

# Studies on Organolanthanide Complexes. Part 55.<sup>1</sup> Synthesis of Furan-bridged Bis(cyclopentadienyl) Lanthanide and Yttrium Chlorides, and Ligand and Metal Tuning of Reactivity of Organolanthanide Hydrides (*in situ*)

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Four new complexes  $[\{Ln[\overline{OCH(CH_2C_5H_4)CHCHCH(CH_2C_5H_4)}]Cl\}_2]$  ( $Ln = Y, Yb, Sm$  or  $Nd$ ) were synthesised by using furan-bridged bis(cyclopentadienes) as ancillary ligands and characterized by elemental analyses, mass, IR and  $^1H$  NMR spectroscopy. The spectra indicate that these complexes are chloride-bridged dimers and the two furan-bridged cyclopentadienyl rings co-ordinate to each metal in a chelating fashion with intramolecular co-ordination between the oxygen atom and the metal. The effects of the bridging chain and the central metal upon the reactivity of organolanthanide hydrides generated *in situ* from the  $[Ln(C_5H_5)_2Cl]-NaH$  system were investigated. The reactivity can be tuned not only by varying the ligands but also by taking advantage of the lanthanide contraction. The ligand tunability varies for different reactions. More reactive organolanthanide hydride species (*in situ*) can be obtained by both 'ligand tuning' and 'metal tuning', *i.e.* by selecting the appropriate ancillary ligands and the early lanthanide metals.

In recent years the chemistry of organolanthanide hydrides has become one of the most active research fields of organolanthanide chemistry and it has been found that the Ln-H bond is highly reactive and can (1) catalyse the hydrogenation<sup>2-7</sup> and polymerization<sup>8-16</sup> of alkenes and alkynes, (2) activate CO<sup>17-19</sup> and C-H,<sup>17,20-24</sup> C-C,<sup>25</sup> C-O and Si-O<sup>20</sup> bonds, (3) catalyse the hydrosilylation<sup>26-28</sup> and hydroboration<sup>29</sup> of olefins, (4) catalyse the hydroamination/cyclization of aminoolefins,<sup>30-32</sup> (5) catalyse the dehydrooligomerization of silanes<sup>33</sup> and (6) catalyse the cyclization of 1,5- and 1,6-dienes.<sup>34</sup> However, it is just this high reactivity that makes it challenging to prepare and manipulate these hydrides. We have previously demonstrated that the organolanthanide hydrides generated *in situ* from the reaction of  $Ln(C_5H_5)_3$  or  $Ln(C_5H_5)_2Cl$  with sodium hydride in tetrahydrofuran (thf) exhibited comparable reactivity and were effective for the reduction, catalytic hydrogenation and isomerization of alkenes,<sup>35-39</sup> catalytic dehalogenation of organic halides<sup>40-42</sup> and deoxygenation of heteroatom oxides,<sup>43</sup> avoiding the difficulty of the preparation and manipulation of these highly reactive hydrides. This stimulated us to undertake a further search for much more reactive organolanthanide hydride species (*in situ*).

On the other hand, in our previous papers<sup>44-53</sup> we suggested that ring-bridged bis(cyclopentadienyl) ligands are effective in preventing the complexes from undergoing intermolecular ligand redistribution. Also that the rigidity of the bridging chain and intramolecular co-ordination of the heteroatom in the bridging chain would decrease the torsional mobility of the cyclopentadienyl ring and open the co-ordination sphere around the central metal, and therefore might facilitate the availability of co-ordination sites for other substrates and enhance the possibility of acquiring more stable, but also more reactive, organolanthanide species. What about the reality? In order to answer this question and to acquire more reactive hydride species (*in situ*), we have investigated the effect of the properties of the bridging chain on the reactivity of the hydride species, which are generated *in situ* from the reaction of ring-bridged bis(cyclopentadienyl) lanthanide chlorides with sodium hydride in thf, toward the reduction of oct-1-ene and the

catalytic dechlorination of benzyl chloride, together with the central metal tuning of the reactivity of these hydrides. The synthesis and characterization of furan-bridged bis(cyclopentadienyl) lanthanide and yttrium chlorides are also reported.

