## Dinuclear Chlorido-, Alkyl(chlorido)-, and Hydridoyttrium Complexes Supported by µ-Bridging-Silyl-Linked Bis(amidinate) Ligands

## Grigorii G. Skvortsov,<sup>[a]</sup> Alexei O. Tolpyguin,<sup>[a]</sup> Georgy K. Fukin,<sup>[a]</sup> Anton V. Cherkasov,<sup>[a]</sup> and Alexander A. Trifonov<sup>\*[a]</sup>

Keywords: Rare earths / N ligands / Alkyl complexes / Hydrido complexes / Structure elucidation

A chloridoyttrium complex supported by a silyl-linked bis-(amidinate) ligand,  $[(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2$ (YCl)<sub>2</sub>(µ-Cl)]<sup>-</sup>[Li(thf)<sub>4</sub>]<sup>+</sup> (2) (thf = tetrahydrofuran), was synthesized by the reaction of equimolar amounts of anhydrous YCl<sub>3</sub> and lithium amidinate  $[(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2Li_3]^-$ [Li(thf)<sub>4</sub>]<sup>+</sup> (1) in thf at 20 °C. Complex 2 was isolated after recrystallization from a thf/hexane mixture in 72 % yield. Single-crystal X-ray structure analysis has revealed that 2 is a dinuclear compound composed of a discrete complex anion  $[(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2(YCl)_2(\mu-Cl)]^-$ , containing one  $\mu$ -bridging and two terminal chloride ligands, and a cation  $[Li(thf)_4]^+$ . The formation of a dimeric structure results from the coordination of amidinate fragments of the same dianionic ligand on two different yttrium ions and the presence of a  $\mu$ -bridging chloride ligand. Alk-

#### Introduction

A unique combination of properties, exceptional reactivity, and promising catalytic activity have given a strong impetus to the development of the organometallic chemistry of the rare earth metals in the past two decades.<sup>[1]</sup> Rare earth alkyl and hydrido complexes mediate a wide range of catalytic transformations of unsaturated substrates,<sup>[2]</sup> and their enhanced reactivity enables stoichiometric reactions of hydrocarbon activation,<sup>[3]</sup> alkane functionalization,<sup>[4]</sup> and C-F bond activation.<sup>[5]</sup> Both stability and reactivity of rare earth hydrocarbyl and hydrido complexes are largely determined by coordination and steric saturation of the electrophilic metal center, and this emphasizes the importance of the design of new ancillary ligand sets. A fine balance between ligand electronic and steric factors needs to be maintained in order to control reactivity of lanthanide complexes. Until recently, growing attention has been paid to non-cyclopentadienyl ligand frameworks, because they offer a greater variety of ligand topologies and their steric and electronic properties may be readily modified within a wide range.[6]

 [a] G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences Tropinina 49, 603950 Nizhny Novgorod, GSP-445, Russia Fax: +7-831-462-7497 E-mail: trif@iomc.ras.ru ylation of 2 with one equivalent of Me<sub>3</sub>SiCH<sub>2</sub>Li in toluene afforded an alkyl(chlorido)yttrium complex, [Me<sub>2</sub>Si{NC(Ph)- $N(2,6-iPr_2-C_6H_3)_2_2[Y(thf)](\mu-Cl)[Y(CH_2SiMe_3)]$  (3). X-ray crystal structure investigation has shown that 3 is a dimeric complex as a result of the "spanning" coordination mode of the *ansa*-bis(amidinate) ligands and the presence of one  $\mu^2$ chloride ligand, while the alkyl group remains terminal. Treatment of the in situ generated alkyl derivative  $[Me_{2}Si\{NC(Ph)N(2,6\mathchar`iPr_{2}\mathchar`-C_{6}H_{3})\}_{2}]_{2}[Y(CH_{2}SiMe_{3})]_{2}$  (4) with PhSiH<sub>3</sub> in toluene results in the formation of the corresponding hydridoyttrium complex [Me<sub>2</sub>Si{NC(Ph)N(2,6-*i*Pr<sub>2</sub>- $C_{6}H_{3}$ }<sub>2</sub> $Y(\mu$ -H)]<sub>2</sub> (**5**), which was isolated after recrystallization from toluene in 73% yield. According to the X-ray crystal structure analysis,  ${\bf 5}$  adopts a dimeric structure with two  $\mu\text{-}$ bridging bis(amidinate) and two  $\mu^2$ -hydrido ligands.

Monoanionic chelating amidinate ligands have been widely employed in transition metal coordination and organometallic chemistry<sup>[7]</sup> and were found to form a suitable coordination environment for isolable hydrocarbyl, hydrido, and cationic alkyl rare earth species.<sup>[8]</sup> Tridentate amidinate ligands containing an additional donor group in the side chain allowed synthesis of mono- and bis(alkyl)yttrium complexes (both neutral and ionic).<sup>[9]</sup> Lanthanide hydrido and cationic alkyl species supported by amidinate ligands have proved to be efficient catalysts for various olefin (polymerization,<sup>[8f,8g]</sup> hydroamination,<sup>[10]</sup> hydrosilylation,<sup>[11]</sup> hydroboration<sup>[12]</sup>) and diene (polymerization)<sup>[13]</sup> transformations. As demonstrated by the example of metallocene-type lanthanide complexes, a transposition from a bis(cyclopentadienyl) to a linked bis(cyclopentadienyl) ligation system results in a considerable opening of the metal coordination sphere<sup>[2a,2e,14]</sup> and effects large increases in rates of olefin insertion into the M-R bond<sup>[2a,2e]</sup> and of olefin hydrogenation.<sup>[14]</sup> To date, several linked bis(amidinate) ligand frameworks have been described,<sup>[15]</sup> and some of them have been successfully employed in the synthesis of lanthanide complexes.<sup>[16]</sup> In order to synthesize new highly reactive rare earth alkyl and hydrido complexes possessing enhanced catalytic activity in olefin polymerization, we focused on silyl-linked bis(amidinate) ligands. Herein we report the synthesis, structure and reactivity of new dimeric chlo-



# FULL PAPER

rido-, alkyl(chlorido)-, and hydridoyttrium complexes supported by  $\mu$ -bridging-silyl-linked bis(amidinate) ligands.

