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Dicyclopentadienyl-yttrium and -aluminium hydridochloride complexes. Crystal and molecular structure of $[(\eta^5\text{-}C_5H_5)_2Y(\mu_2\text{-}Cl)(\mu_3\text{-}H)Y(\eta^5\text{-}C_5H_5)_2](\mu_2\text{-}H)_2AlH \cdot NEt_3 \cdot C_6H_6$: a new type of coordination of the AlH_4 moiety

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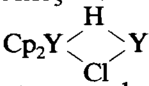
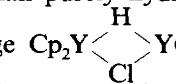
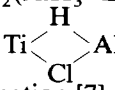
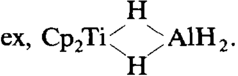
Abstract

The interaction of two equivalents of Cp_2YCl with one equivalent of $LiAlH_4$ gives the hydride complex $(Cp_2YH)_2(AlH_3OEt_2)_2$ (I), described previously, or the hydrido-chloride complexes $(Cp_2Y)_2AlH_4Cl \cdot L$ ($L = NEt_3$ (II), and $L = THF$ (III)). The complexes II and III can also be obtained from the reaction Cp_2YCl and $AlH_3 \cdot L$. The X-ray data indicate that complex II is made up of the fragment  $Cp_2Y\overset{H}{\underset{Cl}{<>}}YCp_2$, linked to the $AlH_3 \cdot NEt_3$ moiety via two μ_2 and μ_3 hydrogen atoms, and solvated benzene molecules. On the basis of the IR data complex III is assigned the following structure $Cp_2Y(\mu_2\text{-}H)_2Al(Cl)(\mu_2\text{-}H)_2YCp_2 \cdot 2THF$.

Introduction

The alumohydride complexes of the transition and rare earth metals have attracted attention in regard to the chemistry of heteronuclear compounds because of their potential, or already established catalytic activity, in processes involving hydrogen transfer. Of these compounds the 17-electron alumohydride complexes of titanocene, which are catalysts for the isomerization and hydrogenation of olefins [1,2], are the most notable. Unfortunately, the attempts undertaken to synthesize the alumohydride complexes of yttriecene have led only to the electron-saturated compounds of the type $((C_5H_5)_2YX)_2(AlH_3L)_n$(I), where $X = Cl$, $n = 1$, 2 [3,4], $X = H$, $n = 2$ [4–6], $C_5H_5 = Cp$, $L = Et_2O$, THF, NEt_3. The structures of all these complexes contain a stable dimeric fragment, $(Cp_2YX)_2$, connected to the two $AlH_3 \cdot L$ fragments by bridging hydrogen bonds, which endow the yttrium atoms with an 18-electron environment. This is probably the main reason for the lack of any noticeable catalytic activity by these compounds in hydrogenation and isomerization reactions. Taking into account the fact that the combined bridges are, as a rule, more labile than purely hydride or purely haloid ones, complexes with the heteronuclear bridge  $Cp_2Y\overset{H}{\underset{Cl}{<\;>}}YCp_2$, e.g. the complex $(Cp_2Y)_2AlH_4Cl$, should have properties different from those of the complex $(Cp_2YX)_2(AlH_3 \cdot L)_2$. In fact, the complex $(Cp_2Ti)_2AlH_4Cl$, which is presumed to have the  $Ti\overset{H}{\underset{Cl}{<\;>}}Al$ linkage in solution, shows a high catalytic activity during olefin hydrogenation [7], which is in contrast to the inactive complex,  $Cp_2Ti\overset{H}{\underset{H}{<\;>}}AlH_2$.

Here we report the results of a study of the reaction between Cp_2YCl and $LiAlH_4$ (with a reagent ratio of 2 : 1) and describe the crystalline products formed; the parallel synthesis of the products from Cp_2YCl and $AlH_3 \cdot L$ is also discribed.

Experimental

The synthesis and study of the complexes as carried out under conditions, such that contact with air by compounds studied was precluded, was as described previously [3,5].

Synthesis of $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$

Method A. To a solution of 1.2 g of Cp_2YCl (4.6 mmol) in 70 ml of benzene was added with stirring a mixture of 9 ml of $LiAlH_4$ (2.3 mmol) and 1 ml of triethylamine in diethyl ether. An hour later the precipitated lithium chloride was filtered off through a glass filter. The solution was evaporated to about 25 ml, decanted from the precipitate, and the volume reduced to about 10 ml, and kept for 48 h for crystallization. The white crystals (0.5 g) were separated from the solution and dried in vacuo. More crystals, but of an irregular hexagonal form, were isolated from the mother liquor. Anal. Found: Y, 25.74; Al, 3.77; Cl, 5.29. $(Cp_2Y)_2ClAlH_4 \cdot NEt_3 \cdot C_6H_6$ calc.: Y, 26.0; Al, 3.94; Cl, 5.18%.