## Results and Discussion

**Synthesis of Furan-bridged Bis(cyclopentadienyl) Lanthanide and Yttrium Chlorides 1-4.**—Four new furan-bridged bis(cyclopentadienyl) lanthanide and yttrium chlorides **1-4** were prepared (Scheme 1) in high yields by treating anhydrous  $LnCl_3 \cdot n\text{thf}$  ( $n = 0, 3$  or  $4$ ) with the disodium salt  $\overline{OCH(CH_2C_5H_4Na)CHCHCHCH_2C_5H_4Na}$  under the given conditions. The disodium salt was obtained from the reaction of  $Na(C_5H_5)$  with 2,5-bis(chloromethyl)furan followed by treatment with an excess of sodium sand or sodium hydride. The disubstituted furan was synthesised by chloromethylation of 2-chloromethylfuran according to the literature method,<sup>54</sup> or by the replacement of the OH groups of furan-2,5-dimethanol by treatment with  $SOCl_2$  in chloroform. The whole procedure is presented in Scheme 1.

Using the furan-bridged bis(cyclopentadienes) as ancillary ligands, complexes of the type  $[\{Ln[\overline{OCH(CH_2C_5H_4)CHCHCH(CH_2C_5H_4)}]Cl\}_2]$  are readily accessible for neodymium and the later rare-earth metals. However, efforts to obtain their lanthanum and praseodymium congeners with reasonable purity under similar conditions have failed. For praseodymium the content of chlorine in the obtained product is half that required for the pure chloride, and only a quarter for lanthanum.

These complexes are still sensitive to air and moisture. They do not sublime at  $< 5 \times 10^{-4}$  mmHg ( $6.65 \times 10^{-2}$  Pa) because of their prior decomposition.

The electron impact (EI) mass spectra of these complexes were measured and the data are presented in Table 1. Although complexes **1**, **2** and **4** ( $Ln = Y, Yb$  or  $Nd$ ) do not exhibit the dimeric parent molecular ion  $[2M]^+$ , the relative intensity of the latter for complex **3** ( $Ln = Sm$ ) is very strong. Since these metals generally show similar chemistry, this suggests that the

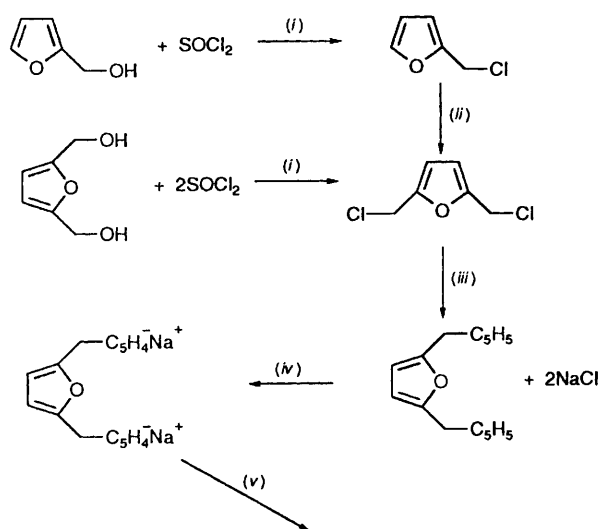
complexes may be dimers in the solid and/or vapour states. Except for complex **4** which does not show a monomeric molecular ion  $[M]^+$ , the mass spectra of all the complexes give very high relative intensity peaks for  $[M]^+$  and  $[M - Cl]^+$ , indicating that these lanthanide chlorides are relatively stable and the Ln-Cl bond is probably more easily cleaved under the EI conditions. This feature is in agreement with our previous observations for the complexes  $[Ln\{(C_5H_4CH_2CH_2)_2O\}Cl]^{48}$ ,  $[Ln\{(C_5H_4CH_2CH_2)_2NMe\}Cl]^{53}$  and  $[Ln\{2,6-(C_5H_4CH_2)_2C_5H_3N\}Cl]^{52}$  with a heteroatom in the bridging chain, but differs from those of complexes  $[Ln\{(C_5H_4CH_2)_2CH_2\}Cl] \cdot thf^{44}$ ,  $[Ln\{(C_5H_4CH_2CH_2)_2CH_2\}Cl] \cdot thf^{47}$  and  $[Ln\{m-(C_5H_4CH_2)_2C_6H_4\}Cl] \cdot thf^{51}$  without a heteroatom and  $[Ln(C_5H_4Me)_2Cl]$  and  $[Ln(C_5H_5)_2Cl]^{55}$  without a bridging chain, and