#### **Results and Discussion**

The metathesis reaction of anhydrous yttrium chloride (YCl<sub>3</sub>) with lithium amidinate [(Me<sub>2</sub>Si{NC(Ph)N(2,6-*i*Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}<sub>2</sub>)<sub>2</sub>Li<sub>3</sub>]<sup>-</sup>[Li(thf)<sub>4</sub>]<sup>+</sup> (1)<sup>[15b]</sup> in a 2:1 molar ratio in thf (20 °C, 14 h) afforded the bis(amidinato)chlorido complex [(Me<sub>2</sub>Si{NC(Ph)N(2,6-*i*Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}<sub>2</sub>)<sub>2</sub>(YCl)<sub>2</sub>(µ-Cl)]<sup>-</sup>[Li-(thf)<sub>4</sub>]<sup>+</sup> (2) in 72% yield (Scheme 1). Complex 2 was isolated as colorless air- and moisture-sensitive crystals and was authenticated by elemental analysis, solution NMR studies, and single-crystal X-ray diffraction studies. Complex 2 is highly soluble in thf, 1,2-dimethoxyethane, and toluene, but insoluble in hexane.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of complex **2** in C<sub>5</sub>D<sub>5</sub>N at 25 °C show the expected sets of resonances due to the amidinate ligand and the coordinated thf molecules. The presence of lithium in complex **2** was confirmed by its <sup>7</sup>Li NMR spectrum, which contains a single resonance at  $\delta$  = 3.3 ppm.

Colorless transparent crystals of complex **2** suitable for single-crystal X-ray diffraction studies were grown by slow condensation of hexane into a concentrated thf solution at room temperature. Complex **2** was isolated as the hexane solvate  $[\{(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2(YCl)_2(\mu-Cl)\}^{-}\{Li(thf)_4\}^+] \cdot (C_6H_{14})_{0.5}$ .

The molecular structure of **2** is depicted in Figure 1, and the crystal and structural refinement data are listed in Table 1. Surprisingly the X-ray crystal structure investigation revealed that complex **2** adopts a dimeric structure as a result of a "spanning" ligation pattern: each of the two dianionic amidinate ligands is  $\mu$ -coordinated to two different yttrium atoms (Figure 1). Such  $\mu$ -bridging coordination of potentially chelating ligands is seldom observed and was formerly described for a few lanthanide complexes containing single-atom-linked *ansa*-bis(cyclopentadienyl) ligands.<sup>[17]</sup> It is noteworthy that linked bis(amidinate) ligands featuring a longer (CH<sub>2</sub>)<sub>3</sub> linker between functional groups can display dual coordination behavior and act as both chelating and  $\mu$ -bridging ligands, depending on the nature of the third ligand bound to the lanthanide atom.<sup>[16,18]</sup> Complex 2 contains three chloride ligands: two of them are terminal, while the third is µ-bridging between two yttrium atoms and thus participates in the formation of the dinuclear structure. The terminal Y-Cl bonds [2.5855(7) and 2.5803(6) Å] are predictably shorter than the bridging ones [2.7037(6) and 2.6961(7) Å], and the lengths of both types of bond are in good agreement with the corresponding values previously reported for yttrium metallocene complexes.<sup>[19]</sup> The Y-N bonds in complex 2 are in the region of 2.3539(18)-2.3960(16) Å [the average bond length is 2.371(2) Å] and are slightly longer than the related distances in monomeric yttrium amidinate complexes.<sup>[8,16]</sup> The N-C bond lengths within the amidinate ligands have very similar values, which indicates negative charge delocalization in the NCN fragments.



Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of **2** showing the atom numbering scheme. Hydrogen atoms and the  $[\text{Li}(\text{thf})_4]^+$  cation are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y(1)–N(2) 2.3539(18), Y(1)–N(3) 2.3573(16), Y(1)–N(1) 2.3667(18), Y(1)–N(4) 2.3719(19), Y(1)–Cl(1) 2.5855(7), Y(1)–Cl(3) 2.7037(6), Y(2)–N(8) 2.3628(19), Y(2)–N(7) 2.369(2), Y(2)–N(6) 2.389(2), Y(2)–N(5) 2.3960(16), Y(2)–Cl(2) 2.5803(6), Y(2)–Cl(3) 2.6961(7), N(1)–C(1) 1.341(2), N(2)–C(1) 1.340(3), N(3)–C(20) 1.344(3), N(4)–C(20) 1.329(3), N(7)–C(60) 1.334(3), N(8)–C(60) 1.340(3), N(5)–C(41) 1.326(3), N(6)–C(41) 1.334(3), N(2)–Y(1)–N(1) 57.39(6), N(3)–Y(1)–N(4) 57.56(7), N(8)–Y(2)–N(7) 57.24(7), Y(2)–Cl(3)–Y(1) 111.59(2), N(4)–Si(1)–N(5) 108.65(9), N(1)–Si(2)–N(8) 105.69(9).



Scheme 1.



Tabl	le 1	. Cry	stallograp	hic data	a and	l structure	refinement	details	for	2, 3	3 an	d	5
------	------	-------	------------	----------	-------	-------------	------------	---------	-----	------	------	---	---

Compound	2	3	5
Empirical formula	$C_{99}H_{139}Cl_{3}LiN_{8}O_{4}Si_{2}Y_{2}$	C <sub>101</sub> H <sub>141</sub> ClN <sub>8</sub> OSi <sub>3</sub> Y <sub>2</sub>	$C_{80}H_{102}N_8Si_2Y_2$
Formula weight	1852.47	1780.76	1409.70
<i>T</i> [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	PĪ	PĪ	$P2_1/n$
<i>a</i> [Å]	14.5217(5)	14.7966(10)	14.0342(10)
<i>b</i> [Å]	17.5020(6)	16.9858(12)	11.2920(8)
<i>c</i> [Å]	23.6035(11)	20.1565(14)	24.0172(16)
a [°]	111.6460(10)	88.1090(10)	90
β [°]	90.4680(10)	86.6220(10)	90.448(2)
γ [°]	113.9820(10)	68.9250(10)	90
Volume [Å <sup>3</sup> ]	5005.6(3)	4718.5(6)	3806.0(5)
Z	2	2	2
$\rho_{\text{calcd.}} [\text{g cm}^{-3}]$	1.229	1.253	1.230
Absorption coefficient [mm <sup>-1</sup> ]	1.309	1.341	1.595
<i>F</i> (000)	1962	1896	1488
Crystal size [mm]	$0.29 \times 0.27 \times 0.18$	$0.15 \times 0.12 \times 0.07$	$0.29 \times 0.24 \times 0.07$
$\theta$ range for data collection [°]	2.23 to 26.00	1.75 to 26.00	2.46 to 26.00
Index ranges	$-17 \le h \le 17;$	$-18 \le h \le 18;$	$-17 \le h \le 17;$
	$21 \le k \le 21;$	$20 \le k \le 20;$	$13 \le k \le 13;$
	$-29 \le l \le 29$	$-24 \le l \le 24$	$-29 \le l \le 29$
Reflections collected	42982	40553	31870
Independent reflections	19470	18382	7460
R <sub>int</sub>	0.0477	0.0691	0.1352
Completeness to $\theta$ [%]	98.9	99.2	99.7
Data/restraints/parameters	19470/156/1219	18382/5/1009	7460/6/446
Goodness-of-fit on $F^2$	1.040	1.006	1.002
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0584, wR2 = 0.1275	R1 = 0.0784, wR2 = 0.2029	R1 = 0.0556, wR2 = 0.0934
R indices (all data)	R1 = 0.1083, wR2 = 0.1409	R1 = 0.1219, wR2 = 0.2228	R1 = 0.1289, wR2 = 0.1039
Largest diff. peak and hole [e Å <sup>-3</sup> ]	1.040/-0.791	1.773/-3.664	0.652/-0.657

