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# SYNTHESIS AND MOLECULAR STRUCTURE OF SOLVATED HYDRIDE COMPLEXES OF ALUMINIUM AND DI-$\eta^5$-CYCLOPENTADIENYLYTTRIUM

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## Summary

A series of hydride complexes of di-$\eta^5$-cyclopentadienyl-yttrium and -aluminium solvated by a Lewis base, viz. $Cp_2YAlH_4NEt_3$ (I), $Cp_2YAlH_4THF$ (II), $Cp_2YAlH_4OEt_2$ (III) and $(Cp_2YAlH_4)_2OEt_2$ (IV), ($Cp = \eta^5$-cyclopentadienyl) was synthesized. An X-ray study of compounds I and IV was performed, yielding the coordinates of the heavy atoms. The positions of the hydrogen atoms were determined accordingly from the IR data and also by comparison with the analogous hydridohalide complexes $(Cp_2YCl)_2AlH_3L$. The structures of I and IV may be represented by the following formulae: $[(\eta^5\text{-}C_5H_5)_2Y(\mu_3\text{-}H)]_2[(\mu_2\text{-}H)AlH_2NEt_3]_2$ (I) and $\{[(\eta^5\text{-}C_5H_5)_2Y]_2(\mu_3\text{-}H)\}[(\mu_2\text{-}H)_2AlH_2][(\mu_2\text{-}H)_2AlHOEt_2]$ (IV).

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## Introduction

The transition metal aluminium hydrides stabilized by cyclopentadienyl ($\eta^5$) ligands are convenient models for the study of reactive sites in Ziegler-type systems [1]. Spectral analysis of titanium [2] and niobium [3] aluminium hydrides ($Cp_2MAlH_4$) and zirconium hydridoaluminium hydride ($Cp_2Zr(H)AlH_4$) [4] suggests that in these compounds the M and Al atoms are connected via a double hydrogen bridge, $\mathrm{M}\Big\langle\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\Big\rangle\mathrm{M}$. With $Cp_2YAlH_4 \cdot nEt_2O$, however, the type of bonding between the metal atoms is likely to be more complex, and to involve a homometallic double bridge, $\mathrm{Y}\Big\langle\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\Big\rangle\mathrm{Y}$, and an ordinary heterometallic hydrogen bridge, Y–H–Al [5]. The double bridge is a close analogue of the chlorine and alkyl bridges [6–8] and

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is very common in the chemistry of rare-earth elements and yttrium.

This paper reports the results of X-ray and IR analyses of a series of aluminium hydride complexes with dicyclopentadienylyttrium of composition $Cp_2YAlH_4L$, where the basicity of the ligand L increases in the order $Et_2O < THF \lesssim NEt_3$.

## Results and discussion

The interaction of $[(\eta^5\text{-}C_5H_5)_2YCl]_2$ with $MAlH_4$ (where M = Li, Na) in the presence or in the medium of a Lewis base (L) results in the formation of bimetallic complexes of empirical formula $(\eta^5\text{-}C_5H_5)_2YAlH_4L_n$, where $L = NEt_3$ (I), THF (II), $Et_2O$ (III), $n = 1$ and $L = Et_2O$ (IV), $n = 0.5$. When stored, these solvates easily decompose to give aluminium metal (the stability of these compounds increases with the basicity of L). For this reason we failed to localize the hydride atoms. The suggested structure of these complexes was derived from IR spectral data and by comparison of structurally-similar compounds, viz. the yttrium and aluminium hydridohalide complexes $[(\eta^5\text{-}C_5H_5)_2Y(\mu_2\text{-}Cl)]_2[(\mu_2\text{-}H)AlH_2NEt_3]_2$ (V) [9], $\{[(\eta^5\text{-}C_5H_5)_2Y(\mu_2\text{-}Cl)]_2[(\mu_2\text{-}H)_2AlHEt_2O]\}_n$ (VI) [10], and a number of monometallic hydride complexes of the rare-earth elements and yttrium.

The X-ray data suggest that complex I consists of centrosymmetric, isolated dimer molecules $((Cp_2YAlH_4NEt_3)_2)$. This confirms the conclusion that dimerization and polymerization (as a limiting case) are typical of the structural chemistry of the rare-earth elements. Table 1 lists the main interatomic bond lengths and valence angles. Fig. 1 shows the arrangement of the atoms in I (the empty circles represent experimentally-determined atoms). The Y and Al atoms are located in the bisector plane of $Cp_2Y$ wedge-shaped sandwiches, while the N atoms deviate somewhat (0.11 Å) from this plane. In general, the arrangement of the heavy atoms in I is similar to their arrangement in $(Cp_2YCl)_2(AlH_3NEt_3)_2$ (V) (the atoms of V are shown in Fig. 1 by a dashed line). The Y–Y distance in I is considerably shorter than that in V, where the yttrium atoms are connected via chlorine atoms, but is comparable with that in the dimeric compound $[(\eta^2\text{-}C_5H_4Me)_2Y(\mu_2\text{-}H)]_2 \cdot 2THF$ (VII) with a double

