gallium Trichloride at Various Temperatures[a, b]

Compound	77 K		195 K	273 K
$(CH_3)_3P{\cdot}GaCl_3$	16.10 [9]	16.15[c]	15.97 [11]	15.85 [11]
	16.25 [5]		16.07 [7]	15.92 [7]
$(C_2H_5)_3P{\cdot}GaCl_3$	15.82 [10]	16.11[c]	15.75 [7]	15.60 {7}
	16.19 [10]		16.04 [6]	15.87 {6}
	16.32 [7]		16.17 [7]	15.98 {8}

[a] Frequencies are given in MHz and are estimated to be within ±5 kHz. The corresponding ^{37}Cl frequencies were found to be in good agreement with the ratio of quadrupole moments $Q_{35}/Q_{37} = 1.2688$. [b] Values in brackets are peak to peak signal to peak to peak noise ratios obtained with a 10-s recording time constant while those in braces were measured with 10- and 18-s time constants in series. [c] Weighted mean.

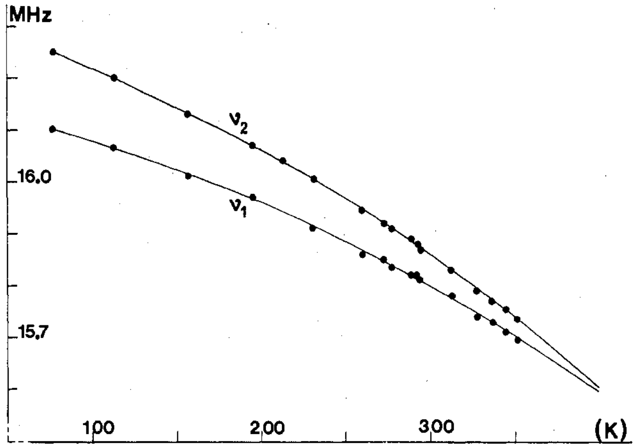

Figure 1. Temperature dependence of the ^{35}Cl NQR frequencies for $(CH_3)_3P{\cdot}GaCl_3$.

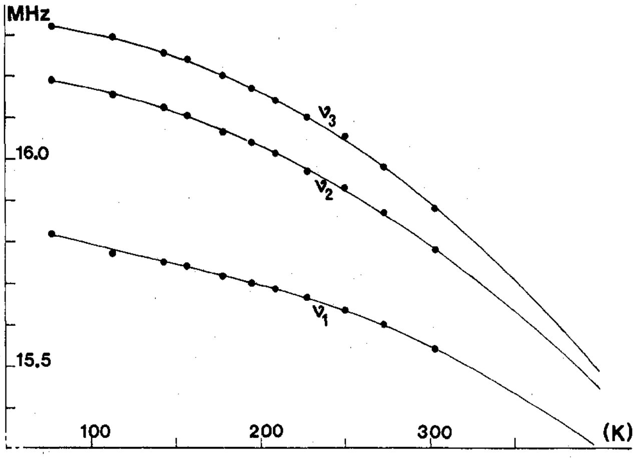

Figure 2. Temperature dependence of the ^{35}Cl NQR frequencies for $(C_2H_5)_3P{\cdot}GaCl_3$.

Following the example of Pies and Weiss,[14] least-squares fitting of the results to a number of functions, $\nu = f(T)$, was attempted. The polynomial expressions

$$\nu(T) = a_0 + a_1T + a_{-1}/T \tag{1}$$

and

$$\nu(T) = a_0 + a_1T + a_{-1}/T + a_2T^2 \tag{2}$$

were analyzed on a Hewlett-Packard Model 9821A programmable calculator while a nonlinear regression library

Table II. Parameters Obtained from Least-Squares Analyses of the Experimental NQR Frequency vs. Temperature Data

