

Studies on organolanthanide complexes

XXXVIII *. New organolanthanide hydrides: synthesis and reactivity towards alkenes, alkynes and organic halides

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Abstract

The reaction of $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2]\text{LnCl}$ with NaH in THF at 45°C generates the dimeric organolanthanide hydrides, $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnH}]_2$ (Ln = Gd, Er, Yb, Lu, Y), in good yield. These new complexes have been fully characterized by elemental analyses, mass spectrometry, IR and NMR spectroscopy. The hydrides can react with alkenes and alkynes. A more active system, organolanthanide hydride/NaH, is able not only to reduce specifically the terminal carbon-carbon double bond but also to catalyse dehalogenation of organic halides.

Introduction

Recently, many organolanthanide hydrides have been reported, most of them synthesized via hydrogenolysis of pure neutral complexes containing Ln–C σ -bond or by β -H elimination reactions, for example, $[\text{Cp}_2\text{NdH} \cdot \text{THF}]_2$ [1], $[\text{Cp}_2\text{LuH} \cdot \text{THF}]_2$ [2–4], $[(\text{C}_5\text{H}_4\text{R})_2\text{LnH} \cdot \text{THF}]_2$ (R = H, CH₃; Ln = Y, Er, Lu) [5], $[(\text{C}_5\text{Me}_5)_2\text{LnH}]_2$ (Ln = Lu [6], Sm [7], La, Nd [8,9]), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{LnH}]_2$ (Ln = Nd, Sm, Lu) [10], $[\text{Cp}_2\text{YbH} \cdot \text{THF}]_2$, $[(\text{Cp}_2\text{YbH})_3\text{H}][\text{Li}(\text{THF})_4]$ [11], $[(\text{Cp}_2\text{ErH})_3\text{Cl}][\text{Li}(\text{THF})_4]$ [12], $[(\text{Cp}_2\text{YH})_3\text{H}][\text{Li}(\text{THF})_4]$ [13], $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-H})]_3$ and $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-H})(\text{THF})]_2$ [14]. Under some circumstances, however, it is not possible to prepare pure Ln–C σ -bonded complexes. Therefore, a third method for direct synthesis of organolanthanide hydrides has been developed involving the reaction of Cp_2LnCl with certain reducing agents containing H[−]. For example, $(\text{C}_5\text{H}_3\text{R}_2)_2\text{LnCl}$ reacted with NaBH₄ to form a complex, $(\text{C}_5\text{H}_3\text{R}_2)_2\text{-Ln}(\text{BH}_4)(\text{THF})$ (R = H [3,15], SiMe₃ [16]); Cp_2YCl and Cp_2LuCl reacted with LiAlH₄ in the presence of NEt₃, giving $[(\text{Cp}_2\text{Y})_2(\mu\text{-Cl})(\mu^3\text{-H})(\mu^2\text{-H})_2\text{Al} \cdot \text{NEt}_3]$ [17]

* For Part XXXVII see ref. 27.

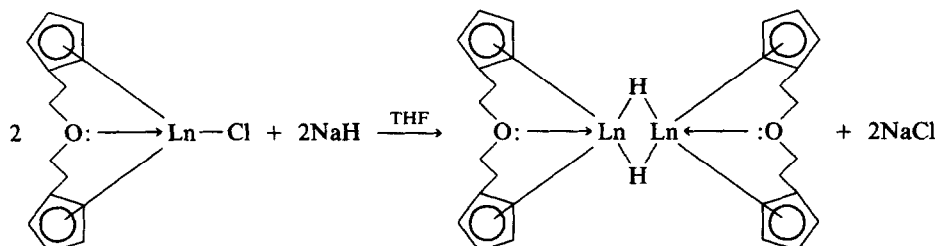
or $[(\text{Cp}_2\text{Lu})_2(\mu^3\text{-H})_2(\mu^2\text{-H})_2(\text{AlH}_2)_2(\text{NEt}_3)]$ [18]; the reaction of Cp_2LuCl with NaH or Na produced $[\text{Na}(\text{THF})_6][\text{Cp}_3\text{LuHLuCp}_3](\text{THF})_2$ [3] or $[\text{Cp}_2\text{LuH} \cdot \text{THF}]_2$ [4]. The results imply that the reduction of Cp_2LuCl with NaH may be a valuable and useful method for the synthesis of neutral organolanthanide hydride. Now our interest has focussed on the investigation of the reaction of organolanthanocene chloride with NaH .

