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On the synthesis of monopentamethylcyclopentadienyl derivatives of yttrium, lanthanum, and cerium

Martin Booij, Niklaas H. Kiers, Hero J. Heeres, and Jan H. Teuben *

Groningen Centre for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

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Abstract

Two routes leading to monopentamethylcyclopentadienyl-yttrium, -lanthanum and -cerium complexes have been explored. Transmetallation of $LnCl_3(THF)_x$ with Cp^*Li ($Cp^* = C_5Me_5$) proved useful only in some particular cases. Acid–base reactions of homoleptic complexes LnR_3 with Cp^*H generally gave Cp^*_2LnR compounds, although Cp^*LnR_2 complexes were observed as intermediates. The mono-Cp^* complex $Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2$ was obtained from $Y(o\text{-}C_6H_4CH_2NMe_2)_3$ and Cp^*H, and is the first salt-free mono-Cp^* yttrium complex with two carbyl ligands.

Introduction

The organometallic chemistry of group 3 and lanthanide elements is a subject of much interest, and synthetic and reactivity studies have increased rapidly in the last ten years [1*,2]. The chemistry has been limited mainly to di- and tri-cyclopentadienyl systems, with bis-pentamethylcyclopentadienyl ($Cp^* = C_5Me_5$) compounds, Cp^*_2LnR, as the most studied. Although these compounds undergo very interesting reactions, the presence of two bulky Cp^* ligands on the metal centre appears to limit the reactivity considerably. An example of this is provided by the reactions of Cp^*_2ScR [3] with olefins. With ethene rapid polymerization takes place, but higher olefins appear not to insert into the Sc–C bond. Oligomerization takes place when the space available around the metal centre is increased by bridging between the cyclopentadienyl ligands, and this suggested to us that monocyclopentadienyl compounds of group 3 and lanthanide elements might be of considerable interest for the oligomerization and polymerization of olefins. We thus decided to examine the virtually unexplored chemistry of monocyclopentadienyl compounds [4] and to devise a general method for the synthesis of salt-free Cp^*LnR_2 complexes (Ln = Y,

* Reference numbers with asterisks indicate notes in the list of references.

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La, and Ce; R = halide, alkoxide, amide, carbyl, etc.). The results are reported below.

Results and discussion

Treatment of $LnCl_3(THF)_x$ (Ln = Y, La, and Ce) with Cp^*Li in a 1/1 ratio gave crystalline products for Ln = La and Ce (eq. 1).

$$LnCl_3(THF)_x + Cp^*Li \xrightarrow{THF} Cp^*LnCl_3 \cdot Li(THF)_2 \quad (1)$$

(**1a**: Ln = La; **1b**: Ln = Ce)

For Ln = Y the reaction gave a complex mixture of various pentamethylcyclopentadienyl-containing products, as indicated by the appearance of several ^1H NMR signals in the Cp^* region (δ 1.7–2.2 ppm). Isolation and identification of individual components was not attempted. The ^1H (Table 1) and ^{13}C NMR (Experimental section) spectra of **1a** and **1b** each show only signals from one Cp^* ligand along with the signals from coordinated THF. The lowering of the THF C–O–C stretching modes by ca. 20 cm^{-1} relative to that for free THF indicates that this ligand is coordinated to Li [5]. These spectral data confirm the proposed stoichiometry although elemental analyses show that **1a** contains 1.3 mole of LiCl per mole of La. This extra LiCl is apparently tightly bonded, as it could not be removed by recrystallisation. In contrast to our results, Bruno et al. isolated $[Cp^*CeCl_2(THF)_x]_y$ without incorporated LiCl from the reaction between Cp^*Li and unsolvated $CeCl_3$ [4k]. This indicates that the nature of the complexation of the lanthanide halide may be crucial in determining the nature of the product.

