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ALUMOHYDRIDE COMPLEX OF YTTRIUM WITH THREE-COORDINATED HYDROGEN ATOMS. THE CRYSTAL AND MOLECULAR STRUCTURE OF $\{[(\eta^5\text{-}C_5H_5)_2Y(\mu_3\text{-}H)][(\mu_2\text{-}H)AlH_2\cdot OC_4H_8]\}_2$

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Summary

The structure of the "alumohydride" tetrahydrofuronate of yttrium bis(η^5-cyclopentadienyl) was determined using X-ray analysis. The dimeric molecule involves the $Cp_2Y(\mu_3\text{-}H)_2YCp_2$ metallocycle, connected to the $AlH_3\cdot THF$ groups via the μ_2- and μ_3-hydrogen atoms (Y–μ_3-H 2.17, 2.23 Å; Al–μ_3-H 2.00 Å). The Y, Al and O atoms, as well as the bridging H atoms, are situated within the bisector plane of the wedge-like sandwiches Cp_2Y.

Introduction

The structural chemistry of transition metal alumohydrides, which is of both theoretical and practical interest, has in the past been studied rather poorly. Previously we synthesized solvates of the "alumohydride" of yttrium biscyclopentadienyl with the overall formula $(C_5H_5)_2YAlH_4\cdot L$, where L = NEt_3 (I), C_4H_8O (II), Et_2O (III), and $(Cp_2YAlH_4)_2\cdot OEt_2$ (IV) [1]. The X-ray study of I and IV showed that these compounds lack the isolated AlH_4 groups, which are characteristic of ionic alumohydrides of the alkali and alkali-earth metals, but the Lewis base molecule is bonded to the aluminium atom [1]. In this case the hydrogen atoms failed to be localized, and the nature of the linkage between the alumohydride group and the yttrium atom was established using IR spectroscopy and comparing the structural data for I and IV with those of the similar complexes $[(Cp_2YCl)_2AlH_3\cdot OEt_2]_n$ (V) [2], $(Cp_2YCl)_2(AlH_3\cdot NEt_3)_2$ (VI) [3], and $[(C_5H_4Me)_2YH\cdot THF]_2$ (VII) [4].

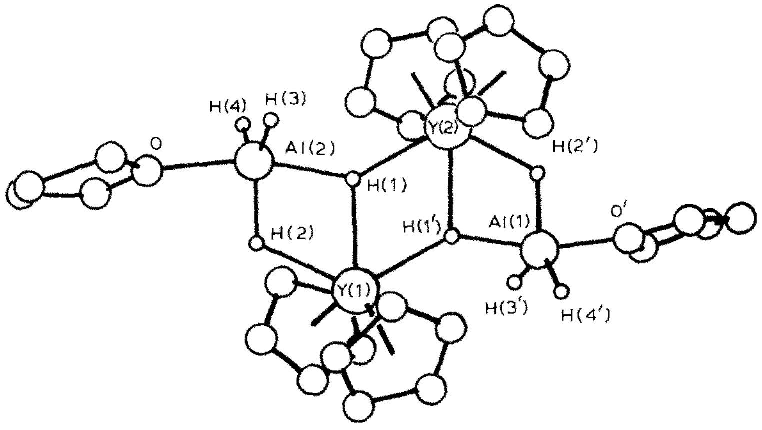

Fig. 1. Molecular structure of $\{[(\eta^5\text{-}C_5H_5)_2Y(\mu_3\text{-}H)][(\mu_2\text{-}H)AlH_2 \cdot OC_4H_8]\}_2$.

The present paper reports the X-ray data for the $(Cp_2YH)_2(AlH_3 \cdot THF)_2$ (II) complex obtained previously by us, which confirm the proposed structure for the $Cp_2YAlH_4 \cdot L$ type complexes suggested in ref. 1.

Results and discussion

Colourless, transparent crystals of the tetrahydrofuronate alumohydride of yttrium biscyclopentadienyl, $(C_5H_5)_2YAlH_4 \cdot C_4H_8O$, were isolated by fractional crystallization from the solution obtained upon interaction of stoichiometric quantities of Cp_2YCl and $NaAlH_4$ in THF. The crystals are composed of dimeric, symmetrical $\{[(\eta^5\text{-}C_5H_5)_2YH][AlH_3 \cdot OC_4H_8]\}_2$ molecules (II) (Fig. 1). The Y, Al, O, H(1), and H(2) atoms are situated practically in one plane *, which is the bisector plane for both wedge-like sandwiches Cp_2Y.