**Table 1** Mass spectral data for complexes 1-4

Fragment <sup>b</sup>	<i>m/z</i> <sup>a</sup>			
	1 (M = Y)	2 (Yb)	3 (Sm)	4 (Nd)
$[2M]^+$			818 (21)	
$[2M - Cl]^+$			783 (4)	
$[M]^+$	346 (8)	431 (37)	409 (6)	
$[M - HCl]^+$	310 (20.5)	395 (100)	373 (69)	364 (16)
$[C_{10}H_{10}ClLn]^+ + 1$		340 (5.5)	318 (7)	
$[M - Cl - C_6H_7]^+$		317 (13)	295 (21)	
$[L]^+$	224 (42.5)	224 (42)	224 (100)	224 (40)
$[LnCl]^+$		209 (35)	187 (27)	
$[L - C_5H_5]^+$	159 (100)	159 (52)	159 (99)	159 (10)
$[L - C_6H_7]^+$	145 (15.5)	145 (4)	145 (12)	
$[Ln]^+$		174 (6)	152 (8)	
$[C_6H_7O]^+$	95 (12)	95 (8)	95 (29)	95 (20)
$[C_6H_6]^+ - 1$	77 (33)	77 (27)	77 (51)	77 (32)
$[C_5H_5]^+$	65 (40)	65 (12)	65 (80)	65 (42)

<sup>a</sup> Mass number is based upon <sup>89</sup>Y, <sup>174</sup>Yb, <sup>152</sup>Sm, <sup>142</sup>Nd, <sup>35</sup>Cl, <sup>16</sup>O, <sup>12</sup>C and <sup>1</sup>H. Relative intensities (%) in parentheses.

<sup>b</sup> L =  $\overline{OCH(CH_2C_5H_5)CHCH(CH_2C_5H_5)}$ .



**Scheme 1** (i)  $CHCl_3$ , pyridine; (ii)  $(CH_2O)_n$ , HCl,  $ZnCl_2$ ,  $CHCl_3$ ; (iii)  $2Na(C_5H_5)$ , thf, 0 °C; (iv) 2Na (or NaH), thf, room temperature; (v)  $2LnCl_3 \cdot nthf$ ,  $n = 0$ , Ln = Y **1** or Yb **2**;  $n = 3.2$ , Ln = Sm **3**;  $n = 4$ , Ln = Nd **4**

might result from intramolecular co-ordination between the heteroatom and the central metal. The presence of very high relative intensity peaks due to  $[L]^+$  and  $[L - C_5H_5]^+$  [ $L = C_4H_2O(CH_2C_5H_5)_{2-2,5}$ ] is another feature of these complexes, which differs from our previous results for the above-mentioned heteroatom-containing ring-linked bis(cyclopentadienyl) lanthanide and yttrium chlorides.<sup>48,52,53</sup>

There are two isomers **I** and **II** for these dimeric ring-linked bis(cyclopentadienyl) lanthanide chlorides. Based on detailed analysis of their mass fragmentation, Fischer and his co-workers<sup>56</sup> found that the mass spectra of type **I** complexes give relatively strong peaks  $[M]^+$  and  $[M - Cl]^+$  while those of type **II** complexes exhibited no such peaks but those of binuclear fragments without chlorine atoms. Comparison of the present results with those of Fischer leads to the conclusion that the present chlorides are of type **I**, the two furan-bridged cyclopentadienyl rings each coordinating to one metal ion in a chelating fashion and the two metal ions being linked by two bridging chloride ligands, as shown in Scheme 1.