Molecular structure determinations would answer the question of whether **1a** and **1b** are indeed mono-Cp^*Ln complexes, but both **1a** and **1b** readily lose THF upon drying, and we could not obtain crystals suitable for X-ray diffraction studies. For synthetic applications it is important to know whether these compounds can serve as a source of the Cp^*Ln moiety. Therefore we tried to replace the remaining Cl ligands by various bulky lipophilic groups R (e.g. R = CH_2SiMe_3, $CH(SiMe_3)_2$ and $N(SiMe_3)_2$), but found that isolation of compounds of the type $Cp^*LnR_2 \cdot L_n$ from the reaction mixtures is very difficult. For R = $N(SiMe_3)_2$ and Ln = La we identified LnR_3 (NMR) as the major reaction product, and no trace of Cp^*LnR_2 was detected. For Ln = Ce and R = $N(SiMe_3)_2$ the reaction did occur, and the desired complex **2c** was obtained (eq. 2), along with some $Ce[N(SiMe_3)_2]_3$.

$$Cp^*CeCl_3 \cdot Li(THF)_2 + 2\ NaN(SiMe_3)_2 \xrightarrow{THF} Cp^*Ce[N(SiMe_3)_2]_2 + LiCl + 2\ NaCl \quad (2)$$

(**2c**)

These results reflect the high mobility of Cp^* and R ligands in these coordinatively unsaturated compounds. This has also been observed for late lanthanides [4l]. Another case in which **1a** and **1b** serve as source of the Cp^*Ln-unit is in their reactions with K_2COT (COT = cyclooctatetraene). The sandwich complexes Cp^*LnCOT were made in this way (eq. 3).

$$Cp^*LnCl_3 \cdot Li(THF)_2 + K_2COT \xrightarrow{THF} Cp^*LnCOT + 2\ KCl + LiCl \quad (3)$$

(**3a**: Ln = La; **3b**: Ln = Ce)

From these results we conclude that metathetical reaction between $LnCl_3(THF)_x$ and Cp^*Li is not a useful general route to Cp^*Ln complexes. An alternative approach was based on acid-base reactions of homoleptic [6] complexes LnR_3 with Cp^*H (eq. 4).

$$LnR_3 + Cp^*H \rightarrow Cp^*LnR_2 + RH \quad (4)$$

These reactions can be monitored easily by NMR spectroscopy, even in apolar solvents such as benzene-d_6, and the problem of salt incorporation in the product is avoided by using a salt-free starting material.

The homoleptic amido-complexes $Ln[N(SiMe_3)_2]_3$ [7] were found to react with Cp^*H in THF to give bis(pentamethylcyclopentadienyl) complexes (eq. 5).

$$2\ Ln[N(SiMe_3)_2]_3 + 2\ Cp^*H \xrightarrow{\text{THF-}d_8,\ 120\,^\circ C} Cp^*_2LnN(SiMe_3)_2 + Ln[N(SiMe_3)_2]_3 + 2\ HN(SiMe_3)_2 \quad (5)$$

(**4a**: Ln = Y;
4b: Ln = La;
4c: Ln = Ce)

Monopentamethylcyclopentadienyl intermediates $Cp^*Ln[N(SiMe_3)_2]_2$ (**2a**: Ln = Y, **2b**: Ln = La, **2c**: Ln = Ce) were observed during the reaction (See Table 1).

The fact that the $Cp^*_2LnN(SiMe_3)_2$ complexes are the major products raises the question of whether the $Cp^*Ln[N(SiMe_3)_2]_2$ complexes disproportionate to $Cp^*_2LnN(SiMe_3)_2$ and $Ln[N(SiMe_3)_2]_3$ or the introduction of the second Cp^* ligand is faster than the first. The former seems to be the case, since we observed that pure **2c** disproportionated under the reaction conditions (120 °C, THF-d_8) into $Cp^*_2CeN(SiMe_3)_2$ and $Ce[N(SiMe_3)_2]_3$.

