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SYNTHESIS AND COORDINATION CHEMISTRY OF PERMETHYLYTTROCENE CHLORIDE *

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Summary

Permethylyttrocene chlorides $Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot 2OEt_2$ and $Cp^{\star}_2Y(\mu\text{-}Cl)_2Na \cdot OEt_2$ have been prepared from $YCl_3 \cdot 3THF$ and $Cp^{\star}Li$ or $Cp^{\star}Na$. The former can be converted into $Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot TMEDA$ and $Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot DME$. The latter reacts with TMEDA to give $Cp^{\star}_2Y(\mu\text{-}Cl)_2Na \cdot TMEDA$ and with THF to give $Cp^{\star}_2YCl \cdot THF$. In the reactions of $Cp^{\star}_2YCl \cdot THF$ with pyridine, acetone, and $Al_2Cl_2Et_4$ the THF molecule is replaced and the new complexes $Cp^{\star}_2YCl \cdot NC_5H_5$, $Cp^{\star}_2YCL \cdot OCMe_2$, and $Cp^{\star}_2Y(\mu\text{-}Cl)_2\,AlEt_2$ are formed. At 220 ° C and 0.03 mmHg $Cp^{\star}_2YCl \cdot THF$ loses THF and $(Cp^{\star}_2YCl)_2$ sublimes out.

Introduction

The combination of our interest in the chemistry of organic derivatives of early transition metals [1] and the appearance of unexpected interesting results in organolanthanoid chemistry [2-5] led us to study permethylyttrocene derivatives. This metal was chosen because yttrium and the late lanthanoids often show very related chemical behaviour [6-8]. We here report the synthesis and coordination chemistry of permethylyttrocene chloride. Reactions involving substitution of the chloride ligand are reported elsewhere [9,10].

Results and discussion

Synthesis

Our first objective was replacement of chlorine in $YCl_3 \cdot 3THF$ by a $Cp^{\star}$ ligand * by use of the reagents $Cp^{\star}Li$ or $Cp^{\star}Na$. Use of these reagents in 1/1

* In this paper the following abbreviations are used: $Cp^{\star} = \eta^5\text{-}C_5Me_5$; $Cp^{\prime\prime} = \eta^5\text{-}C_5H_3(1,3\text{-}SiMe_3)_2$; $Cp = \eta^5\text{-}C_5H_5$; TMEDA = *N,N,N´,N´*-tetramethylethylene-diamine; DME = dimethoxyethane.

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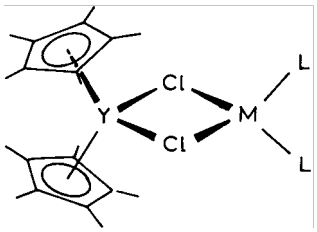


Fig. 1. The general structure of $Cp^{\star}_2Y(\mu\text{-}Cl)_2ML_2$ complexes.

stoichiometry results in mixtures of, presumably, $Cp^{\star}YCl_2$ and $Cp^{\star}_2YCl$ complexes. Reactions with two equivalents of $Cp^{\star}M$ do, however, yield permethylyttrocene chlorides (eq. 1).

$$2Cp^{\star}M + YCl_3 \cdot 3THF \xrightarrow[\text{reflux}]{\text{THF}} \xrightarrow{Et_2O} Cp^{\star}_2Y(\mu\text{-}Cl)_2ML + MCl \quad (1)$$
(**1**, M = Li, L = $2OEt_2$;
2, M = Na, L = OEt_2)

The yttrocene chlorides isolated contain a salt molecule, which appears to coordinate to yttrium as a result of the distinct Lewis acidity of this metal. Salt incorporation of this type is quite common in Group 3 and *f*-element chemistry [8]. Although no attempts have been made to study the structures of complexes **1** and **2**, it is assumed that they are symmetric and include bridging chlorine ligands (Fig. 1) as in analogous late lanthanoid complexes [2,11,12]. The salt complexes were isolated in good yields and are useful starting materials for the synthesis of permethylyttrocene alkyls [9].

