

Structure and reactivity of mono- and dinuclear diiminate zinc alkyl complexes

Scott D. Allen, David R. Moore, Emil B. Lobkovsky, Geoffrey W. Coates*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14850-1301, USA

Received 3 May 2003; received in revised form 7 June 2003; accepted 7 June 2003

Abstract

The synthesis, structure and reactivity of several diiminate ligands are presented. The syntheses of five representative β -diiminate (BDI) zinc alkyl complexes and one β -oxo- δ -diiminate (BODDI) zinc alkyl are described. BDI ligands with varying backbone and *N*-aryl substituents display different solid state structures. [(BDI)ZnR] are synthesized by the reaction of (BDI)H with ZnR₂ in quantitative yield. Previously reported (BDI-1)ZnEt is a three-coordinate monomer in the solid state whereas [(BDI-3)ZnEt]_∞ [(BDI-3) = 2-((2,6-diisopropylphenyl)amido)-3-cyano-4-((2,6-diisopropylphenyl)imino-2-pentene)] and [(BDI-4)ZnEt]_∞ [(BDI-4) = 2-((2,6-diethylphenyl)amido)-3-cyano-4-((2,6-diethylphenyl)imino-2-pentene)] form one dimensional coordination polymers. The bimetallic complex [(BODDI-1)(ZnEt)₂] [(BODDI-1) = 2,6-bis((2,6-diisopropylphenyl)amido)-2,5-heptadien-4-one] is prepared through the reaction of (BODDI-1)H₂ with two equivalents ZnEt₂. Both [(BDI)ZnEt] and [(BODDI)ZnEt] complexes react with acetic acid to give the acetate complexes in moderate to high yields, offering a superior synthetic route to these complexes. [(BDI)ZnR] [BDI = (BDI-3) or 1,1,1-trifluoro-2-((2,6-diisopropylphenyl)amido)-4-((2,6-diethylphenyl)imino-2-pentene), (BDI-5)] complexes react with MeOH to produce [(BDI)Zn(μ-OMe)₂Zn(μ-OMe)₂] in moderate yields. The molecular structures of [(BDI-3)ZnEt], [(BDI-4)ZnEt], [(BODDI-1)(ZnEt)₂], [(BODDI-1)Zn₂(μ-OAc)₂], [(BDI-3)Zn(μ-OMe)₂Zn(μ-OMe)₂] and [(BDI-5)Zn(μ-OMe)₂Zn(μ-OMe)₂] have been determined by X-ray diffraction.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Zinc alkyl complexes; Diiminate ligands; Reactivity

1. Introduction

β -Diiminate (BDI) ligands (Scheme 1) continue to gain attention in coordination chemistry [1]. BDI ligands are uninegative, chelating ligands that provide a suitable steric environment to prevent bis-ligation to metals. The appeal for using these ligands stems from the ease of synthesis and the variety of steric and electronic modifications available to the ligand framework. These attributes have facilitated the synthesis of a wide array of main group and transition metal complexes. The synthesis and isolation of complexes containing metals in unusual oxidation states, preparation of structural models for protein active sites, and the development of catalysts for a diverse range of poly-

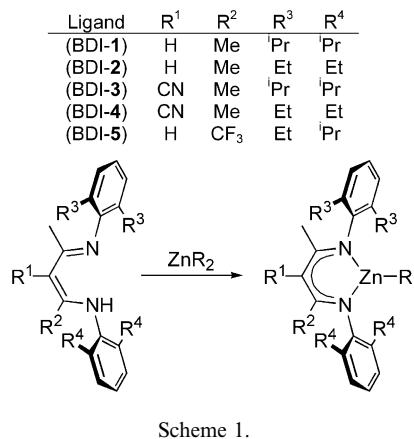
merizations are some of the recent accomplishments using this ubiquitous ligand set [1].

Of particular interest to our group is the polymerization of cyclic esters and the alternating copolymerization of epoxides and carbon dioxide using well-defined, single site catalysts. BDI ligands have been the scaffold for a wide variety of (BDI)MX (M = Zn, Mg, Ca, Sn; X = N(TMS)₂, OMe, O^{*i*}Pr, OAc) complexes and have shown to be efficient initiators for the polymerization of lactide [2–4], β -butyrolactone [5], and the alternating copolymerization of epoxides and CO₂ [6]. Even though Zn alkyls [7] are poor initiators for these polymerizations, they are crucial intermediates in the synthesis of the active initiators. [1]

Our interest in the chemistry of (BDI)ZnR complexes is twofold. First, we look to exploit the Zn–C functionality as a route to new initiating groups in this class of polymerization catalysts. Second, we continue to probe the chemistry of well-defined BDI metal alkyls as

* Corresponding author. Tel.: +1-607-255-5447; fax: +1-607-255-4137.

E-mail address: gc39@cornell.edu (G.W. Coates).



potential catalysts for other polymerizations and organic transformations [6c–f]. We have previously seen dramatic variation in catalytic activity depending on the BDI ligand substituents. Herein we report the synthesis, structure, and reactivity of several representative diiminate zinc alkyl complexes.

2. Results and discussion

2.1. Synthesis and structure

The synthesis and isolation of monomeric, low valent zinc complexes is rare, but the use of bulky chelating ligands such as BDI and tris(pyrazolyl)borate (TPB) [8] has allowed for the study of such complexes. The synthesis of (BDI)ZnR complexes is accomplished through the reaction of (BDI)H with excess ZnR₂ (R = Et, Me). Removal of the volatiles in vacuo yields the (BDI)ZnR complexes (Scheme 1) in quantitative conversions as observed by ¹H-NMR spectroscopy.

We have previously reported the synthesis [6a,c–e] and structure [6c] of monomeric, three-coordinate (BDI)ZnEt compounds [9]. [(BDI-1)ZnEt] [6c] has bond lengths and angles that are similar to related zinc alkyl complexes.

Typically, (BDI)ZnR complexes are oils or waxy solids and highly soluble in common organic solvents. As a result, crystallization is often difficult. (BDI)ZnR complexes modified with CF₃ groups on the backbone (such as (BDI-5) and the related BDI ligands with all ethyl or isopropyl aryl groups) are crystalline, but poor crystal quality and twinning problems preclude data collection. BDI ligands bearing cyano groups on the three-position of the backbone, however, form highly crystalline Zn alkyl complexes. The X-ray crystal structures of [(BDI-3)ZnEt]_∞ and [(BDI-4)ZnEt]_∞ are shown in Figs. 1 and 2, respectively, along with selected bond lengths and angles in Tables 1 and 2. This high crystallinity results from the formation of infinite one-dimensional coordination polymers where the CN group

on the backbone of one complex links to an open zinc coordination site of another complex. Both [(BDI-3)ZnEt]_∞ (crystal containing two molecules of toluene per unit cell) and [(BDI-4)ZnEt]_∞ have different backbone configurations, however, and these are depicted as cartoons in Fig. 3. Although [(BDI-1)ZnEt] possesses a trigonal planar arrangement around the zinc, [(BDI-3)ZnEt]_∞ and [(BDI-4)ZnEt]_∞ attain distorted tetrahedral geometries due to donation from the CN moiety. The CN–Zn bond is 2.15 Å for [(BDI-3)ZnEt]_∞ (average of the three CN–Zn bonds in the unit cell) and 2.11 Å for [(BDI-4)ZnEt]_∞, which are within the expected limits for Zn–N coordination bonds of this type [10].