Compound	Line	N	Eq	a_0, MHz	a_1,[a] MHz K^{-1}	a_{-1}, MHz K	a_2, MHz K^{-2}	b,[b] MHz	c, K	σ_M, kHz
$(CH_3)_3P \cdot GaCl_3$	ν_2	17	1	16.578	-2.27×10^{-3}	−12.46				7.55
			2	16.256	-4.78×10^{-4}	+3.73	-2.94×10^{-6}			2.40
			3	16.251				8.07×10^{-1}	334.2	6.27
			4	16.348	$\alpha = 5.76 \times 10^{-4}$			$p = 4.85 \times 10^{-3}$	$q = 71.8$	3.57
	ν_1	16	1	16.375	-1.81×10^{-3}	−10.96				7.53
			2	16.113	-3.44×10^{-4}	+2.23	-2.47×10^{-6}			4.46
			3	16.099				7.14×10^{-1}	363.3	6.49
			4	16.179	$\alpha = 5.97 \times 10^{-4}$			$p = 4.71 \times 10^{-3}$	$q = 89.9$	3.75
$(C_2H_5)_3P \cdot GaCl_3$	ν_3	11	1	16.840	-2.83×10^{-3}	−23.90				12.06
			2	16.262	$+8.07 \times 10^{-4}$	+2.94	-6.89×10^{-6}			4.25
			3	16.315				1.98	525.3	7.40
			4	16.455	$\alpha = 1.11 \times 10^{-3}$			$p = 1.38 \times 10^{-2}$	$q = 281.1$	3.58
	ν_2	11	1	16.621	-2.51×10^{-3}	−18.90				9.46
			2	16.172	$+3.14 \times 10^{-4}$	+1.93	-5.35×10^{-6}			3.58
			3	16.186				1.42	461.5	6.21
			4	16.315	$\alpha = 9.62 \times 10^{-4}$			$p = 1.27 \times 10^{-2}$	$q = 241.5$	3.36
	ν_1	11	1	15.996	-1.38×10^{-3}	−5.98				9.68
			2	15.515	$+1.65 \times 10^{-3}$	+16.33	-5.73×10^{-6}			2.37
			3	15.817				4.78×10^{-1}	314.0	9.06
			4	15.870	$\alpha = 8.02 \times 10^{-4}$			$p = 4.34 \times 10^{-3}$	$q = 113.4$	6.40

[a] The units of α are K^{-1}. [b] The parameter p is a dimensionless quantity.

Table III. Quantities Derived from Least-Squares Fitting of the ^{35}Cl NQR Data to Equation 4

Compound	Line	NQR freq at 0 K, MHz	Eff moment of inertia, A, kg m^2	Optimum lib freq (0 K),[a] cm^{-1}
$(CH_3)_3P \cdot GaCl_3$	ν_2	16.301	3.47×10^{-45}	49.9
	ν_1	16.141	2.86×10^{-45}	62.4
$(C_2H_5)_3P \cdot GaCl_3$	ν_3	16.341	3.12×10^{-46}	195.2
	ν_2	16.211	3.93×10^{-46}	167.7
	ν_1	15.835	2.45×10^{-45}	78.8

[a] Optimum single librational frequency at absolute zero expressed as a wavenumber.

program BMDP3R[15] was used, on the CIRCE IBM 370/168 system at Orsay, France, for the following equations:

$$\nu(T) = \nu_0 - b/(\exp(c/T) - 1) \tag{3}$$

and

$$\nu(T) = \nu_0[1 - (p/(1 - \alpha T))(0.5 + 1/(\exp(q(1 - \alpha T)/T) - 1))] \tag{4}$$

where $\nu(T)$ is the nuclear quadrupole resonance frequency and T the absolute temperature; the remaining quantities are parameters to be optimized. Equations 1 and 3 are the simplest expressions which may be derived from the Bayer theory[16,17] and represent a constant-volume situation. An approximate but direct approach to the problem of transformation to the constant-pressure case is to consider the temperature variation of the lattice vibrational modes, ω_i, resulting from thermal expansion of the sample.[6,18,19] It is customary to assume a linear relationship between the lattice frequencies and temperature. This may be formulated as

$$\omega_i(T) = \omega_i(0)(1 - \alpha T) \tag{5}$$

Equation 4 may be derived by substitution of this expression into the normal Bayer equation, whence for a single vibrational mode

$$p = 3h/8\pi^2 A\omega(0) \tag{6}$$

and

$$q = h\omega(0)/k \tag{7}$$

where h is Planck's constant, k Boltzmann's constant, and A represents an effective moment of inertia. With this simplified treatment it is therefore possible to estimate the parameters α, A, $\omega(0)$, and the quadrupole resonance frequencies in a rigid lattice, ν_0, and at absolute zero, $\nu_0(1 - p/2)$, by means of a least-squares fit of the experimental data to eq 4.

The results for eq 1–4 are collected in Tables II and III. All attempts to extend the analysis to more than one vibrational mode failed; too many parameters are needed for successful convergence with the available data. The treatment given here is probably the best which can be carried out on the existing data set without making assumptions concerning the nature of the lattice modes and introducing values for the associated moments of inertia into the calculation.[20]

In order to deduce with confidence all the parameters by means of a curve-fitting process in which two librational motions are considered, it would be necessary to extend the range of measurements, ideally to 4 K, since it is in the low–temperature region that the quadrupole resonance frequency is most dependent on low-frequency lattice modes.[19]

Returning to Figures 1 and 2, a marked convergence of the resonance lines as temperature is increased is evident for both compounds; in the case of $(CH_3)_3P \cdot GaCl_3$ extrapolation of the curves gives an intersection or coalescence temperature in the region of 420 K. An interesting difference between the two sets of curves is to be seen if the variations in gradient with temperature are considered. Much larger changes occur for the triethyl adduct (a factor of 3:1 between 100 and 300 K) and it would appear that there are significant differences in the parameters contributing to the NQR temperature dependence for these two compounds.

