

## SYNTHESIS OF PERMETHYLYTTROCENE ALKYL COMPLEXES

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### Summary

Reaction of  $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})_2 \cdot 2\text{OEt}_2$  (**1**) with MeLi gives the new complexes  $\text{Cp}_2^*\text{Y}(\mu\text{-Me})(\mu\text{-Cl})\text{Li} \cdot 2\text{OEt}_2$  (**3**),  $\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{Li} \cdot \text{OEt}_2$  (**4**) and  $\text{Cp}_2^*\text{YMe} \cdot \text{THF}$  (**5**) depending on the reaction conditions and stoichiometry. Salt incorporation is also observed when Grignard reagents react with  $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$  (**2**), e.g.  $\text{Cp}_2^*\text{YMe} \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**6**),  $\text{Cp}_2^*\text{YCH}_2\text{Ph} \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**7**) and  $\text{Cp}_2^*\text{Y}(\eta^1\text{-CH}_2\text{C-Me}=\text{CH}_2) \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**9**) being formed. The reaction of **2** with (2,6-xylyl)MgBr gives  $\text{Cp}_2^*\text{YCl} \cdot [\text{MgBr}_2 \cdot 2\text{THF}]$  (**8**) and not the expected ytrocene aryl. From the IR spectra of the complexes **6**, **7**, **8**, and **9** it is concluded that the THF ligand is coordinated to magnesium. The dimeric  $[\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{AlMe}_2]_2$  is obtained from  $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$  and  $\text{LiAlMe}_4$ . A  $^1\text{H}$  NMR study has yielded the thermodynamic parameters  $\Delta H^\circ$  ( $41.5 \pm 1.2 \text{ kJ mol}^{-1}$ ) and  $\Delta S^\circ$  ( $30.2 \pm 2.4 \text{ e.u.}$ ) for the dimer–monomer equilibrium of this complex. Above ca.  $75^\circ\text{C}$  the monomeric  $\text{Cp}_2^*\text{Y}(\mu\text{-Me}_2)\text{AlMe}_2$  appears to dissociate into an ion pair  $\text{Cp}_2^*\text{Y}^+$  and  $\text{AlMe}_4^-$ . The compounds  $\text{Cp}_2^*\text{YMe} \cdot \text{THF}$  and  $[\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{AlMe}_2]_2$  are active catalysts for polymerization of ethene but not of propene. The initial activities for ethene polymerization of these complexes are 229 and  $125 \text{ g mmol}^{-1} (\text{Y}) \text{ h}^{-1} \text{ atm}^{-1}$ , respectively, at  $30^\circ\text{C}$ . Above  $75^\circ\text{C}$   $[\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{AlMe}_2]$  loses its activity, but regains it when the temperature is lowered.

### Introduction

As described in an earlier paper [1], our first objective in organoyttrium chemistry was to synthesize monomeric yttrium carbyls  $\text{Cp}_2^*\text{YR}$  by metathetical reactions between  $\text{Cp}_2^*\text{YCl}$  or one of its precursors [2] and Grignard or organolithium compounds (eq. 1). Exploratory work revealed that synthesis of  $\text{Cp}_2^*\text{YR}$  in this



manner would not be simple and that, if accessible, these coordinatively highly unsaturated 14 electron compounds would be extremely strong Lewis acids, which would give very stable complexes with a variety of bases, from normal Lewis bases like THF to salt molecules such as LiCl or NaCl [2]. In this respect yttrium seems more related to the 4f-elements [3,4] than to its Group 3 congener Sc [5] or its Group 4 analogue Ti [6].

Preliminary work, in which  $[\text{Cp}_2^*\text{YCl}]_2$ ,  $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})_2\text{Li} \cdot 2\text{OEt}_2$  (**1**) and  $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$  (**2**) were treated with a variety of organo-lithium and Grignard reagents gave monomeric  $\text{Cp}_2^*\text{YR}$  only when R was a large ligand such as  $\text{N}(\text{SiMe}_3)_2$  or  $\text{CH}(\text{SiMe}_3)_2$  [1]. For smaller ligands R the results were more complicated, and monomeric 14 electron compounds  $\text{Cp}_2^*\text{YR}$  could not be obtained: the products isolated invariably contained complexed salts ( $\text{LiCl}$ ,  $\text{MgX}_2$ ) and ether bases ( $\text{Et}_2\text{O}$ , THF), their exact nature depending on stoichiometry of the reagents and experimental conditions.

In this paper we report a number of well-characterized compounds isolated from these reactions.