[(BDI-3)ZnEt]_∞ crystallizes with three (BDI-3)ZnEt molecules and two molecules of toluene in the unit cell. The C(32)–N(3)–Zn(1) angle is essentially linear at 179.1°, which orients the BDI complexes perpendicular to each other along the chain. Additionally, the steric bulk of the aryl isopropyl groups causes each complex along the chain to twist ~90° relative to the subsequent BDI ligand plane (Fig. 1).

[(BDI-4)ZnEt]_∞ crystallizes with only one molecule in the asymmetric unit cell and has similar bond lengths and angles as [(BDI-3)ZnEt]_∞. The major difference is in the CN coordination to Zn which is significantly bent with C(8)–N(3)–Zn(1) = 151.9°, unlike the linear coordination of the CN group of [(BDI-3)ZnEt]_∞. The lower steric bulk of the diethyl aryl groups does not force the molecules along the chain to orient themselves perpendicular to the chain and they remain parallel in a ‘zig-zag’ pattern. The geometry about the Zn atom is a similar distorted tetrahedron as [(BDI-3)ZnEt]_∞.

The crystallographic data are shown in Table 3, and a comparison of these alkyl complexes with [(BDI-1)ZnEt] is shown in Table 4. Even as coordination polymers, the Zn–C and Zn–N bond lengths in [(BDI-3)ZnEt]_∞ and [(BDI-4)ZnEt]_∞ are very similar to [(BDI-1)ZnEt]. The major difference is in the N–Zn–N angle which is more acute in both [(BDI-3)ZnEt]_∞ and [(BDI-4)ZnEt]_∞ by about 6°.

Given the bimetallic nature of epoxide/CO₂ copolymerization using [(BDI)ZnOR]₂ catalysts [6d], we have synthesized a variation of the BDI ligands that can accommodate two Zn centers. These β-oxo-δ-diimine (BODDI; Scheme 2) ligands have been known for quite some time containing both *N*-alkyl [11] and *N*-aryl [12] substituents.

Metal complexes of this class of ligands, however, are limited to macrocyclic ligand dimers [13] where two BODDI molecules are strapped together through the nitrogens by a short alkyl chain. Monomeric, bimetallic complexes of these ligands have yet to be explored. The BODDI ligands were prepared through the reaction of diacetylacetone with the desired aniline as shown in Scheme 2 [14].

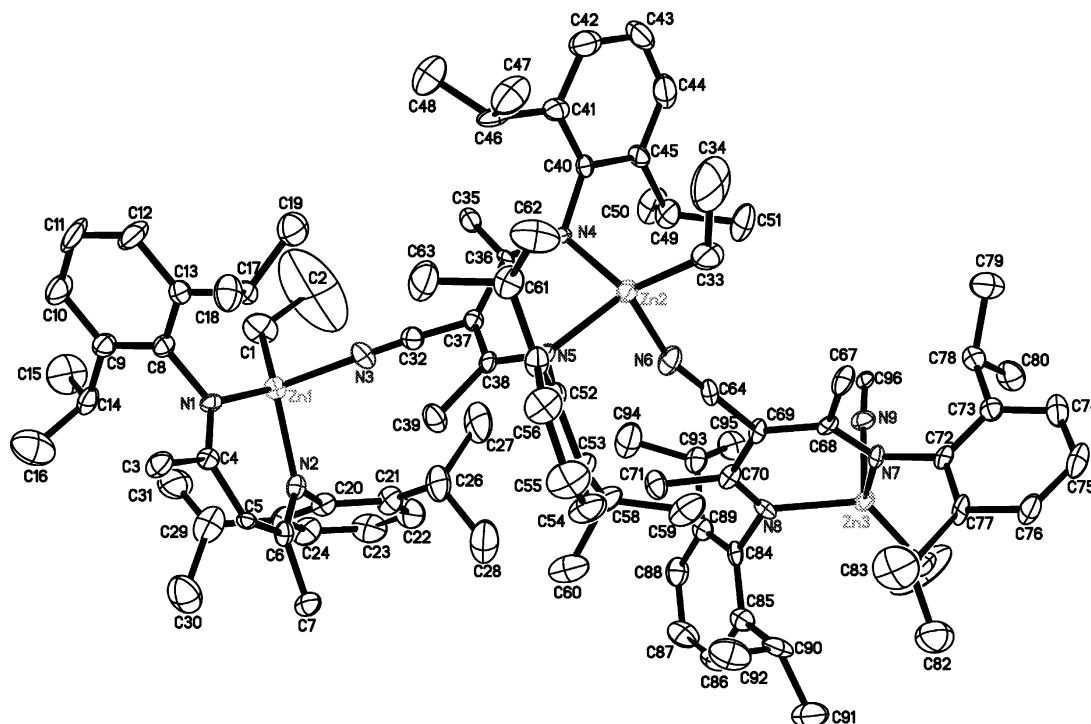


Fig. 1. ORTEP drawing of $[(\text{BDI-3})\text{ZnEt}]_{\infty}$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level. Solvent molecules omitted for clarity.

The reactivity of $(\text{BODDI-1})\text{H}_2$ is similar to the reactivity of BDI ligands, and the ZnEt derivative can be synthesized using the same method. The X-ray structure of $[(\text{BODDI-1})(\text{ZnEt})_2]$ is shown in Fig. 4 with selected bond lengths and angles in Table 5. $[(\text{BODDI-1})(\text{ZnEt})_2]$ crystallizes as a monomer with two similar complexes in the unit cell, and has similar bond lengths as the analogous $[(\text{BDI-1})\text{ZnEt}]$. A comparison between the bond lengths and angles is shown in Table 4. The extended BODDI backbone is planar as in the BDI complexes. To alleviate the steric repulsions of the neighboring ZnEt groups, each Zn atom sits on opposite sides of the plane of the BODDI ligand. Zn(1) sits 0.62 \AA above the plane described by N(1), C(3), and O(1) while Zn(2) sits 0.50 \AA below the plane described

by N(2), C(5) and O(1). This is also made evident by the dihedral angles of C(3)–C(4)–O(1)–Zn(1) and C(5)–C(4)–O(1)–Zn(2) which are 24.19 and 23.68° , respectively. Both Zn atoms adopt a trigonal planar geometry. The atoms C(8), N(1), O(1) and Zn(1) and C(10), N(2), O(1) and Zn(2) are highly coplanar with the Zn atoms sitting only 0.04 \AA above their respective planes.