Attempts to alkylate complex 2 with Me<sub>3</sub>SiCH<sub>2</sub>Li (toluene, 0 and 20 °C) at various molar ratios of reagents were undertaken and revealed noticeable differences in reactivity of the chlorine atoms in the substitution reaction. One chlorine atom was easily substituted by an alkyl fragment when the reaction with an equimolar amount of Me<sub>3</sub>SiCH<sub>2</sub>Li was carried out in toluene at 20 °C; even with a short reaction time (1 h) was enough in this case (Scheme 2). Filtration of the reaction mixture and subsequent recrystallization of the solid residue from a toluene/hexane mixture at -20 °C afforded the alkyl(chlorido) complex [Me<sub>2</sub>Si{NC(Ph)N(2,6*i*Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}<sub>2</sub>]<sub>2</sub>[Y(thf)]( $\mu$ -Cl)[Y(CH<sub>2</sub>SiMe<sub>3</sub>)] (3) in 61% yield. The second chlorine atom proved to be more difficult to substitute. The reaction of **2** with a twofold molar excess of Me<sub>3</sub>SiCH<sub>2</sub>Li in toluene with stirring at 20 °C for 3 h resulted in the formation of alkyl(chlorido) complex **3**, which was isolated after recrystallization from toluene at -20 °C in 27% yield. Alkylation of **2** with an equimolar amount of Me<sub>3</sub>SiCH<sub>2</sub>Li can also be conducted in hexane at room temperature and allows isolation of **3** in 43% yield. Complex **3** was isolated as a highly air- and moisture-sensitive colorless crystalline solid. It is highly soluble in thf and toluene and shows modest solubility in hexane. The methylene protons of the alkyl group attached to the yttrium atom appear in the <sup>1</sup>H NMR spectrum of complex **3** (400 MHz,



Scheme 2.

## FULL PAPER

 $C_6D_6$ , 25 °C) as two doublets of doublets at  $\delta = -0.12$  and -0.03 ppm [dd,  ${}^2J_{\rm H,H}$ = 11.2 Hz,  ${}^2J_{\rm Y,H}$  = 3.2 Hz]. This is indicative of two diastereotopic CH<sub>2</sub> protons obviously resulting from the chirality of complex **3**. In the  ${}^{13}$ C NMR spectrum, the corresponding carbon atom gives rise to a doublet at  $\delta = 34.9$  ppm ( ${}^1J_{\rm Y,C} = 38.5$  Hz). Unlike complex **2**, all the methyl groups of the isopropyl substituents are nonequivalent and give rise to sixteen doublets in the  ${}^{1}$ H NMR spectrum. Complex **3** proved to be quite a robust compound:  ${}^{1}$ H NMR monitoring in a C<sub>6</sub>D<sub>6</sub> solution at ambient temperature (25 °C) showed that decomposition of the complex did not exceed 10% over one month.

Clear transparent crystals of **3** suitable for single-crystal X-ray structure investigation were obtained by slow cooling of a concentrated toluene/hexane (1:10) solution to  $0 \,^{\circ}$ C. Complex **3** crystallizes as a solvate containing one molecule of toluene and one molecule of hexane. The molecular structure of **3** is shown in Figure 2, and the crystal and structural refinement data are listed in Table 1.



Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of **3** showing the atom numbering scheme. Hydrogen atoms and CH<sub>2</sub> groups of thf are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y(1)–N(1) 2.361(3), Y(1)–N(3) 2.383(3), Y(1)–N(2) 2.400(2), Y(1)–C(81) 2.404(3), Y(1)–N(4) 2.434(2), Y(1)–Cl(1) 2.7714(8), Y(2)–N(5) 2.314(3), Y(2)–N(8) 2.338(2), Y(2)–O(1S) 2.358(2), Y(2)–N(6) 2.385(2), Y(2)–N(7) 2.400(3), Y(2)–Cl(1) 2.6586(9), N(1)–Y(1)–N(2) 57.26(9), N(3)–Y(1)–N(4) 56.30(9), N(5)–Y(2)–N(6) 57.89(9), Y(2)–Cl(1)–Y(1) 111.64(3), N(1)–Si(2)–N(8) 106.86(13), N(4)–Si(1)–N(5) 108.51(13).

The X-ray diffraction study revealed that complex 3 has a dimeric structure analogous to the parent complex 2, which results from the coordination of the amidinate fragments of one dianionic ligand on two different yttrium cations. Existence of the dimeric structure is also supported by the presence of the  $\mu$ -bridging chloride ligand, while the alkyl group remains terminal. To the best of our knowledge, complex 3 is a rare example of a dimeric alkyl(chlorido) rare earth metal compound that includes terminal alkyl groups and a  $\mu^2$ -chlorine bridge.<sup>[20]</sup> The coordination environments of the yttrium atoms in complex 3 are different; each contains four nitrogen atoms of two amidinate fragments; however, the coordination sphere of one yttrium atom also includes a  $\sigma$ -bonded alkyl group and a  $\mu^2$ -bridging Cl ligand, while the second yttrium atom is coordinated by a thf molecule in addition to the chloride anion. Since none of the yttrium atoms in the parent chlorido complex 2 is coordinated by a thf molecule and the alkylation was carried out in toluene, one can conclude that  $[Li(thf)_4]^+$  is the sole source of the thf molecule coordinated to Y in 3. The average length of the Y–N bonds in 3 (2.375 Å) is close to that observed in 2 (2.371 Å) and is slightly longer than the related distances in previously reported monomeric yttrium amidinate complexes.<sup>[8,16]</sup> The bond lengths within the Y(1)-Cl(1)-Y(2) moiety [Y(1)-Cl(1) 2.7714(8), Y(2)-Cl(1) 2.6586(9) Å] in 3 are similar to those observed in a related dimeric metallocene-type complex, Cp\*<sub>2</sub>Y(µ-Cl) YClCp\*<sub>2</sub> [2.776(5) and 2.640(5) Å],<sup>[19b]</sup> while the Y(2)-Cl(1)-Y(1) bond angle [111.64(3)°] is remarkably larger than that in Cp\*<sub>2</sub>Y(µ-Cl)YClCp\*<sub>2</sub> [93.4(2)°].<sup>[19b]</sup> The Y-C bond in 3 [2.404(3) Å] is slightly shorter than those in Y-CH<sub>2</sub>SiMe<sub>3</sub> derivatives (2.414–2.425 Å).<sup>[21]</sup>