Crystallographic Data and Description of the Structure. The refined unit cell parameters are given in Table IV which also includes details of the experimental conditions. Final atomic coordinates and anisotropic temperature factors appear in Table V while the interatomic distances and angles are listed in Table VI. Variations of the crystallographic parameters with temperature are plotted in Figure 3, and a projection of the unit cell onto the 100 plane is shown in Figure 4. The structure confirms both the existence of a P–Ga dative bond and the slight departure, expected on the basis of the NQR data, of the molecular unit from strict threefold symmetry. The gallium–phosphorus bond length of 2.353 (2) Å lies between the sum of the single bond covalent atomic radii (2.30

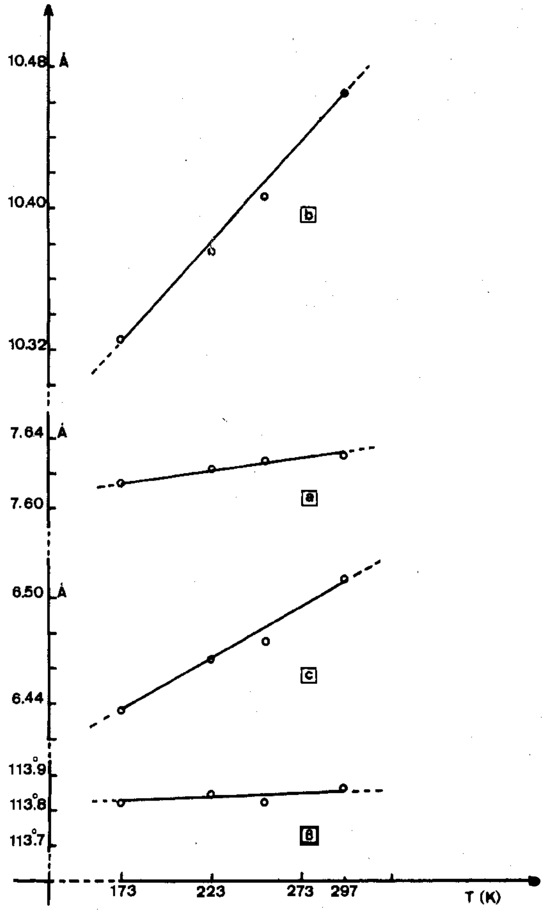

Figure 3. Temperature variation of the unit cell parameters for $(CH_3)_3P{\cdot}GaCl_3$.

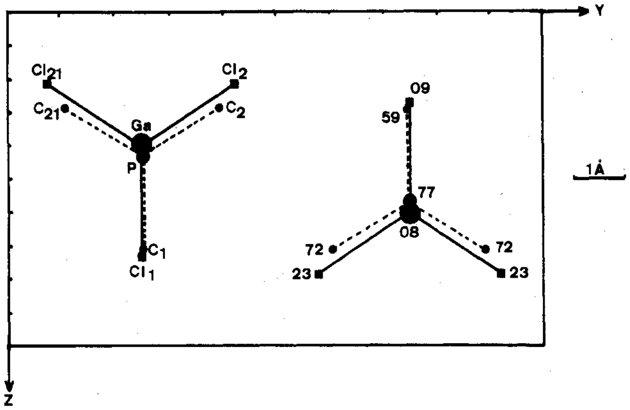

Figure 4. Projection onto (100) illustrating the packing of $(CH_3)_3P{\cdot}GaCl_3$ molecules along the *a* axis.

Å) and the values cited by Golubinskaya et al. (2.492 Å estimated and 2.52 Å found by gas-phase electron diffraction).[21] A particularly interesting feature of this structure is that the molecules adopt an eclipsed conformation (see Figures 4 and 5), whereas all previous x-ray determinations of compounds in the series have shown the expected staggered conformation.[2,4]

Discussion

The ^{35}Cl NQR frequencies reported here are among the lowest known for gallium trichloride adducts, indicating that phosphines are extremely good donors toward $GaCl_3$. This is in agreement with NMR measurements of formation constants for various chloroalkylgallium/Lewis base systems.[22] In fact, the values cited here lie in the range observed for the $GaCl_4^-$ ion, the average ^{35}Cl resonance frequency for $Ga^+(GaCl_4)^-$ being 16.161 MHz at 77 K for example.[23] The dependence of the NQR frequency on donor ability may be