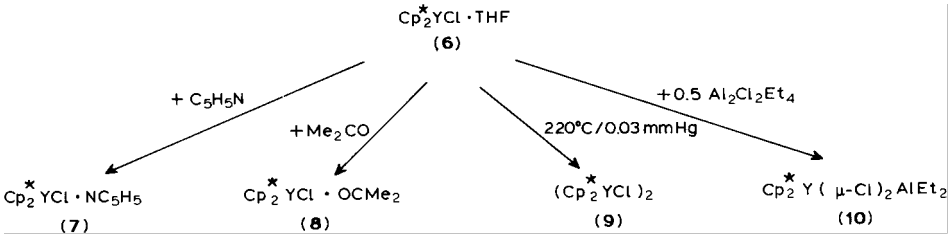
Attempts to remove the complexed salt molecule were successful in only one case. When **1** or **2** was heated in vacuum, no sublimation of $(Cp^{\star}_2YCl)_2$ was observed, in contrast to the results from $Cp^{\star}_2Y(\mu\text{-}Cl)_2K \cdot 2THF$ [13] and $Cp^{\prime\prime}_2Y(\mu\text{-}Cl)_2Li \cdot 2THF$ [14]. The use of the bidentate ligands TMEDA or DME gave complexes in which the salt is still present but the Et_2O ligands have been replaced (eq. 2).

$$Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot 2OEt_2 + L \xrightarrow{Et_2O} Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot L + 2Et_2O \quad (2)$$
(**4**, L = TMEDA;
5, L = DME)

Reaction of **2** with TMEDA yields $Cp^{\star}_2Y(\mu\text{-}Cl)_2Na \cdot TMEDA$ (**3**), without any salt removal. The only successful salt removal reaction involved treatment of **2** with an equivalent of THF, which gave the monomeric $Cp^{\star}_2YCl \cdot THF$ (**6**) (eq. 3).

$$Cp^{\star}_2(\mu\text{-}Cl)_2Na \cdot OEt_2 + THF \xrightarrow{\text{toluene}} Cp^{\star}_2YCl \cdot THF + NaCl + Et_2O \quad (3)$$
(**6**)

In this reaction the NaCl molecule is replaced by THF, a stronger base. The analogous reaction between **1** and THF does not yield a salt-free complex but instead a mixture of complexes in which one or two Et_2O ligands have been replaced. This indicates that LiCl interacts more strongly with the yttrocene chloride than does NaCl.

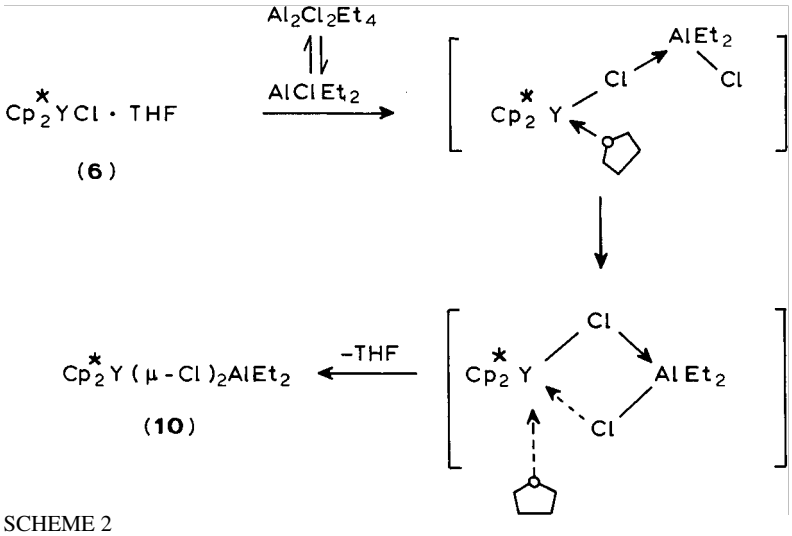


SCHEME 1

In addition to being a good starting material for the synthesis of yttrocene carbyls [9,10], **6** is also a convenient precursor for other permethyl-yttrocene chloride complexes (Scheme 1). Strong Lewis bases such as pyridine and acetone displace THF from its coordination site to give $Cp^{\star}_2YCl \cdot NC_5H_5$ (**7**) and $Cp^{\star}_2YCl \cdot OCMe_2$ (**8**). On heating in vacuum at 220 ° C, **6** loses THF, and $(Cp^{\star}_2YCl)_2$ sublimes out. Treatment of **6** with half a mole of $Al_2Cl_2Et_4$ yields the monomeric $Cp^{\star}_2Y(\mu\text{-}Cl)_2AlEt_2$ (**10**). This reaction shows that the formation of a $Y(\mu\text{-}Cl)_2Al$ moiety is preferred over THF coordination. It is noteworthy that formation of $AlClEt_2 \cdot THF$ is not observed here. However, when one mole of $Al_2Cl_2Et_4$ per yttrium is used the product is an inseparable mixture of **10** and $AlClEt_2 \cdot THF$. These findings lead us to propose a mechanism (Scheme 2) in which the first step is the formation of a single yttrium-aluminium chloride bridge. Such a bridge has been observed by Lobkovskii et al. [15] in the case of $(Cp_2YCl)_2AlH_3 \cdot OEt_2$. In the subsequent step the THF molecule will be eliminated with formation of the second chloride bridge.