Method B. To of a solution of $AlH_3 \cdot NEt_3$ (4.7 mmol) in benzene (25 ml) prepared as described in ref. 8, was added an equimolar amount of a solution of Cp_2YCl in 90 ml of benzene. After 24 h the solution was filtered and evaporated to about 15 ml. The precipitated crystals were separated from solution and dried in vacuo. The IR spectrum of the crystals was identical with that of the compound obtained by Method A. Found: Y, 25.57; Al, 3.87; Cl, 5.25%.

Synthesis of $(Cp_2Y)_2AlH_4Cl \cdot 2THF$

Method A. To a solution of 1.27 g of Cp_2YCl (4.99 mmol) in 50 ml of THF was added 10 ml of a solution of aluminium hydride (5.1 mmol) in THF and the white precipitate (0.6 g) that formed was filtered off and dried. The volume of the solution was reduced to about 10 ml by evaporation and an extra 0.3 g of the compound was isolated. Anal. Found: Y, 27.3; Al, 4.0; Cl, 5.8; C, 46.1; H, 5.55. $(Cp_2Y)_2AlH_4Cl \cdot 2C_4H_8O$ calc.: Y, 27.40; Al, 4.16; Cl, 5.46; C, 51.8; H, 6.21%.

Method B. To a solution of 1.13 g of Cp_2YCl (4.44 mmol) in 80 ml of THF was added dropwise 8 ml of $LiAlH_4$ (2.2 mmol) in THF. The solution was evaporated to 30 ml, and 100 ml of benzene was added. A small amount of a colloidal precipitate

Table 1

Coordinates of atoms ($\times 10^4$) and equivalent isotropic thermal parameters B_{iso}^{eq} (Å $\times 10^3$) [a]

Atom	*x*	*y*	*z*	B_{iso}^{eq}
Y(1)	3312(1)	6166(1)	3934(1)	43(1)
Y(2)	3022(1)	6112(1)	601(1)	43(1)
Al	1813(2)	4940(1)	2411(2)	43(1)
C(1)	4796(9)	5744(7)	3600(10)	70(6)
C(2)	4324(8)	5382(6)	4515(14)	72(6)
C(3)	4433(11)	5823(10)	5416(11)	93(8)
C(4)	4971(12)	6475(8)	5047(17)	106(9)
C(5)	5213(8)	6440(8)	3926(14)	85(7)
C(6)	1814(10)	6591(8)	4182(10)	96(8)
C(7)	2612(11)	7095(6)	4666(12)	85(7)
C(8)	2909(9)	6852(6)	5600(11)	84(6)
C(9)	2294(10)	6182(7)	5787(11)	92(7)
C(10)	1611(9)	6014(6)	4911(12)	94(7)
C(11)	4853(9)	6191(2)	287(14)	102(8)
C(12)	4609(9)	6476(6)	−622(12)	114(7)
C(13)	3919(10)	5952(9)	−1264(8)	133(10)
C(14)	3791(11)	5370(9)	−635(22)	108(9)
C(15)	4334(14)	5520(9)	257(15)	94(8)
C(16)	1564(9)	6590(7)	814(9)	83(7)
C(17)	1180(8)	5954(7)	251(14)	85(7)
C(18)	1595(11)	6022(8)	−794(12)	90(7)
C(19)	2226(10)	6690(8)	−920(9)	88(7)
C(20)	2220(8)	7039(5)	72(11)	88(6)
N	1463(5)	3874(4)	2330(6)	49(3)
C(21)	1247(8)	3539(5)	3464(9)	66(5)
C(22)	385(8)	3633(6)	4060(9)	83(6)
C(23)	585(7)	3634(5)	1554(9)	63(5)
C(24)	155(7)	2867(5)	1322(10)	79(5)
C(25)	2285(7)	3699(5)	1778(9)	66(5)
C(26)	3260(8)	3957(6)	2380(11)	83(6)
Cl	3970(2)	7098(1)	2186(2)	62(1)
C(27)	2404(8)	8473(6)	7376(9)	97(6)
C(28)	1704(9)	8387(6)	6582(11)	97(7)
C(29)	1101(9)	8762(8)	6722(13)	103(7)
C(30)	1170(11)	9182(8)	7642(15)	123(9)
C(31)	1915(11)	9256(7)	8395(12)	106(7)
C(32)	2511(9)	8909(7)	8259(10)	99(7)
H(1)	2630(57)	5852(42)	2327(61)	6(27)
H(2)	893(57)	5022(41)	2576(61)	66(27)
H(3)	2142(53)	4927(38)	1193(65)	36(27)
H(4)	2337(53)	4964(38)	3696(65)	12(27)

[a] Equivalent isotropic *B* defined as one third of the trace of the ortogonalized *B*(*I*,*J*) tensor.