2.2. Reactivity

We have taken advantage of the reactivity of the ethyl groups of $[(\text{BDI})\text{ZnEt}]$ complexes towards alcohols and carboxylic acids as a synthetic route to the corresponding alkoxides and carboxylates (Scheme 3) [6a,c–e]. BDI ligands 1–5 undergo clean reactions and high conver-

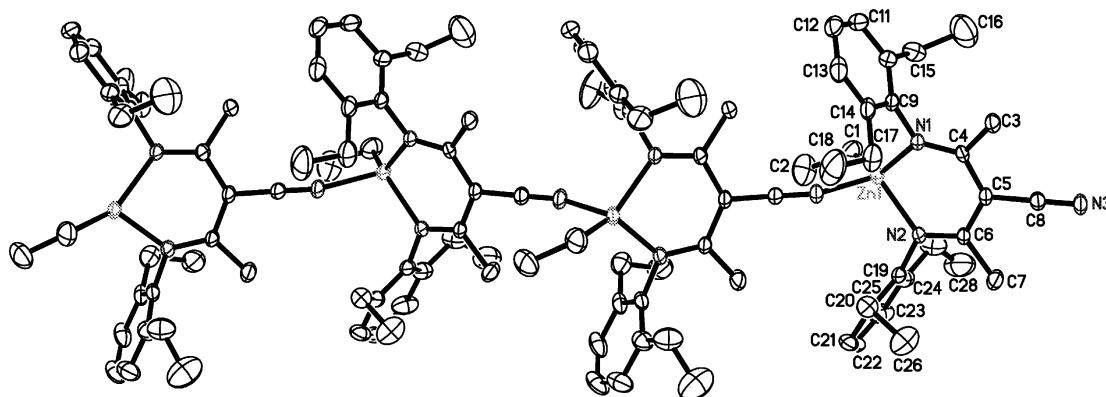


Fig. 2. ORTEP drawing of $[(\text{BDI-4})\text{ZnEt}]_{\infty}$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level.

Table 1
Selected bond lengths (Å) and bond angles (°) of [(BDI-3)ZnEt]_∞

<i>Bond lengths</i>			
Zn(1)–C(1)	1.962(6)	Zn(2)–N(6)	2.160(5)
Zn(1)–N(1)	2.044(5)	N(4)–C(36)	1.301(7)
Zn(1)–N(2)	2.051(5)	N(5)–C(38)	1.311(7)
Zn(1)–N(3)	2.136(5)	Zn(3)–C(65)	1.970(6)
N(1)–C(4)	1.288(7)	Zn(3)–N(7)	2.045(5)
N(2)–C(6)	1.310(7)	Zn(3)–N(8)	2.056(5)
Zn(2)–C(33)	1.956(7)	Zn(3)–N(9)	2.154(5)
Zn(2)–N(4)	2.033(4)	N(7)–C(68)	1.302(7)
Zn(2)–N(5)	2.038(5)	N(8)–C(70)	1.307(7)
<i>Bond angles</i>			
C(2)–C(1)–Zn(1)	114.7(7)	C(40)–N(4)–Zn(2)	115.1(3)
N(1)–Zn(1)–N(2)	91.85(19)	C(52)–N(5)–Zn(2)	116.9(4)
C(32)–N(3)–Zn(1)	179.0(5)	C(66)–C(65)–Zn(3)	117.2(5)
C(8)–N(1)–Zn(1)	113.7(4)	N(7)–Zn(3)–N(8)	91.87(18)
C(20)–N(2)–Zn(1)	114.1(4)	C(96)–N(9)–Zn(3)	176.4(5)
C(34)–C(33)–Zn(2)	121.6(6)	C(72)–N(7)–Zn(3)	117.6(3)
N(4)–Zn(2)–N(5)	91.49(18)	C(84)–N(8)–Zn(3)	114.9(3)

Table 2
Selected bond lengths (Å) and bond angles (°) of [(BDI-4)ZnEt]_∞

<i>Bond lengths</i>			
Zn(1)–C(1)	1.995(5)	N(2)–C(6)	1.305(4)
Zn(1)–N(1)	2.042(2)	C(5)–C(8)	1.418(4)
Zn(1)–N(2)	2.042(3)	N(3)–C(8)	1.146(4)
Zn(1)–N(3A)	2.114(3)	C(4)–C(5)	1.436(4)
N(1)–C(4)	1.308(4)	C(5)–C(6)	1.437(4)
<i>Bond angles</i>			
C(1)–Zn(1)–N(1)	129.97(15)	C(19)–N(2)–Zn(1)	113.99(18)
C(1)–Zn(1)–N(2)	124.26(17)	N(1)–Zn(1)–N(2)	91.22(10)
C(1)–Zn(1)–N(3A)	105.35(17)	N(3)–C(8)–C(5)	177.7(4)
C(9)–N(1)–Zn(1)	113.36(18)		

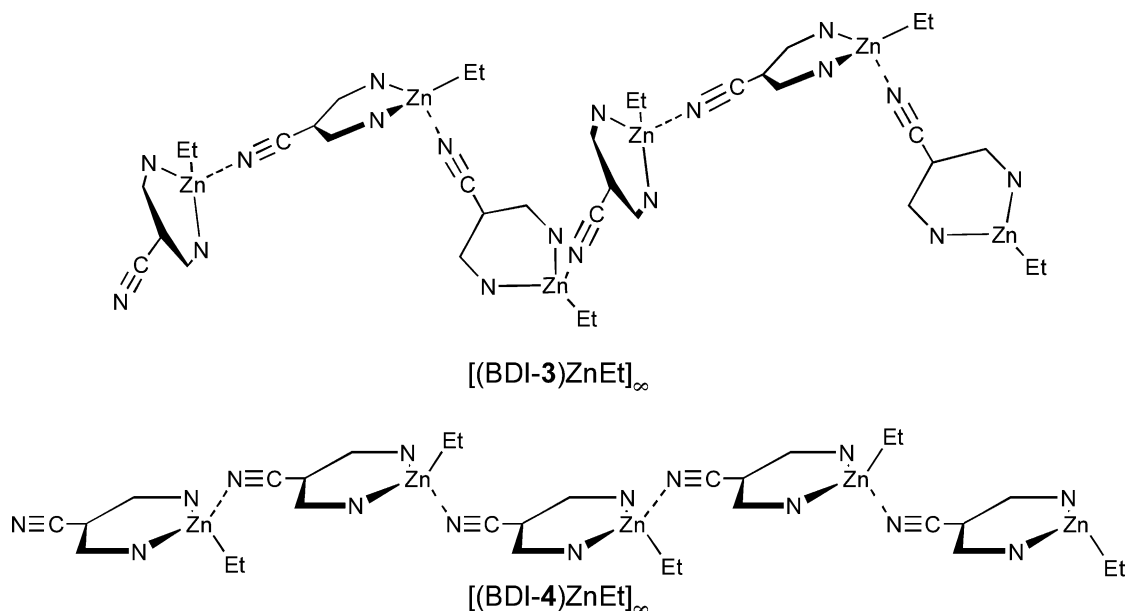


Fig. 3. Depictions of the backbone orientations in [(BDI-3)ZnEt]_∞ and [(BDI-4)ZnEt]_∞.