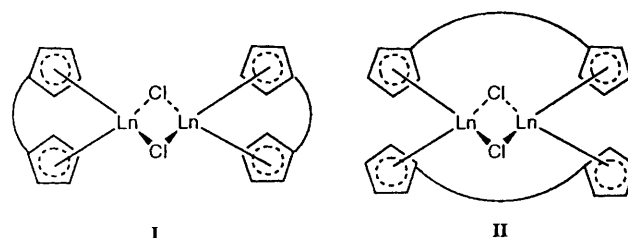
The IR spectra of complexes 1-4 and of the precursor disodium salt were measured from 4000 to 180  $cm^{-1}$  and showed very similar features. There are characteristic cyclopentadienyl absorptions, indicating that these groups co-ordinate in a  $\eta^5$  fashion. The C-O-C stretching vibrations are assigned at about 1195  $cm^{-1}$  and shifted to lower frequency compared with that of the disodium salt,  $\Delta\nu = 40-50 cm^{-1}$ . This implies the formation of an intramolecular co-ordination bond between the oxygen atom of the furan bridge and the central metal ion.<sup>49</sup>

The <sup>1</sup>H NMR spectra of complex **1** and of the precursor disodium salt were measured using  $[^2H_8]thf$  as solvent. The results are shown in Table 2. It can be seen that when the complex is formed the signals of the hydrogen atoms of the furan ring are split into two peaks, indicating that they are chemically inequivalent. Furthermore, the two  $CH_2$  groups are also chemically inequivalent and give signals at  $\delta$  3.51 and 3.61 respectively. This inequivalence might result from the dissociation of the dimer in thf and the co-ordination of thf to the metal (Scheme 2). To verify this, the spectrum was run in non-Lewis base solvents such as  $CDCl_3$  and  $C_6D_6$ . Unfortunately, complex **1** is unstable in  $CDCl_3$  giving a complicated spectrum, and is hardly soluble in hydrocarbon solvents such as benzene. When compared with the disodium salt, the signals of the two furan-ring hydrogen atoms in complex **1** shift to lower field with  $\Delta\delta = 0.79$  and 0.69 implying the existence of an intramolecular co-ordination bond,<sup>49,52,53</sup> which is also responsible for the above-mentioned inequivalence.

Therefore, using furan-bridged bis(cyclopentadienyls) as ancillary ligands, complexes of type **I** are readily accessible for neodymium and the later lanthanides.

**Table 2** Proton NMR data for complex **1** and the disodium salt ( $\delta$  in  $[^2H_8]thf$ ,  $SiMe_4$  reference)

Compound	$C_5H_4$	Furan ring	$CH_2$
<b>1</b>	6.15 (m, 4 H)	6.59 (m, 1 H)	3.61 (m, 2 H)
	5.93 (m, 4 H)	6.49 (m, 1 H)	3.51 (m, 2 H)
Disodium salt	5.36-5.50 (m, 8 H)	5.80 (s, 2 H)	3.67 (s, 4 H)



*Tuning of the Reactivity of Organolanthanide Hydrides (in situ) towards Reduction of Oct-1-ene.*—In our laboratory, a series of ring-bridged bis(cyclopentadienyl) ligands have been used to acquire the early lanthanide derivatives.<sup>44–53</sup> The ultimate aim of this approach is to obtain not only relatively stable but also more reactive organolanthanide species. What about the reactivity of these bis(cyclopentadienyl) lanthanide derivatives? Based on our studies<sup>35–43</sup> on the reactivity of organolanthanide hydrides generated *in situ* we investigated the ligand and metal tuning of the reactivity of organolanthanide hydrides, generated *in situ* from the reaction of these complexes with sodium hydride, toward reduction of oct-1-ene (Table 3).

From Table 3 it can be seen that the properties of the bridging chains strongly affect the reactivity. The complexes  $[Y\{(C_5H_4CH_2)_2Cl\}Cl]\cdot thf$ ,  $[Y\{(C_5H_4CH_2CH_2)_2CH_2\}Cl]\cdot thf$  and  $[Y\{m-(C_5H_4CH_2)_2C_6H_4\}Cl]\cdot thf$  show no reactivity toward the reduction, the reactivity of  $[Y\{\overline{OCH(CH_2C_5H_4)CHCHCH(CH_2C_5H_4)}\}Cl]$  is very low, while  $[Y\{(C_5H_4CH_2CH_2)_2O\}Cl]$  and  $[Y\{(C_5H_4CH_2CH_2)_2NMe\}Cl]$  show very high reactivity and are much more reactive than  $[Y(C_5H_5)_2Cl]$ .