TABLE 1

INTERATOMIC LENGTHS AND VALENCE ANGLES IN $(Cp_2YAlH_4NEt_3)_2$ (I) AND $(Cp_2YAlH_4)_2OEt_2$ (IV)

(E E–N(I), O(IV); C(1), C(2), C(3), C(4): centres of the Cp-rings)

| $d$(Å) | I | IV | $\omega$(°) | I | IV |
|---|---|---|---|---|---|
| Y(1)–Al(1) | 3.308(11) | 3.546(8) | Al(1)–Y(1)–Al(2) | 121.3(1) | 94.4(1) |
| Y(1)–Al(2) | 4.108(11) | 3.207(7) | Al(1)–Y(2)–Al(2) | 121.3(1) | 94.2(2) |
| Y(2)–Al(1) | 4.108(11) | 3.583(8) | Y(1)–Al(1)–Y(2) | 58.7(2) | 75.6(2) |
| Y(2)–Al(2) | 3.308(11) | 3.196(7) | Y(1)–Al(2)–Y(2) | 58.7(2) | 86.3(2) |
| $(Y\text{–}C)_{mean}$ | 2.64 | 2.62 | Y(1)–Al(2)–E | 172.7(3) | 128.3(6) |
| Al–E | 2.127(26) | 1.936(18) | Y(2)–Al(2)–E | 127.9(5) | 130.0(6) |
| $(C\text{–}E)_{mean}$ | 1.50 | 1.52 | $(C\text{–}Al\text{–}E)_{mean}$ | 110.9 | 121.6 |
| $(C\text{–}C)_{mean}$ | 1.38 | 1.36 | $(C\text{–}C\text{–}C)_{mean}$ | 108.0 | 107.9 |
| Y(1)···Y(2) | 3.700(4) | 4.378(8) | C(1)–Y(1)–C(2) | 127.5 | 127.4 |
| Al(1)···Al(2) | 6.780(9) | 4.972(8) | C(3)–Y(2)–C(4) | 127.5 | 130.0 |
| | | | [Y(1)Al(2)Y(2)–Al(2)E] | 176.9 | 120.0 |
| | | | [Y(1)Al(2)Y(2)–Y(1)Al(1)Y(2)] | 180.0 | 149.0 |

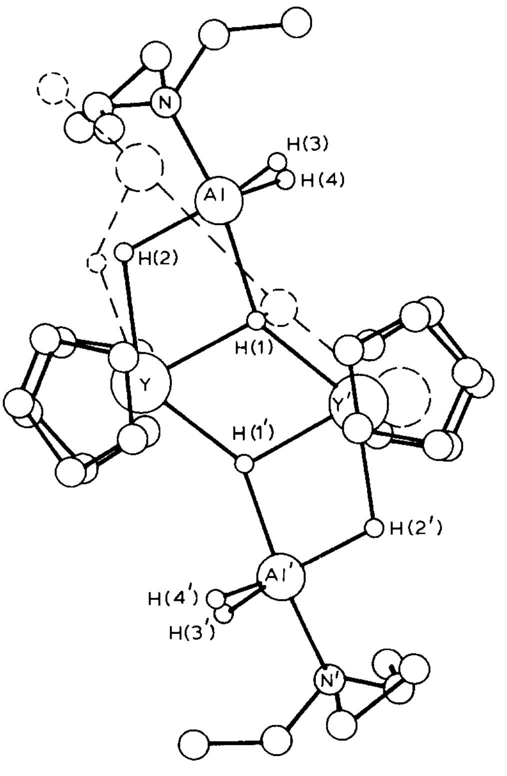


Fig. 1. The structure of the $[(C_5H_5)_2YAlH_4NEt_3]_2$ complex.

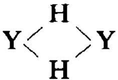
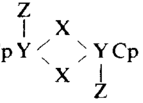
hydrogen bond,  $Y\overset{H}{\underset{H}{<\;>}}Y$ [11] (see Table 2). This allowed us to conclude that a similar structural fragment must be realized in compound I. Since the Y–H distance in the hydride complexes of yttrium with known structures V [9], VI [10], VII [11] and $Y(BH_4)_3 \cdot 3THF$ [12] undergoes only slight changes (2.1–2.3 Å), it can be assumed that in the double hydrogen bridge of I this distance is equal to 2.2 Å. The Y ··· Al distance in I is also considerably shorter than that in either V or VI (see Table 2), where these atoms are connected via an ordinary hydrogen bridge, Y–H–Al. At the same time, this distance is too large for direct metal–metal contact. The presence of the Y–H–Al bridge in structure I was unambiguously proved by IR spectroscopy. The absorption bands at 1275 and 1661 $cm^{-1}$ correspond to $\nu(Y\text{–}H^b)$ and $\nu(Al\text{–}H^b)$, respectively, and are very specific since their positions in the row of compounds I–III and V, VI is practically independent of the nature of ligand L (see Table 3). This indicates the similarity of the Y–H–Al fragment structure in all these compounds. Therefore, we can assume that the Y–H and Al–H distances in I are equal to those found for $(Cp_2YCl)_2(AlH_3NEt_3)_2$ (V). In accordance with these considerations, the values of the valence angles H(1)–Y–H(2) are close to those of the Cl–Y–H angles in complexes V and VI and the O–Y–H angles in complex VII. Also, the Y–H(2)–Al angle is considerably smaller than that in compounds V and VI (see Table 2) and close to the Ti–H–Al angle in the complex $[CpTi(C_5H_4)HAlEt_2]_2$ (101°) [13]. This difference led us to the conclusion that the