Table IV

1. Physical and Crystallographic Data[a]

Formula: $(CH_3)_3P{\cdot}GaCl_3$
Mol wt 252.14
Crystal system: monoclinic
Space group: $P2_1/m$
$Z = 2$
$a = 7.621$ (5) [7.630 (7)] Å
$b = 10.377$ (8) [10.465 (9)] Å
$c = 6.465$ (7) [6.510 (9)] Å
$\beta = 113.84$ (7)° [113.86 (9)°]
$V = 467.6$ (1.2) [475.4 (1.5)] Å^3
$\rho_{\text{exptl}} = 1.75$ (2) g/cm^3
$\rho_X = 1.76$ g/cm^3
Absorption factor: $\mu_{(\lambda \text{Mo})} = 40$ cm^{-1}
Morphology: parallelepiped; 0.019 × 0.041 × 0.006 cm
Min and max absorption corrections: 0.23, 0.63

2. Data Collection

Temperature: 223 K [297 K]
Radiation: molybdenum $\lambda(K\bar{\alpha})$ 0.71069 Å
Monochromatization: oriented graphite crystal
Crystal-detector distance: 208 mm
Detector window: height[b] = 4 mm, width[b] = $3.10 + 0.70 \tan \theta$
Takeoff angle:[b] 3.5°
Scan mode: θ, θ
Max Bragg angle: $\theta = 30°$
Scan angle: $\Delta\theta = \Delta\theta_0 + B \tan \theta$, $\Delta\theta_0{}^b = 1.30$, $B^b = 0.35$
Values determining the scan speed: SIGPRE[b] = 0.400, SIGMA[b] = 0.020, VPRE[b] = 5°/min, TMAX[b] = 90 s
Control: intensity
  Reflections: $0\bar{6}0$, 033, 330
  Periodicity: 3600 s
Control: orientation
  Reflections: 060, 005, 501
  Periodicity: 100 reflections

3. Conditions for Refinement

Reflections for the refinement of the cell dimensions: 25
Recorded reflections: 1522 [1558]
Independent reflections: 1423 [1457]
Utilized reflections: 924 [732] with $I > 3\sigma(I)$
Refined parameters: 57 [43]
Reliability factors: $R = \Sigma |k|F_o| - |F_c||/\Sigma k|F_o| = 0.038$ [0.063] (with $w = 4F_o{}^2/\sigma^2(F_o{}^2)$), $R_w = [\Sigma w(k|F_o| - |F_c|)^2/\Sigma wk^2F_o{}^2]^{1/2} = 0.047$ [0.068]

[a] Data are given for the structure at 223 K; values obtained at 297 K are enclosed in brackets. [b] Cf. A. Mosset, J. J. Bonnet, and J. Galy, *Acta Crystallogr., Sect. B*, 33, 2639 (1977).

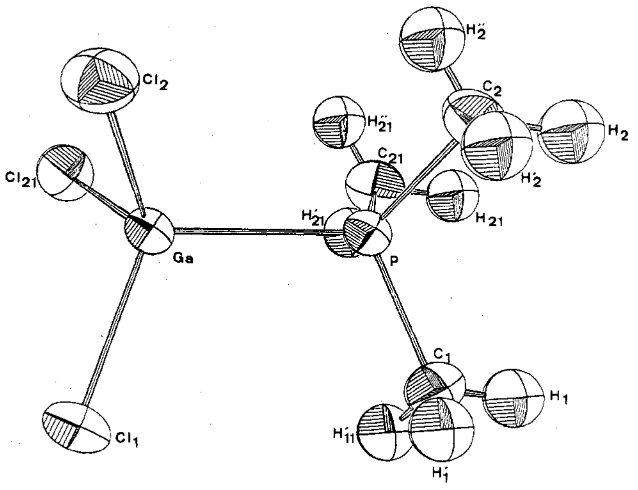

Figure 5. A perspective view of an isolated molecule $(CH_3)_3P{\cdot}GaCl_3$. Thermal ellipsoids are scaled to include 50% probability. The subscripts 11 and 21 are given to atoms which occupy positions related by the mirror plane to those labeled 1 and 2, respectively.