We would like here to report the syntheses of seven new organolanthanide hydrides with 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl ligand and to discuss the reactivities of these hydrides with alkenes, alkynes and organic halides.

Results and discussion

Synthesis

1,1'-(3-Oxa-pentamethylene)dicyclopentadienyl lanthanide chloride reacts with excess of sodium hydride or sodium deuteride in THF at 45°C over a period of a week to give the corresponding organolanthanide hydride (1–5) in good yield.



(Ln = Gd (1), Er (2), Yb (3), Lu (4), Y (5); H = D for 4a and 5a)

These complexes are soluble in THF, but insoluble in hydrocarbons such as hexane at room temperature. They decompose at 80°C and are highly sensitive to air and moisture.

The MS of seven new complexes show a parent monomeric molecular ion (M^+) (except for 3) and some related fragments such as $[M - \text{H}]^+$, Ln^+ and others (Table 1) because the dimers of hydrides are easily dissociated. However, in contrast to what is observed in other 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl lanthanide

Table 1

Mass spectra of $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnH}]_2^a$

Fragment	H = H Ln = Gd	H Er	H Yb	H Lu	H Y	D Lu	D Y
$[M]^+$	358 (7.21)	368 (29.69)		376 (0.70)	290 (15.44)	377 (0.94)	291 (1.09)
$[M - \text{H}]^+$	357 (5.29)	367 (27.58)	374 (0.42)	375 (3.82)	289 (100.0)	375 (47.01)	289 (77.11)
$[\text{C}_7\text{H}_8\text{OLn}]^+$	265 (4.68)	275 (9.64)		283 (1.59)	197 (11.10)	283 (4.91)	197 (22.14)
$[\text{C}_7\text{H}_6\text{Ln}]^+$		257 (1.97)		265 (0.32)	179 (0.65)	265 (0.86)	179 (4.34)

^a Recorded at EI. T 50–300, EM = 1.3 kV. Based on the greatest abundance of isotopes. m/z (rel. intensity).

complexes [19–21], the relative intensity of the fragments containing lanthanide metal in these hydrides is lower, but among these, special attention should be given to the fragments of $[M - H]^+$ with the highest relative intensity. The reason for this may be the less favourable volatility and thermal stability of the hydrides, and the weak Ln–H bond.

The IR spectrum analyses imply the presence of an intramolecular coordination bond from the oxygen atom of 1,1'-(3-oxa-pentamethylene) bridge to lanthanide metal [19,21,26]. However, the IR spectra of hydrides (4 and 5) and deuterides (4a and 5a) are almost the same and exhibit no very strong broad characteristic absorption peaks [5]. This may result from the overlap of the absorption band of 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl ligand with that of Ln–H, or from the exchange of deuterides with a hydrogen source like the paraffin oil [9,22], or from both these factors. Unfortunately, it is not possible to assign an absorption band in these hydrides to Ln–H.

In comparison with the ^1H -NMR spectra of the corresponding deuterides, chemical shifts at 4.50 ppm can be assigned to Lu–H (4.69 [5] or 5.05 ppm [4] in $[\text{Cp}_2\text{LuH} \cdot \text{THF}]_2$, 4.99 ppm [5] in $[(\text{MeC}_5\text{H}_4)_2\text{LuH} \cdot \text{THF}]_2$) and to Y–H at 2.57 ppm which overlap with that of the 1,1'-(3-oxa-pentamethylene) bridge (2.02 ppm in $[\text{Cp}_2\text{YH} \cdot \text{THF}]_2$, 2.31 ppm in $[(\text{MeC}_5\text{H}_4)_2\text{YH} \cdot \text{THF}]_2$ [5], 1.98 ppm in $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-H})_3]$, 2.82 ppm in $[(1,3\text{-Me}_2\text{C}_5\text{H}_3)_2\text{Y}(\mu\text{-H})(\text{THF})]_2$ [14]). The ^1H -NMR spectrum of 3 has also been measured and found to exhibit four groups of broad bands, and the band at 2.91 ppm may represent the chemical shift of $\text{Yb}^{\text{III}}\text{-H}$.