## Results and discussion

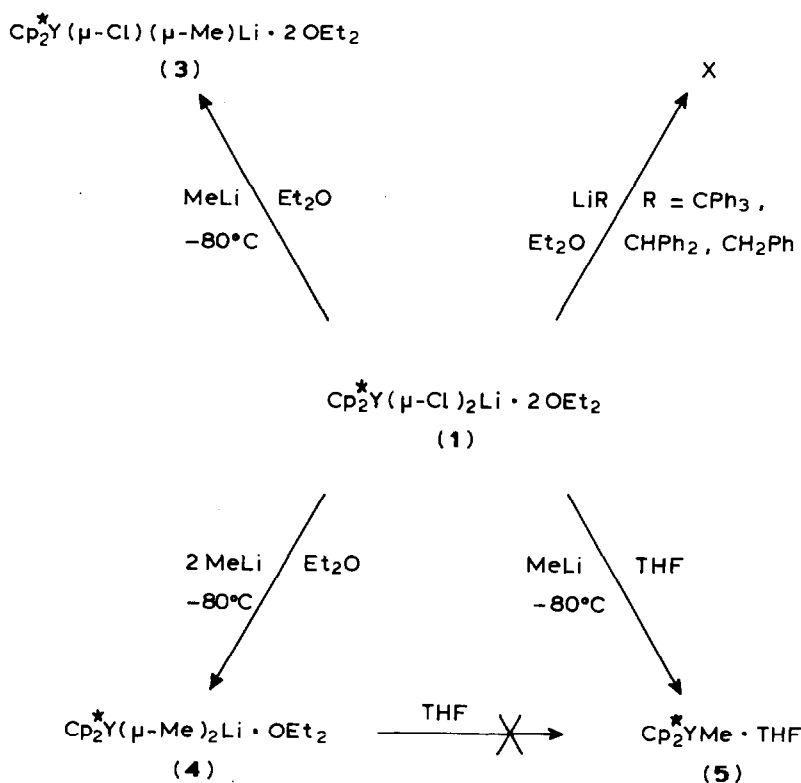
### Synthesis

Reaction of  $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})_2\text{Li} \cdot 2\text{OEt}_2$  (**1**) [2] with MeLi gives several products depending on the ratio of the reagents and other reaction conditions. When the reaction is carried out in  $\text{Et}_2\text{O}$  with one or two moles of MeLi per mole of **1**, the compounds  $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})(\mu\text{-Me})\text{Li} \cdot 2\text{OEt}_2$  (**3**) or  $\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{Li} \cdot \text{OEt}_2$  (**4**) can be isolated. The lithium-free complex  $\text{Cp}_2^*\text{YMe} \cdot \text{THF}$  (**5**) is obtained from **1** and MeLi in THF at  $-80^\circ\text{C}$ . The lithium-containing complexes **3** and **4** cannot be simply converted into **5**, e.g. by dissolving them in THF.

It is evident that LiCl and LiMe are acting as strong bases in these complexes and are very difficult to remove. Thus, organolithium reagents with a small hydrocarbyl group are unsatisfactory for producing  $\text{Cp}_2^*\text{YR}$  complexes. Lithium reagents with large hydrocarbyl ligands, such as  $\text{R} = \text{CPh}_3$ ,  $\text{CHPh}_2$ , and  $\text{CH}_2\text{Ph}$ , gave neither  $\text{Cp}_2^*\text{YR}$  compounds nor their LiCl complexes,  $\text{Cp}_2^*\text{YR} \cdot \text{LiCl} \cdot n\text{OEt}_2$ , under conditions that readily yielded the ytrocene carbyls mentioned above (i.e. stirring for several hours in  $\text{Et}_2\text{O}$  or THF at room temperature).

Grignard reagents could be a useful alternative, since even if the magnesium halide is complexed with  $\text{Cp}_2^*\text{YR}$  initially it could possibly be removed by complexation with 1,4-dioxane [7]. In a first approach MeMgCl in THF was used for reaction with  $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$  (**2**), and a  $\text{MgCl}_2$  adduct  $\text{Cp}_2^*\text{YMe} \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**6**) was, indeed, obtained. The use of the benzyl Grignard,  $\text{PhCH}_2\text{MgCl}$  in THF gave  $\text{Cp}_2^*\text{YCH}_2\text{Ph} \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**7**). Again attachment of a hydrocarbyl ligand to yttrium and complexation of the magnesium salt takes place. An attempt to introduce the large 2,6-xylyl ligand using the Grignard method failed; addition of (2,6-xylyl) $\text{MgBr}$  to **2** in  $\text{Et}_2\text{O}$  gave an instant reaction, but instead of the expected introduction of the organic ligand, complexation of  $\text{Cp}_2^*\text{YCl}$  with  $\text{MgBr}_2$  took place and  $\text{Cp}_2^*\text{YCl} \cdot [\text{MgBr}_2 \cdot 2\text{THF}]$  (**8**) was isolated. Prolonged reaction times (up to 72 h at  $20^\circ\text{C}$ ) did not result in substitution, indicating that either **8** or (2,6-xylyl) $_2\text{Mg}$  is quite inert in this system.

An approach to formation of salt-free complexes  $\text{Cp}_2^*\text{YR}$  by use of a group R



SCHEME 1

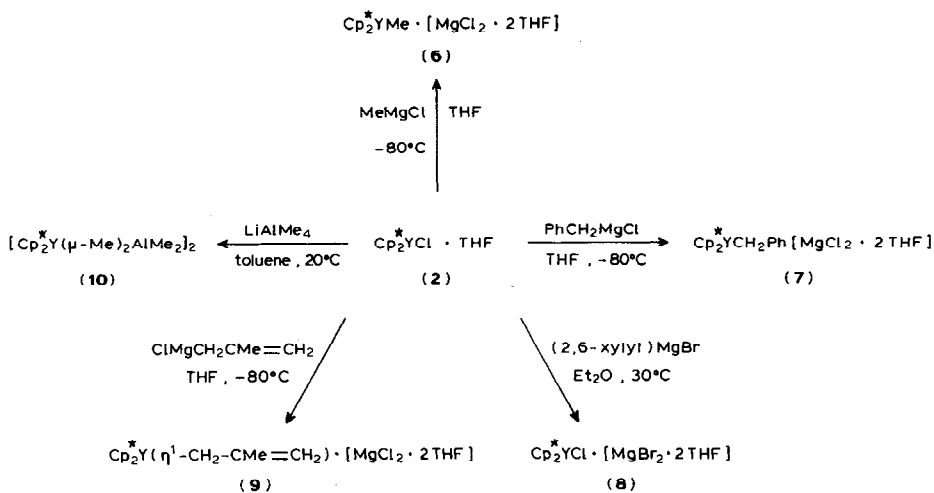
capable of extra internal complexation was then examined. The allylic Grignard, 2-methyl-2-propenylmagnesium chloride was treated with **2** to give the complex  $\text{Cp}_2^*\text{Y}(\eta^1\text{-CH}_2\text{CMe}=\text{CH}_2) \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**9**). Spectroscopic evidence (vide infra) clearly shows that the allyl ligand is  $\eta^1$ -coordinated. It is noteworthy that salt complexation is so strong that it even prevents  $\eta^3$ -allylic coordination.