Table 2

Bond lengths (Å) and bond angles (°) in $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$ (II)

Y(1)-Y(2)	3.951(3)	Al-N	2.087(8)
Y(1)-Al	3.244(3)	Y(2)-Al	3.245(3)
Y(1)-Cl	2.756(5)	Y(2)-Cl	2.753(5)
Y(1)-H(1)	2.13(7)	Y(2)-H(1)	2.13(7)
Y(1)-H(4)	2.41(8)	Y(2)-H(3)	2.44(8)
Y(1)-CpI [a]	2.36	Y(2)-CpIII	2.37
Y(1)-CpII	2.35	Y(2)-CpIV	2.35
Al-H(1)	1.85(7)	N-C(21)	1.49(1)
Al-H(2)	1.42(9)	N-C(23)	1.51(1)
Al-H(3)	1.52(8)	N-C(25)	1.51(2)
Al-H(4)	1.69(8)	$(C-C)_{av}$ (in Cp rings)	1.37
Y(1)-Cl-Y(2)	91.6(1)	Y(1)-H(1)-Y(2)	136
Cl-Y(1)-H(1)	63.8	Cl-Y(2)-H(1)	63.8
H(1)-Y(1)-H(4)	62.6	H(1)-Y(2)-H(3)	58.2
Y(1)-H(4)-Al	103	Y(2)-H(3)-Al	108
Y(1)-H(1)-Al	109	Y(2)-H(1)-Al	109
H(1)-Al-H(2)	100(4)	H(2)-Al-H(3)	117(4)
H(1)-Al-H(3)	83(4)	H(2)-Al-H(4)	108(4)
H(1)-Al-H(4)	84(3)	H(3)-Al-H(4)	135(4)
H(1)-Al-N	155(3)	H(3)-Al-N	84(3)
H(2)-Al-N	104(3)	H(4)-Al-N	91(3)
Al-N-C(21)	112.6(6)	C(21)-N-C(23)	112.2(7)
Al-N-C(23)	103.8(6)	C(21)-N-C(25)	109.3(8)
Al-N-C(25)	110.8(5)	C(23)-N-C(25)	108.0(7)
Y(1)-Al-N	134.4(3)	Y(2)-Al-N	128.9(2)
CpI-Y(1)-CpII	129.0	CpIII-Y(2)-CpIV	128.9
Y(1)-Y(2)-H(1)/ Y(1)-Y(2)-Cl	148	Y(1)-H(1)—Cl/ Y(2)-H(1)-Cl	160

[a] CpI is the root-mean-square plane of the Cp-ring C(1)-C(5).

was filtered off, the solution was reduced in volume to 20 ml. The white microcrystalline precipitate was filtered and dried. The IR spectrum of the precipitate was identical to that of the compound obtained by Method A. Anal. Found: Y, 27.2; Al, 4.3; Cl, 5.6.

Determination of the structure of $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$

The X-ray analysis of a crystal, packed in a glass capillary, was performed using "Nicolet P3" diffractometer (Mo-K_α irradiation, graphite monochromator, $\theta/2\theta$ scan to $2\theta \leqslant 48°$). The crystals are monoclinic, $a = 14.538(3)$, $b = 20.721(7)$, $c = 11.793(3)$ Å, $\gamma = 110.65(2)°$, space group $P2_1/b$, $Z = 4$, $\rho = 1.37$ g/cm^3. 1408 reflections with $I \geqslant 3\sigma(I)$ of the 2639 independent ones were used in the calculations, extinction was neglected ($\mu_{Mo} = 37.2$ cm^{-1}). The structure was solved by combination of the direct method and the Patterson method, and refined by the least-squares method to an anisotropic-isotropic (for H atoms) approximation up to $R = 0.050$ ($R_w = 0.047$). The atomic coordinates are listed in Table 1, the main interatomic distances and bond angles are given in Table 2.

Results and discussion

According to the literature data, the interaction of the equimolar amounts of Cp_2TiCl and $LiAlH_4 \cdot L$ ($L = OEt_2$, THF, NEt_3) (eq. 1) gives the 17-electron complexes $(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2AlH_2$ [9]:

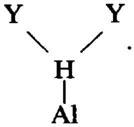
$$(Cp_2TiCl)_2 + 2LiAlH_4 \xrightarrow{L} 2Cp_2TiH_2AlH_2 \cdot L + 2LiCl \qquad (1)$$