sions (50–87%) to the corresponding acetates when reacted with acetic acid. Even the highly organized coordination polymers of [(BDI-3)ZnEt]_∞ and [(BDI-4)ZnEt]_∞ do not hinder the reaction with acetic acid and form the corresponding acetate complexes in moderate to high yields. These complexes crystallize as acetate-bridged dimers, as shown in Scheme 3, and are mixtures of monomers and dimers in solution, the ratio of which depends on the ligand, solvent, concentration, and temperature [6a,c,e,f]. Synthetically, this method is superior to the previously used method of reacting (BDI)Li with Zn(OAc)₂ [6c].

[(BODDI-1)(ZnEt)₂] reacts similarly with acetic acid to yield the expected acetate complex [(BODDI-1)Zn₂(μ-OAc)₂] (Scheme 2). An X-ray crystal structure of this complex is shown in Fig. 5 and selected bond lengths and angles are shown in Table 6. [(BODDI-1)Zn₂(μ-OAc)₂] exists as a μ,η²-diacetate complex in the solid state. The Zn atoms in this complex are highly coplanar with the ligand framework unlike [(BODDI-1)(ZnEt)₂], where the Zn atoms are on opposite sides of the ligand plane. Both Zn atoms only sit 0.007 Å above the ligand plane with dihedral angles of 1.661° for Zn(1)–O(3)–C(3)–C(4) and 1.737° for Zn(1A)–O(3)–C(3)–C(4A).

The reactivity of (BDI)ZnR complexes with aliphatic alcohols, however, is less predictable. Formation of [(BDI)Zn(μ-OMe)]₂ is observed when the ZnEt complexes of BDI ligands 1, 2 [6c] and 4 [6d] are reacted with MeOH. On the other hand, reaction of MeOH with either [(BDI-3)ZnEt]_∞ or [(BDI-5)ZnEt] leads to [(BDI)Zn(μ-OMe)]₂Zn(μ-OMe)₂ (Scheme 3). [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂ and [(BDI-5)Zn(μ-OMe)]₂Zn(μ-OMe)₂ are isolated in moderate crystallized yields of 34–57%, indicating they are not minor by-

Table 3
Crystal data and structure refinements for all structures

	[(BDI-3)ZnEt] _∞	[(BDI-4)ZnEt] _∞	[(BODDI-1)(ZnEt) ₂]	[(BODDI-1)Zn ₂ (μ-OAc) ₂]	[(BDI-3)Zn(μ-OMe)] ₂ Zn(μ-OMe) ₂
Molecular formula	C ₉₆ H ₁₃₄ N ₉ Zn ₃ ·2C ₇ H ₈	C ₂₈ H ₃₇ N ₃ Zn	C ₇₀ H ₁₀₄ N ₄ O ₂ Zn ₄	C ₃₅ H ₄₈ N ₂ O ₅ Zn ₂	C ₁₂₈ H ₁₈₄ N ₁₂ O ₈ Zn ₆ ·C ₆ H ₁₄
Formula weight	1794.51	480.98	1295.05	707.49	2497.26
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions					
<i>a</i> (Å)	14.739(4)	12.0199(15)	15.3677(12)	16.263(2)	12.3899(3)
<i>b</i> (Å)	37.863(9)	16.111(2)	13.8273(11)	13.6025(19)	23.8946(5)
<i>c</i> (Å)	19.329(5)	14.3174(17)	32.591(3)	17.052(3)	24.7560(6)
α (°)	90	90	90	90	71.025(1)
β (°)	102.324(4)	108.943(3)	99.8150(10)	108.257(7)	78.747(1)
γ (°)	90	90	90	90	82.885(2)
<i>V</i> (Å ³)	10539(4)	2622.4(6)	6824.0(9)	3582.3(10)	6783.1(3)
<i>Z</i>	4	4	4	4	2
ρ_{calc} (Mg m ⁻³)	1.131	1.218	1.261	1.312	1.223
μ (Mo K α) (mm ⁻¹)	0.726	0.955	1.433	1.379	1.100
<i>F</i> (000)	3852	1024	2752	1488	2660
Crystal size (mm ³)	0.50 × 0.10 × 0.10	0.40 × 0.30 × 0.20	0.60 × 0.20 × 0.10	0.40 × 0.20 × 0.10	0.20 × 0.10 × 0.05
θ Range (°)	1.08–20.82	2.19–28.28	1.27–26.41	2.52–26.37	0.90–23.82
Index ranges	–14 ≤ <i>h</i> ≤ 14, –37 ≤ <i>k</i> ≤ 7, –19 ≤ <i>l</i> ≤ 19	–16 ≤ <i>h</i> ≤ 15, –18 ≤ <i>k</i> ≤ 21, –17 ≤ <i>l</i> ≤ 19	–17 ≤ <i>h</i> ≤ 19, –8 ≤ <i>k</i> ≤ 17, –40 ≤ <i>l</i> ≤ 40	–15 ≤ <i>h</i> ≤ 19, –16 ≤ <i>k</i> ≤ 16, –21 ≤ <i>l</i> ≤ 9	–14 ≤ <i>h</i> ≤ 14, –26 ≤ <i>k</i> ≤ 26, –28 ≤ <i>l</i> ≤ 28
Data collected	47471	18111	39410	9384	44587
Unique data	11037	6510	13919	3300	18608
<i>R</i> _{int}	0.0781	0.0408	0.0722	0.0593	0.0557
Goodness-of-fit	1.283	1.086	0.918	1.047	1.021
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0917, <i>wR</i> ₂ = 0.1517	<i>R</i> ₁ = 0.0510, <i>wR</i> ₂ = 0.1228	<i>R</i> ₁ = 0.0501, <i>wR</i> ₂ = 0.1076	<i>R</i> ₁ = 0.0520, <i>wR</i> ₂ = 0.1119	<i>R</i> ₁ = 0.0566, <i>wR</i> ₂ = 0.1151
<i>R</i> indices (all data) [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.1133, <i>wR</i> ₂ = 0.1590	<i>R</i> ₁ = 0.0830, <i>wR</i> ₂ = 0.1351	<i>R</i> ₁ = 0.1178, <i>wR</i> ₂ = 0.1281	<i>R</i> ₁ = 0.0739, <i>wR</i> ₂ = 0.1198	<i>R</i> ₁ = 0.0995, <i>wR</i> ₂ = 0.1304
$\rho_{\text{min}}-\rho_{\text{max}}$ (e Å ⁻³)	0.444 and –0.388	0.893 and –0.778	0.827 and –0.637	1.014 and –0.677	0.585 and –0.378

products. An X-ray crystal structure of [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂ is shown in Fig. 6 with selected bond lengths and angles in Table 7.

