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Synthesis and Structural Characterization of β-Diketiminato Yttrium Complexes and their Application in Epoxide/CO_2-Copolymerization

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Dedicated to Professor Dieter Fenske on the Occasion of his 65th Birthday

Abstract. The β-diketiminato yttrium complexes $[(BDI^{Ph})_2Y\{N(SiHMe_2)_2\}]$ (**1**, BDI^{Ph} = $[PhNC(Me)CHC(Me)NPh]^-$), $[(BDI^{Ph})_3Y]$ (**2**), and $[(C_5Me_5)(BDI^{Ph})Y\{N(SiHMe_2)_2\}]$ (**4**) are available via amine elimination starting from $(BDI^{Ph})H$ and either $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ or $[(C_5Me_5)Y\{N(SiHMe_2)_2\}_2(THF)]$ (**3**). X-ray crystallographic analysis of complexes **1** and **4** revealed a η^5 coordination mode for the β-diketiminato ligand, whereas the distorted octahedral complex **2** displayed pure κ^2 coordination. Complex **3** was also structurally characterized. **1**, **3**, and **4** are moderately active catalysts in the copolymerization of cyclohexene oxide and CO_2. Complex **3** was the most active system (TOF up to 33 h^{-1} at 75 °C, 8.5 atm CO_2) and gave the highest molecular weight and narrowest polydispersity (M_n = 12600 g mol^{-1}, M_w/M_n = 1.6).

Keywords: β-Diketiminato complexes; Yttrium; Amine elimination; Epoxide/CO_2 Copolymerization

Introduction

The organometallic chemistry of the rare earth elements has attracted significant attention in particular due to their high catalytic activity for a wide range of organic transformations [1] and polymerizations [2]. An increasingly important field of research focuses on the development of non-metallocene catalyst systems [3]. Non-cyclopentadienyl ligands can be easily modified in their electronic and steric properties, allowing facile catalyst tuning.

The utilization of CO_2 as a C1 feedstock is an appealing goal in contemporary catalysis research, because CO_2 is naturally abundant, inexpensive, nontoxic and nonflammable [4]. In particular, the metal-catalyzed copolymerization of CO_2 and epoxides has been studied extensively, because the resulting polycarbonates are biodegradable polymers with attractive material properties [5]. Homogeneous catalyst systems based on β-diketiminato zinc [5d, 6] and salen chromium [5b, 7] complexes are most prominent examples of recent developments.

We have recently reported the application of mono(β-diketiminato) and linked bis(β-diketiminato) rare earth metal complexes as catalysts in the epoxide/CO_2 copolymerization [8]. Parallel to our study *Hou* reported the application of mono(cyclopentadienyl) rare earth metal complexes in epoxide/CO_2 copolymerization [9]. In continuation of our studies we report herein the synthesis and structural characterization of mono-, bis- and tris(β-diketiminato) [10] yttrium complexes and their catalytic activity in the copolymerization of cyclohexene oxide and CO_2.

Results and Discussion

β-Diketiminato rare earth metal complexes have been prepared *via* salt metathesis [11]. However, for practical synthetic reasons we decided to utilize the more convenient single-step amine elimination route [8, 12].

Reaction of the trisamido yttrium complex $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ with two equiv of the sterically undemanding phenyl-substituted β-diketiminato ligand $(BDI^{Ph})H$ at 70 °C produced the bis(β-diketiminato) yttrium complex **1** in 4 h (Scheme 1). Complex **1** was poorly soluble in toluene and precipitated as slightly yellow crystals suitable for X-ray diffraction (*vide infra*) in 73 % yield from the reaction mixture. Attempts to perform the reaction at elevated temperatures (100 °C) resulted in the formation of the tris(β-diketiminato) yttrium complex $[(BDI^{Ph})_3Y]$ (**2**) as a by-product. Complex **2** could be obtained selectively by heating $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ with three equiv of $(BDI^{Ph})H$ to 100 °C for 24 h to give **2** in good yield. Interestingly, complex **2** was better soluble in toluene than **1**.

While the NMR spectra of complex **1** do not show any unusual behavior, the ^1H NMR spectrum of complex **2** shows 5 distinct, though slightly broadened signals for the

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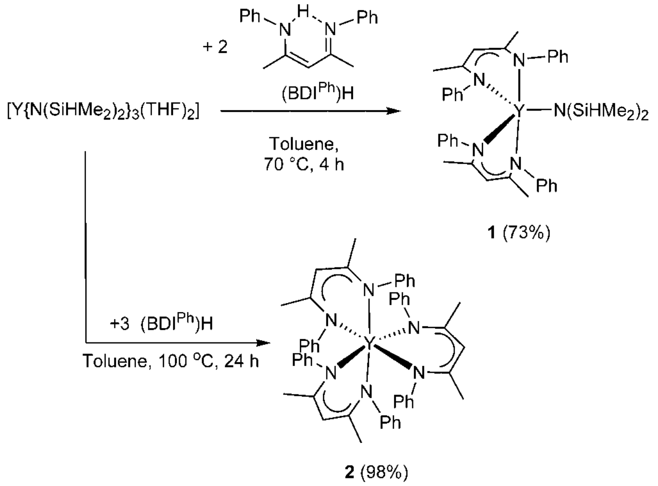


Scheme 1

aromatic ring protons at 25 °C, one of which is significantly shifted to higher field and resonates at 5.23 ppm in C_6D_6 solution. This unusual feature can be readily rationalized by an interaction of a phenyl ring proton with the ring current of an aromatic substituent of a neighboring β-diketiminato ligand. This proposal is supported by a crystallographically observed close proximity of one of the *ortho*-protons in each phenyl substituent to a phenyl substituent of a second β-diketiminato ligand (*vide infra*).

Recrystallization of **2** from toluene afforded single crystals suitable for a X-ray diffraction study. ORTEP diagrams of **1** and **2** are depicted in Figures 1 and 2, while Table 1 and Table 2 give selected metrical parameters.

Table 1 Selected Bond lengths /Å and angles /° of $[(BDI^{Ph})_2Y\{N(SiHMe_2)_2\}]$ (**1**).

