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CRYSTAL AND MOLECULAR STRUCTURE OF AN YTTRIUM DICYCLOPENTADIENYL CHLORIDE COMPLEX WITH TRIETHYLAMINALANE $[\eta\text{-}(C_5H_5)_2YCl \cdot AlH_3 \cdot NEt_3]_2$

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Summary

By treating Cp_2YCl with $AlH_3 \cdot NEt_3$ in benzene we obtained crystals of the complex $(Cp_2YCl \cdot AlH_3 \cdot NEt_3)_2$ (I). The crystals are monoclinic, $a = 12.325(5)$, $b = 18.780(7)$, $c = 8.848(2)$ Å; $\beta = 69.89(2)°$, space group $P2_1/a$, $Z = 2$, $d_{calc.} = 1.33$ g/cm^3. According to the X-ray analysis data (direct method, 1284 reflections with $F > 3\sigma(F)$, R factor = 0.062), the molecule of I is a Cp_2YCl dimer bonded to the $AlH_3 \cdot NEt_3$ groups via H atom bridges between the Y and Al atoms as well as via a weak "secondary" Al=Cl bond. The Cl, Y, Al and H atoms lie in one plane.

Introduction

When we considered the results of the investigation of the structure of polymeric $\{[\eta\text{-}(C_5H_5)_2YCl]_2 \cdot AlH_3 \cdot OEt_2\}_n$ we concluded that the stability and structure of the dinuclear complexes of yttrium dicyclopentadienyl chloride with aluminum hydrides are predominantly controlled by the basicity of the "molecular ligand" $AlH_{3-n}Cl_n \cdot L$, i.e. the negative charge on the hydride atoms [1]. The magnitude of the charge depends both on the accepting power of the substituents on the aluminum atom and the strength of the Lewis base L, which is due to the electron density shift occurring whenever an Al ← L bond is formed. Obviously, the maximum polarity of the Al–H bond will be observed in aluminum hydride complexes with trialkylamines

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which are among the strongest Lewis bases. One should keep in mind, however, that all the molecular complexes of aluminum hydride with a four-coordinate Al atom having a composition $AlH_3 \cdot L$ are, actually, difunctional "molecular ligands", since they have a second reaction site: the electronically unsaturated aluminum atom. It is because of population of the low-lying *d*-orbitals of the Al atom that molecular complexes of the composition $AlH_3 \cdot 2L$ [2] and polymeric $(AlH_3)_n$ with a six-coordinate aluminum atom [3] formed and the complex $\{[(\eta\text{-}C_5H_5)_2YCl]_2 \cdot AlH_3 \cdot OEt_2\}_n$ is additionally stabilized owing to formation of the Al=Cl bond [1].

This paper reports on the results of the X-ray analysis of the complex of $(\eta\text{-}C_5H_5)_2YCl$ with $AlH_3 \cdot NEt_3$, whose composition and structure differs, in accordance with the above, from the structure of the $(\eta\text{-}C_5H_5)_2YCl$ complex with $AlH_3 \cdot OEt_2$.

Results and Discussion

In contrast to the polymeric $\{[(\eta\text{-}C_5H_5)_2YCl]_2 \cdot AlH_3 \cdot OEt_2\}_n$ with a Y : Al ratio of 2 : 1 (Complex I), the structure of the title compound is composed of centro-symmetrical isolated dimers $[(\eta\text{-}C_5H_5)_2YCl \cdot AlH_3 \cdot NEt_3]_2$ (II) and has a Y : Al ratio of 1 : 1 (Fig. 1). The yttrium atom is bonded to two $\eta\text{-}C_5H_5$ ligands forming a 127.7° wedge-like sandwich (Table 2), the angle being practically the same as that found in the structures of I [1] and $[(\eta\text{-}C_5H_5)_2YCl]_2$ [4]. Both wedge-like sandwiches are connected to each other via a double chlorine bridge $\mathrm{Y}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\langle\quad\rangle}}\mathrm{Y}$, that is, in just the same manner as they are in the dimeric dicyclopentadienylyttrium chloride [4] and complex I [1]. As in complex I, the cyclopentadienyl rings in II are disposed asymmetrically with respect to the plane passing through the yttrium atoms and perpendicular to the YCl_2Y' rhomb plane. The angle between Y–Y' and the plane passing through the centers of the Cp rings of the wedge-like sandwich and the yttrium atom is 29.8° (in I 32.3° and 26.1°). This deflection of the Cp rings is no