TABLE 2

THE MAIN BOND LENGTHS AND VALENCE ANGLES IN THE YTTRIUM SURROUNDINGS



| Compound | $d$ (Å) | | | | | | $\omega$(°) | | | | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Y···Y | Y–H[b] | Al–H[b] | Y···Al | Al–E | Al···X | X–Y–X | X–Y–Z | Y–H–Al | $\alpha$[a] | X···Al–E | |
| $[(Cp_2YCl)_2AlH_3OEt_2]_n$ | 4.35 | 2.3 | 1.6 | 3.64 | 1.89 | 3.01 | 74.4 | 64 | 152 | 32.3 | 161 | 10 |
| | | | | 3.91 | | | 75.1 | 71 | 156 | 26.1 | | |
| $[(Cp_2YCl)_2(AlH_3NEt_3)_2]$ | 4.38 | 2.1 | 1.8 | 3.62 | 2.04 | 3.01 | 73.8 | 74 | 136 | 29.8 | 176 | 9 |
| $[(C_5H_4Me)_2YH]_2 \cdot 2C_4H_8O$ | 3.66 | 2.18 | — | — | — | — | 66 | 71 | — | | — | 11 |
| $(Cp_2YH)_2(AlH_3NEt_3)_2$ | 3.70 | 2.1[b] | 1.8[b] | 3.31 | 2.13 | 2.1[c] | 66[c] | 68[c] | 109[c] | 26 | 177[c] | This work |
| | | 2.2[b] | | | | | | | | | | |
| $(Cp_2YAlH_4)_2OEt_2$ | 4.38 | 2.2[b] | 1.6[b] | 3.20 | 1.94 | 2.1[c] | 67[c] | 75[c] | 113[c] | 1.6 | 120[c] | This work |
| | | | | 3.57 | | | | | 139 | | | |

[a] The angle between the C(1)–Y–C(2) plane and the Y–Y axis. [b] Values taken from refs. 9–11. [c] Calculated on the basis of the data in b.

TABLE 3

THE VIBRATION FREQUENCIES IN THE IR ABSORPTION SPECTRA ($cm^{-1}$) OF THE ALUMINIUM HYDRIDES OF YTTRIUM DICYCLOPENTADIENYL AND THEIR ASSIGNMENTS [a]

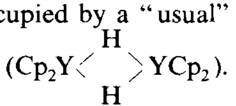
| $(Cp_2YH)_2$-$(AlH_3NEt_3)_2$ (I) | $(Cp_2YH)_2$-$(AlH_3C_4H_8O)_2$ (II) | $(Cp_2YH)_2$-$(AlH_3OEt_2)_2$ (III) | $(Cp_2YAlH_4)_2$-$OEt_2$ (IV) | Assignment |
|---|---|---|---|---|
| | | 406(296) | 400 | $\delta(Y_2HAl)$ |
| 418 | | | | |
| 475 | | | | |
| 530 | | | | |
| 565 | 560 | 520 | 515 | $\nu$(Al-O, Al-N) |
| 648(463) | 635 | 647(462) | 620 | |
| | | | 663 | $\delta(MH_2)$ |
| 705(523) | 695 | 714(530) | 727 | |
| 765 | 767 | 777 | 775 | |
| 783 | 780 | 798 | | Cp |
| 880 | | | 835 | |
| | 877 | 873(635) | 915 | $\nu(Y_2HAl)$ |
| 901 | 919 | 892 | | L |
| 1018 | 1010 | 1010 | 1010 | Cp |
| 1040(735) | 1069 | | | $\nu(Y_2HAl)$ |
| 1055 | | 1050 | 1065 | |
| | | 1085 | 1092 | L |
| 1170 | | | | $NEt_3$ |
| 1190 | 1187 | | 1190 | $\nu(YHAl)$ |
| 1275(910) | 1288 | 1301(945) | 1365 | $\nu(Y-H^b)$ |
| 1299 | | | | $NEt_3$ |
| | | | 1580 | $\nu(Al-H^b)$ |
| 1661(1200) | 1650 | 1662(1207) | 1660 | |
| | | | 1780 | $\nu(Al-H^t)$ |
| 1816(1308,1328) | 1813 | 1863(1345) | 1835 | |