In order to achieve replacement of both chlorine atoms by alkyl groups and to obtain complex  $[Me_2Si\{NC(Ph)-N(2,6-iPr_2-C_6H_3)\}_2]_2[Y(CH_2SiMe_3)]_2$  (4), numerous essays of alkylation of 2 with Me\_3SiCH\_2Li were undertaken (Scheme 3). As mentioned above, substitution of both chloride ligands in 2 is difficult to accomplish. Moreover, alkyl derivatives of rare earth metals are known to be rather thermally unstable, which restricts reaction time and conditions. Therefore, reactions of 2 with Me\_3SiCH\_2Li (1:2 molar ratio) were carried out in toluene (or hexane) at 0 °C over 24 h. Filtration of the reaction mixture and removal of the sol-



Scheme 3.

European Journal of Inorganic Chemistry



Scheme 4.

vent afforded an off-white amorphous solid. Unfortunately all of our attempts to obtain crystalline samples of  $[Me_2Si-{NC(Ph)N(2,6-iPr_2-C_6H_3)}_2]_2[Y(CH_2SiMe_3)]_2$  (4) and to isolate the alkyl species in analytically pure form failed.

Our challenge was to synthesize a new hydrido complex supported by a linked bis(amidinate) ligation system and to investigate its catalytic behavior in olefin polymerization. The most common synthetic route to rare earth hydrido complexes is the reaction of the parent alkyl derivatives with either dihydrogen<sup>[2c,2f]</sup> or phenylsilane.<sup>[22]</sup> Because of the difficulties of isolating alkyl complex **4**, it was generated in situ and used in the synthesis of the related hydrido derivatives as a toluene (or hexane) solution after the separation of LiCl. The  $\sigma$ -bond metathesis reaction of **4** with two equivalents of PhSiH<sub>3</sub> was carried out in toluene at room temperature over 1 h (Scheme 4). Slow cooling of the concentrated toluene solution to -20 °C afforded the hydride complex [Me<sub>2</sub>Si{NC(Ph)N(2,6-*i*Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}<sub>2</sub>Y(µ-H)]<sub>2</sub> (**5**) as a colorless crystalline solid in 73% yield.

Complex 5 was isolated as a highly air- and moisturesensitive colorless crystalline solid. After crystallization, it becomes insoluble in common organic solvents. Treatment of 5 with thf or pyridine results in a chemical reaction and gas evolution. An NMR spectrum of 5 could not be obtained, because of the low solubility of 5 in organic solvents. Clear colorless crystals of 5 suitable for a single-crystal X-ray diffraction study were obtained by slow cooling of the concentrated toluene solution to -20 °C. The molecular structure of 5 is shown in Figure 3, and the crystal and structural refinement data are listed in Table 1. X-ray analysis revealed that complex 5 does not contain Lewis bases and, as 2 and 3, adopts a dimeric structure as a result of the "spanning" coordination mode of the bis(amidinate) ligands. However, in this case two  $\mu^2$ -bridging hydride ligands are also present in the coordination spheres of the yttrium atoms.

Despite the fact that the presence of small ligands such as hydrido or chlorido in the metal coordination sphere favors "spanning" coordination of *ansa*-bis(cyclopentadienyl) ligands, to date just a couple of hydrido rare earth complexes having "flyover dimer" structures have been reported.<sup>[17a,17c]</sup> The planar tetranuclear  $Y_2H_2$  core in **5** is symmetric and features unique geometric parameters: the Y–H



Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of 5 showing the atom numbering scheme. Hydrogen atoms [except H(1) and H(1A)] are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y(1)–N(3) 2.324(2), Y(1)–N(2) 2.325(2), Y(1)–N(1) 2.371(2), Y(1)–N(4) 2.381(2), Y(1)–H(1) 2.55(2), Y(1)–Y(1A) 3.4661(5), N(3)–C(20) 1.352(3), N(4)–C(20) 1.327(3), N(1)–C(1) 1.319(3), N(2)–C(1) 1.345(3), N(2)–Y(1)–N(1) 57.44(6), N(3)–Y(1)–N(4) 57.62(7), Y(1)–H(1)–Y(1A) 83.9(2), H(1)–Y(1)–H(1A) 96.1(2).

bonds [2.55(2) Å] are the longest, while the Y–Y distance [3.4661(5) Å] is the shortest among the known dimeric hydridoyttrium complexes. For comparison, see: [{Me<sub>2</sub>Si(2- $Me-C_{9}H_{5}Y$  (thf)( $\mu$ -H)]<sub>2</sub> [2.09(3), 2.13(3); 3.6524(3) Å],<sup>[17c]</sup>  $[(C_5Me_4)Me_2Si(NCMe_3)Y(thf)(\mu-H)]_2$ [1.98(4)-2.48(4);3.627(1) Å],<sup>[23]</sup>  $[{PhC(NSiMe_3)_2}_2Y(\mu-H)]_2$ [2.11(3) -2.19(3) Å],<sup>[8a]</sup> [(MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Y(thf)( $\mu$ -H)]<sub>2</sub> [3.66(1); 2.17(8), 2.19(8) Å],<sup>[24]</sup>  $[(1,3-Me_2-C_5H_3)_2Y(thf)(\mu-H)]_2$  [2.03(7), 2.27(6); 3.68(1) Å],<sup>[25]</sup>  $[(2,4,7-Me_3-C_9H_4)_2Y(\mu-H)]_2$  [2.09(4)– 2.14(7) Å].<sup>[26]</sup> Angle Y(1)-H(1)-Y(1A) is much smaller than analogous angles in other dimeric hydridoyttrium complexes; for comparison, see:  $[Ln{(Me_3Si)_2NC(NiPr)_2}_2(\mu-$ H)]<sub>2</sub> [104.6(2)°],<sup>[27]</sup> [Y( $\eta^5$ : $\eta^1$ -C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>SiMe<sub>2</sub>NCMe<sub>3</sub>)- $(thf)(\mu-H)_2 [122.5(2)^\circ]_{,[28]} [Ln{(Me_3Si)_2NC(NcHex)_2}_2(\mu-$ H)]<sub>2</sub> [120.1(2)°].<sup>[29]</sup> The average Y-N bond length in 5 [2.35(5) Å] is slightly shorter than those in the related complexes 2 and 3, and this shortening obviously results from the small size of the hydrido ligand.