The homoleptic alkyl complexes $Ln[CH(SiMe_3)_2]_3$ (Ln = La, Ce) [8*] reacted with Cp^*H in benzene-d_6 to give mixtures of $Ln[CH(SiMe_3)_2]_3$, $Cp^*Ln[CH(SiMe_3)_2]_2$ and $Cp^*_2LnCH(SiMe_3)_2$.

$$LnR_3 + Cp^*H \xrightarrow{\text{benzene-}d_6} m\ Cp^*LnR_2 + 0.5(1-m)Cp^*_2LnR + 0.5(1-m)LnR_3 + RH \quad (6)$$

(**5a**: Ln = La; **5b**: Ln = Ce)

(**6a**: Ln = La, $m = 0.33$; R = $CH(SiMe_3)_2$
6b: Ln = Ce, $m = 0.55$)

The reaction was carried out at room temperature, and took between 48 h (Ln = Ce) and 120 h (Ln = La) for consumption of all the Cp^*H. Under these conditions the introduction of the second Cp^* ligand is competitive with the first. This follows from the fact that after all the Cp^*H had disappeared, the $Cp^*Ln[CH(SiMe_3)_2]_2$ present in the mixture did not disproportionate to give $Cp^*_2LnCH(SiMe_3)_2$ and $Ln[CH(SiMe_3)_2]_3$. The synproportionation of $Cp^*_2LnCH(SiMe_3)_2$ and $Ln[CH(SiMe_3)_2]_3$ was not attempted because of the thermal instability of $Cp^*Ln[CH(SiMe_3)_2]_2$ and $Ln[CH(SiMe_3)_2]_3$. The sterically more congested $Y[CH(SiMe_3)_2]_3$ is interesting because there may be a higher kinetic barrier for the second Cp^* introduction. Unfortunately, it was not possible to prepare this compound by the route that gave the La and Ce analogues [8*].

Table 1

^{1}H NMR data for compounds **1–8**

Compound	Ln = Y	Ln = La	Ln = Ce
$Cp^*LnCl_3 \cdot Li(THF)_2$ [a,c]		2.04(s) ($C_5(CH_3)_5$)	1.36(s) ($\Delta\nu_{1/2}$ 8 Hz)
(1)		3.62(m) (αH THF)	
		1.77 (m) (βH THF)	
$Cp^*LnCOT/THF\text{-}d_8$ [a]		1.59(s) (15H, $C_5(CH_3)_5$)	2.60(s) ($\Delta\nu_{1/2}$ 53 Hz, 15H, $C_5(CH_3)_5$)
(3)		6.32(s) (8H, C_8H_8)	0.90(s) ($\Delta\nu_{1/2}$ 114 Hz, 8H, C_8H_8)
$Ln[N(SiMe_3)_2]_3$ [a]	0.20(s) ($Si(CH_3)_3$)	0.19(s) ($Si(CH_3)_3$)	−2.01(s) ($\Delta\nu_{1/2}$ 38 Hz, ($Si(CH_3)_3$)
$Cp^*Ln[N(SiMe_3)_2]_2$ [a]	2.07(s) (15H, $C_5(CH_3)_5$)	2.06(s) (15H, $C_5(CH_3)_5$)	5.03(s) ($\Delta\nu_{1/2}$ 28 Hz, 15 H, $C_5(CH_3)_5$)
(2)	0.15(s) (36H, $Si(CH_3)$)	0.13(s) (36H, $Si(CH_3)$)	−5.42(s) ($\Delta\nu_{1/2}$ 30 Hz, 36H, $Si(CH_3)$)
$Cp_2^*LnN(SiMe_3)_2$ [a]	1.97(s) (30 H, $C_5(CH_3)_5$)	2.00(s) (30H, $C_5(CH_3)_5$)	3.54(s) ($\Delta\nu_{1/2}$ 5 Hz, 30H, $C_5(CH_3)_5$)
(4)	0.10(s) (18H, $Si(CH_3)$)	0.05(s) (18H, $Si(CH_3)$)	−11.26(s) ($\Delta\nu_{1/2}$ 18 Hz, 18H, $Si(CH_3)$)
$Ln[CH(SiMe_3)_2]_3$ [b]		0.27(s) (54H, $Si(CH_3)$)	−2.22(s) ($\Delta\nu_{1/2}$ 15 Hz, 54H, $Si(CH_3)$)
		−0.37(s) (3H, $CH(SiMe_3)_2$)	33.8(s) ($\Delta\nu_{1/2}$ 120 Hz, 3H, $CH(SiMe_3)_2$)
$Cp^*Ln[CH(SiMe_3)_2]_2$ [b]		1.98(s) (15H, $C_5(CH_3)$)	2.84(s) ($\Delta\nu_{1/2}$ 28 Hz, 15H, $C_5(CH_3)$)
(5)		0.25(s) (36H, $Si(CH_3)$)	−7.61(s) ($\Delta\nu_{1/2}$ 300 Hz, 36H, $Si(CH_3)$)
		−0.76(s) (2H, $CH(SiMe_3)_2$)	(α-CH protons not observed)
$Cp_2^*LnCH(SiMe_3)_2$ [b]		1.98(s) (15H, $C_5(CH_3)$)	3.64(s) ($\Delta\nu_{1/2}$ 10 Hz, 15H, $C_5(CH_3)$)
(6)		1.92(s) (15H, $C_5(CH_3)$)	3.29(s) ($\Delta\nu_{1/2}$ 10 Hz, 15H, $C_5(CH_3)$)
		0.21(s) (18H, $Si(CH_3)$)	−10.50(s) ($\Delta\nu_{1/2}$ 9 Hz, 18H, $Si(CH_3)$)
		−0.40(s) (1H, $CH(SiMe_3)_2$)	39.4(s) ($\Delta\nu_{1/2}$ 70 Hz, 1H, $CH(SiMe_3)_2$)
$Ln(o\text{-}C_6H_4CH_2NMe_2)_3$ [b,c]	2.15(s) (18H, $N(CH_3)$)		
(7)	3.44(s) (6H, CH_2)		
	6.96(m), 7.17(m), 8.20(m) (12H, C_6H_4)		
$Cp^*Ln(o\text{-}C_6H_4CH_2NMe_2)_2$ [b,c]	1.91(s) (15H, $C_5(CH_3)_5$)		
(8)	1.99(s) (6H, $N(CH_3)$)		
	2.24(s) (6H, $N(CH_3)$)		
	3.02(d) (^2J(H–H) 14.1 Hz, 2H, CH_2)		
	3.82(d) (^2J(H–H) 14.1 Hz, 2H, CH_2)		
	6.93(m), 7.83(m) (8H, C_6H_4)		