Reactions with alkenes

$[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnH}]_2$ reacts with 1-hexene in THF to form the corresponding hexyl complex, which can be hydrolysed to hexane (Table 2). The yield of hexane depends upon the reaction temperature, and the concentration of the hydrides as well as that of the rare earth metal. Of these hydrides, organolutetium hydride exhibits the best reactivity.

Table 2

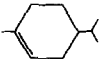
Reduction of 1-hexene by $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnH}]_2/\text{NaH}$ (THF, 65 °C)

Ln	$[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnH}]_2$ /1-Hexene/NaH (molar ratio)	Yield of hexane (%) ^a after time (h)	
		24	48
Gd	1/1/0	49	52
Yb	1/1/0	51	52
Lu	1/1/0	69	76
Y	1/1/0	54	57
Y	2/1/0	94	100
Lu	1/2/4	54	76
Lu	1/1/4	83	100
Y	1/1/4	90	100
Y	1/8/8	24 (10)	27 (40)
Y	1/20/8	9 (2)	10 (20)

^a The yield in brackets is that of *trans*-2-hexene, GLC yield.

Table 3

Reduction of $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YH}]_2/\text{NaH}$ with alkenes ^a

Substrate	Product	Yield (%) ^b
$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	$n\text{-C}_6\text{H}_{14}$	90
$n\text{-C}_{13}\text{H}_{27}\text{CH}=\text{CH}_2$	$n\text{-C}_{15}\text{H}_{32}$	> 95
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$	> 95
<i>trans</i> - $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$	no reaction ^c	
cyclohexene	no reaction ^c	
4-vinylcyclohexene	4-ethylcyclohexene	95
		31

^a $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YH}]_2/\text{alkene}/\text{NaH} = 1/1/4$ (molar ratio), THF, 65°C, 24 h. ^b GLC yield. ^c The starting olefin was recovered.

It is surprising that the yield of hexane can be greatly increased by addition of NaH to the reaction mixture, and the system $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LnH}]_2/\text{NaH}$ can also catalyze the isomerization of 1-hexene to 2-hexene.

5/NaH, as a more active system, can specifically reduce terminal alkenes. The rate of reaction is observed to correlate with the steric bulk of the substrate (Table 3).

Reactions with alkynes

The reaction of 5 with terminal alkynes like $\text{C}_6\text{H}_5\equiv\text{CH}$ does not involve Y-H addition across the unsaturated carbon-carbon bond. Instead, metallation at the acidic terminal position occurs to generate hydrogen and after hydrolysis, an alkynide complex, shown by GC analysis to afford only $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ without $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$. The ¹H-NMR data on this alkynide complex are as follows: δ (ppm) 2.51, 3.85, 4.07, 5.72, 6.00, 7.20, 7.31.

However, the 5/NaH system reacted with $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ in THF at 65°C for 12 h giving after hydrolysis only *trans*-stilbene in quantitative yield (GC-IR analysis). The result is very different from that of the reaction of $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{YH}]_2$ with $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ [23].

Reactions with organic halides

All the organolanthanide hydrides can react rapidly with CH_3I to produce CH_4 , which is a hallmark of the presence of a metal-hydrogen bond [24]. Other organic halides have been tested with these hydrides.

The reaction of 5 with equimolar amounts of *p*-bromotoluene in THF at 65°C for 13 h gives only 6% of toluene; even after reaction for 48 h, no further toluene is produced. At the same time, the starting bromide is recovered. After the addition of NaH to the reaction mixture, however, *p*-bromotoluene can be quantitatively reduced to toluene (Table 4). The rate of reduction depends upon the position of the halogen atom and on the bonding energy of the carbon-halogen bond in the substrates, and decreases in the following order:

p-bromotoluene > *m*-bromotoluene > *o*-bromotoluene

$\text{R-I} > \text{R-Br} \gg \text{R-Cl}, \text{R-F}$

(R = aryl, alkyl)

Table 4

Dehalogenation of organic halides by $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YH}]_2/\text{NaH}^a$