In attempts to introduce the hydrocarbyl ligands by use of organoaluminium compounds we observed incorporation of the alkyl aluminium chloride, as might have been expected from the results with other alkylating reagents. In general the mixtures of products could not be resolved but the reaction of **2** with  $\text{LiAlMe}_4$  in toluene gave  $[\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{AlMe}_2]_2$  (**10**) as the sole product. Complex **10** shows a very interesting behaviour in solution which can be interpreted in terms of a dimer-monomer-ionic equilibrium (vide infra).

The reactions discussed here are represented in Schemes 1 and 2.

#### *Spectroscopic characterization*

All the new complexes reported here have the usual bent metallocene structure with two  $\eta^5\text{-Cp}^*$  ligands, as can be seen from the IR and NMR data. The IR spectra show clearly the characteristic  $\eta^5\text{-Cp}^*$  absorptions at 2720w, 1485m, 1365m, 1020m, 800w and 595w  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum in each case shows only one singlet (Table 1), located between  $\delta$  1.78 and 2.13 ppm, for the two  $\text{Cp}^*$  ligands. The



SCHEME 2

positions are normal for permethyl-yttrocene derivatives [1,2]. The fact that only one resonance is observed indicates that the  $\text{Cp}^*$  ligands are equivalent, and that additional ligands bonded to yttrium are in the equatorial plane of the bent metallocene. Fast dynamic processes in less symmetric molecules leading to spectroscopic equivalence of the  $\text{Cp}^*$  ligands cannot be excluded, however.

A more detailed assignment of the structures and especially of the nature of the complexation of the salts or metal alkyls, as well as the number and identity of the bridging ligands is very difficult from the spectroscopic data available. In the case of the  $\text{MgBr}_2$  complex **8** it is effectively impossible. For the other complexes in which

TABLE 1  
 $^1\text{H}$  NMR DATA FOR THE NEW COMPLEXES <sup>a</sup>

Complex	$\text{Cp}^*$	R	L
3	2.13(s,30H)	-1.41(d,3H, <sup>2</sup> J(YH) 3.5,Me)	1.09(t,12H, <i>J</i> (HH) 7.0, $\beta$ -Et) 3.18(q,8H, $\alpha$ -Et)
4	1.78(s,30H)	-1.80(d,6H, <sup>2</sup> J(YH) 2.0,Me)	1.09(t,6H, <i>J</i> (HH) 7.1, $\beta$ -Et) 3.22(q,4H, $\alpha$ -Et)
5	2.00(s,30H)	-0.66(d,3H, <sup>2</sup> J(YH) 2.3,Me)	1.16(m,4H, $\beta$ -THF) 3.22(m,4H, $\alpha$ -THF)
6	2.04(s,30H)	-0.73(d,3H, <sup>2</sup> J(YH) 3.0,Me)	1.37(m,8H, $\beta$ -THF) 3.82(m,8H, $\alpha$ -THF)
7	2.00(s,30H)	1.87(d,2h, <sup>2</sup> J(YH) 5.0,YCH <sub>2</sub> ) 7.03-7.18(m,5H,Ph)	1.28(m,8H, $\beta$ -THF) 3.56(m,8H, $\alpha$ -THF)
9	2.00(s,30H)	1.57(d,2H, <sup>2</sup> J(YH) 2.4,YCH <sub>2</sub> ) 2.13(s,3H,C-Me) 2.85(s,2H,C=CH <sub>2</sub> )	1.29(m,8H, $\beta$ -THF) 3.64(m,8H, $\alpha$ -THF)

<sup>a</sup> 90 MHz spectra in  $\text{C}_6\text{D}_6$  at 20 °C,  $\delta$  in ppm,  $\delta(\text{TMS}) = 0.0$ , coupling constants (*J*) in Hz.

alkyl ligands are involved the NMR spectra strongly indicate that these are bonded to yttrium.

The methyl ligand resonances of the complexes **3**, **4**, **5** and **6** are at rather high field: **3**,  $\delta$  -1.41; **4**,  $\delta$  -1.80; **5**,  $\delta$  -0.66; **6**,  $\delta$  -0.73 ppm. The signals are split into doublets owing to second order coupling with the yttrium nucleus ( $^{89}\text{Y}$ , mono-isotopic,  $I = 1/2$  [8]). The coupling constants ( $^2J(\text{YH})$ ): **3**, 3.5; **4**, 2.0; **5**, 2.3; **6**, 3.0 Hz) are comparable with that found for  $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$  ( $^2J(\text{YH})$  2.3 Hz) [1]. This convincingly demonstrates that the methyl ligands in **3**, **4**, **5** and **6** are bonded to yttrium.