The same starting materials, but taken in a 2 : 1 ratio, in ether or in a mixture of OEt_2 and C_6H_6, gave an unsolvated three-nuclear complex, $(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(Cl)(\mu_2\text{-}H)_2Ti(\eta^5\text{-}C_5H_5)_2$, which was isolated as an individual compound [7]. If $(Cp_2TiCl)_2$ is replaced in this reaction by $(Cp_2YCl)_2$, which is similar to the former in structure but different in that the yttrium atom has a vacant $1a_1$ orbital (in $(Cp_2TiCl)_2$ this orbital is occupied by a single electron), then with a Y : Al ratio of 1 : 1, the reaction proceeds according to the eq. 1a, which is similar to eq. 1, but the structure of the 18-electron complexes (type I) differs radically from that of their titanium analogs, as follows from data in the literature [5,6,10].

$$(Cp_2YCl)_2 + 2\ LiAlH_4 \xrightarrow{L} (Cp_2YH)_2(AlH_3 \cdot L)_2 + 2\ LiCl \qquad (1a)$$

The complex $(Cp_2YH)_2(AlH_3 \cdot OEt_2)_2$ crystallizes from solution not only when the reagents are present so as to maintain a $Cp_2YCl : LiAlH_4$ ratio of 1 : 1, but also when this ratio is 2 : 1. The formation of coordination- and electron-saturated compounds is evidently the reason why the system ($2Cp_2YCl + LiAlH_4$/ether) shows no catalytic activity in the hydrogenation and isomerization of α-olefins. Nevertheless, hexene-1 does interact with this system and gives alkyl complexes, which liberate hexane upon hydrolysis.

When the ether in this system is replaced by a stronger base, such as THF or a tertiary amine, the stability of the complexes with a Y to Al ratio of 2 to 1 increases. Thus reaction 1a when carried out in the presence of triethylamine, yields a complex of composition $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$ (II). In tetrahydrofuran the direction of the reaction also changes with the change in Y : Al ratio; in this case the reaction yields a compound which is similar to the titanium derivative but solvated with two THF molecules, $(Cp_2Y)_2AlH_4Cl \cdot 2THF$ (III).

The IR spectrum for II, in the region of the metal–hydrogen bond vibration region showed the same set of absorption bands as in the spectrum of the complex $(Cp_2YH)_2(AlH_3 \cdot NEt_3)_2$ (Ia) [5] (Fig. 1). From this fact and by analogy with ref. 5, it can be concluded that the aluminium atom in II is penta-coordinated and solvated with a NEt_3 molecule. The presence of an absorption band at 1047 cm^{-1}, which was assigned in the complexes of type I to $\nu(Y_2HAl)$ [5], in the spectrum for II shows that the yttrium atoms are linked to the aluminium atom via a three-coordinated hydrogen atom,  . These conclusions were confirmed by the direct structural study on II.

According to the X-ray data, the crystal of II is made up of $(Cp_2Y)_2AlH_4Cl \cdot NEt_3$ and solvated benzene molecules, which occupy the lattice interstices. The molecule