Organic halide	Reaction time (h)	Product	Yield (%) ^b
<i>o</i> -bromotoluene	12	toluene	70
<i>m</i> -bromotoluene	12	toluene	80
<i>p</i> -bromotoluene	12	toluene	~ 100
iodobenzene	1.5	benzene	~ 100
bromobenzene	12	benzene	88
chlorobenzene	48	benzene	trace ^c
fluorobenzene	48	no reaction	
α -iodonaphthalene	5	naphthalene	~ 100
β -bromonaphthalene	12	naphthalene	~ 100
<i>p</i> -chloriodobenzene	1.5	chlorobenzene	~ 100
<i>p</i> -bromochlorobenzene	12	chlorobenzene	~ 100
<i>p</i> -bromoanisole	12	anisole	~ 100
1-iodopentane	3	pentane	~ 100
1-bromohexane	12	hexane	> 95
1-bromohexadecane	12	hexadecane	~ 100
benzyl bromide	12	toluene	~ 100

^a $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YH}]_2/\text{halide}/\text{NaH} = 1/2/4$ (molar ratio); THF, 65 °C. ^b GLC yield. ^c Starting organic halide recovered.

Therefore, it is easy to effect highly selective reduction of organic iodides or bromides into the corresponding compounds in the presence of chlorine or fluorine atoms.

It has been reported that NaH is able to reduce organic iodide, but this requires a long reaction time [25]. No toluene is detectable by GC after refluxing excess NaH with *p*-bromotoluene in THF for 12 h.

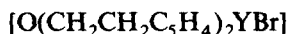
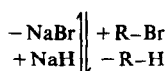
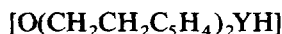
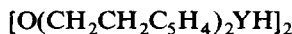
It is noteworthy that **5**/NaH system can also catalyze the dehalogenation of organic bromides, and here NaH acts as a hydrogen source. This is the first example of catalytic dehalogenation of organic halides via the organolanthanide hydride/NaH system. The results are listed in Table 5. Scheme 1 shows the catalytic cycle.

In conclusion, we have demonstrated a convenient and valuable direct synthesis of the dimeric organolanthanide hydrides. The chemistry of these hydrides has also been studied.

Table 5

Catalytic dehalogenation of organic bromides by $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YH}]_2/\text{NaH}$ (THF, 65 °C)

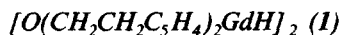
RBr	$[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{YH}]_2/\text{RBr}/\text{NaH}$ (molar ratio)	Reaction time (h)	Product	Yield (%)
<i>p</i> -bromoanisole	1/10/20	13.5	anisole	~ 100
1-bromohexadecane	1/10/20	24	hexadecane	~ 100
<i>p</i> -bromoanisole	1/20/40	24	anisole	~ 100
1-bromohexadecane	1/20/40	24	hexadecane	~ 100



Scheme 1. Catalytic cycle.

Experimental

All procedures were performed in Schlenk tubes in an atmosphere of dry, oxygen free argon. Solvents were dried and freed of oxygen by refluxing, kept over sodium or blue sodium benzophenone and distilled under argon prior to use. The 1,1'-(3-oxa-pentamethylene)dicyclopentadienyl lanthanide chlorides were prepared as previously described [19]. Sodium hydride was washed with THF or pentane and dried in vacuum. 1-Hexene was dried over Na/K alloy and distilled under argon. The other alkenes, alkynes and organic halides were dried over molecular sieves activated by heating overnight under vacuum. Diphenylethyne was used in the form in which it was received. Infrared spectra were recorded on a Perkin-Elmer 983 or a Digilab FTS-20/E using Nujol and Fluorolube mulls. ^1H -NMR spectra were obtained on a Varian XL-200 referenced to internal Me_4Si . THF- d_8 was dried over Na/K alloy and degassed by freeze-thaw cycles on a vacuum line. The mass spectra and GC/MS were obtained on a Finnigan 4021 spectrometer. Gas chromatographic analyses were performed on a 103-type instrument equipped with a 10-m β,β' -oxydipropionitrile column for identification of the products of reduction and isomerization, respectively, or with a 2-m XE-60 column. Complexometric metal and C,H analyses were carried out as previously described [19].