Table V. Fractional Atomic Coordinates and Thermal Parameters ×10^4 for $(CH_3)_3P\cdot GaCl_3$, with Esd's in Parentheses[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	0.9176 (1)	$^1/_4$	0.8981 (1)	87 (2)	55 (1)	179 (2)	0	50 (2)	0
	0.9131 (3)	$^1/_4$	0.8932 (3)	113 (6)	84 (3)	255 (7)	0	72 (5)	0
P	0.2350 (3)	$^1/_4$	0.9243 (3)	91 (4)	57 (2)	170 (5)	0	47 (4)	0
	0.2300 (7)	$^1/_4$	0.9200 (7)	108 (13)	97 (6)	232 (16)	0	65 (12)	0
Cl(1)	0.9130 (3)	$^1/_4$	0.2317 (3)	181 (5)	100 (2)	201 (5)	0	99 (4)	0
	0.9102 (7)	$^1/_4$	0.2248 (7)	236 (17)	123 (7)	300 (17)	0	134 (15)	0
Cl(2)	0.7710 (2)	0.4212 (2)	0.7157 (2)	163 (3)	75 (2)	275 (5)	33 (2)	71 (3)	32 (2)
	0.7662 (5)	0.4195 (3)	0.7117 (5)	201 (12)	115 (5)	396 (14)	98 (6)	94 (10)	44 (6)
C(1)	0.408 (1)	$^1/_4$	0.214 (1)	118 (17)	98 (10)	201 (22)	0	8 (16)	0
	0.400 (3)	$^1/_4$	0.214 (3)	218 (56)	112 (21)	204 (58)	0	−2 (44)	0
C(2)	0.277 (1)	0.3904 (6)	0.788 (1)	160 (13)	71 (7)	293 (19)	−16 (8)	106 (13)	18 (9)
	0.272 (2)	0.392 (1)	0.786 (2)	191 (42)	91 (14)	354 (45)	−43 (21)	113 (37)	50 (22)

	x	y	z	B, Å^2		x	y	z	B, Å^2
HC(1)	0.53 (2)	$^1/_4$	0.20 (2)	4.4	H'C(2)	0.26 (1)	0.479 (7)	0.85 (1)	4.4
H'C(1)	0.39 (1)	0.316 (7)	0.29 (1)	4.4	H''C(2)	0.40 (1)	0.380 (7)	0.80 (1)	4.4
HC(2)	0.19 (1)	0.390 (7)	0.61 (1)	4.4					

[a] Data are given for the structure at 223 K and, when appropriate, 297 K (second line). [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table VI. Molecular Parameters for Crystalline $(CH_3)_3P\cdot GaCl_3$ with Esd's in Parentheses

Atoms	Distance, Å	Atoms	Angle, deg	Atoms	Angle, deg
Ga–P	2.353 (2) [2.347 (5)]	Cl(1)–Ga–P	110.96 (9) [110.58 (20)]	C(1)–P–Ga	111.49 (34) [110.54 (60)]
Ga–Cl(1)	2.171 (2) [2.177 (5)]	Cl(2)–Ga–P	109.02 (6) [109.04 (13)]	C(2)–P–Ga	111.11 (26) [110.88 (44)]
Ga–Cl(2)	2.176 (2) [2.174 (4)]	Cl(1)–Ga–Cl(2)	109.09 (6) [109.13 (13)]	C(1)–P–C(2)	107.89 (31) [108.14 (52)]
P–C(1)	1.794 (9) [1.822 (16)]	Cl(2)–Ga–Cl(21)	109.64 (10) [109.93 (20)]	C(2)–P–C(21)	107.17 (50) [108.17 (79)]
P–C(2)	1.794 (7) [1.824 (11)]				
C(1)–HC(1)	0.89 (11)	P–C(1)–HC(1)	104 (7)	HC(1)–C(1)–H'C(1)	114 (6)
C(1)–H'C(1)	0.94 (8)	P–C(1)–H'C(1)	111 (5)	HC(2)–C(2)–H'C(2)	108 (8)
C(2)–HC(2)	0.98 (8)	P–C(2)–HC(2)	112 (5)	HC(2)–C(2)–H''C(2)	105 (6)
C(2)–H'C(2)	0.80 (8)	P–C(2)–H'C(2)	115 (6)	H'C(2)–C(2)–H''C(2)	113 (7)
C(2)–H''C(2)	0.94 (7)	P–C(2)–H''C(2)	104 (5)		

[a] Data are given for the structure at 223 K; values obtained at 297 K are enclosed in brackets.

explained qualitatively as follows: the greater the electronic charge transferred, along the coordination bond to the Lewis acid, the lower the effective electronegativity of the central metal acceptor atom will be; therefore, the ionicity of the gallium–chlorine bond increases with donor strength and, consequently, the resonance frequency decreases. The NQR frequencies of the phosphine derivatives are substantially (6–12%) lower than those for the corresponding oxygen or sulfur containing adducts.[1,24] Analysis of the weighted mean frequency data by means of the Townes and Dailey treatment[25] permits the estimation of charge densities on chlorine; see Table VII. The absolute quantities derived from this calculation must be regarded as approximate; however, the relative variation in ionic character given in the final column of the table undoubtedly reflects actual differences in the chemical properties of the ligands. Clear distinctions exist between ether, sulfide, and arsine while the best donors, amine and phosphine, are comparable. For the amine and phosphine adducts an estimated additional charge of approximately 0.25 electron, distributed over three atoms, is transferred from gallium to chlorine when compared to the free Lewis acid reference adopted here.