Characterisation

The spectra of the yttrocenes described in this paper conclusively confirm the pentahapto bonding of the $Cp^{\star}$ ligands in all the complexes. The IR spectra show



SCHEME 2

TABLE 1

^{1}H NMR DATA FOR $Cp^\star_2YCl \cdot L$ COMPLEXES [a]

Compound	$Cp^\star$	L
$Cp^\star_2Y(\mu\text{-}Cl)_2Li \cdot 2OEt_2$ (**1**)	1.83(s, 30H)	1.07(t,12H, ^3J(HH) 7.1 Hz, β-Et)
		3.27(q, 8H, α-Et)
$Cp^\star_2Y(\mu\text{-}Cl)_2Na \cdot OEt_2$ (**2**)	2.09(s, 30H)	1.25(t, 6H, ^3J(HH) 7.1 Hz, β-Et)
		3.35(q, 4H, α-Et)
$Cp^\star_2Y(\mu\text{-}Cl)_2Na \cdot TMEDA$ (**3**)	2.22(s, 30H)	1.62(s, 4H, NCH_2)
		1.84(s, 6H, NMe_2)
$Cp^\star_2Y(\mu\text{-}Cl)_2Li \cdot TMEDA$ (**4**)	2.19(s, 30H)	1.78(s, 4H, NCH_2)
		2.00(s, 6H, NMe_2)
$Cp^\star_2Y(\mu\text{-}Cl)_2Li \cdot DME$ [b] (**5**)	1.91(s, 30H)	3.20(s, 6H, OMe)
		3.41(s, 4H, OCH_2)
$Cp^\star_2YCl \cdot THF$ (**6**)	2.01(s, 30H)	1.19(m,4H, β-THF)
		3.35(m,4H, α-THF)
$Cp^\star_2YCl \cdot NC_5H_5$ (**7**)	1.94(s, 30H)	6.59(m,2H, *o*-H)
		6.88(m,1H, *p*-H)
		8.35(m,2H, *m*-H)
$Cp^\star_2YCl \cdot OCMe_2$ (**8**)	1.99(s, 30H)	1.63(s, 6H, $OCMe_2$)
$(Cp^\star_2YCl)_2$ (**9**)	2.01(s)	
$Cp^\star_2Y(\mu\text{-}Cl)_2AlEt_2$ (**10**)	1.89(s, 30H)	0.53(q, 4H, ^3J(HH) 8.1 Hz, α-Et)
		1.40(t, 6H, β-Et)

[a] 90 MHz spectra in C_6D_6 at 20 ° C; shifts in δ(ppm); δ(TMS) = 0. [b] In THF-d_8 at 20 ° C.

the characteristic absorptions of a bis η^5-pentamethylcyclopentadienyl compound at ca. 2720w, 1485m, 1365m, 1020m, 800w and 595w cm^{-1}. The NMR spectra indicate that the $Cp^\star$ ligands are equivalent, showing only one resonance in the ^{1}H NMR (Table 1) and two in the $^{13}C\{^1H\}$ NMR spectra (Table 2); this means that the chloride as well as the other ligands are coordinated in the equatorial plane of the bent permethylyttrocene (Fig. 1). The chemical shifts of the $Cp^\star$ ligands in the ^{1}H NMR spectra are found in the range from δ 1.83 to 2.22 ppm. In the $^{13}C\{^1H\}$ NMR spectra the methyl carbons of the $Cp^\star$ ligand resonate between δ 11.26 and 12.00 ppm, whereas the ring carbon atom resonances appear between δ 117.32 and 120.38 ppm. These values are in similar ranges to those found in the fully characterized complexes $Cp^\star_2YN(SiMe_3)_2$ and $Cp^\star_2YCH(SiMe_3)_2$ [9], and support the normal bent metallocene structure for the chlorides.