A 150-ml Schlenk flask with a Teflon stopcock was charged with 1.35 g (3.44 mmol) of $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2]\text{GdCl}$, 166.2 mg (6.93 mmol) of NaH, 49 ml of THF and a magnetic stir bar, and was then closed. The reaction mixture was stirred for 7 days at 45°C and then centrifuged. Concentration of the clear THF solution followed by diffusion of pentane at 0°C afforded a white product which was washed with 8 ml of pentane and dried in vacuum to give 0.91 g (74.0%) of **1** as a white solid. Anal. Found: C, 47.48; H, 5.61; Gd, 43.98. $\text{C}_{28}\text{H}_{34}\text{O}_2\text{Gd}_2$ calcd.: C, 46.90; H, 4.78; Gd, 43.86%. IR (cm^{-1}): 220s, 245s, 350s, 425m, 488m, 758vs, 823s, 890m, 1037s, 1063s, 1185w, 1195s, 1237m, 1249w, 1271s, 1326s, 1377s, 1436m, 2874s, 2920s, 3071m.

$[O(CH_2CH_2C_5H_4)_2ErH]_2$ (2)

The above procedure was carried out with 1.10 g (2.73 mmol) of $[O(CH_2CH_2C_5H_4)_2]ErCl$, 144.0 mg (6.00 mmol) of NaH and 40 ml of THF. Yield of 0.46 g (46.0%) of 2 as orange-red crystals was obtained. Anal. Found: C, 43.51; H, 4.25; Er, 45.68. $C_{28}H_{34}O_2Er_2$ calcd.: C, 45.62; H, 4.65; Er, 45.38%. IR (cm^{-1}): 345w, 391w, 433m, 487w, 766vs, 824s, 891w, 1038s, 1063vs, 1101m, 1195m, 1236m, 1271m, 1327m, 1376s, 1436m, 2872s, 2919s, 3076m.

$[O(CH_2CH_2C_5H_4)_2YbH]_2$ (3)

The procedure for the preparation of 1 was followed with 1.51 g (3.69 mmol) of $[O(CH_2CH_2C_5H_4)_2]YbCl$, 186.2 mg (7.76 mmol) of NaH and 52 ml of THF: yield 1.12 g (81.3%) of 3 as red crystals. Anal. Found: C, 44.98; H, 4.87; Yb, 46.27. $C_{28}H_{34}O_2Yb_2$ calcd.: C, 44.92; H, 4.58; Yb, 46.23%. IR (cm^{-1}): 487m, 769vs, 826s, 891m, 1013s, 1016vs, 1104s, 1153m, 1195s, 1250m, 1272m, 1326s, 1377s, 1438m, 2871s, 2924s, 3080m. 1H -NMR (THF- d_8): δ (ppm) 5.47 (br); 3.51 (br); 2.91 (br); 2.55 (br).

$[O(CH_2CH_2C_5H_4)_2LuH]_2$ (4)

The above procedure was carried out with 1.32 g (3.21 mmol) of $[O(CH_2CH_2C_5H_4)_2]LuCl$, 154.3 mg (6.43 mmol) of NaH and 45 ml of THF, yielding 0.91 g (75.3%) of 4 as colourless crystals. Anal. Found: C, 44.19; H, 5.00; Lu, 46.06. $C_{28}H_{34}O_2Lu_2$ calcd.: C, 44.68; H, 4.55; Lu, 46.50%. IR (cm^{-1}): 230s, 350s, 380m, 430m, 487m, 768vs, 826s, 892s, 1038s, 1063vs, 1103s, 1185m, 1195s, 1236m, 1249w, 1271s, 1327w, 1376s, 1438m, 2873s, 2920s, 3080m. 1H -NMR (THF- d_8): δ (ppm) 5.76 (m, C_5H_4); 4.50 (s, Lu-H-Lu); 3.96–3.85, 2.63 (m, OCH_2CH_2).

$[O(CH_2CH_2C_5H_4)_2LuD]_2$ (4a)

The above procedure was repeated with 1.11 g (2.70 mmol) of $[O(CH_2CH_2C_5H_4)_2]LuCl$, 148.7 mg (5.95 mmol) of NaD and 40 ml of THF, to yield 0.81 g (80.1%) of 4a as colourless crystals. Anal. Found: C, 45.53; H, 4.62; Lu, 46.43. $C_{28}H_{32}D_2O_2Lu_2$ calcd.: C, 44.57; H, 4.27; Lu, 46.38%. IR (cm^{-1}): 230s, 380s, 432s, 487m, 764vs, 813s, 854m, 890s, 1037s, 1063vs, 1102s, 1185m, 1195s, 1237m, 1249w, 1271s, 1327w, 1376s, 1437m, 2872s, 2920s, 3078m. 1H -NMR (THF- d_8): δ (ppm) 5.72 (m, C_5H_4); 3.95–3.86, 2.62 (m, OCH_2CH_2).