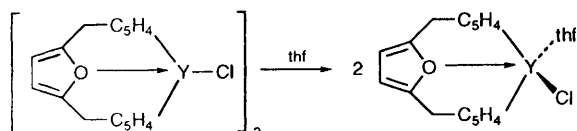
As previously reported,<sup>35,39</sup> the mechanism of the reduction of oct-1-ene is as follows. Complexes  $[Ln(C_5H_5)_2Cl(thf)_n]$  ( $n = 0$  or 1) react with sodium hydride in thf generating organolanthanide hydrides, to which oct-1-ene co-ordinates, and the subsequent insertion of the C=C bond into the Ln–H  $\sigma$  bond produces a compound containing a Ln–C  $\sigma$  bond, which is protolysed to give octane. The reactivity observed in these reductions is determined largely by the ‘cone angle of reaction’ formed by the two cyclopentadienyl rings in the bent metallocenes. The wider this angle the more reactive the complex is likely to be, and conversely a smaller angle will result in less reactive complexes.<sup>6</sup> For the systems  $[Y\{(C_5H_4CH_2)_2Cl\}]\cdot thf$ ,  $[Y\{(C_5H_4CH_2CH_2)_2CH_2\}]\cdot thf$  and  $[Y\{m-(C_5H_4CH_2)_2C_6H_4\}]\cdot thf$ , with NaH, because the reaction was carried out in thf, co-ordinated thf did not dissociate and just obstructed the ‘cone angle of reaction’, resulting in the olefin being incapable of co-ordinating to the metal and subsequently inserting into the Ln–H  $\sigma$  bond. The greater reactivity of  $[Y\{(C_5H_4CH_2CH_2)_2O\}Cl]$  and  $[Y\{(C_5H_4CH_2CH_2)_2NMe\}Cl]$  with NaH might be due to the larger ‘cone angle of reaction’ which results from the change of the orientation of cyclopentadienyl rings arising from the

intramolecular co-ordination between the oxygen or nitrogen atom and the metal, and no external thf co-ordinating to the metal and obstructing the angle. In addition, the increase of the electron density on the metal resulting from the intramolecular co-ordination decreases its hardness. According to the hard and soft acid and base principle, the olefins will be easier to co-ordinate and the reaction readily occurs. However, the  $[Y\{\overline{OCH(CH_2C_5H_4)CHCHCH(CH_2C_5H_4)}\}Cl]-NaH$  system is much less reactive and after a period plenty of pale yellow unidentified solid was produced. The reason for this defect is unclear. Therefore, the reactivity of the organolanthanide hydrides generated *in situ* can be adjusted by varying the ligands on the metal. Metal tuning of reactivity can also be achieved by taking advantage of the well known lanthanide contraction. The early lanthanide hydrides (*in situ*) are much more active than the later ones (Table 3, entries 7–10). Since early lanthanides have larger ionic radii, bent metallocenes incorporating these metals will have larger ‘cone angles of reaction’. All other factors being equal, early lanthanide hydrides thus provide greater reactivity relative to those of the late lanthanides and yttrium.

*Tuning of the Reactivity of Organolanthanide Hydrides (in situ) towards Catalytic Dechlorination.*—Since catalytic dehalogenation of organic halides is one of the most important and fundamental transformations in synthetic organic chemistry and environmental decontamination, we have also examined the tunability of the organolanthanide hydride (*in situ*) toward the dechlorination of benzyl chloride, by varying the ligands and central metals. The results are summarized in Table 4.

From Table 4 it can be seen that all the complexes exhibit high catalytic activity in the order  $[Y\{(C_5H_4CH_2CH_2)_2O\}Cl] > [Y\{(C_5H_4CH_2CH_2)_2CH_2\}Cl]\cdot thf > [Y\{\overline{OCH(CH_2C_5H_4)CHCHCH(CH_2C_5H_4)}\}Cl] > [Y(C_5H_5)_2Cl] > [Y\{(C_5H_4CH_2CH_2)_2NMe\}Cl] > [Y\{m-(C_5H_4CH_2)_2C_6H_4\}Cl]\cdot thf$ . This is different from the results for the oct-1-ene reduction, indicating the tunability of these organolanthanide hydride species (*in situ*) varies for the different reactions. Different reaction mechanisms are probably responsible for these results. Nevertheless, the lanthanide metals show the similar tunability trends in both reactions.