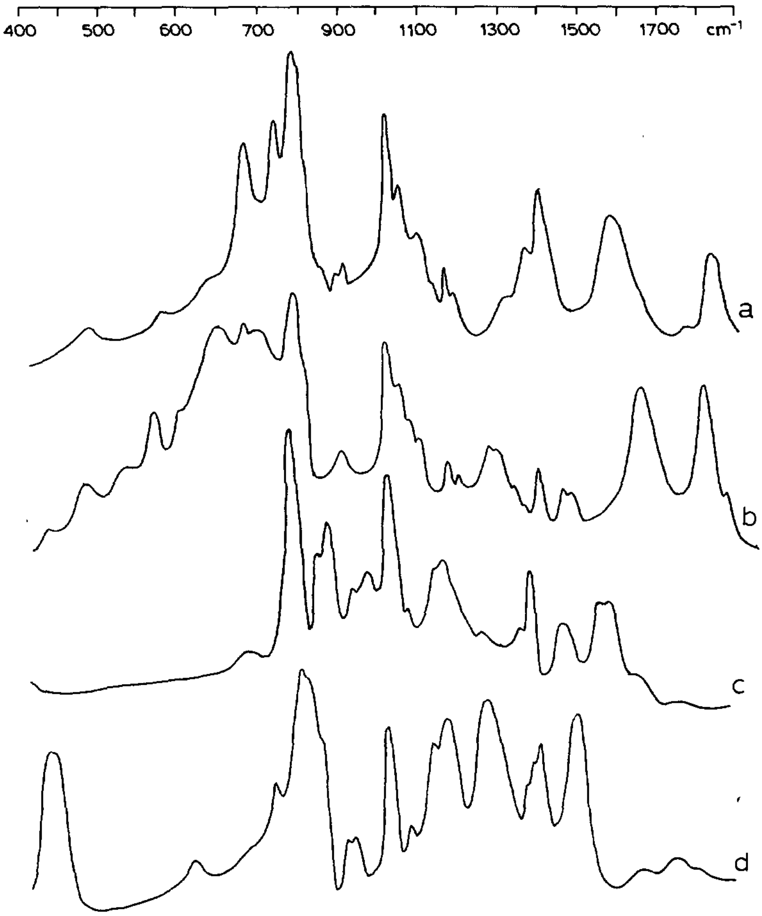


Fig. 1. IR spectra (KBr) of complexes: a – $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$ (II); b – $(Cp_2YH)_2(AlH_3 \cdot NEt_3)_2$ (Ia); c – $(Cp_2Y)_2AlH_4Cl \cdot 2THF$ (III); d – $(Cp_2Ti)_2AlH_4Cl$ [7].

II is made up of a $Cp_2Y\overset{H}{\underset{Cl}{\langle\,\rangle}}Cp_2$ fragment with the combined hydrido-chloride bridges, linked to the $AlH_3 \cdot NEt_3$ moieties via the bridging hydrogen atoms (Fig. 2). The parameters of the bent sandwiches Cp_2Y in II (the Cp–Y–Cp angle, average Y–C distance) (Table 2) are close to the corresponding parameters for the molecules $(Cp_2YH)_2(AlH_3 \cdot NEt_3)_2$ (Ia) (127.5° and 2.64 Å) [5] and $(Cp_2YCl)_2(AlH_3 \cdot NEt_3)_2$ (IV) (127.7° and 2.64 Å) [4]. In contrast to the metallocycles $Y\overset{H}{\underset{H}{\langle\,\rangle}}Y$ in I [5,6] and $Y\overset{Cl}{\underset{Cl}{\langle\,\rangle}}Y$ in IV [4], the metallocycle $Y\overset{H}{\underset{Cl}{\langle\,\rangle}}Y$ in II is not planar and is bent along the H(1)–Cl axis to give an angle of 160° between the Y atoms.

From structural data it follows unambiguously that the second part of the $AlH_3 \cdot NEt_3$ molecule is linked to the $Cp_2Y\overset{H}{\underset{Cl}{\langle\,\rangle}}YCp_2$ fragment by the H(1)–Al bond. In this case, the donor hydride atom H(1) acquires a three-coordinated

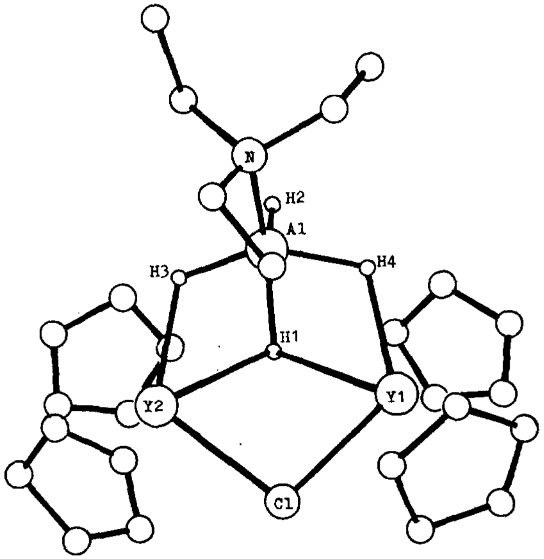


Fig. 2. Molecular structure of the complex $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$ (II).

environment, just as in the complexes of type I. However, in contrast to the latter complexes, the fragment $Y_2(\mu_3\text{-}H)Al$ in II is symmetric, and the M–H bond lengths in it are somewhat less than those found in $(Cp_2YH)_2(AlH_3 \cdot OC_4H_8)_2$ (Ib). Thus the Al–H bond length in II is 1.85(7) Å, as compared to 2.0 Å in Ib [6], and the Y–H bond length in II is 2.13 Å, as compared to 2.18(6) and 2.30(6) in Ib [6].

As in all the known complexes of $AlH_3 \cdot L \cdot L'$, such as, $(Cp_2YH)_2(AlH_3 \cdot NEt_3)_2$ [5] and $(Cp_2TiAlH_4)_2Me_2NC_2H_4NMe_2$ [11], the aluminium atom in II is found in the trigonal-bipyramidal environment $[H_4N]$. The angle formed by the axial ligands, N–Al–H(1), is 155.4°. The coordination polyhedron of the nitrogen atom, consisting of the atoms C(21), C(23), C(25) and Al, is almost a regular tetrahedron. The Al–N bond length in II (2.09(2) Å) is shorter than that in Ia (2.13(3) Å), but is longer than in the complex $(Cp_2YCl)_2(AlH_3 \cdot NEt_3)_2$ (2.05(1) Å), in which the aluminium atom is also coordinated by the weak secondary bond, Cl ··· Al [4].