$[O(CH_2CH_2C_5H_4)_2YH]_2$ (5)

The suspension of $[O(CH_2CH_2C_5H_4)_2]YCl$ (0.90 g, 2.77 mmol) and KH (0.44 g, 11.0 mmol) in 40 ml of THF was stirred for 10 days at room temperature and then filtered. Concentration of the clear THF solution to about 18 ml followed by diffusion of pentane at 0°C afforded 0.58 g (71.2%) of 5 as colourless crystals. Anal. Found: C, 58.23; H, 5.67; Y, 29.57. $C_{28}H_{34}O_2Y_2$ calcd.: C, 57.94; H, 5.90; Y, 30.64%. IR (cm^{-1}): 228w, 269s, 432m, 487m, 764vs, 813s, 854m, 890s, 1037s, 1063vs, 1102s, 1195s, 1237m, 1249m, 1271m, 1376s, 1437m, 2875s, 2923s, 3075m. 1H -NMR (THF- d_8): δ (ppm) 5.75 (m, C_5H_4); 4.09–3.97, 2.57 (m, OCH_2CH_2); 2.57 (Y-H-Y, overlapped).

$[O(CH_2CH_2C_5H_4)_2YD]_2$ (5a)

This complex was prepared from $[O(CH_2CH_2C_5H_4)_2]YCl$ and NaD by following the above procedure as for 5. It was isolated as white crystals, yield 68.3%. Anal.

Found: C, 57.41; H, 5.57; Y, 30.18. $C_{28}H_{32}D_2O_2Y_2$ calcd.: C, 57.75; H, 5.54; Y, 30.53%. IR (cm^{-1}): 220w, 275s, 405s, 767vs, 891s, 1037s, 1062s, 1101s, 1194s, 1271m, 1302m, 1376s, 1436w, 2880s, 2923s, 3078m. 1H -NMR (THF- d_8): δ (ppm) 5.76 (m, C_5H_4); 4.09–3.91, 2.57 (m, OCH_2CH_2).

Reactions with 1-hexene

A 3-ml Schlenk tube with a Teflon stopcock was charged with 0.10 mmol of $[O(CH_2CH_2C_5H_4)_2LnH]_2$, 0.10 mmol of 1-hexene and 1.0 ml of THF, and was then closed. The reaction mixture was stirred at 65°C. The amount of hexane generated was determined by GC-MS after 24 h and again after 48 h.

Reactions with alkenes

The aforementioned Schlenk tube was charged with 0.10 mmol of $[O(CH_2CH_2C_5H_4)_2YH]_2$, 0.40 mmol of NaH, 0.10 mmol of alkene and 1.0 ml of THF and was then closed. The reaction mixture was stirred for 24 h at 65°C. The products, after hydrolysis, were analysed by GC-MS or GC-IR.

Reaction with $C_6H_5C\equiv CH$

In a 5-mm NMR tube, 9.5 μ l (0.087 mmol) of $C_6H_5C\equiv CH$ was added to a solution of 27.0 mg (0.093 mmol) of **5** in 0.40 ml of THF- d_8 and the tube was then sealed. The reaction mixture was heated at 45°C for 12 h. The product was analysed by 1H -NMR.

Reaction with $C_6H_5C\equiv CC_6H_5$

Following the same procedure as for alkenes above, **5** (83.8 mg, 0.145 mmol) was treated with $C_6H_5C\equiv CC_6H_5$ (25.5 mg, 0.143 mmol) and NaH (12.3 mg, 0.513 mmol) in 1.40 ml of THF for 12 h at 65°C.

Reactions with CH_3I

In a 25-ml Schlenk flask equipped with a rubber stopcock, 20 μ l (0.32 mmol) of CH_3I was added to a solution of $[O(CH_2CH_2C_5H_4)_2LnH]_2$ (0.20 mmol) in 2 ml of THF at room temperature. The gas released was determined by GC.

