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THE MOLECULAR STRUCTURE OF A COMPLEX OF TETRAMETHYLCYCLOBUTADIENE AND ALUMINIUM CHLORIDE, CONTAINING A σ-Al—C BOND

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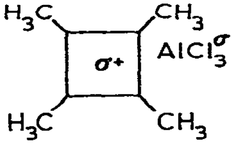
Summary

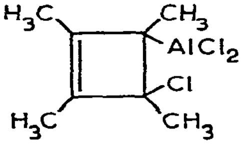
The molecular structure of the primary reaction product of 2-butyne and aluminium chloride has been deduced from single crystal X-ray diffraction data (1148 reflections) ($a = 15.664(8)$; $b = 10.886(4)$, $c = 7.222(2)$ Å, $Z = 4$, space group *Pnma*). The aluminium chloride is coordinated via a σ-aluminium carbon bond (1.979 Å) to a non-planar tetramethylcyclobutadiene moiety. The bond length pattern indicates a charge dislocation within the four-membered ring.

Introduction

The trimerisation of 2-butyne in the presence of aluminium chloride to yield hexamethyl-Dewar-benzene was formulated [1] as proceeding via an intermediate complex $(CH_3—C)_4AlCl_3$ (I). Later, II or III were postulated to be possible structures for the intermediate [2].



(I)



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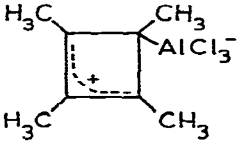

(III)

Detailed NMR studies [3] gave evidence for structure III. In addition, the temperature dependence of the NMR spectrum was interpreted in terms of variable degrees of migration of the $AlCl_3$ part on top of the ring system. As it was possible to grow suitable crystals of the compound in question, we undertook an X-ray structural analysis in order to gain information about the detailed molecular conformation. Besides its interest as an intermediate product in the above reaction, the compound might be suitable as a model for the intermediates postulated for Friedel-Crafts alkylation reactions.

Results and discussion

The structure of the title compound, together with the numbering scheme and major distances and angles, is shown in Fig. 1. Distances and angles, together with standard deviations, are given in Table 1. A stereoscopic representation of the thermal vibration ellipsoids is given in Fig. 2.

The analysis clearly reveals the bonding situation to be that indicated by the spectral data, and confirms the formation of the four-membered ring system, including an aluminium—carbon σ-bond. The $AlCl_3$ group is σ-bonded to the four-membered ring such that one chlorine atom is located opposite the positively charged part of the molecule. The molecule possesses crystallographic *m*-symmetry (C_s), with the atoms Al, Cl1, C1, C3, H51 and H72 located on a mirror plane. The geometry of the Al—Cl unit is almost ideally tetrahedral. Two equivalent Al—Cl bond lengths (2.126 Å) are similar to those found in other $AlCl_4^-$ complexes (2.125 [4], 2.120 [5], 2.13 [6] Å) whereas the bond from Al to the chlorine atom topping the cation is slightly elongated [2.141(2) Å]. The Al—C bond length of the σ-bond agrees well with those found in non-bridged Al—C systems [7—10]. The angles at C1 suggest a distorted sp^3 environment. The four-membered ring is folded; the dihedral angle between the positively charged part C2—C3—C2* and C2—C1—C2* is 31.5°. Furthermore, a severe strain is

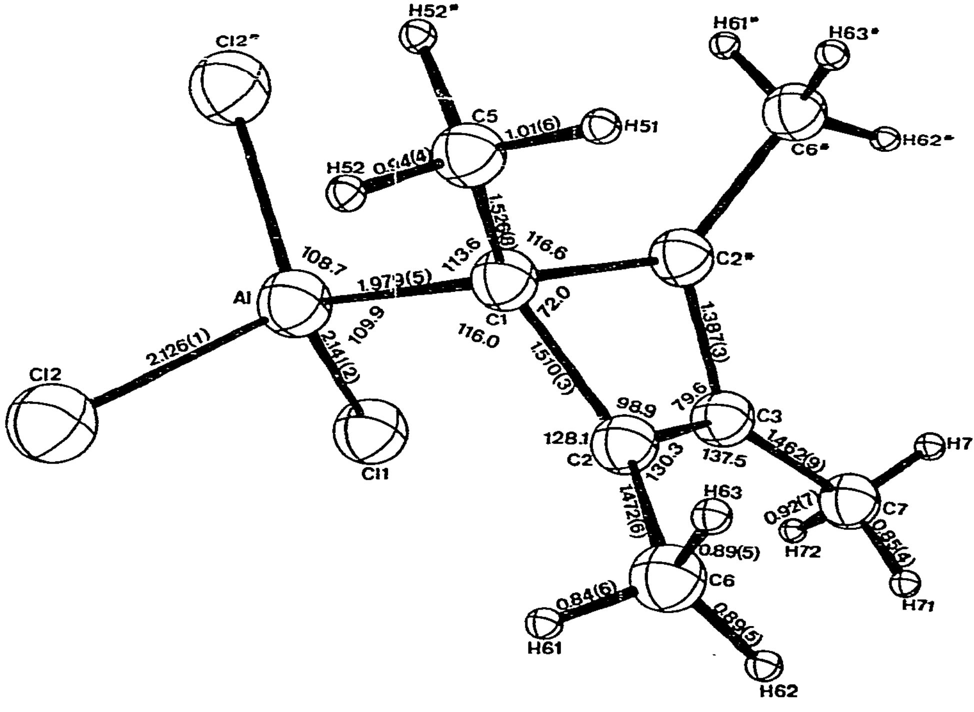

Fig. 1. The molecular structure of $[C{-}CH_3]_4^+AlCl_3^-$.