These complexes consist of two [(BDI)Zn(μ-OMe)] molecules bridged by a Zn(μOMe)₂. All Zn atoms are distorted tetrahedra and the BDI ligands are arranged so that they are nearly perpendicular to each other. X-ray analysis reveals [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂ (Fig. 6) and [(BDI-5)Zn(μ-OMe)]₂Zn(μ-OMe)₂ are isostructural with only slight variations in bond lengths and angles. In [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂,

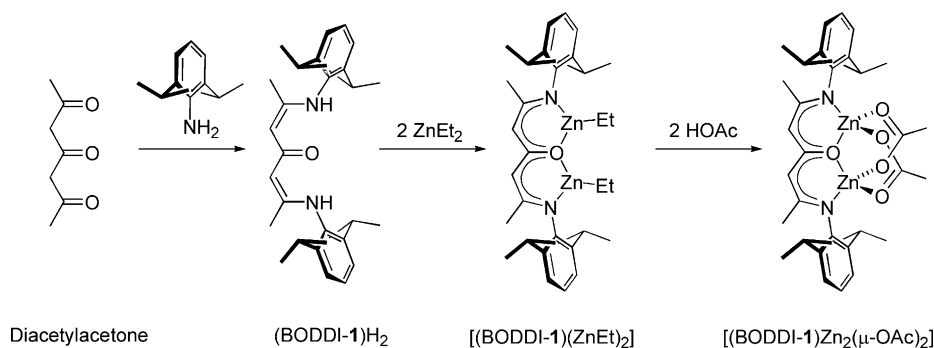
there are two similar complexes in the unit cell as well as a disordered molecule of hexane. The two Zn–O–Zn–O moieties are nearly planar with a sum of the internal angles equal to 359.3°. The planes intersect at 68.5 and 72.4° through the center Zn atom for [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂ and [(BDI-5)Zn(μ-OMe)]₂Zn(μ-OMe)₂, respectively. The distal Zn atoms are distorted tetrahedra with compressed O–Zn–O and N–Zn–N bond angles of 83 and 97° for [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂ and 82 and 98° for [(BDI-5)Zn(μ-OMe)]₂Zn(μ-OMe)₂. The internal Zn atom is also a

Table 4
Comparison of zinc alkyl complexes

	[(BDI-1)ZnEt]	[(BDI-3)ZnEt] _∞ ^a	[(BDI-4)ZnEt] _∞	[(BODDI-1)(ZnEt) ₂]
<i>d</i> (Zn–C)	1.963(5)	1.963(3)	1.995(5)	1.956(5)/1.950(5)
<i>d</i> (Zn–N1)	1.979(3)	2.041(1)	2.042(2)	1.922(3)
<i>d</i> (Zn–N2)	1.943(3)	2.048(8)	2.042(3)	1.926(3)
N–Zn–N	97.07(12)	91.73(9)	91.22(10)	92.92(13)/94.03(13) ^b

^a Bond lengths and angles are averages over the three molecules in the unit.

^b N–Zn–O angles.



Scheme 2.

Table 5
Selected bond lengths (Å) and bond angles (°) of [(BODDI-1)(ZnEt)₂]

Bond lengths			
Zn(1)–N(1)	1.922(3)	Zn(2)–O(1)	2.004(3)
Zn(1)–C(8)	1.956(5)	O(1)–C(4)	1.334(5)
Zn(1)–O(1)	2.007(3)	N(1)–C(2)	1.344(5)
Zn(2)–N(2)	1.926(3)	N(2)–C(6)	1.332(5)
Zn(2)–C(10)	1.950(5)	Zn(1)–Zn(2)	3.4026(8)
Bond angles			
N(1)–Zn(1)–O(1)	92.92(13)	C(12)–N(1)–Zn(1)	116.5(3)
N(2)–Zn(2)–O(1)	94.03(13)	C(24)–N(2)–Zn(2)	116.3(3)
Zn(2)–O(1)–Zn(1)	115.94(14)		
Dihedral angles			
C(3)–C(4)–O(1)–Zn(1)	24.3(5)	C(5)–C(4)–O(1)–Zn(2)	23.4(5)

distorted tetrahedron with bond angles of 83.0, 83.4, 130.3 and 140.4° for $[\{(BDI-3)Zn(\mu-OMe)\}_2Zn(\mu-OMe)_2]$, and 82.5, 82.5, 124.4 and 132.7° for $[\{(BDI-5)Zn(\mu-OMe)\}_2Zn(\mu-OMe)_2]$. These complexes are thermally stable in solution for days at elevated temperatures. Heating a toluene solution of $[\{(BDI-5)Zn(\mu-OMe)\}_2Zn(\mu-OMe)_2]$ for five days at 110 °C does not liberate free $[Zn(OMe)_2]_{\infty}$.

Due to the unpredictable reactions of alcohols with (BDI)ZnR, facile and predictable routes to (BDI)ZnOR complexes continue to be a goal. One route envisioned was the reaction of an aldehyde or ketone with (BDI)ZnR to give the corresponding alkoxide via Scheme 4. The addition of alkyl Zn groups from ZnR_2 across aldehydes and ketones is well-documented [15], but neither (BDI-1)ZnR nor (BDI-2)ZnR (R = Me, Et) react with benzaldehyde to give the corresponding alkoxide.