The positions of the non-hydrogen atoms within the molecule II are very close to those in the molecule of the amine complex I. In addition, almost total coincidence of the vibrational frequencies for the metal–hydrogen bonds is observed in the IR spectra of both complexes which thus proved to be the structural analogues, as we had supposed previously [1]. The main structural feature of II is the dimer $Cp_2YH_2YCp_2$ connected to two aluminium hydride tetrahydrofuronate molecules. The geometry of the wedge-like sandwiches Cp_2Y, having a staggered conformation, is, on the whole, common to yttrium biscyclopentadienyl complexes. The Y ··· C distance and the CpYCp angle (Table 1) are close to the corresponding values (2.36 Å and 127.5°) for the ether-solvated complex $[(Cp_2YCl)_2AlH_3 \cdot OEt_2]_n$ (V) [2].

The Y ··· Y distance in II (3.753 Å) is close to the analogous value for M ··· M in the yttrium biscyclopentadienylhydride complexes I (3.70 Å) [1] and VII (3.66 Å) [4] with the nine-coordinated yttrium atoms (with C_5H_5 being assumed to occupy three coordination positions). The length of the Y–H bond for the dimer moiety $Cp_2YH_2Cp_2$ of II (Table 1) is close to that of the Y–H bond in complex VII (2.17

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* The Al atoms are slightly deviated from this plane (by ca. 0.1 Å).

TABLE 1

BOND LENGTHS, d (Å)

Bond	d	Bond	d
Y(1)-Y(2)	3.753(1)	Al-O	1.972(1)
Y(1)-Al(2)	3.242(3)	Al-H(1)	2.0(1)
Y(1)-Al(1)	3.989(3)	Al-H(2)	1.57(6)
Y(1)-H(1)	2.18(6)	Al-H(3)	1.49(6)
Y(1)-H(1′)	2.3(6)	Al-H(4)	1.46(8)
Y(1)-H(2)	2.17(6)		

and 2.19 Å) [4]. The YH_2Y metallocycle is more asymmetric than that of VII.

The geometry of the aluminium hydride monotetrahydrofuronate moiety is distinctly different from that of usual tetrahedral alanes $AlH_3 \cdot L$, as in the case of the $AlH_3 \cdot OEt_2$ moiety in complex V [2]. The AlH_3 moiety, in which one of the hydrogen atoms, H(2), is a bridging atom while the other two are terminal, belongs to the plane perpendicular to the Al–O axis. The HAlH angles within the AlH_3 moiety are close to 120° (Table 2), i.e. the coordination polyhedron for the aluminium atom is a distorted trigonal bipyramid. The one axial position is occupied by the oxygen atom of the tetrahydrofurane molecule which is practically unaffected on complex-forming. The second axial position is occupied by H(2) belonging to the YH_2Y metallocycle.

The Al–H(1) distance is equal to 2.0 Å (2.1 Å for I [1]); while being noticeably greater than the Al–μ_2-H(2) distance (1.6 Å) it, nevertheless, corresponds to the direct electrovalent Al–H interaction.

Thus, H(1) in molecule II is a three-coordinated atom. It should be noted that in certain clusters involving the μ_3-hydrogen atom the latter is situated off the plane formed by the metal atoms, whereas in I, II and the $[(Cp_2ErH)_3Cl]^-$ anion [5] the hydrogen atom belongs to this plane. The data obtained substantiate the suggestion, put forward in ref. 1, on the presence of the μ_3-H within the structures of complexes I–IV. The solvates of yttrium alumohydride biscyclopentadienyl are the first examples of compounds in which the μ_3-atoms are connected with both transition and non-transition metals, and the first representatives of aluminium hydride compounds involving three-coordinated hydrogen atoms.

TABLE 2

BOND ANGLES, ω (°)

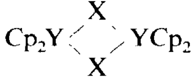
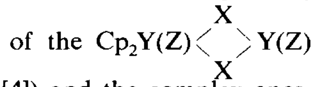
Angle	ω	Angle	ω
Y(1)-H(2)-Al(2)	120(3)	H(4)-Al(2)-H(2)	122(3)
Y(1)-H(1)-Y(2)	117(3)	H(4)-Al(2)-H(3)	121(4)
Y(1)-H(1)-Al(2)	102(3)	H(1)-Al(2)-O	164(2)
Y(2)-H(1)-Al(2)	142(3)	H(1)-Al(2)-H(3)	86(3)
H(2)-Al(2)-H(1)	77(3)	H(1)-Al(2)-H(4)	99(3)
H(2)-Al(2)-O	88(2)		
H(3)-Al(2)-O	98(2)		
H(4)-Al(2)-O	93(3)		
H(3)-Al(2)-H(2)	116(3)		

The Al–μ_3-H bond is longer, and, correspondingly, less strong than the Al–μ_2-H bond (1.57 Å). The latter fact is in agreement with the literature data on the weakening of the M–H bond in the μ_3-bridge as compared with the μ_2-bridge, as well as with the noticeable shift (by ca. 230 cm^{-1}) of the frequency $\nu(Y_2HAl)$ (1069 cm^{-1}) as compared with the frequency ν(Y–H–Al) [1].