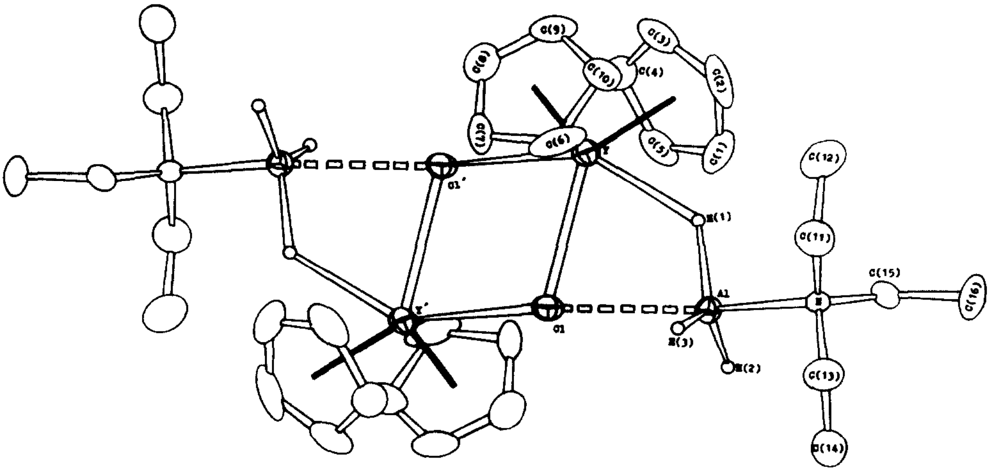


Fig. 1. The structure of the $[(\eta\text{-}C_5H_5)_2YCl \cdot AlH_3 \cdot NEt_3]_2$ molecule.

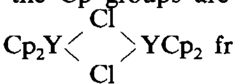
TABLE 1

COORDINATES OF Y, Cl, Al, N($\times 10^4$) C and H ($\times 10^3$) atoms AND THE EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

$B_{\text{iso.}}^{\text{equiv.}} = 4/3 \sum_i \sum_j b_{ij} a_i a_j$

Atom	x	y	z	$B_{\text{iso.}}^{\text{equiv.}}$
Y	3616(1)	4605(1)	4199(1)	3.0
Cl	4344(3)	4625(2)	6760(3)	4.4
Al	2077(3)	3856(2)	8121(4)	2.7
N	526(7)	3333(4)	8899(9)	2.6
C(1)	170(2)	539(1)	530(2)	6.3
C(2)	166(2)	505(1)	394(4)	7.3
C(3)	239(2)	528(1)	268(3)	5.8
C(4)	304(1)	576(1)	299(2)	4.8
C(5)	267(2)	589(1)	460(3)	6.6
C(6)	398(1)	322(1)	378(2)	4.9
C(7)	507(1)	356(1)	298(2)	5.4
C(8)	496(2)	391(1)	166(2)	5.4
C(9)	389(2)	379(1)	167(2)	6.0
C(10)	328(1)	339(1)	291(2)	4.8
C(11)	505(1)	280(1)	767(1)	5.4
C(12)	27(2)	313(1)	628(2)	10.4
C(13)	52.(1)	288(1)	30(2)	4.3
C(14)	54(2)	330(1)	170(2)	7.3
C(15)	−47(1)	384(1)	936(1)	3.9
C(16)	−166(1)	354(1)	11(2)	6.6
H(1)	228	415	608	4
H(2)	190	446	924	1
H(3)	287	330	840	3

doubt due to the coordination by the yttrium atom of one more ligand: the H atom located practically within the bisector plane of the wedge like sandwich.

As a result of complexing with $AlH_3 \cdot NEt_3$, the yttrium atom acquires an eighteen-electron configuration and thus engages all its valence orbitals. The geometry of its surroundings then becomes the same as in electronically-saturated niobium and tantalum trihydrides [5]. Naturally, the increase of the coordination number of the yttrium atom to nine (on the assumption that the Cp groups are tridentate ligands) results in a certain increase in bulk of the  $Cp_2Y\overset{Cl}{\underset{Cl}{\langle\;\rangle}}YCp_2$ fragment as compared with an individual dimer molecule $(Cp_2YCl)_2$, in which the yttrium atom has the coordination number of 8 (a 16-electron configuration). Thus the lengths of the Y–C and Y–Cl bonds increase from 2.60 and 2.68 Å [4] to 2.64 and 2.77 Å, respectively. The YCl_2Y' rhomb becomes, as it does in complex I, somewhat stretched along the diagonal Y–Y′: ClYCl′, 81.4° in $(Cp_2YCl)_2$, reduces to 73.8° in complex II.