It would be expected on the basis of this result that the gallium–chlorine bond lengths in the trialkylphosphine complexes are greater than the corresponding values in the reference compound, $GaCl_3$. In fact the x-ray structure determination of Ga_2Cl_6 by Wallwark and Worral[26] reveals a mean gallium–terminal chlorine distance of 2.06 Å which is in good agreement with the predicted trend. Although the dimerization of gallium trichloride prevents an exact comparison, a substantial increase in the Ga–Cl bond length, of the order of 0.1 Å, is indicated when the free Lewis acid is complexed with very effective donors such as tertiary amines and phosphines.

Table VII. Parameters Derived from the Townes and Dailey Analysis of the NQR Data

Compound	Weighted mean NQR frequency at 77 K	Calcd charge on chlorine, electrons	% change in ionic character
$GaCl_3$ (terminal Cl)	20.750	0.622	Ref
$(CH_3)_2O\cdot GaCl_3$	17.893	0.674	8.4
$(CH_3)_2S\cdot GaCl_3$	17.143	0.688	10.6
$(CH_3)_3As\cdot GaCl_3$	16.463	0.700	12.6
$(CH_3)_3P\cdot GaCl_3$	16.150	0.706	13.5
$(CH_3)_3N\cdot GaCl_3$	16.132	0.706	13.5

Of general chemical interest is the change in ligand geometry on complexation; an increase in the CPC angle from 98 to 108° is seen when the present data are compared to the values derived by Bryant and Kuczkowski from microwave measurements on the free phosphine at 195 K.[27] By contrast there is no significant difference between the phosphine structure reported here and that of the BCl_3 complex.[3] Both $GaCl_3$ and BCl_3 are presumably such good acceptors that near-maximum bonding rearrangements are produced in each case. Poorer acceptors would be expected to induce smaller changes in the CPC angle; this appears to be so in $(CH_3)_3P\cdot BH_3$ where a value of 105° is found[28] but the possibility of a supplementary interaction between phosphorus and the borane group in this compound should be borne in mind.[29]

Table VIII. Available Unit Cell Data for Complexes in the Series $R_3D{\cdot}ACl_3$

Compd	*a*, Å	*b*, Å	*c*, Å	*β*, deg	*V*, Å^3	Conform	Ref
$(CH_3)_3N{\cdot}BCl_3$	6.677	10.247	6.502	116.18	399.2	Staggered	2
$(CH_3)_3N{\cdot}AlCl_3$[a]	7.31	10.66	6.81	118.0	468.6	Staggered	4
$(CH_3)_3P{\cdot}BCl_3$	6.957	10.630	6.476	112.76	441.6	Staggered	3
$(CH_3)_3P{\cdot}GaCl_3$	7.630	10.465	6.510	113.86	475.4	Eclipsed	This work

[a] Values for this compound have been changed according to the convention $a > c$.

Reference to the standard deviation of the mean, σ_m, values given in Table II shows that the empirical quadratic equation given by Pies and Weiss describes the present NQR temperature data very effectively. A quadratic dependence may be derived by the truncation of a polynomial expansion for the exponential term. This would imply that such a parameterization is restricted by the high-temperature approximation but the fit above 77 K is nevertheless very gratifying and the possibility of using linear regression techniques is a considerable advantage. Many trials were needed to obtain successful convergence with eq 4 using the nonlinear program BMDP3R and the determination of suitable initial values for the various parameters by means of a programmable calculator was found to be of some assistance. The two compounds are clearly distinguished by the final values for the optimized parameters of this equation; in particular the differences in the coefficients *p* and *q* should be noted; these are of fundamental importance as may be seen from the derived quantities given in Table III. In this treatment the effective moment of inertia and optimum librational frequency are calculated. Each has the significance of a weighted mean of a number of discrete, like quantities which constitute the physical reality. However, the results obtained are of the expected order of magnitude. Furthermore comparison of the values deduced for $\omega(0)$ to far-infrared data for $(CH_3)_3P{\cdot}GaCl_3$, viz., 145 cm^{-1}, $GaCl_3$ def (e), 127 cm^{-1} $GaCl_3$ def (a_1), and 53 cm^{-1} P–$GaCl_3$ rock (e)[30] is extremely interesting. It would appear that the ligand rocking mode makes dominant contribution to the vibrational averaging of electric field gradient at the chlorine nuclei in the case of the trimethyl compound whereas the deformation of the $GaCl_3$ moiety is the more important for the two high-frequency $(C_2H_5)_3P{\cdot}GaCl_3$ lines. It is reasonable to assume that large amplitude ligand rocking modes might be prohibited to the bulky triethylphosphine group but this does not explain the apparent unimportance of the $GaCl_3$ deformation mode in $(CH_3)_3P{\cdot}GaCl_3$.