Complexes **3** and **5** and systems **2**-MAO and **3**-MAO (toluene, 20 °C, 0.5 bar, [complex]/[MAO] = 1:250) showed no activity in ethylene polymerization. Complex **5** was found to be inert in styrene polymerization (toluene, 20 °C).

### Conclusions

Here we have summarized our attempts to employ the dianionic SiMe<sub>2</sub>-linked bis(amidinate) ligand system for the synthesis of new chlorido-, alkyl(chlorido)-, and hydridovttrium complexes. Similar to those with single-atom-linked ansa-bis(cyclopentadienyl) ligands, yttrium complexes containing the bis(amidinate) analogue [Me<sub>2</sub>Si{NC(Ph)N- $(2,6-i\Pr_2-C_6H_3)$ <sup>2</sup><sup>2-</sup> adopt dimeric structures resulting from a "spanning" ligation pattern. Chlorido complex 2 consists of a discrete dinuclear complex anion [(Me2Si- $\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2(YCl)_2(\mu-Cl)^-$ , which contains one µ-bridging and two terminal chloride ligands, and a cation  $[\text{Li}(\text{thf})_4]^+$ . The terminal chloride ligand was easily substituted by an alkyl group when 2 was treated with an equimolar amount of Me<sub>3</sub>SiCH<sub>2</sub>Li to afford a dinuclear alkyl(chlorido) complex [Me<sub>2</sub>Si{NC(Ph)N(2,6-*i*Pr<sub>2</sub>- $C_6H_3$ ]<sub>2</sub>]<sub>2</sub>[Y(thf)]( $\mu$ -Cl)[Y(CH<sub>2</sub>SiMe<sub>3</sub>)] (3). Treatment of the in situ generated alkyl derivative [Me2Si{NC(Ph)N(2,6 $iPr_2-C_6H_3$ ]<sub>2</sub>[Y(CH<sub>2</sub>SiMe<sub>3</sub>)]<sub>2</sub> (4) with PhSiH<sub>3</sub> in toluene allowed the formation of the dimeric hydridoyttrium complex  $[Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2Y(\mu-H)]_2$  (5) containing two  $\mu^2$ -hydrido ligands. Further studies on the synthesis of alkoxido- and amidolanthanide species supported by a linked bis(amidinate) ligand system and investigation of their catalytic activity in ring opening polymerization of cyclic esters are currently in progress.

### **Experimental Section**

All experiments were performed in evacuated tubes by using standard Schlenk techniques, with rigorous exclusion of traces of moisture and air. After being dried over KOH, thf was purified by distillation from sodium/benzophenone ketyl; hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. C<sub>6</sub>D<sub>6</sub> was dried with sodium/potassium alloy and condensed in vacuo into NMR tubes prior to use. C<sub>5</sub>D<sub>5</sub>N was dried with CaH<sub>2</sub> and condensed in vacuo into NMR tubes prior to use. 2,6-Diisopropylaniline, Me<sub>2</sub>SiCl<sub>2</sub>, and benzonitrile were purchased Acros. Anhydrous YCl<sub>3</sub>,<sup>[30]</sup> Me<sub>3</sub>SiCH<sub>2</sub>Li,<sup>[31]</sup> and from  $[(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2Li_3]$  [Li(thf)<sub>4</sub>]<sup>+[15b]</sup> (1) were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded with Bruker Avance DRX-400 and DPX-200 spectrometers in C<sub>6</sub>D<sub>6</sub> or C<sub>5</sub>D<sub>5</sub>N at 25 °C, unless otherwise stated. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally to the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls with a "Bruker-Vertex 70" instrument. Lanthanide metal analyses were carried out by complexometric titration. The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

 $[(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2(YCl)_2(\mu-Cl)]^-[Li(thf)_4]^+ (2): A solution of [(Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2)_2Li_3]^-[Li(thf)_4]^+$ 

(1) (1.56 g, 1.01 mmol) in thf (30 mL) was added to a suspension of YCl<sub>3</sub> (0.40 g, 2.05 mmol) in thf (5 mL) at 20 °C, and the reaction mixture was stirred at room temperature for 14 h. The reaction mixture was filtered, and the solvent was removed in vacuo. The remaining solid was extracted into toluene (50 mL). After filtration of the toluene extract the solvent was removed in vacuo at room temperature. Slow condensation of hexane into a concentrated thf solution afforded colorless crystals of 2. The crystals were washed with cold hexane and dried at ambient temperature in vacuo for 1 h. Yield 1.32 g (72%).  $C_{96}H_{132}Cl_3LiN_8O_4Si_2Y_2$  (1809.41): calcd. C 63.72, H 7.35, N 6.19, Y 9.83; found C 63.98, H 7.61, N 6.08, Y 9.80. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 25 °C):  $\delta$  = 1.01 [d, <sup>3</sup>J<sub>H H</sub> = 6.8 Hz, 12 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.06 [s, 8 H, Si(CH<sub>3</sub>)<sub>2</sub>], 1.15 [m, 12 H,  $CH(CH_3)_2$  and 4 H, Si(CH<sub>3</sub>)<sub>2</sub>], 1.23 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 12 H,  $CH(CH_3)_2$ ], 1.27 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 12 H,  $CH(CH_3)_2$ ], 1.60 (s, 16 H,  $\beta$ -CH<sub>2</sub>, thf), 3.38 [sept,  ${}^{3}J_{H,H} = 6.8$  Hz, 8 H, CH(CH<sub>3</sub>)<sub>2</sub>], 3.64 (s, 16 H, α-CH<sub>2</sub>, thf), 7.06–7.56 (m, together 32 H, Ar). <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N, 25 °C):  $\delta = -0.1$  [Si(CH<sub>3</sub>)<sub>2</sub>], 22.7, 23.6, 23.9, 24.9 [CH(CH<sub>3</sub>)<sub>2</sub>], 25.8 (β-CH<sub>2</sub>, thf), 28.5, 28.7 [CH(CH<sub>3</sub>)<sub>2</sub>], 67.8 (α-CH<sub>2</sub>, thf), 122.7, 127.3, 127.8, 128.1, 128.6, 128.7, 129.4, 130.4, 137.0, 138.9, 139.4, 146.1, 146.4, 154.0, 158.7 [C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>3</sub>(*i*Pr)<sub>2</sub>], 176.4, 176.7 (N-C-N) ppm. <sup>7</sup>Li NMR (155.5 MHz, C<sub>5</sub>D<sub>5</sub>N, 25 °C):  $\delta$  = 3.3 ppm. IR (KBr):  $\tilde{v}$  = 1641 (m), 1578 (s), 1324 (s), 1254 (s), 1212 (s), 1131 (s), 1100 (m), 1043 (s), 976 (s), 886 (s), 831 (m), 783 (m), 695 (s), 638 (s), 487 (s) cm<sup>-1</sup>.