The aluminium atom and the equatorial atoms H(2), H(3), H(4) in II occupy a single plane. The H(2) atom here is terminal while the atoms H(3) and H(4) are also linked to the yttrium atoms. The existence of the H(3)–Y(2) and H(4)–Y(1) interactions is evidenced by a series of structural features in molecule II. Thus, the bend of the metallocycle Y(1)H(1)Y(2)Cl along the H(1)–Cl axis ensures the valent contacts Y(1)–H(4) and Y(2)–H(3), and, on the other hand, provides a slightly distorted coordination polyhedron for the aluminium atom. The distances between the Y and the H(3), and H(4) atoms (2.41 and 2.44 Å, respectively) are essentially greater than the Y–H distances in molecules Ib and Ic (2.12(6) and 2.1(1) Å) [6,5], however, they do coincide, (within experimental error) with the Y–H bond lengths in the complex $(Cp_2YCl)_2AlH_3OEt_2$ (2.4(1) and 2.3(1) Å) [3] where they link the $(Cp_2YCl)_2$ and AlH_3OEt_2 fragments into a polymeric chain.

The atoms H(4), H(1), Cl, Y(1) (and, H(3), H(1), Cl, Y(2)) occupy a single plane (to within 0.15–0.18 Å), which is the bisecting plane of the bent sandwiches Cp_2Y.

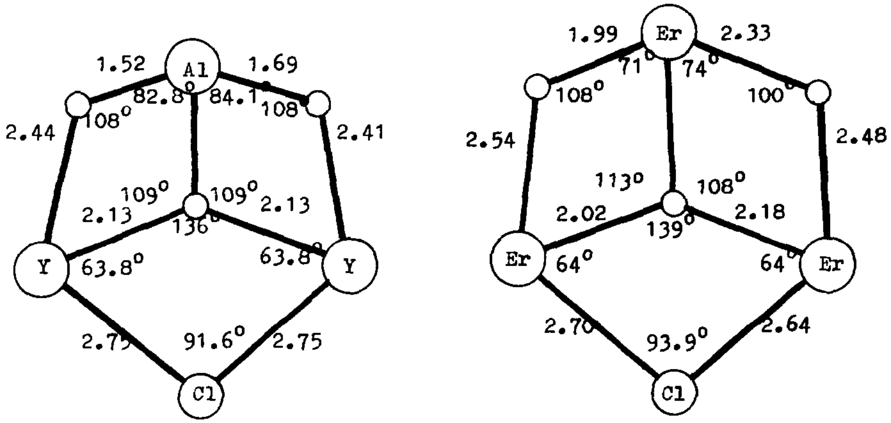


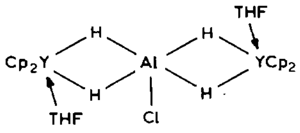
Fig. 3. Structure of the central nucleus of the complex $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$ (II) (a) and the anion $(Cp_2ErH)_3Cl^-$ [14] (b).

In this case, the symmetry axes of the bent sandwiches, which coincide with the central valence orbital $1a_1$ of these fragments, turn out to be directed towards the H(1) atom. The equality between the angles H(1)–Y(1)–Cl (63.8°) and H(1)–Y(1)–H(4) (62.6°) angles, and H(1)–Y(2)–Cl (63.8°) and H(1)–Y(2)–H(3) (58.2°), respectively, which coincide well with the H–Y–H angles in the complex Ic (62 and 63°) [6] and the H–M–H angles in Cp_2MH_3 (M = Nb, Ta) (63°) [12], are also evidence for coordinated H(3) and H(4) atoms in Cp_2YX_3.

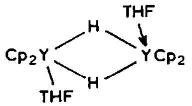
The occurrence of the Al-(μ_2-H) $\cdots$ Y linkages in structure II also follows from the electronic factors, since the existence of such bonds ensures an 18-electron electronic configuration for the yttrium atoms. Thus, in the complex $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$ a new type of coordination for the AlH_4 moiety, i.e. the bonding with two transition metal atoms via one μ_3 and two μ_2 hydrogen atoms was observed for the first time. It should be noted that such coordination by the alumohydride moiety was previously proposed by us for the complex $Cp_2Y(\mu\text{-}AlH_4 \cdot OEt_2)(\mu\text{-}AlH_4)YCp_2$, of which the coordinates for the hydrogen atoms were not determined [5]. It is noteworthy that the values of the Y–Al–O angles in this compound are very close to those of the Y–Al–N angles in the complex II (128.3 and 130.0° and 128.9 and 134.4°, respectively), this fact supports the suggestion put forward previously [5]. For the analog of the alumohydride moiety, BH_4, such coordination was observed only in the complex $Co_2(BH_4)_2(Ph_2P(CH_2)_5PPH_2) \cdot \frac{1}{2}C_6H_6$ [13].