[a] Frequencies for the deuterated complexes are given in parentheses.

type of bonding between the Y and Al atoms in I is more complex compared with that in complexes V and VI. It has been shown [9,10] that in V and VI the Al atom is bonded to a chlorine atom in the fragment $Y\begin{smallmatrix}Cl\\ \langle\quad\rangle\\ Cl\end{smallmatrix}Y$ via a weak "secondary" bond ($r$(Al $\cdots$ Cl) 3.0 Å) which is only slightly shorter than the non-valent contact (3.6 Å). Substitution of the chlorine atoms in $Y\begin{smallmatrix}X\\ \langle\quad\rangle\\ X\end{smallmatrix}Y$ by hydrogen atoms should result in a considerable reduction of the Al-H(1) distance to a definitely valent contact (2.1 Å), provided our assumption about the value of Y-H(1) is correct. In this case, the coordination number of the H atoms in $(Cp_2YH)_2(AlH_3NEt_3)_2$ should be equal to 3 (bonding type ($\mu_3$-H)). A similar type of bonding has been recently discovered in the trinuclear hydrides $[(Cp_2LuH)_3\mu_3\text{-}H]^-[Li(C_4H_8O)_3]^+$ and $[(Cp_2ErH)_2\text{-}(Cp_2ErCl)\mu_3\text{-}H]^-[Li(C_4H_8O)_4]^+$ [14]. In the latter, the Er-Er distance increases only by 0.07 Å compared with the binuclear hydride $(Cp_2ErH)_2 \cdot 2THF$, which contains an $Er\begin{smallmatrix}H\\ \langle\quad\rangle\\ H\end{smallmatrix}Er$ bridge where the coordination number of the H atom is 2

[14]. The presence of the three-coordinated hydrogen atom in structure I is confirmed by the estimated value of the N–Al–H(1) angle which almost coincides with that of the N–Al–Cl angle in complex V (see Table 2), by the "forced" location of the Al atoms in one and the same plane with the Y atoms, and by IR spectral data. The IR spectrum of I exhibits an absorption band which can be assigned to the stretching vibration $\nu(\mathrm{Y{-}H^b})$ of a bridge with a three-coordinated hydrogen atom. This band is located in a lower frequency range than $\nu(\mathrm{Y{-}H^b})$ in the ordinary bridge Al–H–Y (1275 $\mathrm{cm^{-1}}$), and in a lower frequency range than $\nu(\mathrm{Y{-}H^b})$ in the double hydrogen bridge with a two-coordinated H atom (1315 $\mathrm{cm^{-1}}$) in $[(\mathrm{C_5H_4Me})_2\mathrm{YH}]_2 \cdot 2\mathrm{THF}$ [11]. Indeed, the band in the 900–1050 $\mathrm{cm^{-1}}$ range (1040 $\mathrm{cm^{-1}}$ in I) can be observed in all of the complexes of yttrium aluminium hydrides studied (see Table 3). Hydrogen atoms H(3) and H(4) in I are bonded to the Al atom and are terminal, which is in agreement with a large interatomic Al(1) $\cdots$ Y(2) distance. In the IR spectrum of I, these atoms are identified by a wide band with a maximum at 1816 $\mathrm{cm^{-1}}$, which resolves into a doublet in the spectrum of the deuterated complex.

On the basis of these considerations, it follows that the most plausible coordination polyhedron of the Al atom in I, as well as in V and VI, is a trigonal bipyramid with atoms of N and H(1) in axial positions. The strengthening of the "secondary" bond in complexes of $(\mathrm{Cp_2YX})_2(\mathrm{AlH_3NEt_3})_2$ in transition from X = Cl (V) to X = H (I) results in the weakening of the Al–N bond ($r$(Al–N) increases by only 0.08 Å), the length of which becomes close to that of the Al–N bond in complexes with a five-coordinated Al atom, for instance in $\mathrm{AlH_3 \cdot 2NMe_3}$ (2.18 Å) [15]. The geometry of the triethylamine ligand is, in general, typical of such compounds. It should be stressed, however, that the $\alpha$-carbon atoms in the ethyl groups statistically occupy two positions which differ according to the direction of the $\mathrm{C_2H_5}$ groups, "twisting" relative to the Al–N axis. It should also be mentioned that the empirical rule [16] formulated for the molecular and ionic aluminium hydrides with terminal X atoms, which correlates the location of the $\nu(\mathrm{Al{-}H^t})$ band with the coordination number of the Al atom, is invalid for compounds containing bridge hydrogen atoms.