The high sensitivity of NQR to chemical inequivalence is well illustrated in the present study. For $(CH_3)_3P{\cdot}GaCl_3$ the x-ray determinations show only very slight differences in bond lengths for Cl(1) and Cl(2) and indicate that any change in the geometry of the $GaCl_3$ group between 223 and 297 K is limited to variations which are comparable to or less than the sum of the appropriate standard deviations. Yet the quadrupole resonance frequencies for the two chlorine sites differ by 85 and 60 kHz at 223 and 297 K, respectively.

The dominant thermal expansion of the crystallographic *b* axis is considered to be an especially significant result; see Figure 3. A possible clue to the origin of this effect may lie in the fact that the separation parameter between the mirror planes is *b*/2. If Figure 4 is considered, it may be seen that the eclipsed conformation permits a closer approach of two molecules than would be allowed in the case of a staggered configuration. Since the resulting contraction is essentially along the *b* axis, a large coefficient of thermal expansion in this direction is consistent with the structure. Comparison of the unit cell parameters given in Table VIII provides some indication of the effect of this change in conformation. All other known structures of similar compounds are staggered but $(CH_3)_3P{\cdot}GaCl_3$ is the largest molecule so far studied and size is likely to play an important role in the determination of the preferred conformation for a particular adduct. It is clear that for $(CH_3)_3P{\cdot}GaCl_3$ the energy sacrificed in going to the eclipsed position is more than recovered by the resulting decrease in intermolecular interactions while for the other three complexes the return is unfavorable. A striking fact which emphasizes this point is that the length of the *b* axis for $(CH_3)_3P{\cdot}GaCl_3$ is actually shorter than that of $(CH_3)_3N{\cdot}AlCl_3$ in spite of the increase in size of both donor and acceptor atoms. The difference of only 7 Å^3 in the unit cell volumes for these two compounds would also have been most surprising if a structural rearrangement such as that described here had not been observed.

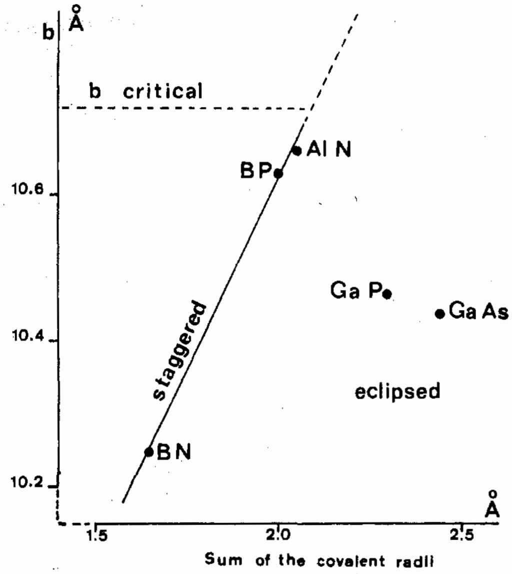

Figure 6. Illustration of the proposed dependence of the *b* parameter on molecular dimensions for the series of compounds $(CH_3)_3D{\cdot}ACl_3$.

Since the NQR data suggest that the three chlorine atoms of $(CH_3)_3P{\cdot}GaCl_3$ become equivalent in the vicinity of 420 K, it is tempting to speculate that in this temperature range a transition from the eclipsed to the staggered conformation occurs as a prelude to the onset of hindered rotation. If this is in fact the case then there should be a critical value of the *b* parameter (estimated to be in the region of 10.7–10.8 Å) defining the stability transition point for the two conformers. It might indeed be possible to use this approach to predict the conformation of other compounds in the same series from the minimum of experimental data by means of a scheme such as Figure 6.

Further studies of this interesting group of compounds and in particular NQR and x-ray results for $(CH_3)_3P{\cdot}GaCl_3$ at elevated temperatures are much to be desired.

Following the suggestions of one of the reviewers for testing the validity of Figure 6, the next compound in the series $(CH_3)_3As{\cdot}GaCl_3$ has been prepared and characterized. Here we report briefly the NQR and x-ray data. On the one hand, the ^{35}Cl quadrupole resonance frequencies (at 77 K, $\nu(^{35}Cl)$ = 16.36 (14) and 16.67 (7) MHz) clearly indicate that the molecule lies on a mirror plane with an eclipsed conformation. On the other hand, the x-ray determinations follow and confirm the following features: at 297 K, the parameters are $a = 7.84 \pm 0.03$ Å, $b = 10.44 \pm 0.04$ Å, $c = 6.52 \pm 0.03$ Å, and $\beta = 113 \pm 0.5°$, and the space group is $P2_1/m$.