The  $^{13}\text{C}$  NMR of **5** confirms this. A first order yttrium-carbon coupling ( $^1J(\text{YC})$  56.2 Hz) is observed on the methyl carbon resonance ( $\delta$  21.36 ppm). This coupling is substantially larger than that observed for  $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$  ( $^1J(\text{YC})$  36.6 Hz), and appears to be the largest so far reported. It is of the same order of magnitude as that for the asymmetric dimer  $\text{Cp}_2^*\text{Y}(\mu\text{-Me})\text{YMeCp}_2^*$  [9]. From the data for **5**, it is possible to assign the smaller coupling ( $^1J(\text{YC})$  42.7 Hz) observed for this dimer to the bridging methyl group, and the larger ( $^1J(\text{YC})$  51.1 Hz) to the terminal methyl ligand.

The benzyl-methylene group in **7** is observed as a doublet ( $^2J(\text{YH})$  5.0 Hz) again indicating a  $\sigma$ -yttrium benzyl bond. The  $\eta^1$ -coordination of the benzyl ligand can also be inferred from the IR spectrum of **9**, which shows the characteristic absorptions for this bonding mode of the benzyl ligand at 1595s, 1170w and 1155w  $\text{cm}^{-1}$  [10].

The propenyl ligand in **9** also has two possible bonding modes. It could be  $\pi$ -bonded to yttrium as an  $\eta^3$ -allyl or  $\sigma$ -bonded as an alkyl with  $\eta^1$ -coordination. The  $^1\text{H}$  NMR spectrum of **9** shows a doublet resonance at  $\delta$  1.57 ppm ( $^2J(\text{YH})$  2.4 Hz), indicating  $\sigma$ -bonding to yttrium. The IR spectrum of **9** is also compatible with  $\eta^1$ -coordination, since the characteristic non-complexed olefinic stretching vibrations [11] are observed at 1620 and 1570  $\text{cm}^{-1}$ .

Although the NMR evidence does not allow definite conclusions whether or not the alkyl ligands are bridging, it is clear that they are all bonded to yttrium. The analogy with the corresponding lanthanum, erbium, ytterbium, and lutetium complexes [12-15], however, suggests that the hydrocarbyl groups probably are bridging. X-ray structure determinations appear to be the only way to prove this unequivocally.

The presence of two acidic metal centers in the  $\text{MgX}_2$  complexes raises the question of whether the THF molecules are coordinated to yttrium or to magnesium. The NMR spectra are not of much help on this point, IR spectroscopy appears to give more guidance. There are small but significant differences in  $\nu_s$  and  $\nu_{as}$  for the COC moiety of ethers coordinated to Mg or to Y. In Mg complexes these THF vibrations are observed between 1030 and 1020 and at 870  $\text{cm}^{-1}$ ; for  $\text{PhMgBr} \cdot 2\text{THF}$  and  $\text{MgBr}_2 \cdot 4\text{THF}$  [16] at 1028 and 869  $\text{cm}^{-1}$ , for  $\text{Cp}^*\text{MgCl} \cdot \text{THF}$  [17] at 1030 and 870  $\text{cm}^{-1}$ , and for the ionic  $[\text{C}_4\text{Ph}_4\text{TiCl}_3][\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]$  [18] at 1020 and 870  $\text{cm}^{-1}$ . When THF is coordinated to Y the COC vibrations are found at 1020 and 860  $\text{cm}^{-1}$  for  $\text{YCl}_3 \cdot 3\text{THF}$  [1],  $\text{Cp}_2\text{YCH}_2\text{SiMe}_3 \cdot \text{THF}$  [19], **5**, and **2**. For the complexes under discussion here the absorptions are at 1030 and 870  $\text{cm}^{-1}$  for **6**, **8** and **9** and at 1035 and 870  $\text{cm}^{-1}$  for **7**. On the criteria formulated above this strongly indicates that the THF molecules in **6**, **7**, **8** and **9** are coordinated to Mg. Thus IR spectroscopy can be a convenient technique in order to distinguish to

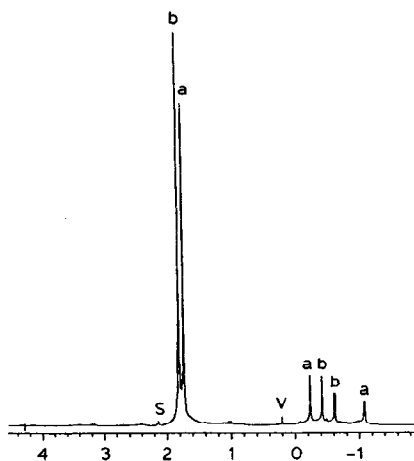


Fig. 1. The  $^1\text{H}$  NMR spectrum of **10** ( $a = \mathbf{10a}$ ,  $b = \mathbf{10b}$ ) at  $20^\circ\text{C}$  in toluene- $d_8$  ( $S = \text{solvent}$ ,  $V = \text{impurity}$ ,  $\delta$  0.26 ppm).

which metal center a THF molecule is coordinated. Unfortunately the potential of this technique is often not appreciated nowadays by organometallic chemists.