Thus the X-ray data and the location of the hydride atoms allowed us to conclude that the compound in question is an alane rather than a tetrahydridoaluminate. In this alane, one coordination position is occupied by a "usual" ligand, e.g. $(\mathrm{NEt_3})$, and the other by an organometallic ligand  $(\mathrm{Cp_2Y}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\langle\;\rangle}}\mathrm{YCp_2})$. This means that its structure should be defined by the formula $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Y}(\mu_3\text{-}\mathrm{H})]_2[(\mu_2\text{-}\mathrm{H})\mathrm{AlH_2NEt_3}]_3$. In this case, the metal atoms become coordinatively and electronically saturated. (The Y atom acquires an 18-electronic configuration in the $\mathrm{Cp_2YH_3}$ fragment [17]; the Al atom attains $sp^3d$ hybridization similar to complexes V and VI.) That the choice of the model suggesting that the yttrium atom involves three ligands in its coordination sphere is correct is also confirmed by the value of the angle $\alpha$ between the plane passing through the centres of the Cp rings, the Y(1) atom and the Y(1)–Y(2) axis (26°). This value is close to the values in complexes V and VI (see Table 2). The direction of the symmetry axis of the $\mathrm{Cp_2Y}$ wedge-shaped sandwich practically coincides with that of the bond Y(1) to the central ligand in the $\mathrm{Cp_2MX_3}$ system (the estimated H(1)–Y(1)–Y(2) angle is 33°). The total valence angle between the terminal ligands in the bisector plane of the wedge-shaped sandwich is 134°, which is comparable to the values found for other hydride complexes with a nine-coordinated yttrium atom (137–138°) (see Table 2) and to $Cp_2MH_3$ hydrides (M = Nb, Ta) (126°) [18]. (The non-bonding contact H ··· H in I is 2.3–2.5 Å and is considerably longer than that in $Cp_2MH_3$ (1.75–1.85 Å) [18].)

No X-ray data are available for the structures of the complexes $(Cp_2YH)_2(AlH_3THF)_2$ (II) and $(Cp_2YH)_2(AlH_3Et_2O)_2$ (III). Taking into account the total coincidence of the IR spectra of I and II (with the exception of the ligand vibrations), one may conclude that the THF complex is a structural analogue of the amine complex. The IR spectrum of monoetherate III, although very similar to those of I and II, is nevertheless somewhat different, exhibiting a narrow singlet at 1863 $cm^{-1}$ pertaining to the $\nu(Al-H^t)$ vibration. This led us to conclude that the type of the bonding in this compound is close to but, nevertheless, different from that in question.

The X-ray data suggest that the $Cp_2YAlH_4 \cdot 0.5Et_2O$ (IV) molecule contains two $Cp_2Y$ wedge-shaped sandwiches and two non-equivalent Al atoms, one of which is connected to the $Et_2O$ molecule (see Fig. 2). The wedge-shaped sandwiches differ in the mutual orientation of the rings (which is crossed with the Y(1) atom and eclipsed with the Y(2) one) and, correspondingly, in the value of the Cp–Y–Cp valence angle (see Table 2). A similar phenomenon is observed in the $[(Cp_2MoH_2)_2Cu][CuCl]_2$ complex, where the orientations of the Cp-rings and the Cp–Mo–Cp angles are different for the two Mo atoms. This results in minimum contact between the hydride and the carbon atom [19]. The symmetry axes of the wedge-shaped sandwiches nearly coincide with the Y(1)–Y(2) axis (the deviation angle α is 1.6°). The bisector planes of the wedge-shaped sandwiches are somewhat deflected from the Y(1)–Y(2) axis to the side of the Al atoms. Unlike structures I, V and VI, in this

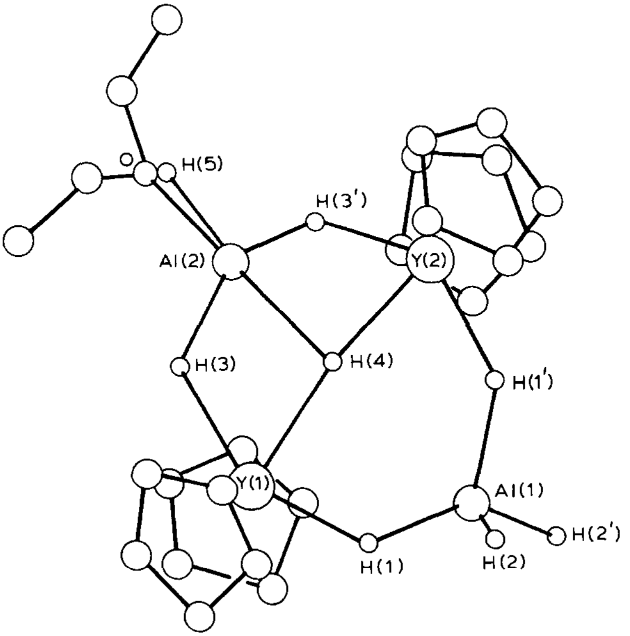


Fig. 2. The structure of the $[(C_5H_5)_2YAlH_4]_2OEt_2$ complex.