When reacted for extended amounts of time (about 24 h) at room temperature, or at higher temperatures (≥ 50 °C), benzaldehyde undergoes a Tishchenko type disproportionation in the presence of [(BDI)ZnR] to yield benzyl benzoate (Scheme 4) [16]. ¹H-NMR spectroscopy shows no change of the (BDI)ZnEt complex, but the reaction goes to completion (even at ratios of benzaldehyde:Zn of 100:1). These reactions are generally initiated with metal alkoxides and it is our belief that protic impurity or aldehyde insertion product is generating a small amount of zinc alkoxide which may be initiating the reaction. This reaction does not occur spontaneously in the absence of the Zn complex and it occurs with other aldehydes. For example, the regioir-

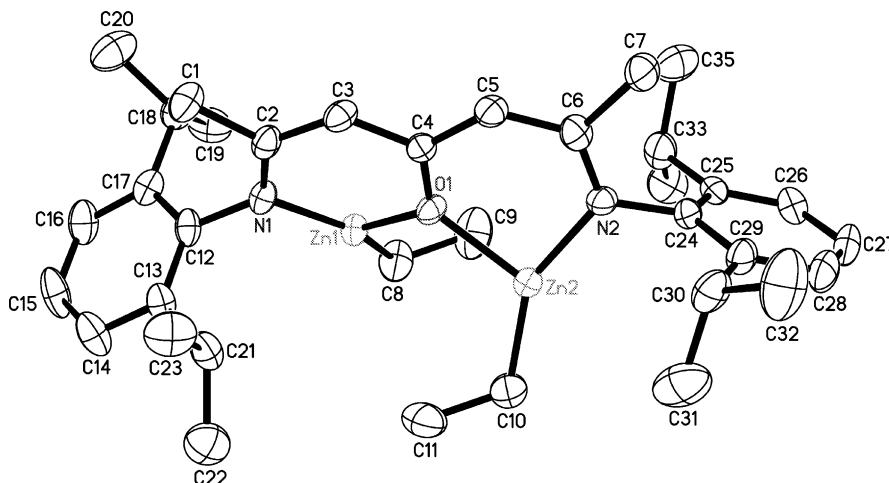
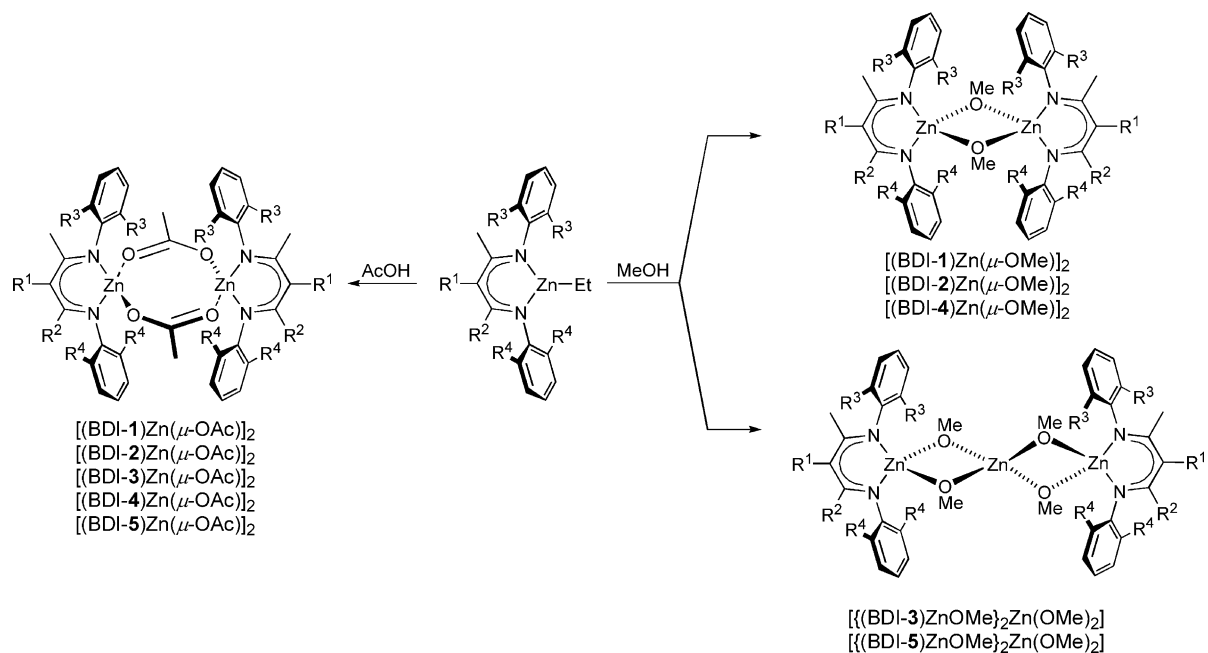


Fig. 4. ORTEP drawing of [(BODDI-1)(ZnEt)₂] (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level.



Scheme 3.

regular polyester can be synthesized from benzene-1,4-dicarboxaldehyde (Scheme 4) [17].

2.3. Summary

In summary, we have reported the synthesis and structure of several new BDI and BODDI zinc alkyl complexes. BDI Zn alkyl complexes with cyano groups on the backbone do not form the expected monomeric species, but form coordination polymers in the solid state. $[(\text{BDI})\text{ZnEt}]$ and $[(\text{BODDI})(\text{ZnEt})_2]$ complexes

react with acetic acid to give the corresponding acetate complexes in moderate to high yields. This synthetic method is superior to previous routes using $(\text{BDI})\text{Li}$ and $\text{Zn}(\text{OAc})_2$. The reaction of MeOH with $[(\text{BDI})\text{ZnR}]$ complexes is unpredictable and the expected $[(\text{BDI})\text{Zn}(\mu\text{-OMe})_2]$ complex is only achieved with some ligand sets, whereas with $(\text{BDI-3})\text{H}$ and $(\text{BDI-5})\text{H}$, $[\{(\text{BDI})\text{Zn}(\mu\text{-OMe})\}_2\text{Zn}(\mu\text{-OMe})_2]$ is formed in moderate yields. New routes to BDI zinc complexes with carboxylate and alkoxide initiators continue to be a goal and further optimization of the synthetic routes to