#### Properties of $[\text{Cp}^*\text{Y}(\mu\text{-Me})_2\text{AlMe}_2]_2$ (**10**)

The  $^1\text{H}$  NMR spectrum of **10** in toluene- $d_8$  at  $20^\circ\text{C}$  clearly reveals the presence of two compounds **10a** and **10b** (Fig. 1). The integration shows that these compounds have the same stoichiometry. The  $\text{Cp}^*$  resonances can be readily assigned (Table 2). In addition the complexes exhibit two different methyl resonances. Both complexes have two bridging methyl groups, which give doublets owing to yttrium–hydrogen coupling, and two terminal methyls are observed as singlets (Table 2). The ratio of the two complexes **10a** and **10b** is approximately 1/4. At  $-50^\circ\text{C}$  the spectrum has changed: the resonances are shifted slightly (Table 2) and the ratio **10a**/**10b** has become 5.8/1. On warming to  $20^\circ\text{C}$  the original spectrum reappears. Thus, **10a** and **10b** are in equilibrium. This equilibrium was studied by  $^1\text{H}$  NMR at various temperatures in order to evaluate  $\Delta H^\circ$  and  $\Delta S^\circ$  [20]. From the plot of  $\ln K_{\text{obs}}$  vs.  $1000/T$  (Fig. 2) with  $K_{\text{obs}} = [\mathbf{10b}]^2/[\mathbf{10a}]$  a  $\Delta H^\circ$  of  $41.5 \pm 1.2$  kJ/mol and a  $\Delta S^\circ$  of  $30.2 \pm 2.4$  e.u. was derived. The value of  $\Delta S^\circ$  is consistent

TABLE 2

$^1\text{H}$  NMR SPECTRA OF  $\text{Cp}^*\text{Y}(\text{AlMe}_2)$  AT VARIOUS TEMPERATURES <sup>a</sup>

Complex	$T$ ( $^\circ\text{C}$ )	$\text{Cp}^*$	$\mu\text{-Me}$	Me
<b>10a</b>	-50	1.66(s)	-1.12( $d, {}^2J(\text{YH})$ 1.0)	-0.16(s)
<b>10b</b>		1.81(s)	-0.65( $d, {}^2J(\text{YH})$ 4.8)	-0.34(s)
<b>10a</b>	20	1.74(s)	-1.08( $d, {}^2J(\text{YH})$ 2.9)	-0.29(s)
<b>10b</b>		1.84(s)	-0.61( $d, {}^2J(\text{YH})$ 4.9)	-0.47(s)
<b>10c</b>	75	1.89(s)		-0.53(s,12H)

<sup>a</sup> 90 MHz  $^1\text{H}$  NMR spectra in toluene- $d_8$  in ppm; coupling constants ( ${}^2J(\text{YH})$ ) in Hz.

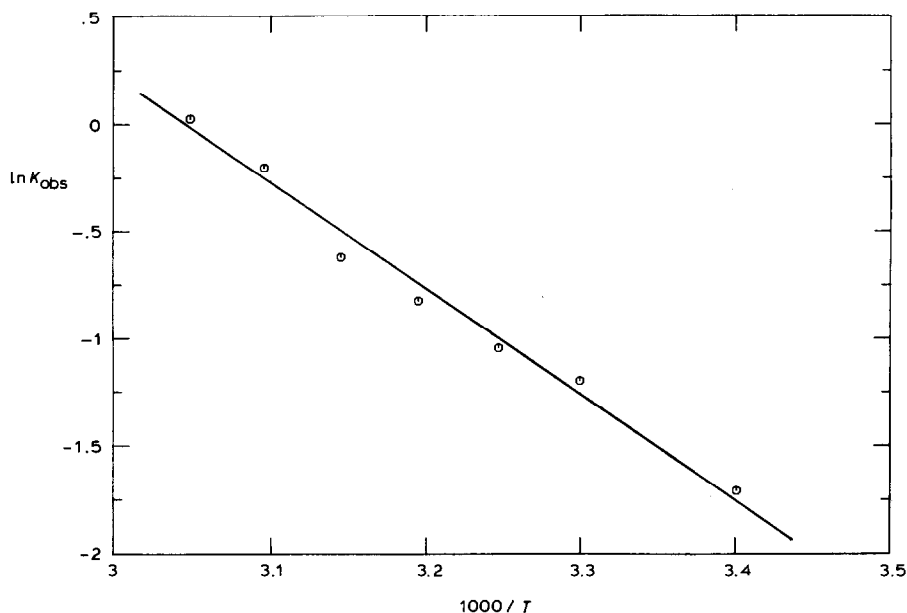
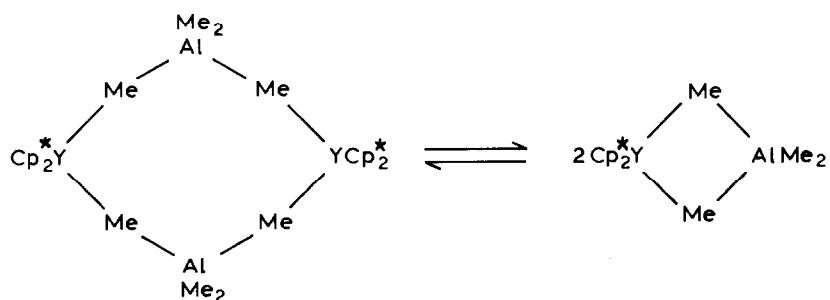


Fig. 2. Plot of  $\ln K_{\text{obs}}$  vs.  $1000/T$  for  $10a \rightleftharpoons 10b$ .

with a dimer–monomer equilibrium (Scheme 3) [21]. The intensities of the resonances of **10a** increase at low temperature, showing that this compound is the dimer.