Y1-N1	2.3591(18)	N2-Y1-N2′	110.22(9)
Y1-N2	2.3169(19)	N1-Y1-N2	77.80(6)
Y1-N3	2.209(3)	N1-Y1-N2′	90.97(6)
Y1···Si1	3.3309(7)	N1-Y1-N3	99.79(5)
Y1···C_{BDI}	3.17−3.42	N2-Y1-N3	124.89(5)
distance of Y from N_2C_3	1.20	Si1-N3-Si1′	127.54(17)
N1-Y1-N1′	160.42(9)	Y1-N3-Si1	116.23(8)

Table 2 Selected Bond lengths /Å and angles /° of $[(BDI^{Ph})_3Y]$ (**2**).

Y1-N1	2.406(4)	N1-Y1-N15	96.66(12)
Y1-N5	2.404(3)	N5-Y1-N6	97.17(12)
Y1-N6	2.397(4)	N5-Y1-N10	88.11(12)
Y1-N10	2.404(4)	N5-Y1-N11	96.05(12)
Y1-N11	2.388(4)	N5-Y1-N15	172.64(12)
Y1-N15	2.404(4)	N6-Y1-N10	77.63(12)
Y1···C_{BDI}	3.41−3.77	N6-Y1-N11	96.99(12)
distance of Y from N_2C_3	0.10−0.11	N6-Y1-N15	88.25(12)
N1-Y1-N5	78.14(12)	N10-Y1-N11	173.61(13)
N1-Y1-N6	174.59(12)	N10-Y1-N15	97.94(13)
N1-Y1-N10	99.36(12)	N11-Y1-N15	78.29(12)
N1-Y1-N11	86.27(12)		

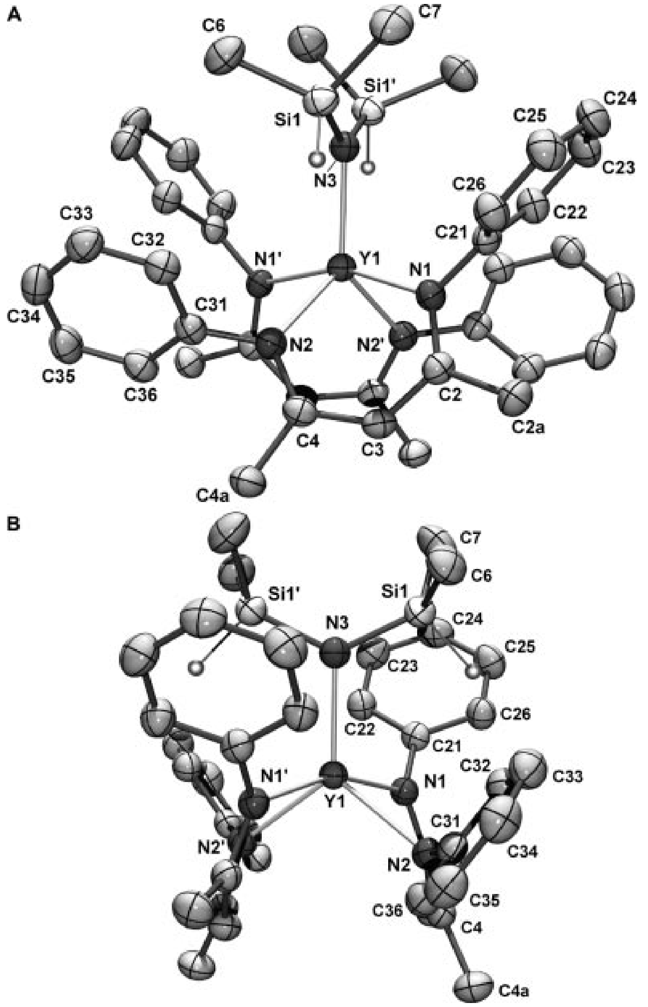


Fig. 1 ORTEP diagram of $[(BDI^{Ph})_2Y\{N(SiHMe_2)_2\}]$ (**1**) a) view from top b) view from the side. Thermal ellipsoids are drawn at the 50 % probability level. All hydrogen atoms, except those attached to silicon, are omitted for clarity.

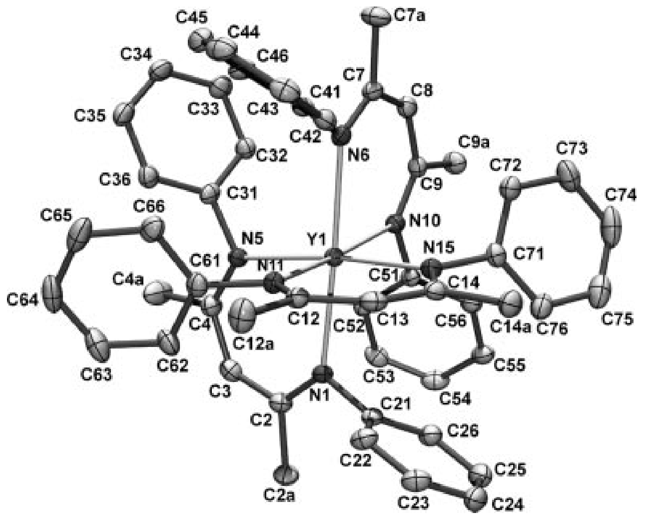
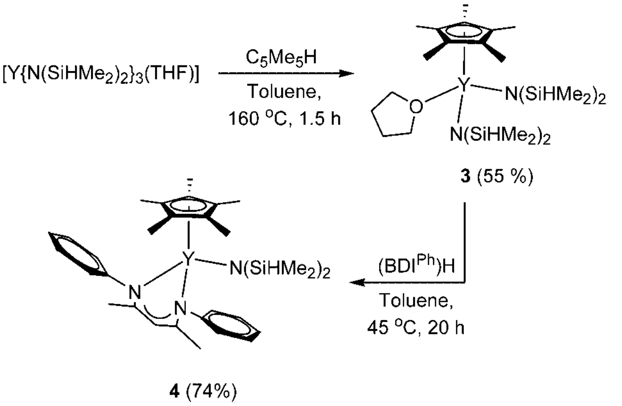


Fig. 2 ORTEP diagram of $[(BDI^{Ph})_3Y]$ (**2**). Thermal ellipsoids are drawn at the 30 % probability level. All hydrogen atoms are omitted for clarity.