 $[Me_2Si\{NC(Ph)N(2,6-iPr_2-C_6H_3)\}_2]_2[Y(thf)](\mu-Cl)[Y(CH_2SiMe_3)]$ (3): A solution of Me<sub>3</sub>SiCH<sub>2</sub>Li (0.04 g, 0.42 mmol) in toluene (30 mL) was added to a suspension of 2 (0.72 g, 0.40 mmol) in toluene (5 mL) at 20 °C, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered, and the solvent was removed in vacuo. The remaining solid was dissolved in a toluene/hexane mixture (1:10, 40 mL). Slow cooling of this toluene/ hexane solution to -20 °C afforded colorless crystals of 3. The crystals were washed with cold hexane and dried at ambient temperature in vacuo for 0.5 h. Yield 0.39 g (61%).  $C_{88}H_{119}CIN_8OSi_3Y_2$ (1602.46): calcd. C 65.96, H 7.49, N 6.99, Y 11.10; found C 66.27, H 7.30, N 6.93, Y 11.02. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 25 °C):  $\delta$  = -1.01 [s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>], -0.64 [s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>], -0.12 [dd,  ${}^{2}J_{H,H}$ = 11.2,  ${}^{2}J_{Y,H}$  = 3.2 Hz, 1 H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>], -0.03 [dd,  ${}^{2}J_{H,H}$  = 11.2,  ${}^{2}J_{Y,H}$  = 3.2 Hz, 1 H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>], 0.38 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ], 0.54 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ], 0.61 [d,  ${}^{3}J_{H,H}$ = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 0.64 [s, 9 H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>], 0.81 [d,  ${}^{3}J_{H,H} = 6.8 \text{ Hz}, 3 \text{ H}, \text{ CH}(\text{C}H_{3})_{2}$ ], 0.83 [d,  ${}^{3}J_{H,H} = 6.8 \text{ Hz}, 3 \text{ H},$  $CH(CH_3)_2$ ], 0.87 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H,  $CH(CH_3)_2$ ], 1.11 [m, 6 H, Si(CH<sub>3</sub>)<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>], 1.18 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.23 [s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>], 1.27 [m, 7 H, CH(CH<sub>3</sub>)<sub>2</sub> and β-CH<sub>2</sub>, thf], 1.38 [d,  ${}^{3}J_{H,H} = 6.8$  Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.46 [d,  ${}^{3}J_{H,H} = 6.8$  Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.50 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.65 [d,  ${}^{3}J_{H,H} = 6.8 \text{ Hz}, 3 \text{ H}, \text{ CH}(\text{CH}_{3})_{2}], 1.67 \text{ [d, } {}^{3}J_{H,H} = 6.8 \text{ Hz}, 3 \text{ H},$  $CH(CH_3)_2$ ], 1.81 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H, CH- $(CH_3)_2$ ], 1.96 [d,  ${}^{3}J_{H,H}$  = 6.8 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 2.98 [sept,  ${}^{3}J_{H,H}$ = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ], 3.13 [sept,  ${}^{3}J_{H,H}$  = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ], 3.40 [sept,  ${}^{3}J_{H,H}$  = 6.8 Hz, 1 H,  $CH(CH_3)_2$ ], 3.72 [sept,  ${}^{3}J_{H,H} = 6.8 \text{ Hz}, 2 \text{ H}, CH(CH_{3})_{2}$ ], 3.78, 4.04 (br. s, each 2 H,  $\alpha$ - $CH_2$ , thf), 4.27 [sept,  ${}^{3}J_{H,H}$  = 6.8 Hz, 2 H,  $CH(CH_3)_2$ ], 6.64–7.70 (m, together 32 H, Ar). <sup>13</sup>C NMR (50 MHz,  $C_6D_6$ , 25 °C):  $\delta$  = 3.0, 3.3, 7.5, 9.6 [Si(CH<sub>3</sub>)<sub>2</sub>], 4.7 [CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>], 22.7, 23.2, 23.3, 24.0, 24.3, 24.4, 24.8, 24.9, 25.2, 25.4, 25.6, 25.8, 26.0, 26.8 [CH(CH<sub>3</sub>)<sub>2</sub>], 25.0 (β-CH<sub>2</sub>, thf), 27.5, 27.6, 27.9, 28.0, 28.2, 28.3, 28.4, 28.6  $[CH(CH_3)_2]$ , 34.9 [d,  ${}^1J_{Y,C}$  = 38.5 Hz,  $CH_2Si(CH_3)_3$ ], 71.6 ( $\alpha$ - $CH_2$ , thf), 122.6, 122.9, 123.1, 123.4, 123.8, 124.3, 124.4, 124.8, 125.1, 125.4, 126.9, 127.5, 128.5, 129.0, 136.4, 136.8, 137.5, 138.2, 138.7, 141.9, 142.0, 142.2, 142.3, 142.8, 142.9, 143.4, 143.6, 143.9 [C<sub>6</sub>H<sub>5</sub>,



 $C_6H_3(iPr)_2$ ], 176.2, 177.2, 177.8, 178.7 (N-*C*-N) ppm. IR (KBr):  $\tilde{v} = 1626$  (s), 1578 (m), 1318 (s), 1251 (s), 1209 (m), 1131 (m), 1100 (s), 1043 (m), 976 (s), 862 (m), 825 (s), 777 (s), 698 (m), 638 (s), 487 (s) cm<sup>-1</sup>.