As in I, the fragments $Cp_2YCl_2YCp_2$ and $AlH_3 \cdot NEt_3$ are also bonded in the compound under consideration by the secondary Al---Cl bond whose length is 3.00 Å. Despite the fact that Al and Cl atoms are quite a long distance apart, the following evidence indicates that there is a weak interaction between them. The Cl, Y, Al and H atoms lie in the same plane and, therefore, any rotation of the

TABLE 2

BONDS LENGTHS d AND VALENCE ANGLES ω IN II

Bond	d(Å)	Bond	d(Å)	Bond	d(Å)
Y–C(1)	2.66(2)	C(1)–C(2)	1.37(3)	Al–N	2.045(9)
Y–C(2)	2.63(2)	C(2)–C(3)	1.24(2)	Al–H(1)	1.8(1)
Y–C(3)	2.66(2)	C(3)–C(4)	1.31(3)	Al–H(2)	1.5(1)
Y–C(4)	2.63(2)	C(4)–C(5)	1.36(2)	Al–H(3)	1.5(1)
Y–C(5)	2.65(2)	C(5)–C(1)	1.48(2)	N–C(11)	1.49(2)
Y–C(6)	2.64(2)	C(6)–C(7)	1.43(2)	N–C(13)	1.50(2)
Y–C(7)	2.63(2)	C(7)–C(8)	1.38(2)	N–C(15)	1.50(2)
Y–C(8)	2.63(2)	C(8)–C(9)	1.38(2)	C(11)–C(12)	1.48(3)
Y–C(9)	2.63(2)	C(9)–C(10)	1.33(2)	C(13)–C(14)	1.47(3)
Y–C(10)	2.65(2)	C(10)–C(6)	1.38(3)	C(15)–C(16)	1.49(2)
Y–Cl	2.710(5)	Y ⋯ Y′	4.38	Y–Cp(1) [a]	2.38
Y–Cl′	2.769	Y ⋯ Al	3.62	Y–Cp(2) [c]	2.37
Y–H(1)	2.1(1)	Al⋯Cl	3.00(1)		
Angle	**ω(°)**	**Angle**	**ω(°)**	**Angle**	**ω(°)**
Cl–Y–Cl′	73.8(1)	Y–H(1)–Al	136(7)	N–Al–H(1)	106(6)
Y–Cl–Y′	106.2(1)	N–Al⋯Cl	176.2(6)	N–Al–H(2)	104(4)
Cl–Y–H(1)	74(4)	$(C–C–C)_{aver.}$	108	N–Al–H(3)	101(6)
Al–N–C(11)	109(1)	C(11)–N–C(13)	103(2)	H(1)–Al–(2)	112(8)
Al–N–C(13)	107(1)	C(11)–N–C(15)	114(1)	H(1)–Al–H(3)	120(7)
Al–N–C(15)	112(1)	C(13)–N–C(15)	112(1)	H(2)–Al–H(3)	113(7)
N–C(11)–C(12)	113(2)	N–C(13)–C(14)	113(1)	H–C(15)–C(16)	118(1)

[a] Cp is the corresponding RMS plane.

$AlH_3 \cdot NEt_3$ molecule about the Y–H direction will increase the distance between Al and Cl (cf. Fig. 1). This means that the $AlH_3 \cdot NEt_3$ fragment cannot be in any other orientation except the one assuring the shortest possible contact between Al and Cl atoms. It is interesting that the lengths of the Y–Cl′ and Y′–Cl bonds that are parallel with the Al–N direction are thereby increased by 0.06 Å. Further, in trialkylaminalanes of composition $AlH_3 \cdot NR_3$ the four-coordinated Al atom has a tetrahedral environment and the Al–N distance in $AlH_3 \cdot NBu_3$ is 1.98(2) Å [6]. When the coordination number of Al in $AlH_3 \cdot 2NMe_3$ rises to 5 the Al–N distance increases to 2.18(1) Å [7]. In our case the interatomic distance Al–N of 2.045(9) Å is intermediate between the values typical of four- and five-coordinated aluminum. The decrease of the valence angles in HAlN compared with the tetrahedral one is indicative of the tendency of AlH_3 to become flatter. The practically total similarity of the geometry of Al in compounds I and II is an important argument in favor of the existence of the secondary Al⋯Cl bond.