In conclusion, the reactivity of the organolanthanide hydrides generated *in situ* from the reaction of complexes  $[Ln(C_5H_5)_2Cl]$  with sodium hydride in thf can be tuned not only by varying the ligands but also by taking advantage of the lanthanide contraction. The ligand tunability of reactivity varies for different reactions. The goal of acquiring more reactive organolanthanide hydrides (*in situ*) can be achieved by both ‘ligand tuning’ and ‘metal tuning’, *i.e.* selecting the appropriate ligands and the early lanthanide metals.



Scheme 2

Table 3 Effects of the bridging chain and metal on the reduction of oct-1-ene<sup>a</sup>

Entry	Complex	Conversion (%) <sup>b</sup>		
		24	44	72 h
1	$[Y(C_5H_5)_2Cl]$	14	20	32
2	$[Y\{(C_5H_4CH_2CH_2)_2CH_2\}Cl]\cdot thf$	0	0	0
3	$[Y\{(C_5H_4CH_2)_2Cl\}]\cdot thf$	0	0	0
4	$[Y\{m-(C_5H_4CH_2)_2C_6H_4\}Cl]\cdot thf$	0	0	0
5	$[Y\{\overline{OCH(CH_2C_5H_4)CHCHCH(CH_2C_5H_4)}\}Cl]_2$	4	4	6
6	$[Y\{(C_5H_4CH_2CH_2)_2O\}Cl]$	64	84	95
7	$[Y\{(C_5H_4CH_2CH_2)_2NMe\}Cl]$	40	66	94
8	$[Yb\{(C_5H_4CH_2CH_2)_2NMe\}Cl]$	7	11	16
9	$[Sm\{(C_5H_4CH_2CH_2)_2NMe\}Cl]$	60	93	100
10	$[Nd\{(C_5H_4CH_2CH_2)_2NMe\}Cl]$	90	95	100

<sup>a</sup> Complex : NaH : oct-1-ene = 2 : 8 : 1. <sup>b</sup> Determined by GC.

**Table 4** Effects of the bridging chain and central metal on the catalytic dechlorination of benzyl chloride

Entry	Complex	Conversion (%) <sup>*</sup>			
		12	18	24	36 h
1	None			10	18
2	[Y(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Cl]	39	62	84	100
3	[Y{(C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> }Cl]·thf	50	82	100	
4	[Y{ <i>m</i> -(C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> }Cl]·thf	10	/	24	41
5	[Y{(C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NMe}Cl]	26	40	63	100
6	[Y{(C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O}Cl]	69	93	100	
7	[{Y[ $\overline{\text{OCH(CH}_2\text{C}_5\text{H}_4\text{)CHCHCH(CH}_2\text{C}_5\text{H}_4\text{)Cl}_2$ ]}]	42	72	98	100
8	[{Yb[ $\overline{\text{OCH(CH}_2\text{C}_5\text{H}_4\text{)CHCHCH(CH}_2\text{C}_5\text{H}_4\text{)Cl}_2$ ]}]	45	63	85	98
9	[{Sm[ $\overline{\text{OCH(CH}_2\text{C}_5\text{H}_4\text{)CHCHCH(CH}_2\text{C}_5\text{H}_4\text{)Cl}_2$ ]}]	57	84	100	
10	[{Nd[ $\overline{\text{OCH(CH}_2\text{C}_5\text{H}_4\text{)CHCHCH(CH}_2\text{C}_5\text{H}_4\text{)Cl}_2$ ]}]	61	92	100	

\* Determined by GC.