The  $^1\text{H}$  NMR spectrum at  $70^\circ\text{C}$  reveals the presence of a third component, which increases rapidly in amount as the temperature is further raised. Even at only  $75^\circ\text{C}$  the spectrum consists simply of two singlets, in an intensity ratio of 5/2 (Table 2). The monomer–dimer equilibrium reappears on cooling. The observed changes in the spectrum at around  $75^\circ\text{C}$  might arise from rapid bridging-terminal site exchange of the methyl ligands as suggested by Holton et al. [22] for  $\text{Cp}_2\text{Y}(\mu\text{-Me})_2\text{AlMe}_2$ . When this process is fast on the NMR time scale an average  $^2J(\text{YH})$  would still be expected, however, and since this is not observed this is a satisfactory explanation. A process that accounts for the absence of yttrium–hydrogen coupling in the high temperature spectrum is the formation of ions (eq. 2).



SCHEME 3

In this case none of the methyl groups of the tetramethyl aluminate ligand are interacting with the yttrium, and consequently no coupling with that nucleus is observed. To test this idea we studied this equilibrium in a polar solvent, in which the ions are stabilized [23] and so should be observed at lower temperatures, and we found that in  $\text{CD}_2\text{Cl}_2$  the two line spectrum was observed even at  $20^\circ\text{C}$ . At low temperature ( $< -10^\circ\text{C}$ ) the dimer–monomer equilibrium is again observed, demonstrating that we are still dealing with the same type of system.

### Reactivity

All the complexes described above are extremely reactive towards oxygen and moisture; the products of these reactions have not been identified. The reactions of the mixed metal complexes with  $\text{H}_2$  and  $\text{CO}$  were examined. Although smooth reactions took place in all cases, mixtures of products were formed, and were too complex to allow identification of the components.

Complexes **5** and **10** show marked activity as catalysts for the polymerization of ethene. The initial activity [24], measured by gas uptake at  $30^\circ\text{C}$  and 1 atm  $\text{C}_2\text{H}_4$  in toluene, is 229 g ( $\text{C}_2\text{H}_4$ )  $\text{mmol}^{-1}$  (Y)  $\text{h}^{-1}$   $\text{atm}^{-1}$  for **5** and 125 g for **10**. At higher temperatures the polymerization activity of **5** increases as expected. Compound **10** behaves completely differently. The ethene polymerization is slower at higher temperatures, and virtually does not take place at all at about  $75^\circ\text{C}$  which can be understood in terms of the predominant presence of ionic species of the tetraalkyl aluminate type at that temperature; as discussed above, under these conditions no yttrium carbon bond is present. Thus, in the ionic situation the essential steps for ethene polymerization, i.e. precomplexation of the olefin followed by insertion into a metal carbon bond, are impossible, both at Y and Al. Lowering of the temperature restores the monomeric species and the polymerization is catalysed as before.

Propene is neither polymerized or oligomerized by **5** or **10**. When **5** was exposed to propene the complex  $\text{Cp}_2^*\text{YCH}_2\text{CHMe}_2 \cdot \text{THF}$  was observed in the mixture ( $^1\text{H}$  NMR [25]) in addition to the starting materials. No insertion of more than one propene molecule, such as was reported by Watson for  $\text{Cp}_2^*\text{YbMe}$  [26] and  $\text{Cp}_2^*\text{LuMe}$  [27], took place. An explanation for this is that the THF molecule present in our system is complexed to yttrium in the *s*-butyl derivative, thus suppressing further complexation of propene completely and subsequently prohibiting the insertion. Attempts to isolate this new complex failed, and only **5** was recovered. This suggests that the propene insertion is reversible. A  $\beta$ -methyl elimination, such as proposed by Watson [27] for related *4f*-element systems, is likely to occur in our system also, thus underlining the relationship of Y to the late *f*-elements.

No formation of  $\text{Cp}_2^*\text{Y}(\eta^3\text{-C}_3\text{H}_5) \cdot \text{THF}$ , which could have been expected from the reaction of  $\text{Cp}_2^*\text{LnH}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) with propene [28], was observed. Again the THF molecule seems to block this reaction by occupying an essential coordination site.

Thus the 16-electron complex **5** is less reactive towards propene than its 14-electron *f*-element congeners.

### Conclusions

The 14-electron systems  $\text{Cp}_2^*\text{YR}$  are extremely strong Lewis acids. They react with virtually all Lewis bases, even with salt molecules such as lithium or mag-



nesium halides. Once complexed, these bases are very difficult to remove. Synthesis of base-free  $\text{Cp}_2^*\text{YR}$  by use of ytrocene chloride precursors and lithium, Grignard or other hydrocarbyl introducing reagents is virtually impossible owing to the more-favoured adduct formation.

The tetramethylaluminate ligand in the  $\text{Cp}_2^*\text{Y}$  system shows a remarkable versatile ligating potential. It can bridge between two  $\text{Cp}_2^*\text{Y}$  units, act as a bidentate ligand for one such unit, or dissociate to produce ionic species at higher temperatures.

The catalytic activity of  $\text{Cp}_2^*\text{YR} \cdot \text{L}$  for the polymerization of olefines parallels closely that of the 4*f*-element analogues. High activity for ethene and no activity for propene polymerization was observed. For propene there is insertion of one molecule, but no propagation occurs.

Yttrium appears to be very useful as a model system for *f*-element chemistry.

## Experimental

All compounds are extremely air-sensitive, and experiments were carried out under nitrogen by glove box (Braun-MB-200) and Schlenk techniques. Solvents (pentane,  $\text{Et}_2\text{O}$ , THF, and toluene) were distilled from Na/K-alloy benzophenone ketyl prior to use.