[a] THF-d_8 (δ 3.57). [b] Benzene-d_6 (δ 7.16) referenced to residual solvent protons. [c] TMS (δ 0.00).

More successful was the preparation of a well defined mono-Cp* complex starting from a homoleptic yttrium compound with the *o*-(dimethylaminomethyl)-phenyl ligand. This compound, $Y(o\text{-}C_6H_4CH_2NMe_2)_3$ (**7**), was easily prepared by the method previously described for Sc and the heavier lanthanides Er, Yb, and Lu [9]. Attempts to prepare the La and Ce analogues by the same route were unsuccessful [9b].

The reaction of **7** with Cp*H showed that only one Cp* ligand was introduced (eq. 7).

$$Y(o\text{-}C_6H_4CH_2NMe_2)_3 + Cp^*H \xrightarrow[45\,^\circ C]{THF} Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2 + C_6H_5CH_2NMe_2 \quad (7)$$

(**8**)

Introduction of a second Cp*-group was not observed even when an excess of Cp*H was used and heating was prolonged (several days at 60 °C). The ^1H NMR spectrum of **8** shows the expected integrated signals for one Cp* ligand for two benzylamine ligands. The $N(CH_3)$ protons give rise to two singlets and the $N(CH_2)$ protons to two doublets, showing that in solution the two benzylamine ligands are equivalent. The conformation of the chelating ligand seems rather rigid since the $N(CH_3)$ and $N(CH_2)$ protons do not simply give two singlets. In the ^{13}C NMR spectrum the Y–C(*ipso*) signal appears as a doublet (^1J(Y–C) 43.4 Hz) indicating that both aryl groups are bonded to one yttrium atom and are not bridging. This makes a monomeric structure for **8** most likely, and thus **8** is an example of a very interesting class of compounds, and we are investigating its structure and reactions.