The coordination of Et_2O, TMEDA and DME has hardly any effect on the $Cp^\star$ part of the NMR and IR spectra of **1**, **2**, **3**, **4**, and **5**. The effects of coordination on the ligands themselves are also relatively small. For example, the IR spectra of these complexes are superimposable on those of their Lu and Yb analogues [11,16].

The complexation of THF in **6** as well as of pyridine in **7** also have hardly any detectable effects on the spectral data for the metallocene moiety, and the same is true for the coordinated Lewis bases themselves. Only very small shifts of the NMR resonances of these ligands compared with those of the free molecules are observed, along with minor changes in the positions of the ligand absorptions in the IR spectra. The IR spectrum of **8** shows the carbonyl stretching vibration of the coordinated acetone at 1680 cm^{-1}, which is considerably lower than in the free molecule (1712 cm^{-1}). This lower wavenumber is indicative of a decrease in the bond order in the carbonyl function, probably due to withdrawal of electron density

TABLE 2

$^{13}C\{^1H\}$ NMR DATA FOR $Cp^{\star}_2YCl \cdot L$ COMPLEXES [a]

Compound	C_5Me_5	C_5Me_5	L
$Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot 2OEt_2$ (**1**)	11.82(q, 125.3)	117.85(s)	15.07(q, 125.7, β-Et) 65.83(t, 140.7, α-Et)
$Cp^{\star}_2(\mu\text{-}Cl)_2Na \cdot$ TMEDA (**3**)	12.00(q, 125.1)	117.35(s)	45.51(q, 134.2, NMe_2) 56.74(t, 133.0, NCH_2)
$Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot$ TMEDA (**4**)	12.01(q, 125.3)	117.57(s)	45.94(q, 134.3, NMe_2) 57.08(t, 132.4, NCH_2)
$Cp^{\star}_2Y(\mu\text{-}Cl)_2Li \cdot$ DME (**5**)	11.93(q, 125.1)	117.68(s)	59.10(q, 141.2, OMe) 71.05(t, 142.5, OCH_2)
$Cp^{\star}_2YCl \cdot$ THF (**6**)	11.70(q, 125.0)	118.10(s)	25.37(t, 133.7, β-THF) 71.97(t, 147.6, α-THF)
$Cp^{\star}_2YCl \cdot NC_5H_5$ (**7**)	11.58(q, 125.3)	117.85(s)	124.51(d, 168.5, *m*-C) 138.37(d, 167.2, *p*-C) 150.15(d, 185.0, *o*-C)
$Cp^{\star}_2YCl \cdot OCMe_2$ (**8**)	11.39(q, 125.1)	117.32(s)	31.06(q, 128.8, CMe) 222.93(d, ^2J(YC) 4.71, OC)
$Cp^{\star}_2Y(\mu\text{-}Cl)_2AlEt_2$ (**10**)	11.26(q, 126.0)	120.38(s)	3.04(t, 141.1, α-Et) 8.71(q, 123.6, β-Et)

[a] 50.3 MHz spectra in C_6D_6 at 20 °C, δ in ppm, J in Hz; δ(TMS) = 0. Multiplicity and coupling constants ^1J(CH) in parentheses.

by the Lewis acid Y. This effect is also manifested in the ^{13}C NMR spectrum of **8**, where the carbonyl carbon resonance at δ 222.93 ppm is shifted downfield with respect to that for free acetone (δ 206.0 ppm), clearly showing the deshielding effect on this carbon atom. The resonance appears as a doublet as a result of second order coupling with the yttrium nucleus (^2J(Y-C) 4.7 Hz) [17]. Coordination hardly affects the methyl group resonance of the acetone ligand (a 0.4 ppm downfield shift is observed in the ^{13}C NMR spectrum). The IR and ^1H NMR spectra of $(Cp^{\star}_2YCl)_2$ (**9**) are identical with those reported by Evans et al. [13].