From the above data it can be seen that II represents a three-metallic complex with a μ_3-hydrogen atom centred in a triangle formed by two Y atoms and one Al atom. In this respect it resembles very closely the three-metallic hydride complexes $(Cp_2LnH)_3R^-Li(THF)_4^+$, with R = H, Ln = Lu, Y; R = Cl, Ln = Er, and $(Cp_2^*YH)_2Cp_2^*ZrH_2$, ($Cp^* = CH_3C_5H_4$) [14,15], having the same central nucleus as II. The only difference is that in II one of the vertices of the triangle is occupied by an atom of a non-transition metal, Al, in place of a rare earth metal atom or Zr. The geometrical parameters of II and of the anion of the complex $(Cp_2ErH)_3Cl \cdot Li(THF)_4$ [14] (the only complex structurally studied) are given in Fig. 3. The figure shows that the geometry of the metallocycles YHClY and ErHClEr is nearly identical (which is supported by the closeness of the covalent radii of yttrium and erbium). The values of angles and bond lengths of that part of complex II that includes Al, obviously differ from the corresponding values for the erbium complex.

The complex $(Cp_2Y)_2AlH_4Cl \cdot 2THF$ (III) crystallizes from solution as a fine powder, hence direct determination of its structure was not possible. However, a different M : L ratio in the complexes II and III, and distinctions in their IR spectra indicate that these compounds have different structure. The IR spectrum of III contains neither the absorption bands corresponding to terminal Al–H bond vibration (1750-1900 cm^{-1}), nor the absorption bands in the region 1000-1100 cm^{-1} referring to M-μ_3-H bond vibrations (see above). At the same time, the spectrum does show the absorption bands $\nu(Al–H^b)$ (1580 cm^{-1}) and $\nu(Y–H^b)$ (1155 cm^{-1}), typical of the Y–H–Al bonds with the μ_2-bridging hydrogen atom [5]. Deformation vibrations were observed only in one broad absorption band at 770 cm^{-1}. Taking into account these data and the composition of the complex, its structure can be suggested to be:



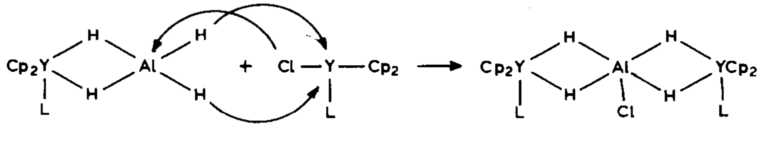
which is close to the structure of the corresponding titanium derivative. The distinction is that in $(Cp_2Ti)_2AlH_4Cl$ the titanium atoms are unsolvated, whereas in III the yttrium atoms coordinate a THF molecule so as to fill the vacant $1a_1$ orbital and thus acquire an 18-electron environment, just as in the complex studied previously [16].



The differing structures of complexes II and III suggests different mechanisms of reaction between $LiAlH_4$ and yttrium bis(cyclopentadienyl) chloride, the path of which is usually determined by solvent nature, or, in general, by the nature of the ligand L. Thus a series of steps leads to the formation of a monomeric and unstable alumohydride (eq. 2),

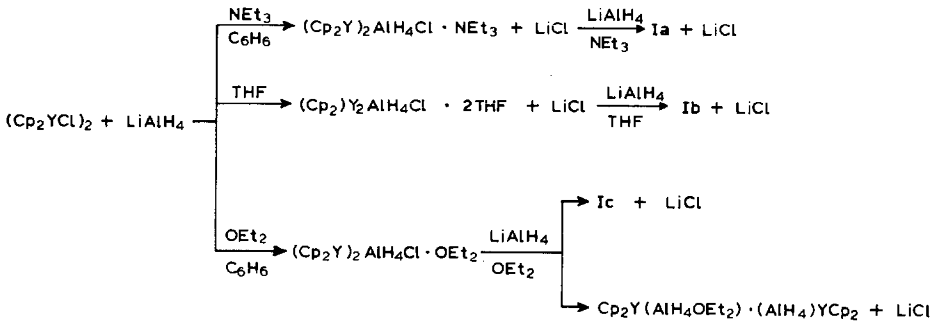
$$Cp_2YCl \cdot L + LiAlH_4 \cdot L \rightarrow Cp_2YAlH_4 \cdot L + LiCl \qquad (2)$$

and then on to its complexing with Cp_2YCl another molecule, followed by an intramolecular rearrangement (eq. 3):



(3)

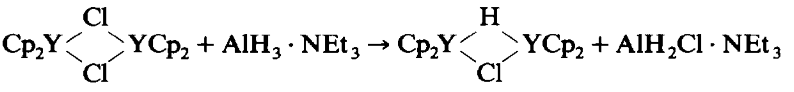
This mechanism for the formation of III is similar, in essence, to that for $(Cp_2Ti)_2AlH_4Cl$, as suggested in ref. 7.