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Registry No. $(CH_3)_3P\cdot GaCl_3$, 19502-93-3; $(C_2H_5)_3P\cdot GaCl_3$, 59400-56-5; $(CH_3)_2O\cdot GaCl_3$, 19379-37-4; $(CH_3)_2S\cdot GaCl_3$, 15171-34-3; $(CH_3)_3As\cdot GaCl_3$, 59400-54-3; $(CH_3)_3N\cdot GaCl_3$, 15555-33-6; $GaCl_3$, 13450-90-3.

Supplementary Material Available: A listing of structure factor amplitudes at two temperatures (12 pages). Ordering information is given on any current masthead page.

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Molecular Structures of Phosphorus Compounds. 6. An Electron Diffraction Study of *tert*-Butylfluorophosphines $Bu^t_nPF_{3-n}$ (n = 1, 2, 3)

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The geometric structures of *tert*-butyldifluorophosphine, di-*tert*-butylfluorophosphine, and tri-*tert*-butylphosphine have been determined in the gas phase by electron diffraction. Successive substitution of fluorine atoms by *tert*-butyl groups results in the lengthening of both P–F and P–C bond distances. The P–F bond lengths increase from 1.589 (3) Å in Bu^tPF_2 to 1.619 (7) Å in Bu^t_2PF. The P–C bond lengths increase even more strongly from 1.822 (12) Å in Bu^tPF_2 to 1.859 (6) Å in Bu^t_2PF to 1.919 (5) Å in Bu^t_3P. The bond angles at the phosphorus atom follow the opposite trend. The CPF angle decreases from 99.0 (0.6)° in Bu^tPF_2 to 96.0 (2.0)° in Bu^t_2PF, and the CPC angle decreases from 113.8 (1.9)° in Bu^t_2PF to 109.9 (0.7)° in Bu^t_3P. The geometric parameters and the configuration of the *tert*-butyl groups are given in the paper. The electron diffraction results are compared with results obtained by CNDO/2 calculations. The effect of steric strain on the geometry caused by the bulky *tert*-butyl groups is discussed.

Introduction

The phosphorus(III) ligands Bu^t_3P, Bu^t_2PF, and Bu^tPF_2 together with PF_3 constitute a complete substitution series, $Bu^t_{3-n}PF_n$ (n = 0–3).

The coordination chemistry of Bu^tPF_2,[1] Bu^t_2PF,[1,2] and Bu^t_3P[1,3,4] has been extensively studied, while the same is true even more for PF_3.[5a]

The coordination compounds synthesized range from transition-metal carbonyl complexes[1,3,5a] and transition-metal halide complexes, e.g., $MX_2(Bu^t_2PF)_2$ (M = Co, Ni; X = Cl, Br, I)[2] and $[Bu^t_3PH][NiBr_3Bu^t_3P]$,[4a] to borane adducts, $Bu^t_{3-n}PF_n\cdot BH_3$ (n = 0–3).[5b] The physical properties of these complexes have been thoroughly investigated.

The NMR spectroscopic properties of members of the series initially mentioned have been discussed in some detail,[1,6] and the Raman and infrared spectra of Bu^tPF_2[7] and Bu^t_2PF[8] have been assigned and interpreted.

UV photoelectron spectra[9] of these ligands show a remarkable decrease of the first vertical ionization potential from 12.3 eV (PF_3) to 7.70 eV (Bu^t_3P).

Finally, CNDO/2 calculations[10] of the differences in electronic energies of the phosphines $Bu^t_{3-n}PF_n$ and the corresponding phosphonium salts $[Bu^t_{3-n}PF_nH]^+$ may be linearly related to the first vertical ionization potentials of the ligand $Bu^t_{3-n}PF_n$.

In order to show to what extent these observations could be explained on the basis of structural parameters of the phosphines $Bu^t_{3-n}PF_n$ (n = 0, 1, 2), a comparative electron diffraction study was undertaken.

Experimental Section

The phosphorus(III) compounds Bu^tPF_2,[11] Bu^t_2PF,[12] and Bu^t_3P[13,14] have been prepared according to the methods described in the literature. Their purity was checked by ^1H NMR, ^{19}F NMR, and ^{31}P NMR spectroscopy, respectively. The scattering intensities were recorded with the Balzers Diffractograph KD-G2[15] for two camera distances (25 and 50 cm) on Ilford N50 plates (18 × 13 cm). Details of the experiment are given in Table I. (Throughout this paper 1 Å = 100 pm and 1 Torr = 101.325/760 kPa.) The electron wavelength was determined by ZnO powder diffraction. For all molecules the s range ($s = (4\pi/\lambda)\sin(\delta/2)$, λ electron wavelength, δ scattering angle) covered in the experiment was $s = 1.4–17\ Å^{-1}$ and $s = 7–34\ Å^{-1}$ for the two camera distances. Two plates for each camera distance were selected for the structure analysis. The optical densities were

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