Conclusions

Reaction of $LnCl_3(THF)_x$ with Cp*Li gives products with a stoichiometry of one Cp* per Ln (Ln = La, Ce). Replacement of the remaining chloride ligands does not provide a general route to stable complexes of the type Cp^*LnR_2 but particular compounds, e.g. $Cp^*Ce[N(SiMe_3)_2]_2$ and Cp*LnCOT (Ln = La, Ce), can be isolated. Reaction of the homoleptic compounds LnR_3 ($R = CH(SiMe_3)_2$, $N(SiMe_3)_2$) with Cp*H efficiently gives Cp^*_2LnR complexes, monopentamethylcyclopentadienyl complexes Cp^*LnR_2 being observed as intermediates. The method is successful for Ln = Y and $R = o\text{-}C_6H_4CH_2NMe_2$ and $Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2$ is obtained. Provided the compounds $Ln(o\text{-}C_6H_4CH_2NMe_2)_3$ become available for other lanthanides, acid base reaction seems likely to provide a satisfactory route to mono-Cp*Ln complexes.

Experimental section

General considerations. All the compounds reported are air-sensitive. Manipulations were performed under nitrogen by standard Schlenk line and glove box techniques (Braun MB-200). IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer as Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90-DS (^1H), a Nicolet NT-200 (^1H and ^{13}C) or a Varian VXR-300 (^1H and ^{13}C) spectrometer. Elemental analyses were carried out in the Micro-Analytical Department of our Laboratory under the supervision of Mr. A.F. Hamminga.

Solvents were distilled from Na/K alloy and degassed prior to use. Cp^*H [10], Cp^*Li [11], $Li(o\text{-}C_6H_4CH_2NMe_2)$ [9a], $LnCl_3(THF)_x$ (Ln = Y [12], La [4m], Ce [13]), K_2COT [14], and $NaN(SiMe_3)_2$ [15*] were prepared by published procedures. Most of the reactions were monitored by NMR spectroscopy. Solutions (ca. 0.1 *M*) were cooled to −196 °C and subsequently sealed under vacuum. The spectra were compared with literature data or with independently-prepared samples (**4a** [12], **4c** [13], **6a** [17], **6b** [13]). Intermediate species were characterized by NMR spectroscopy (See Table 1) only. Full details of the synthesis of **2c** [18] and **3a** [4m] will be described elsewhere.

*$Cp^*LaCl_3 \cdot Li(THF)_2$ (**1a**).* A suspension of 7.43 g (21.6 mmol) of $LaCl_3(THF)_{1.37}$ and 3.00 g (21.1 mmol) of Cp^*Li in 150 ml of THF was stirred for 2 h at room temperature. The solution was than filtered and the solvent removed in vacuum. The residue was washed with 40 ml of pentane and redissolved in the minimum amount of THF. Cooling to −80 °C gave colourless crystals, which lose solvent on drying. Yield: 4.59 g (8.63 mmol) of $Cp^*LaCl_3 \cdot Li(THF)_2$ as a white powder. Concentration of the mother liquor gave a second crop of crystals (1.59 g, 2.99 mmol). Total yield 54%. IR (cm^{-1}): 2720(w), 1170(w), 1070(s), 1045(s), 910(s), 885(s), 715(w), 670(w). ^{13}C NMR (THF-d_8): 120.76 (s, C_5Me_5), 68.21 (t, ^1J(C–H) 146.2 Hz, α-C–THF), 26.33 (t, ^1J(C–H) 131.7 Hz, β-C–THF), 11.84 (q, ^1J(C–H) 125.2 Hz, $C_5(CH_3)_5$). An analytical sample was recrystallized from THF. Anal. Found: C, 39.73; H, 5.72; Cl, 21.63; La: 25.55; Li, 1.62. $C_{18}H_{31}Cl_{3.3}LaLi_{1.3}O_2$ calcd.: C, 39.72; H, 5.74; Cl, 21.39; La, 25.52); Li, 1.66%.