The NMR spectra of **10** permit an unambiguous identification of the bridging ligands in this complex. Bridging ethyl groups should show a first order yttrium coupling to the methylene carbon of the ethyl group, but this is not observed for the complex under discussion. This shows that there are chlorine rather than alkyl bridges. This observation is in agreement with Holton's report [7] that reaction of $(Cp_2YMe)_2$ with $Al_2Cl_2Me_4$ gives $Cp_2Y(\mu\text{-}Cl)_2AlMe_2$ as the only product. Characteristic chloride bridge vibrations are also observed in the IR spectrum. The Al-Cl stretching vibration is found at 540 cm^{-1}, and the bridge deformation vibration at 385 cm^{-1}.

Conclusions

Salt-free permethylyttrocene chloride is not easily accessible by the reaction through $Cp^{\star}$ introducing salts like $Cp^{\star}Li$ and $Cp^{\star}Na$, because $Cp^{\star}_2YCl$ is too strong a Lewis acid, and even complexes with salt molecules like NaCl and LiCl. The complexed salt cannot be easily removed from the complexes. NaCl is displaced by THF, to give $Cp^{\star}_2YCl \cdot$ THF, which is a convenient starting material for the synthesis of other yttrocene chlorides and carbyls. The Lewis bases pyridine and

acetone as well as $AlClEt_2$ replace THF. Coordination of the salt molecules and Lewis bases has little effect on the bonding of the $Cp^\star$ ligand.

In $Cp^\star{}_2Y(\mu\text{-}Cl)_2AlEt_2$ chloride bridges are preferred over alkyl bridges.

Experimental

All the compounds are extremely air-sensitive, and the experiments were carried out under nitrogen, by glove box (Braun-MB-200) and Schlenk techniques. Solvents (pentane, Et_2O, THF and toluene) were distilled from Na/K alloy benzophenoneketyl prior to use. TMEDA and DME were distilled under nitrogen and stored over activated molecular sieves (3 Å). Acetone and pyridine were stored similarly after distillation from $CaCl_2$ or KOH. $Al_2Cl_2Et_4$ was prepared by a published procedure [18]. $Cp^\star H$ was synthesized by Burger's method [19] and converted into $Cp^\star Li$ [20] and $Cp^\star Na$ [9] as described previously. $YCl_3 \cdot 3THF$ was synthesized from Y_2O_3 (Aldrich) [9]. IR spectra (Nujol/KBr) were recorded with a Pye Unicam SP-300 spectrophotometer, and NMR spectra on Nicolet NT 200, Bruker WH-90, and Hitachi Perkin-Elmer R-24B spectrometers. Elemental analyses were carried out at the Micro-Analytical Group of the Chemical Laboratories of this University under the supervision of Mr. A.F. Hamminga, and the results are given in Table 3.

*Synthesis of $Cp^\star{}_2Y(\mu\text{-}Cl)_2Li \cdot 2OEt_2$ (**1**)*

A suspension of 21.60 g of $YCl_3 \cdot 3THF$ (48.6 mmol) and 15.20 g of $Cp^\star Li$ (106 mmol) in 500 ml of THF was refluxed for 6 h. After cooling, THF was evaporated off and the solids extracted with 300 ml of Et_2O. After crystallization at -30 ° C the mother liquor was decanted, and 14.5 g of **1** was isolated as large colourless crystals.

TABLE 3

ELEMENTAL ANALYSES (Found (calc) (%)) OF $Cp^\star{}_2YCl \cdot L$ COMPLEXES

Complex	C	H	Y	Cl	Other
$Cp^\star{}_2Y(\mu\text{-}Cl)_2Li \cdot 2OEt_2$ (**1**)	57.44	8.48	-	-	-
	(57.23)	(8.48)			
$Cp^\star{}_2Y(\mu\text{-}Cl)_2Na \cdot OEt_2$ (**2**)	54.92	7.44	16.86	13.44	-
	(54.64)	(7.65)	(16.71)	(13.30)	
$Cp^\star{}_2Y(\mu\text{-}Cl)_2Na \cdot TMEDA$ (**3**)	55.89	8.47	15.31	12.22	-
	(54.84)	(8.14)	(15.61)	(12.45)	
$Cp^\star{}_2Y(\mu\text{-}Cl)_2Li \cdot TMEDA$ (**4**)	56.33	8.38	16.37	12.94	N 5.02
	(56.43)	(8.38)	(16.06)	(12.82)	(5.06)
$Cp^\star{}_2Y(\mu\text{-}Cl)_2Li \cdot DME$ (**5**)	54.27	7.55	16.82	13.45	Li 1.43
	(54.67)	(7.60)	(16.87)	(13.03)	(1.33)
$Cp^\star{}_2YCl \cdot THF$ (**6**)	61.49	8.20	18.90	7.64	-
	(61.74)	(8.20)	(19.04)	(7.59)	
$Cp^\star{}_2YCl \cdot NC_5H_5$ (**7**)	63.20	7.47	18.50	7.56	-
	(63.26)	(7.44)	(18.76)	(7.48)	
$Cp^\star{}_2YCl \cdot OCMe_2$ (**8**)	59.85	7.84	19.48	8.30	-
	(61.00)	(8.01)	(19.63)	(7.83)	
$(Cp^\star{}_2YCl)_2$ (**9**)	60.58	7.65	22.45	8.89	-
	(60.84)	(7.66)	(22.52)	(8.78)	
$Cp^\star{}_2Y(\mu\text{-}Cl)_2AlEt_2$ (**10**)	55.33	7.86	-	-	-
	(55.93)	(7.82)			