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) WITH THEIR STANDARD DEVIATIONS

Al—Cl1	2.141(2)	Cl1—Al—Cl2	109.3
Al—Cl2	2.126(1)	Cl2—Al—C1	108.7
		Cl1—Al—C1	109.9(2)
Al—C1	1.979(5)	Al—C1—C2	116.0(1)
C1—C2	1.510(3)	Al—C1—C5	113.6(4)
C2—C3	1.387(3)	C5—C1—C2	116.6(1)
C1—C5	1.526(8)	C2—C1—C2*	72.0(3)
C2—C6	1.472(6)	C1—C2—C3	98.9(2)
C3—C7	1.462(9)	C3—C2—C6	130.3(3)
		C2—C3—C7	137.5(1)
		C2—C3—C2*	79.6(3)
C5—H51	1.01(6)		
C5—H52	0.94(4)		
C6—H61	0.84(6)		
C6—H62	0.89(5)		
C6—H63	0.89(5)		
C7—H71	0.85(4)		
C7—H72	0.92(7)		

indicated by markedly different bond lengths and angles within the ring, causing an elongation of the ring system along the mirror plane. As a result, the distance between atoms C2 and C2* is only 1.775(4) Å, indicating a transannular interaction. In contrast, the distance C1—C3 is 2.202(7) Å. Angles and distances at atoms C2 (C2*) and C3 suggest an equivalent hybridisation close to sp^2, thus proving the symmetric dislocation of the positive charge amongst these three atoms. The terminal methyl groups C6 (C6*) are pointing away from the AlCl_3^- fragment and are located 0.350 Å above the plane C1—C2—C3, which forms a dihedral angle of 38.4° with the equivalent plane C1—C2*—C3. The vector C3—C7 is colinear with the vector C1—C3.

Shortest intermolecular contacts (see Table 2 and Fig. 3) are from the AlCl_3^- group to the methyl groups C5, C6, C7 and between the methyl groups C5 and C7.

Experimental

The reaction between 2-butyne and aluminium chloride was carried out as described earlier [3]. Single crystals of the title compound were obtained with difficulty by repeated recrystallisation from methylene chloride/chloroform

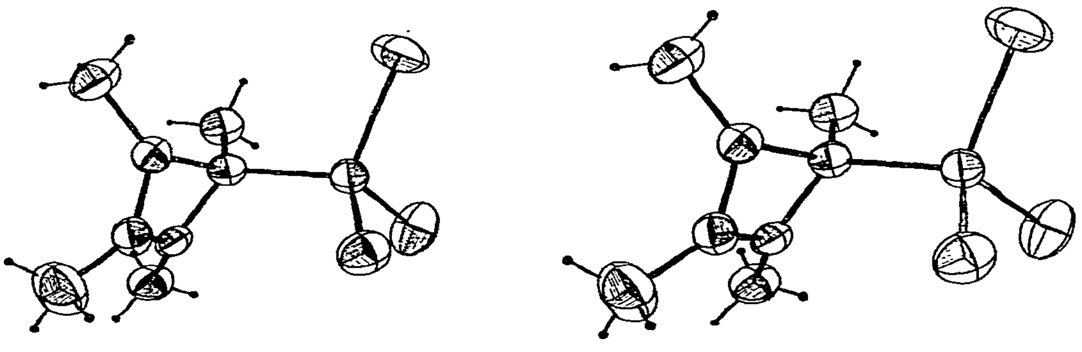

Fig. 2. Stereoscopic representation of the thermal ellipsoids of $[\text{C—CH}_3]_4^+$ AlCl_3^- (50% probability).

TABLE 2

INTERMOLECULAR DISTANCES (Å)

C7—Cl1	3.865(11)	C7—C5	3.422(11)
C3—Cl1	3.848(5)		
C6—Cl1	3.817(5), 3.725(5)		
Cl2—C6	3.842(6)		
Cl2—C5	3.972(1)		

TABLE 3

CRYSTAL DATA

Formula:	$C_8H_{12}AlCl_3$
Molecular weight:	241.5
Crystal size:	0.75 × 0.75 × 0.3 mm
Crystal system:	orthorhombic
Wavelength:	Mo-K_α 0.71069 Å
Unitcell:	$a = 15.664(8)$, $b = 10.886(4)$, $c = 7.222(2)$ Å; $V = 1231.5$ Å^3; $Z = 4$
D_{calc} =	1.303 g cm^{-3}
Systematic absences:	$h00$, $h = 2n$; $hk0$, $h = 2n$; $0k0$, $k = 2n$; $0kl$, $k + l = 2n$; $00l$, $l = 2n$
Space group:	*Pnma*