Reaction with p - $CH_3C_6H_4Br$

A 2-ml Schlenk tube was charged with **5** (43.0 mg, 0.074 mmol), NaH (8.0 mg, 0.333 mmol), p -bromotoluene (25.4 mg, 0.148 mmol) and 0.73 ml of THF and the reaction mixture stirred for 12 h at 65°C. The product was analysed by GC-MS.

Other organic halides were treated with the **5**/NaH system in an analogous manner to that described for p -bromotoluene.

Catalytic dehalogenation of organic bromides

The above procedure for p -bromotoluene was carried out with 0.020 mmol of **5**, 0.80 mmol of NaH, 0.40 mmol of organic bromide and 0.90 ml of THF.

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References

- 1 H. Schumann and G. Jeske, *Angew. Chem.*, 97 (1985) 208.
- 2 H. Schumann and W. Genthe, *J. Organomet. Chem.*, 213 (1981) C7.
- 3 H. Schumann, W. Genthe, E. Hahn, M.B. Hossain and D. van der Helm, *J. Organomet. Chem.*, 299 (1986) 67.
- 4 C. Qian, D. Deng, C. Ni and Z. Zhang, *Inorg. Chim. Acta*, 146 (1988) 129.
- 5 W.J. Evans, J.H. Meadows, A.L. Wayda, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 104 (1982) 2008.
- 6 P.L. Watson and D.C. Roe, *J. Am. Chem. Soc.*, 104 (1982) 6417.
- 7 W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 105 (1983) 1401.
- 8 H. Mauermann, P.N. Swebston and T.J. Marks, *Organometallics*, 4 (1985) 200.
- 9 G. Jeske, H. Lauke, H. Mauermann, P.N. Swebston, H. Schumann and T.J. Marks, *J. Am. Chem. Soc.*, 107 (1985) 8091.
- 10 G. Jeske, L.E. Schok, P.N. Swebston, H. Schumann and T.J. Marks, *J. Am. Chem. Soc.*, 107 (1985) 8103.
- 11 W.J. Evans, R. Dominguez and T.P. Hanusa, *Organometallics*, 5 (1986) 263.
- 12 W.J. Evans, J.H. Meadows and A.L. Wayda, *J. Am. Chem. Soc.*, 104 (1982) 2015.
- 13 W.J. Evans, J.H. Meadows and T.P. Hanusa, *J. Am. Chem. Soc.*, 106 (1984) 4454.
- 14 W.J. Evans, D.K. Drummond, T.P. Hanusa and R.J. Doedens, *Organometallics*, 6 (1987) 2279.
- 15 T.J. Marks and G.W. Grynkewich, *Inorg. Chem.*, 15 (1976) 1302.
- 16 M.F. Lappert, A. Singh, J.L. Atwood and W.E. Hunter, *Chem. Commun.*, (1983) 206.
- 17 A.B. Erofeev, B.M. Bulychev, V.K. Bel'skii and G.L. Soloveichik, *J. Organomet. Chem.*, 335 (1987) 189.
- 18 S.Ya. Knijazhanski, B.M. Bulychev, V.K. Belsky and G.L. Soloveichik, *J. Organomet. Chem.*, 327 (1988) 173.
- 19 C. Qian, Z. Xie and Y.Z. Huang, *J. Organomet. Chem.*, 323 (1987) 285.
- 20 G. Fu, Z. Xie, Y. Xu and C. Qian, *Acta Chim. Sinica (Engl. ed.)* 5 (1989) 431.
- 21 C. Qian, Z. Xie and Y.Z. Huang, *J. Organomet. Chem.*, 398 (1990) 251.
- 22 P.J. Fagan, J.M. Manriquez, E.A. Maatta, A.M. Seyam and T.J. Marks, *J. Am. Chem. Soc.*, 103 (1981) 6650.
- 23 W.J. Evans, J.H. Meadows, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 106 (1984) 1291.
- 24 E.L. Muetterties, *Transition Metal Hydrides*, Marcel Dekker, New York, 1971.
- 25 R.B. Nelson and G.W. Gribble, *J. Org. Chem.*, 39 (1974) 1425.
- 26 H. Schumann, J. Loebel, J. Pickardt, C. Qian and Z. Xie, *Organometallics*, 10 (1991) 215.
- 27 C. Qian, A. Qiu, Y.Z. Huang and W. Chen, *J. Organomet. Chem.*, 412 (1991) 53.