*$Cp^*CeCl_3 \cdot Li(THF)_2$ (**1b**).* A suspension of 0.81 g (2.1 mmol) of $CeCl_3(THF)_{1.95}$ and 0.30 g (2.1 mmol) of Cp^*Li in 30 ml of THF was stirred for 20 h at room temperature. The resulting clear light-green solution was concentrated to ca. 10 ml and 20 ml of pentane was allowed to diffuse slowly into the solution at −20 °C. Yield 0.74 g (1.4 mmol, 66%) of $Cp^*CeCl_3 \cdot Li(THF)_2$ as light-green needles. IR (cm^{-1}): 2710(w), 1375(m), 1040(s), 920(m), 895(m), 670(w). ^{13}C NMR (THF-d_8): 160.8 (s, C_5Me_5), 3.5 (q, ^1J(C–H) 126 Hz, $C_5(CH_3)_5$). Anal. Found: C, 40.56; H, 5.96; Cl, 20.58; Ce, 26.17; Li, 1.42. $C_{18}H_{31}CeCl_3LiO_2$ calcd.: C, 40.57; H, 5.87; Cl, 19.96; Ce, 26.30; Li, 1.30%.

*Cp^*CeCOT (**3b**).* A suspension of 0.48 g (1.2 mmol) of $CeCl_3(THF)_{1.95}$ and 0.19 g (1.3 mmol) of Cp^*Li in 25 ml of THF was stirred for 20 h at room temperature. To the resulting clear light-green solution was added 2.4 ml of a 0.53 *M* K_2COT solution in THF and the solution, immediately became cloudy. The mixture was stirred for an additional 4 h, then the solvent was removed in vacuum and the residue sublimed (10^{-3} torr, ca. 160 °C). Yield: 0.08 g (0.2 mmol, 17%) of Cp^*CeCOT as a brown microcrystalline solid. IR (cm^{-1}): 2710(w), 2110(m), 1850(w), 1740(w), 1600(w), 1375(w), 1320(w), 1300(w), 1170(w), 1155(w), 1020(m), 890(s), 840(m), 800(w), 780(m), 770(m), 755(m), 740(m), 710(s), 620(w). Anal. Found: C, 56.52; H. 6.19. $C_{18}H_{23}Ce$: C, 56.97; H, 6.11%.

*$Cp_2^*LaN(SiMe_3)_2$ (**4b**).* A solution of 2.61 g (5.9 mmol) of $[Cp_2^*LaCl]_n$ [16*] and 1.06 g (5.8 mmol) of $NaN(SiMe_3)_2$ in 50 ml of THF was stirred for 18 h at room temperature. The solvent was removed in vacuum and the residue was sublimed (10^{-2} torr, ca. 120 °C) to give 2.22 g (3.9 mmol, 66%) of $Cp_2^*LaN(SiMe_3)_2$ as white crystals. IR (cm^{-1}): 2740(w), 1375(sh), 1385(m), 1255(s), 1240(s), 1055(s), 865(s), 820(s), 760(s), 680(m), 595(m). ^{13}C NMR (benzene-d_6): 120.82 (s, C_5Me_5), 11.65 (q, ^1J(C–H) 125.1 Hz, $C_5(CH_3)_5$), 3.89 (q, ^1J(C–H) 116.3 Hz, $Si(CH_3)$. Anal.

Found: C, 54.71; H, 8.44; La, 24.15. $C_{26}H_{48}LaNSi_2$ calcd.: C, 54.81; H, 8.49; La, 24.38%.