[Me<sub>2</sub>Si{NC(Ph)N(2,6-*i*Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}<sub>2</sub>Y(µ-H)]<sub>2</sub> (5): A solution of Me<sub>3</sub>-SiCH<sub>2</sub>Li (0.06 g, 0.64 mmol) in toluene (30 mL) was added to a suspension of 2 (0.54 g, 0.30 mmol) in toluene (5 mL) at 20 °C, and the reaction mixture was stirred for 12 h at 0 °C and for 3 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated to 5 mL. PhSiH<sub>3</sub> (0.07 g, 0.65 mmol) was added at -40 °C, and the clear solution was stirred for 1 h at room temperature. Growth of colorless crystals of 5 started in approximately 0.5 h. The toluene solution was allowed to stand at -20 °C for 3 days, and the mother liquor was decanted from the crystalline material. The colorless crystals were washed with cold hexane and dried at ambient temperature in vacuo for 1 h. Yield 0.31 g (73%). C<sub>80</sub>H<sub>102</sub>N<sub>8</sub>Si<sub>2</sub>Y<sub>2</sub> (1409.70): calcd. C 68.16, H 7.29, N 7.95, Y 12.61; found C 68.70, H 7.18, N 7.88, Y 12.72. IR (KBr): v = 1631 (s), 1578 (s), 1248 (s), 1216 (s), 1133 (s), 1098 (s), 972 (s), 932 (m), 916 (m), 894 (s), 828 (s), 776 (m), 625 (m), 541 (s), 489 (s)  $cm^{-1}$ .

X-ray Crystallography: The data were collected with a SMART APEX diffractometer (graphite-monochromated,  $Mo-K_{\alpha}$ -radiation,  $\omega$ - and  $\theta$ -scan technique,  $\lambda = 0.71073$  Å, T = 100 K). The structures were solved by direct methods and were refined on  $F^2$ with the SHELXTL<sup>[32]</sup> package. All non-hydrogen atoms atom were found from Fourier syntheses of electron density and were refined anisotropically, whereas all H atoms in 2, 3, and 5 were placed in calculated positions and were refined in the riding model. The hydride H(1) in 5 was found from Fourier syntheses of electron density and was refined isotropically with fixed  $U_{iso}$  (0.08 Å<sup>2</sup>). SA-DABS<sup>[33]</sup> was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection, and refinement data are shown in Table 1. CCDC-756183, -756184, -756185 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_ request/cif.

#### Acknowledgments

This work is supported by the Russian Foundation for Basic Research (Grant Nos. 08-03-00391-a, 06-03-32728), Program of the Presidium of the Russian Academy of Science (RAS), and the RAS Chemistry and Material Science Division.

- a) S. A. Cotton, *Coord. Chem. Rev.* **1997**, *160*, 93–127; b) M. N. Bochkarev, L. N. Zakharov, G. S. Kalinina, *Organoderivatives of Rare Earth Elements*, Kluwer Academic Publishers, Dordrecht, **1995**, p. 532; c) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–893; d) S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953–1976; e) J. Okuda, *Dalton Trans.* **2003**, 2367–2378; f) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404–2433; g) M. Konkol, J. Okuda, *Coord. Chem. Rev.* **2008**, *252*, 1577–1591; h) Z. Hou, M. Nishiura, T. Shima, *Eur. J. Inorg. Chem.* **2007**, 2535–2545.
- [2] Hydrogenation: a) G. Jeske, H. Lauke, H. Mauermann, H. Schumann, T. J. Marks, J. Am. Chem. Soc. 1985, 107, 8111–8118; b) V. P. Conticello, L. Brard, M. A. Giardello, Y. Tsyji, M. Sabat, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. 1992, 114, 2761–2762; Polymerization: c) G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, T. J. Marks, J. Am. Chem. Soc. 1985, 107, 8091–8103; d) H. Mauermann, P. N. Swepston, T. J. Marks, Organometallics 1985, 4, 200–202;

e) G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann, T. J. Marks, J. Am. Chem. Soc. 1985, 107, 8103–8110; f) G. Desurmont, Y. Li, H. Yasuda, T. Maruo, N. Kanehisha, Y. Kai, Organometallics 2000, 19, 1811–1813; g) Z. Hou, Y. Luo, X. Li, J. Organomet. Chem. 2006, 691, 3114–3121. Hydrosilylation: h) G. A. Molander, J. A. C. Romero, Chem. Rev. 2002, 102, 2161–2185; Hydroamination: i) I. Aillaud, J. Collin, J. Hannedouche, E. Schulz, Dalton Trans. 2007, 5105–5118; j) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, Chem. Rev. 2008, 108, 3795–3892; Hydroboration: k) K. N. Harrison, T. J. Marks, J. Am. Chem. Soc. 1992, 114, 9220–9221; l) E. A. Bijpost, R. Duchateau, J. H. Teuben, J. Mol. Catal. 1995, 95, 121–128.