Concentration of the mother liquor gave a second crop. Overall yield 20.7 g of **1** (35.3 mmol, 73%) IR (cm^{-1}): 2720w, 1480m, 1365m, 1295m, 1185m, 1150m, 1115m, 1090s, 1065s, 1020s, 975w, 910m, 835m, 795m, 720m, 595w, 500m and 385m.

*$Cp^{\star}{}_2Y(\mu\text{-}Cl)_2Na(OEt_2)$ (**2**)*

To a suspension of 2.16 g of $YCl_3 \cdot 3THF$ (4.86 mmol) in 100 ml of THF was added 33.7 ml of a 0.29 *M* solution of $Cp^{\star}Na$ in THF (9.77 mmol), and the mixture was refluxed for 3 h. The solvent was completely removed in vacuo and the solids extracted with 100 ml of Et_2O. The clear solution was stored at -30 ° C overnight and large colourless crystals formed. Isolated 1.56 g of **2** (2.59 mmol, 53%). IR (cm^{-1}): 2720w, 1480m, 1365m, 1320w, 1285w, 1240w, 1160w, 1130w, 1095s, 1075s, 1050m, 1020s, 910w, 860w, 810w, 800w, 795w, 595w and 360m.

*$Cp^{\star}{}_2Y(\mu\text{-}Cl)_2Na \cdot TMEDA$ (**3**)*

To a solution of 1.03 g of **2** (1.71 mmol) in 50 ml of Et_2O at room temperature was added 0.53 ml of TMEDA (3.51 mmol). After 3 h stirring the volatiles were pumped off and the solids dissolved in 15 ml of toluene. Crystallization at -80 ° C afforded 0.56 g of **3** (0.98 mmol, 57%) as pale yellow crystals. IR (cm^{-1}): 2890m, 2870m, 2720w, 1490m, 1415w, 1365m, 1355m, 1290s, 1245w, 1175w, 1155m, 1135m, 1100w, 1080m, 1040s, 1025s, 955s, 930w, 800w, 785s, 775m, 730m, 695w, 595w, 570w and 425m.

*$Cp^{\star}{}_2Y(\mu\text{-}Cl)_2Li \cdot TMEDA$ (**4**)*

A solution of 1.10 g of **1** (1.88 mmol) in 50 ml of Et_2O was treated with 0.40 ml of TMEDA (2.65 mmol) and the mixture stirred for 19 h at room temperature. After evaporation to complete dryness the solids were extracted with 50 ml of Et_2O. Crystallisation at -80 ° C afforded 0.56 g of **4** (1.02 mmol, 54%) as colourless crystals. IR (cm^{-1}): 2720w, 1485m, 1420m, 1405m, 1365m, 1335w, 1315w, 1285s, 1245w, 1180w, 1155m, 1125m, 1095w, 1065m, 1030s, 1015s, 940s, 885w, 800w, 790s, 770m, 630w, 615w, 595w, 480m, 435m and 375m.

*$Cp^{\star}{}_2Y(\mu\text{-}Cl)_2Li \cdot DME$ (**5**)*

A solution of 0.81 g of **1** (1.39 mmol) in 40 ml of Et_2O and 10 ml of DME was stirred for 24 h. The solvents were pumped off and the solids extracted with 30 ml of Et_2O. Crystallisation at -80 ° C gave 0.32 g of **5** (0.60 mmol, 43%) as white crystals. IR (cm^{-1}): 2750w, 2720w, 1490m, 1420m, 1370s, 1365m, 1340w, 1300m, 1270w, 1240w, 1190w, 1140w, 1120m, 1080s, 1030w, 1020m, 980w, 940w, 870m, 835w, 800w, 770w, 665w, 595w, 480w and 420m.