$Y(o\text{-}C_6H_4CH_2NMe_2)_3$ (7). A suspension of 4.10 g (29.2 mmol) of Li(*o*-$C_6H_4CH_2NMe_2$) and 4.40 g (9.8 mmol) of $YCl_3(THF)_3$ in 200 ml of Et_2O was stirred for 18 h at room temperature. The solvent was removed in vacuum, and the residue washed with three portions of 20 ml of Et_2O and extracted with 150 ml of toluene. The toluene was removed in vacuum to leave 3.30 g (6.7 mmol, 69%) of Y(*o*-$C_6H_4CH_2NMe_2)_3$ as a white powder. IR (cm^{-1}): 3040(m), 2760(m), 1420(m), 1370(m), 1290(w), 1230(m), 1170(m), 1145(w), 1090(m), 1035(m), 990(s), 860(m), 750(m), 740(s), 630(w), 500(w). ^{13}C NMR (benzene-d_6): 186.81 (d, ^1J(Y–C) 43.3 Hz, Y–*C*), 146.66 (s, ring *C*–CH_2), 138.55, 125.66, 125.16, 124.73 (all d, ^1J(C–H) 149.6, 157.0, 154.0, and 151.4 Hz respectively, aryl *C*H), 69.71 (t, ^1J(C–H) 133.6 Hz, N(*C*H_2)), 45.87 (q, ^1J(C–H) 135.6 Hz, N(*C*H_3)). Anal. Found:C, 65.64; H, 7.41; N, 8.52; Y, 18.08. $C_{27}H_{36}N_3Y$ calcd.: C, 65.98; H, 7.38; N, 8.55; Y, 18.09%.

$Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2$ (8). A solution of 7.80 g (15.8 mmol) of Y(*o*-$C_6H_4NMe_2)_3$ and 3.0 ml (2.58 g, 19.0 mmol) of Cp^*H in 50 ml of THF was stirred for 3 h at 45°C and than 15 h at room temperature. The solvent was removed in vacuum and the residue was extracted with 300 ml of pentane. The extract was concentrated, and cooled to −30°C to give 3.40 g (6.9 mmol, 44%) of Cp^*Y(*o*-$C_6H_4CH_2NMe_2)_2$ as white needles. IR (cm^{-1}): 3100(w), 2780(m), 2710(m), 1480(m), 1430(m), 1350(m), 1280(w), 1230(w), 1170(w), 1100(m), 1040(w), 1030(m), 1010(m), 990(m), 970(m), 930(w), 830(m), 815(w), 745(s), 740(s), 720(m), 640(w), 620(w), 595(w), 470(m). ^{13}C NMR (benzene-d_6): 187.88 (d, ^1J(Y–C) 43.4 Hz, Y–*C*), 145.94 (s, ring *C*–CH_2), 138.41 (dd, ^1J(C–H) 149.8 Hz, ^3J(C–H) 6.5 Hz, aryl *C*H), 125.19, 125.02, 124.37 (all d, ^1J(C–H) 157.3, 157.2, and 152.1 Hz respectively, aryl *C*H), 118.11 (s, C_5Me_5), 69.84 (t, ^1J(C–H) 134.2 Hz, N(*C*H_2)), 45.37 (q, ^1J(C–H) 135.8 Hz, N(*C*H_3)), 45.32 (q, ^1J(C–H) 137.7 Hz, N(*C*H_3)), 11.60 (q, ^1J(C–H) 125.0 Hz, $C_5(CH_3)_5$). Anal. Found: C, 68.35; H, 7.92; N, 5.41; Y, 18.02 C. $C_{28}H_{39}N_2Y$ calcd.: 68.28; H, 7.98; N, 5.69; Y, 18.05%.

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References and notes

1 In this article the following abbreviations are used: Cp = C_5H_5, Cp^* = C_5Me_5.

2 (a) T.J. Marks and R.D. Ernst in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. III, Pergamon Press, New York, 1982, p. 173. (b) H. Schumann, Angew. Chem. Int. Ed. Engl., 23 (1984) 474; (c) W.J. Evans, Polyhedron, 6 (1987) 803.

3 (a) E. Bunel, B.J. Burger and J.E. Bercaw, J. Am. Chem. Soc., 110 (1988) 976; (b) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

4 (a) S. Manastyrskyj, R.E. Maginn and M. Dubeck, Inorg. Chem., 2 (1963) 904; (b) J.D. Jamerson,