The structure of **1** shows similar features as observed in the bis(β-diketiminato) neodymium complex [{$Me_3SiNC(Ph)CHC(Ph)NSiMe_3$}$_2$NdCl] [11d]. The yttrium atom is coordinated in a distorted trigonal bipyramidal fashion by two β-diketiminato and one amido ligand. One nitrogen atom of each β-diketiminate (N1 and N1′) occupies an axial position, while the other nitrogen atoms (N2 and N2') and the amido ligand (N3) are placed in equatorial positions. Overall, complex **1** has C_2-symmetry in the solid state. The β-diketiminato ligands are bound in the η^5 bonding mode with the yttrium atom being displaced by 1.20 Å out of the N_2C_3 planes and relative short Y···C contacts (3.17−3.41 Å). The β-diketiminato ligand is slightly puckered with C3 being placed slightly out of the N_2C_3 plane by 0.175 Å. The planes of the β-diketiminato ligands have a dihedral angle of 33.9° and the aromatic substituents are oriented perpendicular to these planes. The β-diketiminato ligands are bound slightly unsymmetrical with the axial Y1-N1 bond (2.3591(18) Å) being 0.04 Å longer than the equatorial Y1-N2 bond (2.3169(19) Å). Both bond lengths exceed the typical range for Y-N bonds (2.18−2.32 Å [13]), but are comparable to other β-diketiminato rare earth metal complexes [8, 11], when considering the ionic radius of yttrium. The Y-N bond to the bis(dimethylsilyl)amido ligand is significant shorter (2.209(3) Å) and falls at the lower limit of the typical range of Y-N bonds. The amido ligand shows a weak diagostic β-SiH interaction [14], with a relative close contact to the silicon atoms (3.3309(7) Å), concomitant with a decreased Y-N-Si angle (116.23(8)°) and a slightly widened Si-N-Si angle (127.54(17)°).

Complex **2** adopts a slightly distorted octahedral coordination which can be best compared with related tris(β-diketiminato) samarium and gadolinium complexes [{BDI^{Ph}}$_3$Ln] (Ln = Sm, Gd) [11a]. The β-diketiminato ligands are coordinated in a κ^2-fashion, as indicated by long yttrium-carbon distances (3.41−3.77 Å). The yttrium atom is situated close to the N_2C_3 plane of the β-diketiminato ligands (ca. 0.1 Å) and the β-diketiminato ligands are essentially planar. The Y-N bond lengths to the β-diketiminato ligands (2.39−2.41 Å) are slightly longer than those in complex **1**, in agreement with the higher coordination number in complex **2**. As indicated by NMR spectroscopic evidence (*vide supra*), the protons attached to the aromatic *ortho*-ring carbons C26, C36, C46, C56, C66 and C76 are situated in close proximity (2.56−2.69 Å) above the ring plane of one of a neighboring β-diketiminato phenyl substituent.

We then began to investigate the synthesis of half-sandwich complexes containing one β-diketiminato and one cyclopentadienyl ligand. A convenient precursor for the synthesis are mono(cyclopentadienyl) yttrium diamido complexes reported by *Anwander* and co-workers [15] as base-free species, though no crystallographic data is available. However, we were able to obtain single crystals of the THF-adduct **3** suitable for a X-ray diffraction study (Scheme 2, Figure 3, Table 3).



Scheme 2

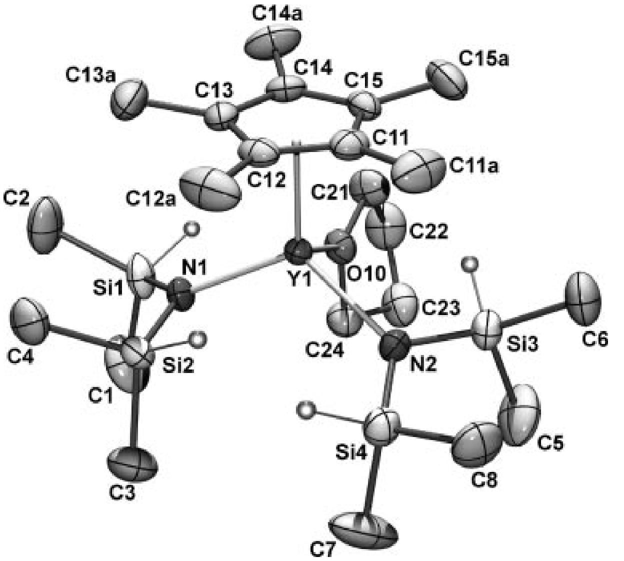


Fig. 3 ORTEP diagram of [(C_5Me_5)Y{$N(SiHMe_2)_2$}$_2$(THF)] (**3**). Thermal ellipsoids are drawn at the 50 % probability level. All hydrogen atoms, except those attached to silicon, are omitted for clarity.

Table 3 Selected Bond lengths /Å and angles /° of [(C_5Me_5)Y{$N(SiHMe_2)_2$}$_2$(THF)] (**3**).

Y1-N1	2.264(2)	N2-Y1-O10	97.24(7)
Y1-N2	2.281(2)	Cp_{cent}-Y1-N1	116.88(8)
Y1-O10	2.3623(19)	Cp_{cent}-Y1-N2	114.99(8)
Y1···Si1	3.636(1)	Cp_{cent}-Y1-O10	116.64(7)
Y1···Si2	3.0929(8)	Si1-N1-Si2	125.39(13)
Y1···Si3	3.3247(8)	Si3-N2-Si4	120.84(13)
Y1···Si4	3.572(1)	Y1-N1-Si1	132.44(12)
Y1-Cp_{cent}	2.367(2)	Y1-N1-Si2	102.15(10)
Y1···C_{Cp}	2.647(3)−2.662(3)	Y1-N2-Si3	112.57(11)
N1-Y1-N2	120.05(8)	Y1-N2-Si4	126.52(12)
N1-Y1-O10	84.95(7)		

Complex **3** adopts a three-legged piano stool arrangement. The Y-N bonds (2.264(2) and 2.281(2) Å) and the