TABLE 4

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS (× 10^4)

Atom	*x*	*y*	*z*
Al	3682(1)	2500(0)	2419(2)
Cl1	4938(1)	2500(0)	1249(3)
Cl2	3024(1)	4108(1)	1557(2)
C1	3755(3)	2500(0)	5155(6)
C2	4434(2)	3315(3)	5987(4)
C3	5114(3)	2500(0)	5935(7)
C5	2887(4)	2500(0)	6111(10)
C6	4318(4)	4449(5)	7067(8)
C7	6018(5)	2500(0)	6438(17)
H51	2890(31)	2500(0)	7506(79)
H52	2544(25)	1843(39)	5723(58)
H61	4057(33)	4946(56)	6378(79)
H62	4817(31)	4709(44)	7499(65)
H63	3926(30)	4342(43)	7949(72)
H71	6193(32)	1885(38)	7064(65)
H72	6336(44)	2500(0)	5377(101)

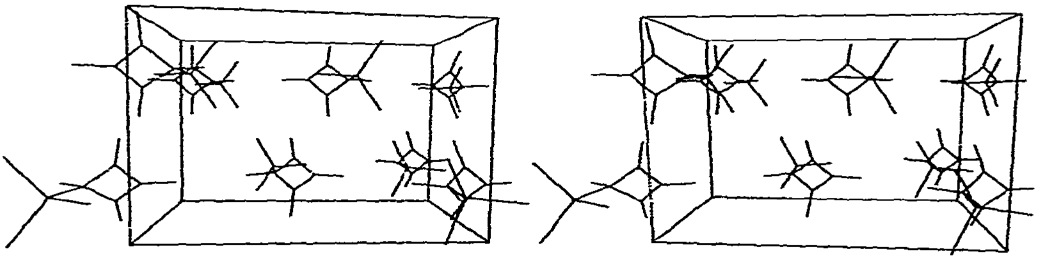

Fig. 3. Stereoscopic view of the unit cell, seen along —c. The *a* axis is horizontal.

TABLE 5

FINAL THERMAL PARAMETERS ($\times 10^3$)

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Al	51.0	39.0	44.0	0	−3.0	0
Cl1	64.0	60.0	56.0	0	15.0	0
Cl2	104.0	78.0	83.0	45.0	1.0	20.0
C1	42.0	39.0	46.0	0	4.0	0
C2	56.0	34.0	39.0	−4.0	3.0	6.0
C3	50.0	50.0	46.0	0	−3.0	0
C5	56.0	65.0	64.0	0	12.0	0
C6	93.0	47.0	63.0	−5.0	6.0	−9.0
C7	58.0	98.0	100.0	0	−21.0	0
H51	56.0	0	0	0	0	0
H52	92.0	0	0	0	0	0
H61	141.0	0	0	0	0	0
H62	99.0	0	0	0	0	0
H63	108.0	0	0	0	0	0
H71	96.0	0	0	0	0	0
H72	101.0	0	0	0	0	0

(1/1) at −30°. A dark red, plate-like crystal was sealed under dry argon in a glass-capillary. All subsequent investigations were carried out using this crystal. The space group and initial cell data were determined from Weissenberg and precession photographs. The crystal was transferred to an automated diffractometer and mounted with b^* coincident to the ϕ-axis. The cell constants, given together with other crystal data in Table 3, were refined by a least-squares procedure using the 2θ maxima of 18 reflections.

Intensity data were collected from one octant ($2\theta \leqslant 50°$) of reciprocal space and reduced to F's as described previously [11]. The fluctuation of a monitor reflection, which was recorded every 40 reflections, was only random. Of 1148 reflections measured, 216 had intensities (I) less than $3\sigma(I)$ and were considered unobserved and excluded from the data set. The structure was solved using multi-solution tangent formula refinement [12] of 283 reflections with $|E| > 1.2$. The most probable solution was indicated by an $R(\alpha)$ value of 0.046. The program used was written by Sheldrick [13], and adapted to our local PDP-10 computer system. All other programs used were described elsewhere [14].

The subsequent E-map clearly revealed the positions of all atoms of the molecule. Isotropic full-matrix weighted least-squares refinement yielded after 5 cycles an R-value of 0.1533 ($R_w = 0.162$). This was followed by 5 cycles of anisotropic refinement resulting in $R = 0.074$ ($R_w = 0.078$). The function minimized was $w(|F_o| - s\cdot|F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. At this stage a difference Fourier synthesis was used to locate all seven hydrogen atoms. The refinement was completed by 5 additional cycles of least-squares treatment, the hydrogen atoms being refined isotropically. The final R-values were 0.054 ($R_w = 0.057$). Final coordinates and thermal vibration parameters are given in Tables 4 and 5. A list of the final F_o/F_c calculation may be obtained from the authors (C.K.). Scattering factors used were those of Cromer and Waber [15] for the heavier atoms, and those of Stewart, Davidson and Simpson [16] for hydrogen atoms.

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