Grignards [29], MeLi [30] and  $\text{LiAlMe}_4$  [31] were prepared by published methods. The syntheses of  $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)$  (**1**) [2] and  $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$  (**2**) [1] have been described previously. NMR spectra were recorded on Nicolet NT-200 and Bruker-WH-90 spectrometers. IR spectra (Nujol/KBr) were recorded with a Pye Unicam SP3-300 spectrophotometer. The results of the elemental analyses, carried out by the Micro-analytical Group of the Chemical Laboratories of this University, are reported in Table 3.

### $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})(\mu\text{-Me})\text{Li} \cdot 2\text{OEt}_2$ (**3**)

A solution of 0.75 g of **1** (1.29 mmol) in 50 ml of  $\text{Et}_2\text{O}$  at  $-80^\circ\text{C}$  was treated dropwise with 1.00 ml of a 1.28 *M* solution of MeLi in  $\text{Et}_2\text{O}$ . The mixture was stirred for 3 h as it warmed to room temperature. After evaporation of the solvent the solids were extracted with 50 ml of  $\text{Et}_2\text{O}$ . The colourless extract was stored overnight at  $-80^\circ\text{C}$  and white crystals formed, and shown to be **3** (0.30 g, 0.53 mmol, 41%). IR ( $\text{cm}^{-1}$ ): 2770w, 2720w, 1485m, 1420m, 1365m, 1300w, 1260w, 1185m, 1150w, 1115w, 1090m, 1060s, 1020m, 910w, 830w, 800w, 790m, 595w, 500m, 380m.

### $\text{Cp}_2^*\text{Y}(\mu\text{-Me})_2\text{Li} \cdot \text{OEt}_2$ (**4**)

A solution of MeLi (12.5 ml, 0.32 *M*) in  $\text{Et}_2\text{O}$  was added dropwise to a stirred solution of 1.13 g of **1** (2.0 mmol) in 50 ml of  $\text{Et}_2\text{O}$  at  $-80^\circ\text{C}$ . The mixture was allowed to warm to room temperature then stirred for 2 h. The solvent was evaporated and the residual solid was extracted with 80 ml of  $\text{Et}_2\text{O}$ . The clear solution was concentrated to ca. 40 ml in vacuo and stored overnight at  $-80^\circ\text{C}$ . Colourless crystals formed, and were filtered off to give 0.60 g of **4** (1.28 mmol, 64%). IR ( $\text{cm}^{-1}$ ): 2760m, 2720w, 1480m, 1365m, 1305w, 1185w, 1145m, 1125w, 1090m, 1060s, 1020m, 910w, 835w, 795w, 595w, 515m, 455m.

TABLE 3

ELEMENTAL ANALYSES FOR THE NEW COMPLEXES (Found (calc) (%))

Complex	C	H	Y	M'	X	
4	66.21 (66.37)	9.81 (9.86)	-	-	-	
5	67.29 (67.25)	9.31 (9.26)	20.17 (19.91)	-	-	
6	55.67 (56.75)	7.85 (8.05)	14.81 (14.48)	3.58 (3.96)	11.19 (11.55)	
7	(60.39) (60.93)	7.80 (7.85)	13.23 (12.89)	3.47 (3.52)	10.36 (10.27)	
8	45.34 (46.51)	6.53 (6.41)	11.31 (12.39)	3.14 (3.36)	3.01 Cl (4.09)	23.39 Br (22.10)
9	58.42 (58.78)	8.17 (9.17)	13.20 (13.60)	3.68 (3.68)	11.00 (10.84)	
10	64.39 (64.56)	9.46 (9.48)	19.90 (19.91)	6.07 (6.04)	-	

*Cp*<sub>2</sub><sup>\*</sup>YMe · THF (5)

A stirred solution of 7.82 g of **1** (13.4 mmol) in 130 ml of THF at  $-80^{\circ}\text{C}$  was treated dropwise with 32.6 ml of a 0.41 M solution of MeLi in Et<sub>2</sub>O (13.4 mmol). The mixture was stirred for 1 h and then allowed to warm gradually to room temperature, after which the solvent was removed in vacuo. The residual solid was extracted with 130 ml of pentane, and the clear solution stored at  $-30^{\circ}\text{C}$ . The colourless crystals were filtered off. Yield: 2.83 g of **5** (6.34 mmol, 48%) M.W. (cryosc, C<sub>6</sub>H<sub>6</sub>): calc 446; found:  $443 \pm 5$ . IR (cm<sup>-1</sup>): 2770w, 2720w, 1480m, 1365m, 1340w, 1295w, 1245w, 1180w, 1125m, 1085m, 1050s, 1020s, 915s, 900m, 860m, 800w, 670w, 595w, 510m, 385s. <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25°C):  $\delta$  11.47 (q, <sup>1</sup>J(CH) 124.8 Hz, C<sub>5</sub>Me<sub>5</sub>), 21.36 (dq, <sup>1</sup>J(CH) 108.2, <sup>1</sup>J(YC) 56.2 Hz, Y-Me), 24.99 (t, <sup>1</sup>J(CH) 133.1 Hz,  $\beta$ -THF), 69.96 (t, <sup>1</sup>J(CH) 148.7 Hz,  $\alpha$ -THF), 115.68 (s, C<sub>5</sub>Me<sub>5</sub>).