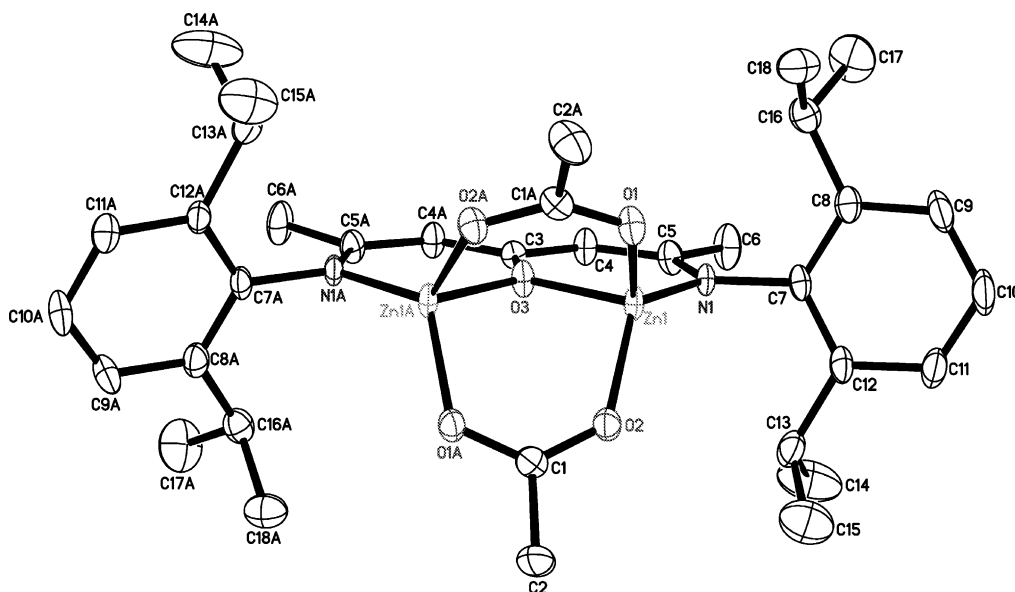


Fig. 5. ORTEP drawing of $[(\text{BODDI-1})\text{Zn}_2(\mu\text{-OAc})_2]$ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level.

Table 6
Selected bond lengths (Å) and bond angles (°) of [(BODDI-1)Zn₂(μ-OAc)₂]

Bond lengths			
Zn(1)–O(1)	1.947(2)	Zn(1)–N(1)	1.927(2)
Zn(1)–O(2)	1.970(2)	N(1)–C(7)	1.448(4)
Zn(1)–O(3)	1.9387(16)	N(1)–C(5)	1.334(4)
Zn(1A)–O(3)	1.9387(16)	O(3)–C(3)	1.322(4)
Zn(1)–Zn(1A)	3.0450(8)	O(1)–C(1A)	1.265(4)
Bond angles			
N(1)–Zn(1)–O(3)	95.55(9)	O(3)–Zn(1)–O(1)	105.14(7)
O(1A)–C(1)–O(2)	125.7(3)	O(3)–Zn(1)–O(2)	100.77(7)
Zn(1)–O(3)–Zn(1A)	103.50(11)	C(5)–N(1)–Zn(1)	121.9(2)
Dihedral angles			
Zn(1)–O(3)–C(3)–C(4)	1.67(15)	Zn(1A)–O(3)–C(3)–C(4A)	1.74(16)

these complexes is underway. Additionally, the catalytic activity of the new class of [(BODDI)Zn₂(μ-OAc)₂] complexes is currently being investigated.

3. Experimental

3.1. General considerations

All manipulations of air- and/or water-sensitive compounds were carried out under dry N₂ using a Braun Labmaster drybox or standard Schlenk line

Table 7
Selected bond lengths (Å) and bond angles (°) of [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂

Bond lengths			
Zn(1)–O(1)	1.963(3)	N(1)–C(29)	1.319(6)
Zn(1)–O(2)	1.916(3)	N(3)–C(33)	1.147(7)
Zn(2)–O(2)	1.968(3)	C(29)–C(30)	1.433(7)
Zn(1)–N(1)	1.959(4)	Zn(1)–Zn(2)	2.8944(9)
Zn(1)–N(2)	1.985(4)		
Bond angles			
O(2)–Zn(1)–O(1)	83.74(14)	Zn(2)–O(1)–Zn(1)	95.85(14)
N(1)–Zn(1)–N(2)	96.63(18)	Zn(1)–O(2)–Zn(2)	96.36(14)
O(1)–Zn(2)–O(2)	83.06(14)	C(5)–N(1)–Zn(1)	118.7(3)
Zn(1)–Zn(2)–Zn(3)	164.01(3)	C(17)–N(2)–Zn(1)	118.0(3)

techniques. ¹H-NMR and ¹³C-NMR spectra were recorded on Varian Inova 400 and Bruker AF 300 spectrometers and referenced versus residual non-deuterated solvent shifts. In some cases, ¹³C-NMR spectra were not obtained due to low solubility.

3.2. Materials

Solvents were purified over solvent columns. All reagents were purchased from Aldrich and used without further purification unless otherwise noted.

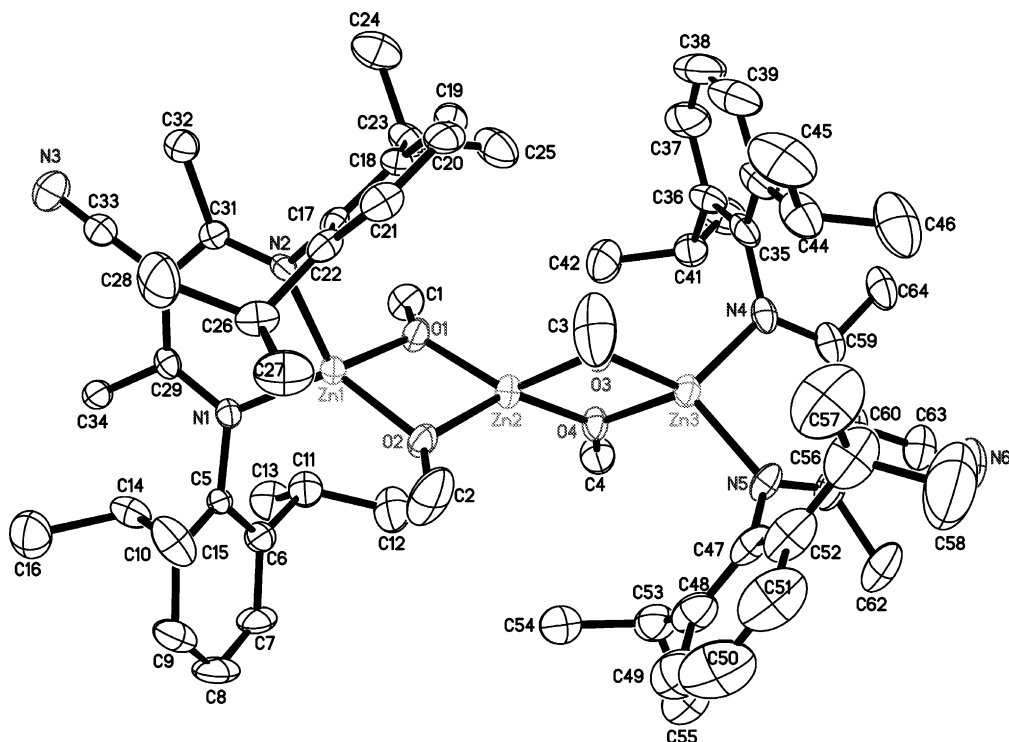
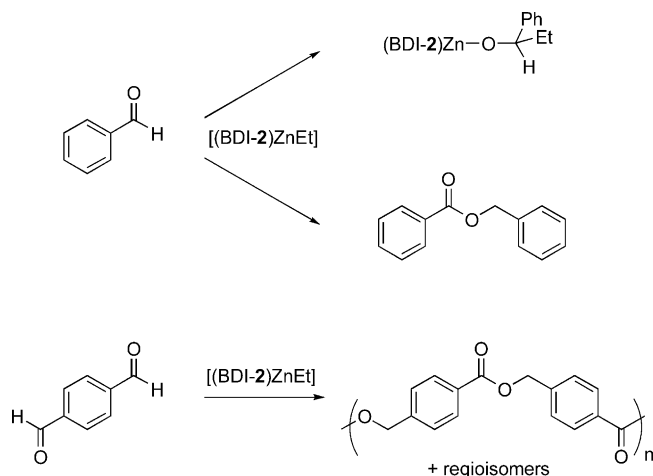


Fig. 6. ORTEP drawing of [(BDI-3)Zn(μ-OMe)]₂Zn(μ-OMe)₂ (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level.