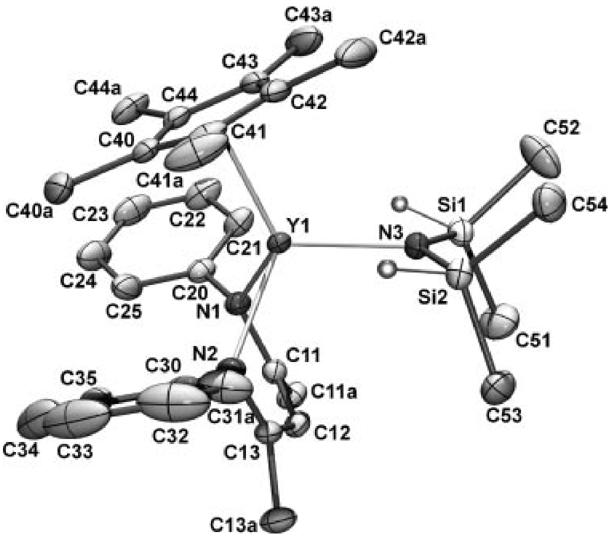


Fig. 4 ORTEP diagram of [$(C_5Me_5)(BDI^{Ph})Y\{N(SiHMe_2)_2\}$] (**4**). Thermal ellipsoids are drawn at the 30 % probability level. All hydrogen atoms, except those attached to silicon, are omitted for clarity.

Table 4 Selected Bond lengths /Å and angles /° of [$(C_5Me_5)(BDI^{Ph})Y\{N(SiHMe_2)_2\}$] (**4**).

Y1-N1	2.3012(18)	Cp_{cent}-Y1-N1	117.37(6)
Y1-N2	2.3236(17)	Cp_{cent}-Y1-N2	119.88(7)
Y1-N3	2.2472(18)	Cp_{cent}-Y1-N3	119.00(7)
Y1···Si1	3.493(1)	N1-Y1-N2	80.53(6)
Y1···Si2	3.1486(7)	N1-Y1-N3	103.21(7)
Y1···C_{Cp}	2.633(2)−2.690(2)	N2-Y1-N3	109.66(7)
Y1-Cp_{cent}	2.373(2)	Si1-N3-Si2	129.98(11)
Y1···C_{BDI}	3.04−3.21	Y1-N3-Si1	124.12(10)
distance of Y from N_2C_3	1.39	Y1-N3-Si2	105.68(9)

Y-O bond (2.3623(19) Å) fall within the usual range found in other amido and THF containing yttrium complexes (Y-N = 2.18−2.32 Å, Y-O = 2.35−2.45 Å [13]), likewise the Y-C_{Cp} and Y-Cp_{cent} distances are quite typical [16]. The geometry of the amido ligands are unsymmetric, indicative of monoagostic β-SiH interactions similar to that found in [$(C_5HPh_4)_2La\{N(SiHMe_2)_2\}$] [14c] or (*R*,*S*)-[$Y(Biphen)\{N(SiHMe_2)_2\}(THF)]_2$ [17]. This interaction is most prominent in the amido ligand containing N1, in which Si2 is in close contact with yttrium (3.0929(8) Å) concomitant with a decreased Y-N-Si angle (Y1-N1-Si2 = 102.15(10)° vs. Y1-N1-Si1 = 132.44(12)°), while the Si1-N1-Si2 angle (125.39(13)°) remains typical. This agostic interaction is less pronounced in the other amido ligand (Y1···Si3 = 3.3247(8) Å, Y1-N2-Si3 = 112.57(11)°, Y1-N2-Si4 = 126.52(12)°, Si3-N2-Si4 = 120.84(13)°).

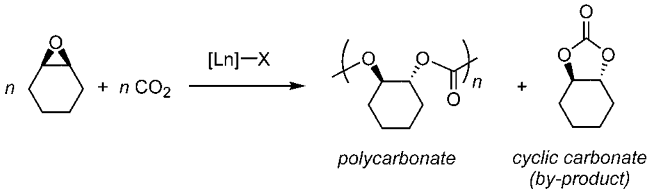
The mono(cyclopentadienyl) yttrium diamido complex **3** reacted cleanly and quantitatively according to ^1H NMR spectroscopy with the β-diketiminato ligand ($(BDI^{Ph})H$) at 45 °C within 20 h to give the THF-free half-sandwich complex **4** in good yield (Scheme 2).

X-ray crystallographic analysis of the half-sandwich complex **4** (Figure 4, Table 4) revealed a three-legged piano stool coordination geometry around yttrium and can be compared to previously characterized [$(C_5H_4CH_3)(BDI^{DIPPh})YbR$] (R = Cl, NPh_2) [11f]. Most noteworthy seems to be the η^5 binding mode of the β-diketiminato ligand, which is comparable to the chloro complex [$(C_5H_4CH_3)(BDI^{DIPPh})YbCl$], but significantly more pronounced than in the corresponding diphenylamido complex [$(C_5H_4CH_3)(BDI^{DIPPh})YbNPh_2$] [11f]. The N_2C_3 plane is oriented perpendicular (88°) to the plane of the cyclopentadienyl ligand, while the two phenyl rings are almost coplanar (dihedral angle 20.4 and 21.9°) to the cyclopentadienyl ring. The β-diketiminato chelating ring is slightly more puckered (C12 is 0.19 Å out of the N_2C_3 plane) than those in the bis(β-diketiminato) complex **1**. Furthermore, the Y···C contacts are shorter (3.04 − 3.21 Å) and the yttrium to N_2C_3 plane distance (1.39 Å) is larger than in complex **1**. The Y-C_{Cp} and Y-Cp_{cent} distances are comparable to those of complex **3** and all Y-N bond lengths fall within the typical range (*vide supra*). Interestingly, the Y-N bonds of the β-diketiminato ligand mark the lower end of the range of Y-N(BDI) bond lengths observed in complexes **1**, **2** and the linked bis(β-diketiminato) complex [$\{C_2H_4(BDI^{Mes})_2\}YN(SiMe_3)_2$] [8b]. The amido ligand displays a monoagostic β-SiH interaction similar to that of complex **3**.

