A GAS ELECTRON DIFFRACTION STUDY OF THE MOLECULAR STRUCTURES OF $(CH_3)_3Ga \cdot N(CH_3)_3$ AND $(CH_3)_3Ga \cdot P(CH_3)_3$

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Summary

The structures of $(CH_3)_3Ga \cdot N(CH_3)_3$ and $(CH_3)_3Ga \cdot P(CH_3)_3$ are determined by electron diffraction in the gas phase. The donor—acceptor bonds, Ga—N and Ga—P, for organogallium complexes are measured and the variation in geometry of the free ligands is discussed.

Recently, the structure of the first inorganic complex containing gallium, $Cl_3Ga \cdot NH_3$, has been determined by electron diffraction [1]. There are no data, however, for organogallium complexes with Group VB alkyl derivatives. In an attempt to obtain more insight into the nature of the Ga—N and Ga—P donor—acceptor bonds, the structures of $(CH_3)_3Ga \cdot N(CH_3)_3$ and $(CH_3)_3Ga \cdot P(CH_3)_3$ have been investigated. Another point of interest is the variation in the geometry of the free donor and acceptor as a result of complex formation. This can be easily done since the structures of the free acceptor $(CH_3)_3Ga$ [2] and the free donors $(CH_3)_3N$ [3] and $(CH_3)_3P$ [4] have been previously studied by electron diffraction. A similar comparison exists for complexes with B—N [5], B—P [6—9], B—As [10] and Al—N [11] bonds. The main molecular parameters of the complexes studied are listed in Table 1.

Donor—acceptor bonds

The Ga—N bond of 2.20Å is significantly longer than the sum (1.95Å) of the atomic radii of Ga (1.30Å) and N (0.65Å) [12]. This is also greater than the value of 2.057Å reported for $Cl_3Ga \cdot NH_3$ [1]. A similar variation has been observed in Al—N complexes [11] as a result of the replacement of chlorine by methyl groups at the Al atom. In X-ray structural studies a number of Ga—N bond lengths have been measured: 1.97(9)Å in $H_3Ga \cdot N(CH_3)_3$ [13]; 2.097(6), 2.182(5) in $HGa \cdot EDTA \cdot H_2O$ [14]; 2.097, 2.105 in $GaCl_3 \cdot$ bipy [15]; 2.034(7), 2.110(6), 2.115(6)Å in $GaCl_3 \cdot$ terpyridyl [16].

TABLE 1

THE MAIN STRUCTURAL PARAMETERS OF THE COMPLEXES $(CH_3)_3Ga \cdot D(CH_3)_3$ AND THEIR COMPARISON WITH THE STRUCTURES OF THE FREE DONORS AND ACCEPTOR

	$(CH_3)_3Ga \cdot N(CH_3)_3$			$(CH_3)_3Ga \cdot P(CH_3)_3$		
	Bond length (Å)	Angle (°)	Δ^a	Bond length (Å)	Angle (°)	Δ^a
Ga—D	2.20 (3)			2.52 (2)		
Ga—C	1.998(4)		+0.031	1.997(8)		+0.030
C—D	1.485(4)		+0.031	1.84 (1)		−0.006
C—Ga—C		116.7	−2.8		117.9	−1.6
C—D—C		109.6	−1.0		102.6	+4.0

$^a\Delta$ is the value of the complex molecule parameter minus the value of free molecule parameter.

We are not aware of any determination of the Ga—P bond distance. Therefore it can be discussed only by analogy with related compounds containing B—N and B—P bonds: B—donor: 1.609Å in $H_3B \cdot N(CH_3)_3$ [5] and 1.901Å in $H_3B \cdot P(CH_3)_3$ [6]. Ga—donor: 2.20 Å in $(CH_3)_3Ga \cdot N(CH_3)_3$ and "χ" in $(CH_3)_3Ga \cdot P(CH_3)_3$.

Assuming that the difference between acceptor—P and acceptor—N bond lengths can be constant one arrives at a value for the Ga—P distance of: $\chi = 2.20 + (1.901 - 1.609) = 2.492$Å. This estimate is in good agreement with the experimental value of 2.52Å while the sum (2.30Å) of the atomic radii [12] is significantly less.

The variation of geometry upon complex formation

Table 1 shows those geometrical effects which are observed if one takes into account the structures of the free ligands. These variations are, at least partially, rationalized in terms of the VSEPR theory [17] keeping in mind that complex formation is accompanied by transfer of electrons away from the donor. According to this theory: in the donor (D) part of the complex the D—C distances should be shorter and the C—D—C bond angle should increase compared to the geometry of the free donor. In the acceptor (A) part the A—C distances should be longer and the C—A—C bond angle should decrease. Studying the variations shown in Table 1 one can see that the predictions of the VSEPR theory are in good agreement with the values for the acceptor part of the complex. On the other hand the behaviour of the donor part is more complicated since $(CH_3)_3N$ shows an "abnormal" variation, observed earlier in complexes with boron [5] and aluminium [11]. $(CH_3)_3P$, however, gives a "normal" variation although the difference in the P—C bonds length is of marginal significance. Much larger variations of 0.027—0.036Å were reported for complexes with boron [6—8]. This is also the case for the $H_3B \cdot As(CH_3)_3$ molecule [10].

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