A.P. Masino and J. Takats, J. Organomet. Chem., 65 (1974) C33; (c) N.M. Ely and M. Tsutsui, Inorg. Chem., 14 (1975) 2680; (d) P.L. Watson, J. Chem. Soc. Chem. Commun., (1980) 652; (e) T.D. Tilley and R.A. Andersen, Inorg. Chem., 20 (1981) 3267; (f) P.L. Watson, J.F. Whitney and R.L. Harlow, Inorg. Chem., 20 (1981) 3271; (g) W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 107 (1985) 941; (h) I. Albrecht, E. Hahn, J. Pickardt and H. Schumann, Inorg. Chim. Acta, 110 (1985) 145, (i) C.S. Day, V.W. Day, R.D. Ernst and S.H. Vollmer, Organometallics, 1 (1982) 998; (j) H. Schumann, I. Albrecht, F.W. Reier and E. Hahn, Angew. Chem. Int. Ed. Engl., 23 (1984) 522; (k) P.N. Hazin, J.C. Huffman, and J.W. Bruno, Organometallics, 6 (1987) 23; (l) I. Albrecht and H. Schumann, J. Organomet. Chem., 310 (1986) C29; (m) P. Bruin, M. Booij, J.H. Teuben and A. Oskam, ibid., 350 (1988) 17; (n) H.J. Heeres, A. Meetsma and J.H. Teuben, J. Chem. Soc. Chem. Commun., (1988) 962.

5 (a) R.J. Kern, J. Inorg. Nucl. Chem., 24 (1962) 1105; (b) K.H. den Haan, Y. Wielstra, J.J.W. Eshuis and J.H. Teuben, J. Organomet. Chem., 323 (1987) 181.

6 P.J. Davidson, M.F. Lappert and R.J. Pearce, Chem. Rev., 76 (1976) 219.

7 D.C. Bradley, J.S. Ghotra and F.A. Hart, J. Chem. Soc. Dalton Trans., (1973) 1021.

8 Recently Lappert et al. described a general route involving reaction of homoleptic aryloxides with $LiCH(SiMe_3)_2$:

$$Ln(OAr)_3 + 3\ LiCH(SiMe_3)_2 \xrightarrow{\text{pentane}} Ln[CH(SiMe_3)_2]_3 + 3\ LiOAr \qquad (5)$$

(OAr = 2,6 di-t-Bu-phenoxo, Ln = La, Sm): M.F. Lappert and R.G. Smith, Proc. Second Intern. Conf. on the Basic and Applied Chemistry of *f*-Transition (Lanthanide and Actinide) and Related Elements, Lisbon, 1987, Abstact No. P(II)1 (See J. Chem. Soc. Chem. Commun., (1988) 1007). The Ce analogue was prepared similarly. For Ln = Y in pentane no reaction was observed and in ether the OAr groups were only partially replaced.

9 (a) L.E. Manzer, J. Am. Chem. Soc., 100 (1978) 8068; (b) A.L. Wayda, J.L. Atwood and W.E. Hunter, Organometallics, 3 (1984) 939.

10 U. Burger, A. Delay and F. Maznot, Helv. Chim. Acta, 57 (1974) 2106.

11 R.S. Threlkel and J.E. Bercaw, J. Organomet. Chem., 136 (1977) 1.

12 K.H. den Haan, J.L. de Boer, J.H. Teuben, A.L. Spek, B. Kojić-Prodić, G.R. Hays and R. Huis, Organometallics, 5 (1986) 1726.

13 H.J. Heeres, J. Renkema, M. Booij, A. Meetsma and J.H. Teuben, Organometallics, in press.

14 H.F. Ebel in E. Müller (Ed.), Methoden der Organischen Chemie (Houben-Weyl), Band XIII-1, Georg Thieme Verlag, Stuttgart, 1970, p. 430.

15 C.R. Krüger and H. Niederprüm in H.F. Holtzclaw Jr. (ed.), Inorganic Synthesis, Vol. VIII, McGraw-Hill, New York, 1966, p. 15. The crude product was vacuum sublimed prior to use.

16 $[Cp_2^* LaCl]_n$ was prepared as described for $[Cp_2^* CeCl]_n$, see ref. 13.

17 G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann and T.J. Marks, J. Am. Chem. Soc., 107 (1985) 8091.

18 H.J. Heeres, R.D. Rogers and J.H. Teuben, manuscript in preparation.