Complexes **1**, **3** and **4** were tested as catalysts in the copolymerization of cyclohexene oxide and CO_2 (Table 5). All complexes showed moderate activity [5d] at 75 °C and 8 atm CO_2 comparable in magnitude to linked bis(β-diketiminato) lanthanum complexes [8]. The best results were obtained when the reactions were performed in a 1:1 (v:v) mixture of cyclohexene oxide and toluene. All catalysts produced polycarbonate with carbonate linkages exceeding 80 %. The half-sandwich complex **3** was the most active catalyst system (Table 5, entries 6 and 8) and produced the polymer with the highest molecular weight (Table 5, entry 7) and narrowest molecular weight distribution. Polymers obtained with the bis(β-diketiminato) complex **1** generally had lower molecular weights and broader molecular weight distributions, but produced the polycarbonate with the highest content in carbonate linkages (93 %, see Table 5, entry 2) in this series. Formation of the cyclic carbonate by-product was largely suppressed (≤ 2 %) under the optimized polymerization conditions; only at higher reaction temperatures (110 °C, Table 5, entry 3) a significant increase to 20 % was observed.

For comparison we also investigated the catalytic activity of the yttrocene [$Cp^*_2Y\{N(SiHMe_2)_2\}$] [14c] in the epoxide/CO_2 copolymerization. Although the catalytic activity of the yttrocene is at the lower end of the catalytic activities observed herein, the resulting polycarbonate possessed the highest percentage of carbonate linkages (95 %, Table 5, entry 11).

Table 5 Rare earth metal catalyzed copolymerization of CO_2 and cyclohexene oxide.



Entry	cat.	[M]/[cat.]	CHO/toluene v:v	$p(CO_2)$ atm	T (°C)	t (h)	TON	TOF h^{-1}	% cyclic carbonate[a)]	% carbonate linkages[a)]	M_n[b)] g mol−1	M_w[b)] g mol−1	M_w/M_n[a)]
1	**1**	1000	1:1	8	50	48	82	1.7	1	87	3500	7600	2.2
2	**1**	1000	1:1	8	75	48	356	7.3	1	93	7460	17200	2.3
3	**1**	1000	1:1	8	110	48	187	3.9	20	80	2430	13200	5.4
4	**1**	1000	1:2	8	75	48	145	3	2	91	2400	12000	5.0
5	**1**	1000	2:1	8	75	48	200	4.2	2	83	3190	8900	2.8
6	**3**	500	1:1	8.5	75	3.5	115	33	2	88	6670	12000	1.8
7	**3**	500	1:1	8.5	75	24	301	12.5	2	88	12600	20000	1.6
8	**3**	1000	1:1	8.5	75	3.5	117	33	2	85	5170	7400	1.4
9	**3**	1000	1:1	8.5	75	24	276	11.5	2	86	6700	12600	1.9
10	**4**	1000	1:1	8	75	24	173	7.2	2	88	nd	nd	nd
11	$[Cp^*_2Y\{N(SiHMe_2)_2\}]$	1000	1:1	8.5	75	48	163	3.4	2	95	7400	19000	2.6

[a)] Determined by ^1H NMR spectroscopy. [b)] Determined by gel permeation chromatography relative to polystyrene standards.

Experimental Part

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. All solvents were purified by distillation from sodium/triglyme benzophenone ketyl under nitrogen. $(BDI^{Ph})H$ [18] $[Y\{N(SiHMe_2)_2\}_3(THF)_n]$ (n = 1 [14a], n = 2 [19]) and $[Cp^*_2Y\{N(SiHMe_2)_2\}]$ [14c] were prepared according to published procedures. Cyclohexene oxide was dried by distillation from CaH_2. NMR spectra were recorded on a Bruker Avance 400 spectrometer (^1H, 400.1 MHz; ^{13}C, 100.6 MHz) at 25 °C. Chemical shifts were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Mass spectra (EI, 70 eV) were obtained using a Finnigan MAT 8200 instrument. Elemental analyses were performed by the Microanalytical Laboratory of this department. Although metal complexes were combusted with V_2O_5 as burning aid, some analyses gave low carbon content repeatedly, presumably due to carbide formation. Molecular weights of the polycarbonates were determined by GPC (Agilent 1100 Series using RI detector, 3 SDV Linear M 5µ columns with 8 × 50 mm, 8 × 300 mm and 8 × 600 mm dimensions) versus polystyrene standards using THF at 35 °C as eluent.

$[(BDI^{Ph})_2Y\{N(SiHMe_2)_2\}]$ (1)

$[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (670 mg, 1.06 mmol) and $(BDI^{Ph})H$ (533 mg, 2.12 mmol) were dissolved in toluene (10 mL) and the mixture was heated to 70 °C for 4 h. The resulting precipitate was filtered, washed with pentane (3 × 6 mL) and dried *in vacuo* to give 560 mg (73 %) of **1** as a slight yellow microcrystalline powder. Melting point: 262 °C dec. $C_{38}H_{48}N_5Si_2Y$ (719.91): C 63.84 (calc. 63.40); H 6.76 (6.72); N 9.58 (9.73) %.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.07 (pt, 8H, aryl-H), 6.91 (t, $^3J_{H,H}$ = 7.4 Hz, 4H, aryl-H), 6.73 (d, $^3J_{H,H}$ = 8.3 Hz, 6H, aryl-H), 5.07 (sept, $^3J_{H,H}$ = 2.9 Hz, 2H, SiH), 4.94 (s, 2H, β-CH), 1.80 (s, 12H, CH_3), −0.09 (d, $^3J_{H,H}$ = 2.9 Hz, 12H, $SiCH_3$). **$^{13}C\{^1H\}$ NMR** (C_6D_6): δ = 164.6 (CH_3CN), 150.0, 128.9, 125.8, 124.2 (aryl), 97.9 (β-CH), 24.2 (CH_3), 2.8 ($SiCH_3$). **MS** (70 eV): m/z = 719 ($[M]^+$, 46 %), 642 ($[M-Ph]^+$, 15 %), 587 ($[(BDI^{Ph})_2Y]^+$, 100 %), 470 ($[(BDI^{Ph})Y(NSiHMe_2)_2]^+$, 49 %), 337 ($[(BDI^{Ph})Y-H]^+$, 26 %).