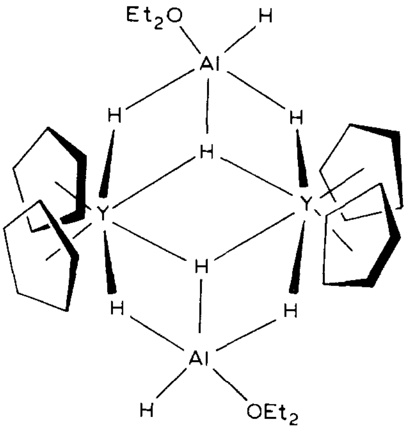


Fig. 3. The proposed structure of the $(C_5H_5)_2YAlH_4OEt_2$ complex

complex the Al atoms deviate from these planes by 0.3–0.5 Å. (The angle between the planes made by Y(1), Y(2), Al(1) and by Y(1), Y(2) and Al(2) is 150°.) It was natural to assume that the Al and Y atoms were connected via the bridge hydrogen atoms, which are symmetrical with respect to the plane $\sigma$ that passes through the Al atoms and is perpendicular to the Y(1)–Y(2) axis (since the Al–Y distances are equal in pairs). Assuming that the Y–H distance is equal to 2.2 Å, and that the Al–H distance equals 1.6 Å (by analogy with complex VI), and taking into account the fact that the hydrogen atoms linked to the Y atoms should be located in the bisector planes of the corresponding wedge-shaped sandwiches [17], we obtained a model of the hydride stereochemistry of the metal atoms presented in Fig. 2. The Al(1)–Y distances in IV (3.57 Å) are very close to those in complexes V and VI (Table 2), which contain ordinary hydrogen bridges, Al–H–Y. Since the Al(1) atom is equidistant with respect to Y(1) and Y(2), one can assume that the Al(1)$H_4$ group involves a bridge which connects both these atoms. This type of bonding through the $AlH_2Et$ group has been observed in $(C_{10}H_8)(CpTi(H)(H_2AlEt)TiCp)$ [20]. This also seems to account for the close values of the Ti–H–Al (135°) and Y–H(1)–Al angles in both compounds. (It should be taken into account that the latter, as well as the other compounds containing the hydrogen atoms, in structure IV was estimated assuming that $r(Y{-}H) = 2.2$ Å and $r(Al{-}H^b) = 1.6$ Å.)

It was natural to assume that the two hydrogen atoms connected to Al(1) were the bridge hydrogens while the other two were terminal. In this case, the coordination polyhedron of the Al(1) atom is a distorted tetrahedron. The H(1)–Al(1)–H(1′) angle is close to the tetrahedral angle, since the Al atom is located outside the bisector plane of the wedge-shaped sandwich.

The Al(2)–Y distance in IV is even shorter than that in I with $\mu_3$-H atoms, which indicates the strengthening of the bond between the Al and Y atoms in the fragment. Indeed, the identical Y(1)–Al(2) and Y(2)–Al(2) distances show that there are two geometrically-equivalent bridges, Y–H(3)–Al(2) (see Fig. 2). The Y–H(3)–Al valence angle (113°) is comparable to its counterpart in molecule I. Geometrical considerations and the orientation of the Al(2)–O bond require the atom of hydrogen which binds to three metallic atoms to be located almost on the Y(1)–Y(2) axis (the H(4)–Y(1)–Y(2) angle is 6°). This is in agreement with a small deviation angle, $\alpha$, made by the planes passing through the centres of the cyclopentadienyl rings and the Y atoms with the Y(1)–Y(2) axis (Table 2). The O–Al(2)–H(4) angle is 120°. This allowed us to assume that H(5) is terminal and located within the plane $\sigma$, while the H(5)–Al(2)–H(4) and H(5)–Al(2)–O angles are also 120°. Thus in this case the coordination polyhedron of the Al(2) atom is also a trigonal bipyramid, with the axial ligands H(3) and H(3′). The value of the H(3)–Al(2)–H(3′) angle (166°) is thus comparable to that of the angle between the axial ligands Cl–Al–O in complex VI [10].

In complex IV, as in I, the yttrium atom coordinates to three hydrogen atoms and becomes coordinatively and electronically saturated. The non-valent contacts H $\cdots$ H are within a reasonable range (2.3–2.7 Å). The values of the H(1)–Y(1)–H(4) and H(3)–Y(1)–H(4) valence angles correlate with those of the X–Y–X and X–Y–Z angles in complexes I and V–VII (Table 2), i.e. structure IV should be defined by the formula $\{[(\eta^5\text{-}C_5H_5)_2Y]_2(\mu_3\text{-}H)\}[(\mu_2\text{-}H)_2AlH_2][(\mu_2\text{-}H)_2AlHEt_2O]$. The proposed model of the hydride stereochemistry of the metallic atoms was confirmed by a difference synthesis, which demonstrated the presence of electron density peaks at some of the estimated positions. We failed, however, to refine the coordinates of these "atoms". Nevertheless, their presence on the electron density map is solid evidence in favour of the proposed structural model for complex IV.