### Experimental

**General.**—All operations were carried out under purified argon using Schlenk techniques. All solvents were refluxed and distilled either over finely divided LiAlH<sub>4</sub> or over blue sodium-benzophenone under argon immediately before use. Anhydrous lanthanide chlorides were prepared from the oxides by the published procedure.<sup>57</sup> 2,5-Bis(chloromethyl)furan was obtained by the literature method<sup>54</sup> based on the chloromethylation of 2-chloromethylfuran, or by the replacement of the OH groups of furan-2,5-dimethanol by treatment with SOCl<sub>2</sub> in chloroform. Sodium cyclopentadienide was prepared in the usual manner from freshly distilled monomeric cyclopentadiene and sodium sand in thf. Sodium hydride (E. Merck, with 20% paraffin oil) was washed with hexane and dried *in vacuo*. The complexes [Y(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl]<sub>2</sub>,<sup>58</sup> [Y{(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>}Cl]·thf,<sup>47</sup> [Y{*m*-(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}Cl]·thf,<sup>51</sup> [Y{(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O}Cl]<sup>48</sup> and [Ln{(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe}Cl]<sub>2</sub> (Ln = Y, Yb, Sm or Nd)<sup>53</sup> were synthesised by our previously reported procedures. Oct-1-ene was used as received and benzyl chloride was dried over anhydrous CaCl<sub>2</sub>.

Melting points or thermal decomposition temperatures were determined in sealed argon-filled capillaries and were uncorrected. Infrared spectra were recorded on Perkin-Elmer 983 and Digilab FTS-20/E Fourier-transform spectrometers with Nujol and Fluorolube mulls and were examined between disc-shaped CsI crystals; the mulls were prepared in an argon-filled glove-box. Mass spectra were recorded on a Finnigan 4021 spectrometer at 50–300 °C and 1.3 kV, <sup>1</sup>H NMR spectra on FX-90Q (90 MHz) or AM-300 (300 MHz) spectrometers referenced to external SiMe<sub>4</sub> in [<sup>2</sup>H<sub>8</sub>]thf. The latter solvent (E. Merck for NMR spectroscopy) was dried over a Na–K alloy and degassed by freeze–thaw cycles on a vacuum line. Gas chromatographic analyses were carried out on a Shanghai Analytical Instrument Factory 103 type gas chromatograph equipped with 10 m β,β'-oxydipropionitrile or 2 m OV-1 columns.

**Syntheses.**—*Disodium furan-2,5-diylbis(methylenecyclopentadienide)*. To a solution of Na(C<sub>5</sub>H<sub>5</sub>) (0.048 mol) in thf (41 cm<sup>3</sup>) was added dropwise a solution of 2,5-bis(chloromethyl)furan (3.97 g, 0.024 mol) in thf (20 cm<sup>3</sup>) at –10 °C and the mixture was stirred for 2 h at room temperature. It was then centrifuged and the sodium chloride formed filtered off. The brown solution thus obtained was allowed to react with sodium sand (2.0 g) in thf (20 cm<sup>3</sup>) at 43 °C for 6 h. A dark red solution of the disodium salt in thf was obtained and was used for subsequent work. After the solvent was removed a light red solid was obtained. <sup>1</sup>H NMR: δ 5.80 (2 H, s, furan), 5.50–5.36 (8 H, m, C<sub>5</sub>H<sub>4</sub>) and 3.67 (4 H, s, 2CH<sub>2</sub>). IR: 3180w, 3057m, 2862s, 2718s, 1607m, 1559s, 1456s, 1281m, 1242m, 1193s, 1129s, 1091s, 1007s, 963s, 928m, 861m, 781s, 721vs, 553w and 280m cm<sup>-1</sup>.

**Complex 1.** A thf solution of 1 equivalent of the disodium salt was added slowly to a suspension of YCl<sub>3</sub> (1.35 g, 6.9 mmol) in thf (40 cm<sup>3</sup>) at –40 °C. The reaction mixture was stirred for 2 h at –40 to –30 °C, then allowed to warm to room temperature and stirred overnight. The Schlenk flask was centrifuged, the precipitate filtered off and the solution reduced in volume to about 15 cm<sup>3</sup>. Addition of hexane (40 cm<sup>3</sup>) gave a light yellow solid which was washed with hexane (2 × 20 cm<sup>3</sup>) and dried *in vacuo* (1.72 g, 72%), m.p. > 250 °C (decomp.) (Found: C, 55.55; H, 4.65; Cl, 10.15; Y, 25.30. C<sub>16</sub>H<sub>14</sub>ClOY requires C, 55.45; H, 4.05; Cl, 10.25; Y, 25.65%). IR: 3097m, 2897s, 1620m, 1560m, 1426s, 1301m, 1198m, 1082m, 1012s, 969m, 890m, 781vs, 722s, 664m, 597m, 407m and 260w cm<sup>-1</sup>. Proton NMR data are in Table 2, mass spectral data in Table 1.