$[(BDI^{Ph})_3Y]$ (2)

$(BDI^{Ph})H$ (188 mg, 0.75 mmol) and $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ (157 mg, 0.25 mmol) were dissolved in toluene (2 mL) and the reaction mixture was heated to 100 °C for 24 h. All volatiles were removed *in vacuo* to afford 205 mg (98 %) of **2** as a yellow powder. This material is pure according to NMR spectroscopic analysis. Crystals suitable for X-ray crystallographic analysis were obtained from a concentrated toluene solution at room temperature. Melting point: 353 °C dec. $C_{51}H_{51}N_6Y$ (837.52): C 72.35 % (calc. 73.19); H 5.85 (6.14); N 10.78 (10.04) %.

^{1}H NMR (C_6D_6): δ = 7.39 (br d, 6H, aryl-H), 7.26 (br t, 6H, aryl-H), 7.09 (br t, 6H, aryl-H), 7.01 (br t, 6H, aryl-H), 5.23 (br d, 6H, aryl-H), 4.84 (s, 3H, β-CH), 1.47 (s, 18H, CH_3). **$^{13}C\{^1H\}$ NMR** (C_6D_6): δ = 164.5 (CH_3CN), 150.8 (aryl), 128.6 (aryl, 2C), 127.8, 127.1, 124.0 (aryl), 98.7 (β-CH), 24.9 (CH_3). **MS** (70 eV): m/z = 836 ($[M]^+$, 14 %), 587 ($[(BDI^{Ph})_2Y]^+$, 100 %), 337 ($[(BDI^{Ph})Y-H]^+$, 10 %).

$[(C_5Me_5)Y\{N(SiHMe_2)_2\}_2(THF)]$ (3)

C_5Me_5H (150 mg, 1.10 mmol) and $[Y\{N(SiHMe_2)_2\}_3(THF)]$ (558 mg, 1.00 mmol) were dissolved in toluene (10 mL) in a round bottom Schlenk-flask and the solution was heated with stirring to 160 °C for 1.5 h. All volatiles were removed *in vacuo* and the product was crystallized from a concentrated pentane solution at −78 °C to give 309 mg (55 %) of **3** as colorless crystals. Melting point: 104 °C.

^{1}H NMR (C_6D_6): δ = 4.61 (m, 4H, SiH), 3.65 (br m, 4H, THF), 2.14 (s, 15H, C_5Me_5), 1.32 (br m, 4H, THF), 0.31 (d, $^3J_{H,H}$ = 2.8 Hz, 24H, $SiCH_3$). **$^{13}C\{^1H\}$ NMR** (C_6D_6): δ = 119.2 (C_5Me_5), 71.0 (THF), 25.3 (THF), 11.8 (C_5Me_5), 3.6 ($SiCH_3$). **MS** (70 eV): m/z = 488 ($[M-THF]^+$, 12 %), 355 ($[(C_5Me_5)Y\{N(SiHMe_2)_2\}-H]^+$, 100 %), 132 ($[N(SiHMe_2)_2]^+$, 7 %).

$[(C_5Me_5)(BDI^{Ph})Y\{N(SiHMe_2)_2\}]$ (4)

To a round bottom Schlenk flask were added **3** (280.4 mg, 0.50 mmol), $(BDI^{Ph})H$ (125.2 mg, 0.50 mmol) and toluene (5 mL).

The reaction mixture was stirred at 45 °C for 20 h. All volatiles were removed *in vacuo*. The product was crystallized at −25 °C from pentane to give 224 mg (74 %) of **4** as yellow crystals. Melting point: 120 °C.

$C_{31}H_{46}N_3Si_2Y$ (605.80): C 60.58 (calc. 61.46); H 7.16 (7.65); N 7.46 (6.94) %.

^{1}H NMR (C_6D_6): δ = 7.17 (m, 4H, aryl-H), 7.01 (m, 6H, aryl-H), 4.87 (s, 1H, β-CH), 4.69 (br m, 2H, SiH), 1.85 (s, 15H, C_5Me_5), 1.68 (s, 6H, CH_3, BDI^{Ph}), 0.26 (d, $^3J_{H,H}$ = 2.9 Hz, 12H, $SiCH_3$). **^{13}C{^{1}H} NMR** (C_6D_6): δ = 165.7 ($CH_3\mathit{C}N$), 150.6, 129.1, 125.6, 124.9 (aryl), 118.9 ($\mathit{C_5}Me_5$), 96.4 (β-CH), 24.9 (CH_3, BDI^{Ph}), 11.8 ($C_5\mathit{Me_5}$), 4.0 ($SiCH_3$). **MS** (70 eV): *m/z* = 605 ($[M]^+$, 4 %), 470 ($[M\text{-}C_5Me_5]^+$, 100 %), 337 ($[(BDI^{Ph})Y\text{-}H]^+$, 10 %).