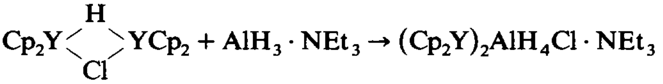
Scheme 1

In benzene and weakly solvating solvents, such as diethyl ether, $LiAlH_4$ reacts with the dimer $(Cp_2YCl)_2$, in which one chlorine atom is replaced by the AlH_4 moiety to give a complex of type II. The use of lithium alumohydride etherate $LiAlH_4 \cdot OEt_2$ instead of $LiAlH_4 \cdot NEt_3$ does not lead to an ether-solvated complex analogous to III, evidently owing to its instability. Still, it can be suggested that this complex exists as an intermediate, judging from the existence of the complex $Cp_2Y(\mu\text{-}AlH_4OEt_2)(\mu\text{-}AlH_4)YCp_2$ [5] in which the chlorine atom has been replaced by the $(\mu_2\text{-}H)_2AlH_2$ moiety.

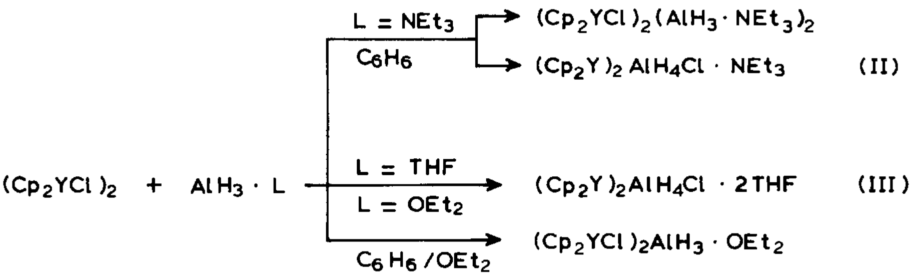
Thus, on the strength of all this evidence, Scheme 1, showing the reactions in the $(Cp_2YCl)_2/LiAlH_4/L$ system is proposed. Complex I can also be obtained in a rather unexpected way, viz. by the interaction of Cp_2YCl and $AlH_3 \cdot NEt_3$. The addition of the alanes $AlH_3 \cdot L$ to $(Cp_2YCl)_2$ is known to lead to the complexes of type I, $(Cp_2YCl)_2(AlH_3 \cdot L)_n$ ($n = 1$, 2) [3,4]. However, if the order in which the reagents are mixed is reversed, i.e. $(Cp_2YCl)_2$ is added to a solution of $AlH_3 \cdot NEt_3$, the complex which forms, $(Cp_2Y)_2AlH_4Cl \cdot NEt_3 \cdot C_6H_6$, is similar to that obtained from the reaction with $LiAlH_4 \cdot NEt_3$. It appears that the first step in this reaction is the replacement of the chlorine atom with a hydrogen, followed by addition to $Cp_2Y\overset{H}{\underset{Cl}{<>}}YCp_2$ of more basic (compared to $AlH_2Cl \cdot NEt_3$) triethylamine:



$$Cp_2Y\overset{Cl}{\underset{Cl}{<>}}YCp_2 + AlH_3 \cdot NEt_3 \rightarrow Cp_2Y\overset{H}{\underset{Cl}{<>}}YCp_2 + AlH_2Cl \cdot NEt_3 \tag{4}$$



$$Cp_2Y\overset{H}{\underset{Cl}{<>}}YCp_2 + AlH_3 \cdot NEt_3 \rightarrow (Cp_2Y)_2AlH_4Cl \cdot NEt_3 \tag{5}$$



Scheme 2

Similarly the reaction between $AlH_3 \cdot OC_4H_8$ and monomeric $Cp_2YCl \cdot L$ in THF yields a product, identical to complex III, but no analogs of complex I are formed, and reaction of $(Cp_2YCl)_2$ with $AlH_3 \cdot OEt_2$ in ether yields only $(Cp_2YCl)_2AlH_3 \cdot OEt_2]_n$. On the basis of the data considered, the interaction in the system $(Cp_2YCl)_2/AlH_3 \cdot L/L$ shown in Scheme 2 is proposed.

Thus, the interaction between yttrium bis(cyclopentadienyl)chloride and the aluminium hydride derivatives in all cases leads to the formation of the coordination- and electron-saturated alumohydride compelxes of yttrium. The distinctions in the structure and stability of these complexes are directed by the difference in basicity of the solvating ligands, $Et_2O < THF < NEt_3$, and by the state (dimer or monomer) of the starting yttrium bis(cyclopentadienyl) chloride in solution.

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