The transition from the weak secondary bond Al $\cdots$ Cl in V to the bridging bond Al–H(1) in II results in the essential weakening of the Al–O bond, which is elongated from 1.89 Å in V [2] up to 1.97 Å in II despite the greater basicity of the THF molecule as compared with Et_2O. Similar elongation of the Al–N bond (by ca. 0.09 Å) was observed upon substitution of Cl for H within the $(Cp_2YX)_2(AlH_3 \cdot NEt_3)_2$ complexes [1,3].

The value of the O–Al–H(1) bond angle (164°) is close to that of the O–Al–Cl angle in V (161°) [2], as well as to the angle between the axial ligands H–Al–H for the oxygen-containing trigonal-bipyramidal polyhedron around the Al atom within complex IV [1]. The values for the similar angle N–Al–μ_3-H and N–Al–Cl within the amine-solvated complexes I and VI are likewise close to each other (177 [1] and 176° [3], respectively).

Besides the bridges involving μ_3-H, the alumohydride groups within II * are bonded to the yttrium atoms via ordinary hydrogen bridges Y–H(2)–Al. The metal–hydrogen bond lengths for the latter compound are close to those found for complexes V [2] and VI [3], and that estimated for complex I [1]. Comparing the Y $\cdots$ Al distances for the complexes $Cp_2YAlH_4 \cdot NEt_3$ (3.30 Å) [1], $Cp_2YAlH_4 \cdot THF$ (3.24 Å), and $(Cp_2YAlH_4)_2 \cdot Et_2O$ (3.20 Å) [1], one can arrive at the conclusion that the former are determined by the strength of the Al–L bond, and vary according to the change in the basicity of the ligands within the series $NEt_3 > THF > Et_2O$. The third valent orbital of the Cp_2Y moiety is used to form the Y–H(2)–Al bridge, which leads to saturation of the coordination capabilities of the yttrium atom and to the latter acquiring an 18-electron configuration. The structure of the Cp_2YH_3 moiety in II is very close to that of the niobium and tantalum trihydrides Cp_2MH_3 [6]. The H(1)YH(2) and H(1)YH(1′) bond angles for II are equal to 62 and 63°, respectively, together equalling 125° (126° for Cp_2MH_3 [7]). In this case, the "unbending" angle formed by the Cp(1)–Y–Cp(2) and the Y–Y axis amounts to 30°, i.e. the symmetry axis of the Cp_2Y moiety practically coincides with the Y–H(1) axis, as in the case of Cp_2MH_3.

It is well known that the characteristic feature of yttrium biscyclopentadienyl complexes is their inclination to dimerize to give metallocycles  $Cp_2Y\overset{X}{\underset{X}{\langle\;\rangle}}YCp_2$ (X = H, Cl, R). It is the presence of the small hydride ligands within the nearest environment of the Y atom that enables 18-electron coordination saturated complexes of the  $Cp_2Y(Z)\overset{X}{\underset{X}{\langle\;\rangle}}Y(Z)Cp_2$ type to be realized. Both the usual ligands (THF [4]) and the complex ones (the alanes $AlH_3 \cdot L$) may serve as the Z ligands.

The results obtained indicate the covalent bonding of the alumohydride group

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* It should be kept in mind that the name "alumohydride" in the case considered is a purely formal one since, as emphasized in ref. 1, the present type of compound has to be singled out as a new type of aluminium hydride compounds, the alanes, which involve the "usual" organic ligands THF, NR_3, Et_2O as one of the ligands, and the organometal as the second ligand.

with the transition metal atom in II and the other alumohydride complexes of Cp_2Y. As distinguished from the AlH_4^- anion groups, the former is solvated with the Lewis base to increase the coordination number of the Al atom to 5. At the same time, the borohydride analogue of complex II, $Cp_2YBH_4 \cdot THF$, as well as the complex $Cp_2LnBH_4 \cdot THF$ (Ln = Yb, Pr, Sm, Nd, La), is solvated at transition metal atom [7] with the bidentate BH_4 group maintained, resulting also in the 18-electron complex. It is the ability to increase the aluminium coordination number up to 5 that, apparently, will determine the distinctions in the structural chemistry of covalent alumohydrides and borohydrides of transition metals.

Experimental

The synthesis of $(Cp_2YH)_2(AlH_3 \cdot OC_4H_8)_2$ was described in ref. 1. Crystals are monoclinic, a 8.750(2), b 11.043(3), c 16.453(3) Å, γ 95.57(2)°, space group $P2_1/b$, $Z = 2$, $d_{calc.}$ 1.36 g cm^{-3}. 1281 reflections were recorded using a Syntex $P\bar{1}$ automatic diffractometer, μ 38.4 cm^{-1} (corrected for extinction). The structure was solved using the direct method and refined in the anisotropic-isotropic (H atoms) approximation up to $R = 0.041$. Atomic coordinates can be obtained from the authors.

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