Crystal structure determination of 1-4

Slight yellow crystals of $[(BDI^{Ph})_2Y\{N(SiHMe_2)_2\}]\cdot C_7H_8$ (**1**·C_7H_8), $C_{45}H_{55}N_5Si_2Y$, 811.03 g·mol^{-1}, were obtained from toluene solution at 25 °C. Crystal size 0.15 × 0.15 × 0.10 mm, monoclinic, *P2/c*, a = 12.1244(2) Å, b = 11.3924(3) Å, c = 15.5232(4) Å, β = 96.030(2)°, V = 2132.29(9) Å^3, Z = 2, ρ_{calcd} = 1.263 g cm^{-3}, μ = 1.460 mm^{-1}, F(000) = 854. Data were collected on a Nonius KappaCCD area detector at 173(2) K up to $2\theta_{max}$ = 55.0° (*Mo-Kα* radiation). 9530 reflections were collected, 4897 were unique [R(int) = 0.0327] of which 3848 were observed [$I > 2\sigma(I)$]. R_1 = 0.0407, wR_2 = 0.1070 (obsd. data), goodness-of-fit on F^2 = 1.040; residual electron density (max/min) 0.547/−0.481 e Å^{-3}. Yellow crystals of $[(BDI^{Ph})_3Y]$ (**2**), $C_{51}H_{54}N_6Y$, 839.91 g·mol^{-1}, were obtained from toluene solution at 25 °C. Crystal size 0.10 × 0.10 × 0.10 mm, monoclinic, *P2₁/c*, a = 18.5156(9) Å, b = 10.5296(3) Å, c = 22.8784(11) Å, β = 103.895(2)°, V = 4329.9(3) Å^3, Z = 4, ρ_{calcd} = 1.288 g cm^{-3}, μ = 1.389 mm^{-1}, F(000) = 1764. Data were collected on a Nonius KappaCCD area detector at 173(2) K up to $2\theta_{max}$ = 50.0° (*Mo-Kα* radiation). 13443 reflections were collected, 7630 were unique [R(int) = 0.0674] of which 4301 were observed [$I > 2\sigma(I)$]. R_1 = 0.0505, wR_2 = 0.1421 (obsd. data), goodness-of-fit on F^2 = 0.891; residual electron density (max/min) 0.424/−0.583 e Å^{-3}. Colorless crystals of $[(C_5Me_5)Y\{N(SiHMe_2)_2\}_2(THF)]$ (**3**), $C_{22}H_{51}N_2OSi_4Y$, 560.92 g·mol^{-1}, were obtained from pentane solution at −35 °C. Crystal size 0.20 × 0.20 × 0.20 mm, monoclinic, *P2₁/n*, a = 10.2388(2) Å, b = 21.0111(5) Å, c = 14.4477(3) Å, β = 96.780(2)°, V = 3086.38(11) Å^3, Z = 4, ρ_{calcd} = 1.207 g cm^{-3}, μ = 2.060 mm^{-1}, F(000) = 1200. Data were collected on a Nonius KappaCCD area detector at 173(2) K up to $2\theta_{max}$ = 55.0° (*Mo-Kα* radiation). 12327 reflections were collected, 7055 were unique [R(int) = 0.0255] of which 5479 were observed [$I > 2\sigma(I)$]. R_1 = 0.0395, wR_2 = 0.1055 (obsd. data), goodness-of-fit on F^2 = 1.027; residual electron density (max/min) 0.420/−0.444 e Å^{-3}. Yellow crystals of $[(C_5Me_5)(BDI^{Ph})Y\{N(SiHMe_2)_2\}]\cdot{}^1/_2C_5H_{12}$ (**4**·$^1/_2C_5H_{12}$), $C_{33.5}H_{51.5}N_3Si_2Y$, 641.37 g·mol^{-1}, were obtained from pentane solution at −78 °C. Crystal size 0.25 × 0.15 × 0.15 mm, triclinic, $P\bar{1}$, a = 9.6017(2) Å, b = 10.0017(4) Å, c = 20.4827(4) Å, α = 80.177(1)°, β = 76.882(1)°, γ = 69.695(1)°, V = 1787.54(9) Å^3, Z = 2, ρ_{calcd} = 1.192 g cm^{-3}, μ = 1.723 mm^{-1}, F(000) = 681. Data were collected on a Nonius KappaCCD area detector at 173(2) K up to $2\theta_{max}$ = 55.0° (*Mo-Kα* radiation). 15491 reflections were collected, 8181 were unique [R(int) = 0.0263] of which 6713 were observed [$I > 2\sigma(I)$]. R_1 = 0.0368, wR_2 = 0.0992 (obsd. data), goodness-of-fit on F^2 = 0.950; residual electron density (max/min) 0.566/−0.426 e Å^{-3}. Cell parameters for **1**−**4** were obtained from 10 frames using a 10° scan and refined with 5127 reflections for **1**, 7697 for **2**, 6280 for **3**, and 7889 reflections for **4**. Lorentz, polarization, and empirical absorption corrections were applied [20a,b] The space groups were determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 using SHELXL-97 [20c]. Non-hydrogen atoms in complex **1**−**4** were refined anisotropically. The methyl group of the toluene solvate in **1** was disordered and was refined with two independent positions (occupation ratio 50 : 50 % by symmetry). The pentane solvate in **4** was split over 6 positions and C103 was set manually to 50 % occupation. Hydrogen atoms were fixed in idealized positions using a riding model, except hydrogen atoms attached to silicon in complex **1** and **3**, which were localized and free isotropically refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature [20d].

Crystallographic data for the structures (**1**: CCDC-642078, **2**: CCDC-642080, **3**: CCDC-642081, **4**: CCDC-642079) have been deposited with the Cambridge Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Typical procedure for the copolymerization of cyclohexene oxide and CO_2

The copolymerization reactions were performed in a Buchi tinyclave reactor. Cyclohexene oxide (3.92 g, 40 mmol) and toluene (4 mL) were added to the reactor in the glovebox under an inert atmosphere of argon. The catalyst (20 μmol) was placed on a glass boat in order to prevent premature mixing. Then the reactor was closed and transferred to a Schlenk-line where the atmosphere was exchanged for 8 atm CO_2. After saturation of the solution with CO_2 was complete, the catalyst was dissolved by tilting the reactor. The system was then heated to the desired temperature. The pressure of CO_2 was maintained at 8 atm. After the specified reaction time the heating was discontinued and the reactor was cooled in an ice bath to 5-10 °C, then the pressure was released and the reaction mixture was quenched by addition of CH_2Cl_2 and MeOH. All volatiles were evaporated *in vacuo* at 80 °C to obtain the polymer product as a crispy solid. The carbonate linkage contents were determined from the intensity of the cyclohexyl methyne proton signals (4.6 ppm for carbonate linkages, 3.3 ppm for ether linkages) in the ^{1}H NMR spectrum of the polymer.

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References

[1] a) G. A. Molander, E. D. Dowdy, *Top. Organomet. Chem.* **1999**, *2*, 119; b) G. A. Molander, J. A. C. Romero, *Chem. Rev.* **2002**, *102*, 2161; c) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673; d) K. C. Hultzsch, *Org. Biomol. Chem.* **2005**, *3*, 1819.

[2] a) H. Yasuda, *Top. Organomet. Chem.* **1999**, *2*, 255; b) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1; c) J. Gromada, J.-F. Carpentier, A. Mortreux, *Coord. Chem. Rev.* **2004**, *248*, 397.