*$Cp^{\star}{}_2YCl \cdot THF$ (**6**)*

THF (0.58 ml) was added to a suspension of 4.31 g of **2** (7.17 mmol) in 100 ml of toluene whereupon the suspension almost disappeared. The NaCl was centrifuged off and the clear yellow solution was transferred to a Schlenk flask. The solvent was evaporated until crystallisation started, and the remaining solution stored overnight at -30 ° C to give 1.61 g of **6** as off-white crystals. Concentration of the mother liquor gave a second crop. Overall yield 2.76 g of **6** (5.92 mmol, 83%). IR (cm^{-1}): 2720w, 1490m, 1365m, 1340w, 1180w, 1035m, 1015s, 915m, 860s, 840m, 800w, 735m, 675m, 595w and 375m.

*$Cp^{\star}_2YCl \cdot NC_5H_5$ (**7**)*

Pyridine (0.25 ml, 3.10 mmol) was added from a syringe to a solution of 0.96 g of **6** (2.06 mmol) in 10 ml of toluene and the mixture was stirred for 6 h. After concentration to approx. 50%, 5 ml of pentane was added and the solids formed were filtered off. Storage of the clear yellow solution overnight at -30 ° C gave 0.58 g of **7** (1.20 mmol, 59%) as an off-white microcrystalline solid. IR (cm^{-1}): 3070w, 3050w, 2720w, 1630w, 1600s, 1565w, 1480m, 1445s, 1365m, 1230w, 1210m, 1150w, 1115w, 1060s, 1035s, 1020m, 1005s, 950w, 880w, 800w, 765s, 705s, 625m, 595w, 425m and 385m.

*$Cp^{\star}_2YCl \cdot OCMe_2$ (**8**)*

A suspension of 0.78 g of **6** (1.69 mmol) in 30 ml of Et_2O was stirred with 0.18 ml of acetone (2.45 mmol) for 2 h. A clear yellow solution formed and this solution was stored at -80 ° C to deposit pale yellow crystals. Isolated 0.27 g of **8** (0.59 mmol, 25%). IR (cm^{-1}): 2720w, 1680s, 1480m, 1420m, 1365m, 1250m, 1170w, 1120w, 1095w, 1060w, 1020m, 920w, 800w, 595w, 540m, 500w, 425w and 385m.

*$(Cp^{\star}_2YCl)_2$ (**9**)*

On heating 1.04 g of **6** (2.33 mmol) at 210-230 ° C/0.03 mmHg complex **9** sublimed out. After washing with pentane *, 0.64 g of **9** (1.61 mmol, 72%) was isolated as a white powder. IR (cm^{-1}): 2720w, 1485m, 1365m, 1270w, 1060w, 1020s, 945w, 800w, 595w, 385m and 360m.

*$Cp^{\star}_2Y(\mu\text{-}Cl)_2AlEt_2$ (**10**)*

A 1.0 *M* solution of $Al_2Cl_2Et_4$ (0.95 ml, 1.90 mmol) in toluene was added with stirring at room temperature to a solution of 0.90 g of **6** (1.93 mmol) in 10 ml of toluene. After 1 h the solvent was reduced in vacuo to approx. 5 ml, and crystallization at -80 ° C gave the crude product. Recrystallisation from 5 ml of pentane gave 0.29 g of **10** (0.52 mmol, 27%) as colourless crystals. IR (cm^{-1}): 2790m, 2720w, 1510m, 1485m, 1405m, 1365m, 1300w, 1260w, 1225m, 1190w, 1060w, 1025s, 1000w, 980s, 945m, 920m, 865m, 800w, 780w, 655s, 595w, 540s and 385s.

Treatment of **6** with double the proportion of $Al_2Cl_2Et_2$ gave an unseparable mixture of **10** and $AlClEt_2 \cdot THF$ (NMR).

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* Without the washing step an impurity, probably $Cp^{\star}H$, is present, and gives rise to a strong absorption in the IR spectrum at 1610 cm^{-1}.

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