The proposed model of the $(Cp_2YAlH_4)_2Et_2O$ structure is in good agreement with the IR spectral data. The spectrum of IV exhibits the absorption bands of the M–H bonds corresponding to the stretching vibrations of both the solvated (1836, 1660, 1365 and 915 $cm^{-1}$) and unsolvated parts of the molecule (1790, 1580 and 1190 $cm^{-1}$). As expected, the intensities of the latter bands are greater. On comparing the IR spectra of "hemietherate" IV and monoetherate III, one should note their resemblance, particularly in the vibration range of the solvated part of molecule I ($\nu(Y_2HAl)$ frequencies at 915 and 873 $cm^{-1}$, correspondingly). The presence in III of a narrow singlet which belongs to the $\nu(Al\text{-}H^t)$ frequencies (1835 $cm^{-1}$) and does not change its shape on deuteration indicates the presence of only one terminal hydrogen atom in structure III. This allowed us to assume that complex III contains two solvated fragments which are present in complex IV, i.e. its structure can be represented as a dimer in which the yttrium atom has four hydrogen ligands (Fig. 3). In this case, geometrical considerations require a considerable change in the values of the Y–H–Y and H′–Y–H valence angles compared with those in IV. Such examples can be found in the structural chemistry of the transition metal bimetallic hydrides. (A similar type of bonding has been observed in $(CH_3C_5H_4)_2Hf(BH_4)_2$ ($r$(Hf–H) = 2.1 Å, $\sphericalangle$ H–Hf–H = 55–57° [21].)

At present, the causes of the formation of the aluminium hydride etherate of dicyclopentadienylyttrium with various degrees of solvation are not completely clear. The formation seems to be related to changes in crystallization conditions. Such a phenomenon is well known in the chemistry of aluminium hydrides. Crystallization from pure ether yields a solvate of $AlH_3 \cdot 0.3Et_2O$, while isolation from the mixed solvent ether/benzene gives a non-solvated aluminium hydride [22].

## Experimental

All experiments with the initial and final compounds were carried out under an argon atompshere or under vacuum. The solvents were distilled before use over

$LiAlH_4$. $LiAlH_4$ and $NaAlH_4$ were purified by recrystallization (98–99%). $Cp_2YCl$ was prepared as described in ref. 7 and purified by vacuum-sublimation. Elemental analyses were carried out as described in ref. 5.

### $Cp_2YAlH_4NEt_3$ (I)

$Cp_2YCl$ (0.63 g; 2.47 mmol) in 60 ml of benzene was added to a stirred solution of 6 ml of $LiAlH_4$ in $Et_2O$ (2.9 mmol) and 0.7 ml (3 mmol) of $NEt_3$. Twenty minutes after the obtained white residue had been filtered, the solution was evaporated twice under vacuum and left overnight whereupon transparent, colourless crystals were deposited which were then separated from the solution and dried under vacuum. Found: Y, 22.78; Al, 6.74. Calculated for $(C_5H_5)_2YAlH_4N(C_2H_5)_3$: Y, 25.31; Al, 7.68%.

### $Cp_2YAlH_4THF$ (II)

$Cp_2YCl$ (0.84 g, 3.3 mmol) in 60 ml of THF was added to a stirred solution of 10 ml (3.4 mmol) of $NaAlH_4$ in THF. The solution was evaporated to a volume of 10 ml, and the white fine crystalline residue obtained was separated. The mother liquid was evaporated to 5 ml and left for 2 days to yield transparent, colourless crystals which were then separated from the solution and dried under vacuum. Found: Y, 27.7; Al, 7.9. Calculated for $(C_5H_5)_2YAlH_4C_4H_8O$: Y, 27.59; Al, 8.37%.

### $Cp_2YAlH_4OEt_2$ (III)

To 1.54 g (6.05 mmol) of $Cp_2YCl$ in 80 ml of benzene was added, dropwise, a solution of 7.8 mmol of $LiAlH_4$ in 25 ml of $Et_2O$. A white residue was obtained which was then filtered. The filtrate was evaporated under vacuum to 30 ml, the same amount of $Et_2O$ was added again, the filtrate was almost evaporated, and then 15 ml of $Et_2O$ was finally added. The next day the ether was separated under vacuum, while the residue was extracted with 15 ml of benzene and evaporated to dryness. Found: Y, 27.7; Al, 9.04. Calculated for $(C_5H_5)_2YAlH_4(C_2H_5)_2O$: Y, 27.40; Al, 8.32%.