[3] a) F. T. Edelmann, *Angew. Chem.* **1995**, *107*, 2647; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2466; b) F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* **2002**, *102*, 1851; c) W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* **2002**, *233−234*, 131; d) K. C. Hultzsch, D. V. Gribkov, F. Hampel, *J. Organomet. Chem.* **2005**, *690*, 4441.

[4] a) W. Leitner, *Angew. Chem.* **1995**, *107*, 2391; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207; b) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259; c) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063; d) W. Leitner, *Coord. Chem. Rev.* **1996**, *155*, 257; e) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27; f) C. Bolm, O. Beckmann, O. A. G. Dabard, *Angew. Chem.* **1999**, *111*, 957; *Angew. Chem. Int. Ed.* **1999**, *38*, 907; g) G. Music, M. Wei, B. Subramaniam, D. H. Busch, *Coord. Chem. Rev.* **2001**, *219−221*, 789; h) H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953.

[5] a) D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155; b) D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps, D. R. Billodeaux, *Acc. Chem. Res.* **2004**, *37*, 836; c) H. Sugimoto, S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561; d) G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784; *Angew. Chem. Int. Ed.* **2004**, *43*, 6618.

[6] a) M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018; b) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738; c) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2599; d) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911.

[7] a) D. J. Darensbourg, J. C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 6335; b) D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers, A. L. Phelps, *Inorg. Chem.* **2004**, *43*, 1831; c) D. J. Darensbourg, R. M. Mackiewicz, D. R. Billodeaux, *Organometallics* **2005**, *24*, 144.

[8] a) D. V. Vitanova, F. Hampel, K. C. Hultzsch, *Dalton Trans.* **2005**, 1565; b) D. V. Vitanova, F. Hampel, K. C. Hultzsch, *J. Organomet. Chem.* **2005**, *690*, 5182.

[9] C. Cui, M. Nishiura, Z. Hou, *Macromolecules* **2005**, *38*, 4089.

[10] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031.

[11] a) D. Drees, J. Magull, *Z. Anorg. Allg. Chem.* **1994**, *620*, 814; b) P. B. Hitchcock, S. A. Holmes, M. F. Lappert, S. Tian, *J. Chem. Soc., Chem. Commun.* **1994**, 2691; c) D. Drees, J. Magull, *Z. Anorg. Allg. Chem.* **1995**, *621*, 948; d) P. B. Hitchcock, M. F. Lappert, S. Tian, *J. Chem. Soc., Dalton Trans.* **1997**, 1945; e) P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood, W. Clegg, *Organometallics* **2001**, *20*, 2533; f) Y. Yao, Y. Zhang, Q. Shen, K. Yu, Organometallics **2002**, *21*, 819; g) D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, H.-G. Schmidt, M. Noltemeyer, *J. Organomet. Chem.* **2002**, *643−644*, 47; h) Y. Yao, M. Xue, Y. Luo, Z. Zhang, R. Jiao, Y. Zhang, Q. Shen, W. Wong, K. Yu, J. Sun, *J. Organomet. Chem.* **2003**, *678*, 108; i) D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, R. Herbst-Irmer, B. Walfort, D. Stalke, *Organometallics* **2003**, *22*, 2279; j) Y. Yao, Y. Zhang, Z. Zhang, Q. Shen, K. Yu, *Organometallics* **2003**, *22*, 2876; k) F. Basuli, J. Tomaszewski, J. C. Huffman, D. J. Mindiola, *Organometallics* **2003**, *22*, 4705; l) Y. Yao, Y.-J. Luo, R. Jiao, Q. Shen, K.-B. Yu, L.-H. Weng, *Polyhedron* **2003**, *22*, 441; m) Z.-Q. Zhang, Y.-M. Yao, Y. Zhang, Q. Shen, W.-T. Wong, *Inorg. Chim. Acta* **2004**, *357*, 3173; n) M. Xue, Y. Yao, Q. Shen, Y. Zhang, *J. Organomet. Chem.* **2005**, *690*, 4685; o) Y. Yao, Z. Zhang, H. Peng, Y. Zhang, Q. Shen, J. Lin, *Inorg. Chem.* **2006**, *45*, 2175.

[12] a) H. W. Görlitzer, M. Spiegler, R. Anwander, *J. Chem. Soc., Dalton Trans.* **1999**, 4287; b) S. Hong, S. Tian, M. V. Metz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 14768.

[13] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228.

[14] a) J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann, R. Anwander, *J. Am. Chem. Soc.* **2000**, *122*, 3080; b) W. Hieringer, J. Eppinger, R. Anwander, W. A. Herrmann, *J. Am. Chem. Soc.* **2000**, *122*, 11983; c) M. G. Klimpel, H. W. Görlitzer, M. Tafipolsky, M. Spiegler, W. Scherer, R. Anwander, *J. Organomet. Chem.* **2002**, *647*, 236.

[15] R. Anwander, M. G. Klimpel, H. M. Dietrich, D. J. Shorokhov, W. Scherer, *Chem. Commun.* **2003**, 1008.

[16] K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845.

[17] D. V. Gribkov, K. C. Hultzsch, F. Hampel, *Chem. Eur. J.* **2003**, *9*, 4796.

[18] H. Bredereck, F. Effenberger, D. Zeyfang, K.-A. Hirsch. *Chem. Ber.* **1968**, *101*, 4036.

[19] a) W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte, R. Anwander, *Organometallics* **1997**, *16*, 682; b) R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck, M. Spiegler, *J. Chem. Soc., Dalton Trans.* **1998**, 847.

[20] a) "Collect" data collection software, Nonius B. V. 1998; b) "Scalepack" data processing software: Z. Otwinowski, W. Minor, *Methods in: Enzymology (Macromolecular Crystallography, Part A)* **1997**, *276*, 307; c) G. M. Sheldrick, *SHELX-97, Program for the refinement of crystal structures*, University of Göttingen, 1997; d) D. T. Cromer, J. T. Waber, in: J. A. Ibers, W. C. Hamilton (Eds.), *International Tables for X-ray Crystallography*, Kynoch, Birmingham, Great Britain, 1974.