*Cp*<sub>2</sub><sup>\*</sup>YMe · [MgCl<sub>2</sub> · 2THF] (6)

A stirred suspension of 0.76 g of **2** (1.63 mmol) in 30 ml of Et<sub>2</sub>O of  $-80^{\circ}\text{C}$  was treated with 1.2 ml of a 1.38 M solution of MeMgCl (1.66 mmol) in THF. The mixture was stirred for 1 h then allowed to warm to room temperature. The solvents were pumped off and the residual solid dissolved in 10 ml of THF. Crystallisation at  $-80^{\circ}\text{C}$  afforded, after washing with pentane, 0.55 g of **6** (0.89 mmol, 55%) as colourless crystals. IR (cm<sup>-1</sup>): 2800m, 2770w, 2720w, 1495m, 1480m, 1425m, 1400w, 1365m, 1345m, 1320w, 1300w, 1260w, 1245w, 1180w, 1110w, 1080m, 1030s, 1020m, 955w, 920m, 870s, 840m, 805w, 675m, 630w, 615w, 595w, 500w, 390s.

*Cp*<sub>2</sub><sup>\*</sup>YCH<sub>2</sub>Ph · [MgCl<sub>2</sub> · 2THF] (7)

A stirred suspension of 1.26 g of **2** (2.70 mmol) in 30 ml of Et<sub>2</sub>O at 0°C was treated with 3.2 ml of a 0.86 M solution of PhCH<sub>2</sub>MgCl (2.75 mmol) in THF. After 18 h stirring at room temperature the solvent was pumped off and the solid

extracted with 40 ml of pentane. The solution was stored overnight at  $-30^{\circ}\text{C}$  and colourless crystals deposited. Isolated: 1.29 g of **7** (1.45 mmol, 54%). IR ( $\text{cm}^{-1}$ ): 3060w, 3000m, 2720w, 1595s, 1585m, 1575w, 1495w, 1485m, 1415w, 1365m, 1345w, 1295w, 1215s, 1170w, 1155w, 1060w, 1030s, 1020s, 995w, 950w, 920s, 885s, 865s, 825w, 800m, 745s, 700s, 595w, 560m, 525w, 435m.

$\text{Cp}_2^*\text{YCl} \cdot [\text{MgBr}_2 \cdot 2\text{THF}]$  (**8**)

A suspension of 0.96 g of **2** (2.05 mmol) in 30 ml of  $\text{Et}_2\text{O}$  was treated at room temperature with 2.2 ml of a 0.95 M solution of (2,6-xylyl)MgBr (2.09 mmol) in  $\text{Et}_2\text{O}$ . After overnight stirring the solvent was evaporated, and the residual solid dissolved in 10 ml of THF. Crystallization at  $-80^{\circ}\text{C}$  afforded 0.66 g of **8** (0.83 mmol, 40%) as colourless crystals. IR ( $\text{cm}^{-1}$ ): 2720w, 1485m, 1365m, 1340w, 1295w, 1260w, 1175w, 1070m, 1025s, 1015s, 950w, 920m, 875m, 860s, 840m, 800w, 670w, 595w.

$\text{Cp}_2^*\text{Y}(\mu^l\text{-CH}_2\text{CMe}=\text{CH}_2) \cdot [\text{MgCl}_2 \cdot 2\text{THF}]$  (**9**)

A stirred solution of 0.83 g of **2** (1.77 mmol) in 20 ml of THF at  $-80^{\circ}\text{C}$  was treated with  $\text{CH}_2=\text{CMeCH}_2\text{MgCl}$  in THF (2.3 ml 0.76 M, 1.77 mmol). After being allowed to warm to room temperature (4 h) the mixture was stirred for 2 h and the solvent removed in vacuo. Extraction with 40 ml of pentane and crystallisation at  $-30^{\circ}\text{C}$  afforded 0.31 g of **9** (0.46 mmol, 26%) as colourless crystals. IR ( $\text{cm}^{-1}$ ): 3060m, 2720w, 1620m, 1570m, 1490m, 1365m, 1340w, 1300w, 1275m, 1180w, 1090w, 1070w, 1030s, 1020m, 990w, 925s, 870s, 825m, 800w, 790s, 695m, 670m, 590s, 540w, 460m, 410m, 385m.

$[\text{Cp}_2^*\text{Y}(\mu\text{-Me})\text{AlMe}_2]_2$  (**10**)

A stirred solution of 1.37 g of **2** (2.92 mmol) in 30 ml of toluene at room temperature was treated with 4.4 ml of a 0.68 M  $\text{Et}_2\text{O}$  solution of  $\text{LiAlMe}_4$  (2.99 mmol). The mixture was stirred for 20 h, then the solids were filtered off and the clear solution stored at  $-80^{\circ}\text{C}$ . After crystallisation 0.72 g of **10** (1.61 mmol, 55%) was isolated as a colourless microcrystals. IR ( $\text{cm}^{-1}$ ): 2800m, 2760w, 2720w, 1480m, 1415m, 1365m, 1335w, 1260w, 1175s, 1090w, 1060w, 1020m, 905s, 895s, 810m, 800w, 780m, 740s, 675s, 620s, 595w, 565s, 545s, 515w.

## References and notes

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- 25 <sup>1</sup>H NMR spectrum of Cp<sub>2</sub>\*YCH<sub>2</sub>CHMe<sub>2</sub>·THF in C<sub>6</sub>D<sub>6</sub> at 20 °C: δ -0.76 (dd, 2H, <sup>2</sup>J(YH) 3.2, <sup>3</sup>J(HH) 7.1, YCH<sub>2</sub>), -0.03 (m, 1H, <sup>3</sup>J(HH) 6.5, CH<sub>2</sub>CHMe<sub>2</sub>), 1.08 (d, 6H, CHMe<sub>2</sub>), 1.30 (m, 4H, β-THF), 2.03 (s, 30H, Cp\*), 3.57 (m, 4H, α-THF).
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