It should be noted that in contrast to the reported data [8], according to which an increase of the coordination number of Al in its hydrides from 4 to 5 must shift the ν(Al–H) band in the IR spectra to lower frequencies (1670–1720 cm^{-1}), we did not observe the predicted shift of ν(Al–H) either in complex I or II (ν(Al–H) in I = 1861 cm^{-1} and in II = 1825 cm^{-1}, i.e., in accordance with the classification [8], within the Al–H bond region typical of a four-coordinated Al atom). This fact may be attributed either to the weakness of the secondary, Al---Cl bond or, which is more probable, to the effect of the Y–H–Al bridge, the formation of which apparently inverts the expected dependence of the position of ν(Al–H) on the coordination number of the Al atom. A similar situation was observed in other compounds which contained bridging and terminal hydrogen atoms bonded to Al: in $Cp_2ReHAlH_3$ [9] and $(AlH_3)_n$ [10]. These observations permit one to conclude that the applicability of the empirical rule proposed [8] is limited only to structures having terminal H atoms.

The geometry of the triethylamine ligand in complex II is somewhat unusual. While in $AlH_3 \cdot NBu_3$ all the C–C bonds in the butyl chains are substantially perpendicular to the Al–N direction [6], in II only two bonds (C(11)–C(12) and C(13)–C(14)) are perpendicular to it, the third bond (C(15)–C(16)) being parallel to the direction. Possibly, such a distortion of the symmetry of the NEt_3 group is due to steric requirements imposed by molecular packing in the crystal.

The results of the investigation of the structure of II and the general characteristics of the formation of bimetallic complexes of the type in question allow us to conclude that addition of atoms possessing stronger accepting properties than the H atom (a chlorine atom, for example) to a molecular ligand $AlH_nX_{3-n} \cdot L$ destabilizes the bimetallic complexes. Thus, while $AlH_2Cl \cdot L$ still forms an unstable compound with Cp_2YCl, $AlHCl_2 \cdot L$ cannot react with this compound at all [11].

Experimental

Preparation of [$Cp_2YCl \cdot AlH_3 \cdot NEt_3)_2$

To a suspension of 2.4 g (9.47 mmol) of Cp_2YCl in 100 ml benzene (dried by boiling and distillation over $LiAlH_4$), stirred by a magnetic stirrer, were added 9.48 mmol of a triethylaminalane solution in 30 ml of benzene. Next day, when all Cp_2YCl was dissolved, the solution was evaporated to a volume of 5–8 ml and left to crystallize. The colorless transparent crystals were isolated from the solution and dried in vacuo. Found: Y, 22.51; Al, 6.47; Cl, 9.49. Calcd. for $Cp_2YClAlH_3NEt_3$: Y, 23.04; Al, 6.99; Cl, 9.19%.

Determination of the structure of ($Cp_2YCl \cdot AlH_3 \cdot NEt_3)_2$

As protection from the effect of atmosphere oxygen and moisture the crystals were placed in thin-walled glass capillaries. Using Mo-K_α radiation the principal crystallographic characteristics were found to be: monoclinic, $a = 12.325(5)$, $b = 18.780(7)$, $c = 8.848(2)$ Å; $\beta = 69.89(2)°$; space group $P2_1/a$, $Z = 2$, $M = 385.7$, $d_{calc.} = 1.33$ g/cm^3.

About 2000 reflections ($2\theta \leqslant 49°$) were collected by means of a four-circle Syntex P$\bar{1}$ diffractometer. The structure was solved by the direct method followed by Fourier syntheses. The positions of H atoms were localized with the help of differential Fourier synthesis. The full-matrix correction by the least-squares method in the unisotropic-isotropic (H atoms) approximation gave an R factor of 0.062 for 1284 reflections with $F > 3\sigma(F)$. The coordinates of symmetrically independent atoms are listed in Table 1.

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