**Complex 2.** The procedure was similar to that for complex 1. A red solid (**2**) was obtained (77%), m.p. > 250 °C (decomp.) (Found: C, 45.55; H, 3.95; Cl, 8.15; Yb, 39.85. C<sub>16</sub>H<sub>14</sub>ClOYb requires C, 44.60; H, 3.30; Cl, 8.25; Yb, 40.15%). IR: 3095m, 2897s, 1618m, 1560s, 1427s, 1375s, 1192m, 1033m, 1009s, 976s, 836m, 783vs, 723s, 406w, 370m, 320w and 254m cm<sup>-1</sup>. Mass spectral data are given in Table 1.

**Complex 3.** A thf solution containing 1 equivalent of the disodium salt was added slowly to a suspension of [SmCl<sub>3</sub>(thf)<sub>3</sub>] (1.59 g, 3.3 mmol) in thf (50 cm<sup>3</sup>) at –40 °C. The reaction mixture was stirred at –40 to –30 °C for 2 h, then allowed to warm to room temperature and stirred overnight. The work-up procedure followed was similar to that for complex 1. Compound **3** was obtained as an orange solid (68%), m.p. > 250 °C (decomp.) (Found: C, 47.65; H, 3.90; Cl, 9.00; Sm, 36.85. C<sub>16</sub>H<sub>14</sub>ClOSm requires C, 47.10; H, 3.45; Cl, 8.70; Sm, 36.85%). IR: 3100m, 2896s, 1610s, 1560s, 1427s, 1375s, 1300m, 1259m, 1194m, 1146m, 1096m, 1033s, 1012s, 969m, 773vs, 722s, 630m, 482m and 427m cm<sup>-1</sup>. Mass spectral data are given in Table 1.

**Complex 4.** The procedure followed was similar to that for complex 3. Compound **4** was afforded as a pale purple solid (71%), m.p. > 250 °C (decomp.) (Found: C, 48.30; H, 4.05; Cl, 8.65; Nd, 35.75. C<sub>16</sub>H<sub>14</sub>ClNdO requires C, 47.80; H, 3.50; Cl, 8.80; Nd, 35.90%). IR: 3100m, 2892s, 1609m, 1558s, 1425s, 1375s, 1287m, 1195m, 1146m, 1033m, 1011s, 968s, 765vs, 364m and 252m cm<sup>-1</sup>. Mass spectral data are given in Table 1.

**Reduction of Oct-1-ene.**—The general procedure was as follows (entry 7 in Table 3). A Schlenk tube (5 cm<sup>3</sup>) equipped with a Teflon stopcock was charged with [Y{(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe}Cl]<sub>2</sub> (106 mg, 0.314 mmol) and NaH (30 mg, 1.23 mmol), and thf (2 cm<sup>3</sup>) and oct-1-ene (0.022 cm<sup>3</sup>, 0.157 mmol) were then added by syringe. The stopcock was closed and the reaction carried out at 45 °C with stirring. At given times, samples were obtained and GC analyses were performed to determine the conversion of oct-1-ene into octane.

*Catalytic Dechlorination of Benzyl Chloride.*—The general procedure was as follows (entry 7 in Table 4). A Schlenk tube (5 cm<sup>3</sup>) equipped with a Teflon stopcock was charged with furan-bridged bis(cyclopentadienyl) yttrium chloride (20 mg, 0.06 mmol) and NaH (58 mg, 2.4 mmol); thf (1.2 cm<sup>3</sup>) and benzyl chloride (0.069 cm<sup>3</sup>, 0.6 mmol) were added by syringe. The stopcock was then closed and the reaction carried out at 65 °C with stirring. At given times samples were obtained and GC analyses were performed to determine the conversion of benzyl chloride into toluene.

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