- [3] a) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, J. Am. Chem. Soc. 1987, 109, 203–219; b) M. Booij, B.-J. Deelman, R. Duchateau, D. S. Postma, A. Mettsma, J. H. Teuben, Organometallics 1993, 12, 3531–3540; c) K. H. den Haan, Y. Wielstra, J. H. Teuben, Organometallics 1987, 6, 2053–2060; d) F.-G. Fontaine, T. Don Tilley, Organometallics 2005, 24, 4340– 4342; e) P. L. Watson, J. Am. Chem. Soc. 1983, 105, 6491–6493; f) H. M. Dietrich, H. Grove, K. W. Törnroos, R. Anwander, J. Am. Chem. Soc. 2006, 128, 1458–1459.
- [4] A. D. Sadow, T. Don Tilley, Angew. Chem. Int. Ed. 2003, 42, 803–805.
- [5] a) E. L. Werkema, E. Messines, L. Perrin, L. Maron, O. Eisenstein, R. A. Andersen, *J. Am. Chem. Soc.* 2005, *127*, 7781–7795; b) L. Maron, E. L. Werkema, L. Perrin, O. Eisenstein, R. A. Andersen, *J. Am. Chem. Soc.* 2005, *127*, 279–292.
- [6] a) F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* 2002, 102, 1851–1896; b) W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* 2002, 233–234; W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* 2002, 131–155; c) P. Mountford, B. D. Ward, *Chem. Commun.* 2003, 1797–1803; d) A. Trifonov, *Russ. Chem. Rev.* 2007, 76, 1051–1072.
- [7] a) F. T. Edelmann, Adv. Organomet. Chem. 2008, 57, 183–352;
  b) M. P. Coles, Dalton Trans. 2006, 985–1001.
- [8] For reviews see: F. T. Edelmann, Chem. Soc. Rev. 2009, 38, 2253-2268; a) R. Duchateau, C. T. Van Wee, A. Meetsma, P. T. Van Duijnen, J. H. Teuben, Organometallics 1996, 15, 2279-2290; b) R. Duchateau, C. T. Van Wee, A. Meetsma, J. H. Teuben, J. Am. Chem. Soc. 1993, 115, 4931-4932; c) R. Duchateau, C. T. Van Wee, J. H. Teuben, Organometallics 1996, 15, 2291-2302; d) J. R. Hagadorn, J. Arnold, Organometallics 1996, 15, 984–991; e) S. Bambirra, M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen, J. H. Teuben, Organometallics 2000, 19, 3197-3204; f) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J. H. Teuben, Chem. Commun. 2003, 522-523; g) S. Bambirra, M. W. Bouwkamp, A. Meetsma, B. Hessen, J. Am. Chem. Soc. 2004, 126, 9182-9183; h) S. Bambirra, F. Perazzolo, S. J. Boot, T. J. J. Sciarone, A. Meetsma, B. Hessen, Organometallics 2008, 27, 704-712.
- [9] S. Bambirra, M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics* 2000, 19, 3197–3204.
- [10] S. Bambirra, H. Tsurugi, D. van Leusen, B. Hessen, *Dalton Trans.* 2006, 1157–1161.
- [11] S. Ge, A. Meetsma, B. Hessen, Organometallics 2008, 27, 3131– 3135.
- [12] E. A. Bijpost, R. Duchateau, J. H. Teuben, J. Mol. Catal. A 1995, 95, 121–128.
- [13] L. Zhang, M. Nishiura, M. Yuki, Y. Luo, J. Hou, Angew. Chem. Int. Ed. 2008, 47, 2642–2645.
- [14] a) C. M. Fendrick, L. D. Schertz, V. W. Day, T. J. Marks, Organometallics 1988, 7, 1828–1838; b) C. M. Fendrick, E. A. Mintz, L. D. Schertz, T. J. Marks, V. W. Day, Organometallics 1984, 3, 819–821.
- [15] a) J.-F. Li, L.-H. Weng, X.-H. Wei, D.-S. Liu, *J. Chem. Soc., Dalton Trans.* 2002, 1401–1405; b) S.-D. Bai, J.-P. Guo, D.-S. Liu, *Dalton Trans.* 2006, 2244–2250; c) M. S. Hill, P. B. Hitch-cock, S. M. Mansell, *Dalton Trans.* 2006, 1544–1553.

# FULL PAPER

- [16] a) S. Bambirra, A. Meetsma, B. Hessen, J. H. Teuben, Organometallics 2001, 20, 782–785; b) J. Wang, Y. Yao, Y. Zhang, Q. Shen, Inorg. Chem. 2009, 48, 744–751; c) C.-L. Pan, W. Chen, Sh. Song, H. Zhang, X. Li, Inorg. Chem. 2009, 48, 6344–6346.
- [17] a) D. Stern, M. Sabat, T. J. Marks, J. Am. Chem. Soc. 1990, 112, 9558–9575; b) N. Höck, W. Oroschin, G. Paolucci, R. D. Fischer, Angew. Chem. Int. Ed. Engl. 1986, 25, 738–739; c) M. G. Klimpel, P. Sirsch, W. Scherer, R. Anwander, Angew. Chem. Int. Ed. 2003, 42, 574–577.
- [18] a) J. Wang, H. Sun, Y. Yao, Q. Shen, *Polyhedron* 2008, 27, 1977–1982; b) J. Wang, F. Xu, T. Cai, Q. Shen, *Org. Lett.* 2008, 10, 445–448.
- [19] a) W. J. Evans, J. W. Grate, K. R. Levan, I. Bloom, T. T. Peterson, R. J. Doedens, H. Zhang, J. L. Aywood, *Inorg. Chem.* 1986, 25, 3614–3619; b) W. J. Evans, T. T. Peterson, M. D. Rausch, W. E. Hunter, H. Zhang, J. L. Aywood, *Organometallics* 1985, 4, 554–559.
- [20] M. P. Hogerheide, D. M. Grove, J. Boersma, J. T. B. H. Jastrzebski, H. Kooijman, A. L. Spek, G. van Koten, *Chem. Eur. J.* 1995, 1, 343–350.
- [21] a) P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* 2003, 22, 3921–3926; b) L. Lavanant, T.-Y. Chou, Y. Chi, C. V. Lehmann, L. Toupet, J.-F. Carpentier, *Organometallics* 2004, 23, 5450–5458; c) X. Liu, X. Shang, T. Tang, N. Hu, F. Pei, D. Cui, X. Chen, X. Jing, *Organometallics* 2007, 26, 2747–2757; d) A. A. Trifonov, T. P. Spaniol, J. Okuda, *Organometallics* 2001, 20, 4869–4874.
- [22] A. Z. Voskoboinikov, I. N. Parshina, A. K. Shestakova, K. P. Butin, I. P. Beletskaya, L. G. Kuz'mina, J. A. K. Howard, *Organometallics* 1997, *16*, 4041–4055.

- [23] a) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* **1999**, *38*, 227–230; b) S. Arndt, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 4690–4700.
- [24] W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter, J. L. Atwood, J. Am. Chem. Soc. 1982, 104, 2008–2014.
- [25] W. J. Evans, D. K. Drummond, T. P. Hanusa, R. J. Doedens, Organometallics 1987, 6, 2279–2285.
- [26] W. P. Kretschmer, S. I. Troyanov, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics* 1998, 17, 284–286.
- [27] A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov, V. N. Glushakova, *Chem. Eur. J.* 2006, *12*, 5320–5327.
- [28] A. A. Trifonov, T. P. Spaniol, J. Okuda, Organometallics 2001, 20, 4869–4874.
- [29] D. M. Lubov, A. M. Bubnov, G. K. Fukin, F. M. Dolgushin, M. Yu. Antipin, O. Pelce, M. Schappacher, S. M. Guillaume, A. A. Trifonov, *Eur. J. Inorg. Chem.* **2008**, 2090–2098.
- [30] M. D. Taylor, C. P. Carter, J. Inorg. Nucl. Chem. 1962, 24, 387– 393.
- [31] H. L. Lewis, T. L. Brown, J. Am. Chem. Soc. 1970, 92, 4664– 4670.
- [32] G. M. Sheldrick, *SHELXTL*, v. 6.12, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin (USA), 2000.
- [33] G. M. Sheldrick, SADABS, v.2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin (USA), 1998.

Received: December 1, 2009 Published Online: March 3, 2010