### $(Cp_2YAlH_4)_2OEt_2$ (IV)

To 2.43 g (9.55 mmol) of $Cp_2YCl$ in 70 ml of benzene was added, dropwise, 6 mmol of a solution of $LiAlH_4$ in 30 ml of $Et_2O$. The next day the precipitated white residue was filtered, and the solution was evaporated under vacuum to one-third of the initial volume. The crystals obtained were separated from the mother liquid and dried under vacuum. Found: Y, 31.3; Al, 10.4. Calculated for $[(C_5H_5)_2YAlH_4]_2(C_2H_5)_2O$: Y, 30.96; Al, 9.39%.

## Determination of the structures

To protect the obtained complexes from the effects of atmospheric oxygen and moisture, the crystals were placed in thin-walled glass capillaries. Experimental data were obtained on an automatic Syntex P$\bar{1}$ diffractometer, $\alpha$Mo-$K_\alpha$ radiation graphite monochromator, using the $\theta/2\theta$ scan method ($2\theta_{max} = 48\%$).

The crystals of $Cp_2YAlH_4NEt_3$ are monoclinic with unit cell dimensions $a = 11.381(4)$, $b = 13.388(4)$, $c = 14.155(2)$ Å, $\gamma = 102.01(3)°$, space group $P2_1/b$, $Z = 4$, and $d = 1.12$ g/cm$^3$. 1351 reflections ($I > 3\sigma(I)$) were considered observed. The structure was solved by the direct method. No absorption correction was applied. The least-squares refinement in the anisotropic approximation (Y, Al, N and C atoms) gave a final *R* factor of 0.072.

The crystals of $(CpYAlH_4)_2OEt_2$ are monoclinic, with unit cell dimensions $a = 18.984(6)$, $b = 16.981(6)$, $c = 8.896(3)$ Å, $\gamma = 81.41(3)°$, sp.g. $P2_1/b$, $Z = 4$ and $d_{calc.} = 1.36$ g/cm$^3$. The structure was solved by the direct method. No absorption correction was applied. The least-squares refinement in the anisotropic approximation (Y, Al, O and C atoms) gave an *R* factor of 0.076 for 1479 reflections with $I > 3\sigma(I)$.

The tables of the positional and thermal parameters of the atoms, and of the full data on the bond lengths and angles may be received upon request from the authors.

## References

1 G.L. Soloveichik and B.M. Bulychev, Uspekhi Khim., 52 (1983) 72.
2 G. Henrici-Olive and S. Olive, J. Organomet. Chem., 23 (1970) 155.
3 J.A. Labinger and Kwai Sam Wong, J. Organomet. Chem., 170 (1979) 373.
4 P.C. Wailes and H. Weigold, J. Organomet. Chem., 24 (1970) 405.
5 A.B. Erofeev, B.M. Bulychev, G.L. Soloveichik and V.B. Polyakova, Koord. Khim., 9 (1983) 190.
6 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev and A.B. Erofeev, Z. Struct. Khim., in press.
7 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood, and W.E. Hunter, H. Chem. Soc., Dalton Trans., (1979) 45.
8 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood, and W.E. Hunter, J. Chem. Soc., Dalton Trans., (1979) 54.
9 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev, A.B. Erofeev, A.I. Gusev and N.I. Kirillova, J. Organomet. Chem., 265 (1984) 167.
10 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev, A.B. Erofeev, and B.K. Belsky, J. Organomet. Chem., 235 (1982) 151.
11 W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 2008.
12 B.G. Segal and S.J. Lippard, Inorg. Chem., 17 (1978) 844.
13 F.N. Tebbe and L.G. Guggenberger, J. Chem. Soc., Chem. Commun., (1973) 227.
14 W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 2015.
15 C.W. Heitsch, C.E. Nordman and R.W. Parry, Inorg. Chem., 2 (1963) 508.
16 R. Dautel and W. Zeil, Z. Electrochem., 64 (1960) 1234.
17 J.W. Lauher and R. Hoffmann, J. Am. Chem. Soc., 98 (1976) 1729.
18 R.D. Wilson, T.F. Koetzle, D.W. Hart, Å. Kvick, D.L. Tipton and R. Bau, J. Am. Chem. Soc., 99 (1977) 1775.
19 E.B. Lobkovskii, A.V. Aripovskii, B.K. Belsky, B.M. Bulychev, Koord. Khim., 8 (1982) 104.
20 L.G. Guggenheimer and F.N. Tebbe, J. Am. Chem. Soc., 95 (1972) 7870.
21 P.L. Johnson, S.A. Cohen, T.J. Marks and J.M. Williams, J. Am. Chem. Soc., 100 (1978) 2709.
22 F.M. Brower, N.E. Matzek, P.F. Reigler, H.W. Rinn, C.B. Roberts, D.L. Schmidt, J.A. Snover and K. Terada, J. Am. Chem. Soc., 98 (1976) 2450.