Scheme 4.

3.3. Ligand synthesis

BDI ligands **1** and **2** [6c] were prepared as previously reported. BDI ligands **3** and **4** were prepared using a modified procedure reported by Corey and Wang [18].

3.3.1. (BDI-3)H

ⁿBuLi (1.6 M in hexane, 1.0 ml, 1.6 mmol) was added dropwise to a solution of (BDI-1)H (0.60 g, 1.43 mmol) in THF (30 ml) at -78°C . After stirring at -78°C for 5 min, the solution was warmed to room temperature (r.t.) and stirred for 1 h. The solution was cooled back down to -78°C and a solution of *p*-toluenesulfonyl cyanide (0.28 g, 1.5 mmol) in THF (10 ml) was added dropwise. The solution was warmed to r.t. and stirred for 10 h. The volatiles were removed in vacuo and the light yellow residue was dissolved in CH_2Cl_2 (50 ml), washed with brine, dried over Na_2SO_4 , filtered, and the solvent was removed in vacuo to leave a light yellow solid. The crude material was crystallized from EtOH at -20°C (0.48 g, 76%). $^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ 14.14 (1H, s, NH) 7.07 (6H, m, ArH), 2.93 (4H, m, $J = 6.5$ Hz, CHMe_2), 1.98 (6H, s, $\alpha\text{-CH}_3$), 1.02 (12H, d, $J = 6.5$ Hz, $\text{CHMeMe} + \text{CHMeMe}$). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 75 MHz): δ 167.4 (iminate C–N), 142.2, 139.0, 126.8, 123.9, 121.5 (aromatic C + CN), 81.4 ($\beta\text{-CH}$), 28.7, 24.2, 23.3, 19.8 ($\alpha\text{-Me} + ^i\text{Pr}$).

3.3.2. (BDI-4)H

$^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ 14.0 (1H, s, NH), 6.94 (6H, m, ArH), 2.27 (8H, m, $J = 7.5$ Hz, CH_2CH_3), 1.89 (6H, s, $\alpha\text{-CH}_3$), 0.98 (12H, t, $J = 7.5$ Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 75 MHz): δ 166.9 (iminate C–N), 140.6, 126.6, 126.2, 121.5 (aromatic C), 81.0 ($\beta\text{-CH}$), 24.8, 19.3, 14.5 ($\alpha\text{-Me} + \text{Et}$).

3.3.3. *N*-(2,6-diethyl)phenyl-acetimine

2,6-Diethylaniline (20.0 g, 134 mmol), 2,2-dimethoxypropane (19.1 g, 183 mmol) and activated 4 Å molecular sieves (12.5 g) were added to 20 ml dry toluene. The mixture was heated for 2 days at 100°C then the sieves were filtered off and the volatiles were removed in vacuo to leave a light yellow oil. The product was isolated by vacuum distillation as a colorless oil (23.4 g, 92%). $^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ 7.00 (3H, m, Ar–H), 2.36 (4H, m, CH_2CH_3), 2.29 (3H, s, CH_3), 1.65 (3H, s, CH_3), 1.15 (3H, s, CH_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 75 MHz): δ 168.6 (C=N), 147.9, 132.1, 126.0, 123.2 (aromatic C), 27.9, 24.6, 21.4, 14.1 (Et + Me).

3.3.4. *N*-(2,6-diisopropyl)phenyl-trifluoromethylacetimidoyl chloride

The preparation for this compound was accomplished using a literature procedure in 80% isolated yield. [19] $^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ 7.21 (3H, s, Ar–H), 2.69 (2H, m, $J = 6.9$ Hz, CHMe_2), 1.21 (12H, m, $\text{CHMeMe} + \text{CHMeMe}$). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 75 MHz): δ 141.2, 136.5, 127.2, 124.2 (aromatic C), 134.6 (q, $^2J_{\text{CF}} = 43$ Hz, C = O), 121.0 (q, $^1J_{\text{CF}} = 264$ Hz, CF_3) 29.4, 23.3 (^iPr).

3.3.5. (BDI-5)H

This compound was prepared using a modified procedure reported by Andersson and co-workers [20]. ⁿBuLi (1.6 M in hexane, 27.7 ml, 44.3 mmol) was added to a solution of diisopropyl amine (4.48 g, 44.3 mmol) in THF (200 ml) at -78°C . The solution was stirred for 30 min and *N*-(2,6-diethyl)phenyl-acetimine (4.0 g, 21.1 mmol) was added in one portion. The solution was stirred for 30 min at -78°C , then warmed to 0°C and stirred for an additional 2 h. *N*-(2,6-diisopropyl)phenyl-trifluoromethylacetimidoyl chloride (6.48 g, 22.2 mmol) was added in one portion and stirred for 45 min at 0°C . The reaction was quenched with saturated NH_4Cl solution (100 ml) and EtOAc (200 ml) and water (100 ml) were added. The organic phase was separated, washed with 1×100 ml NH_4Cl , $1 \times$ brine, dried over Na_2SO_4 , filtered, and the solvent was removed in vacuo to leave a yellow oil. The product was crystallized from EtOH at r.t. to yield yellow needles (6.16 g, 66%). $^1\text{H-NMR}$ (C_6D_6 , 300 MHz): δ 12.18 (1H, s, NH), 7.05 (6H, m, ArH), 5.36 (1H, s, $\beta\text{-CH}$), 3.24 (2H, m, $J = 6.6$ Hz, CHMe_2), 2.42 (4H, m, $J = 7.5$ Hz, CH_2CH_3), 1.41 (3H, s, $\alpha\text{-CH}_3$), 1.29 (6H, d, $J = 6.3$ Hz, CHMeMe), 1.06 (12H, m, $\text{CHMeMe} + \text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6 , 75 MHz): δ 163.6, 149.4 (q, $^2J_{\text{CF}} = 27.3$, iminate C–N) 141.6, 140.3, 138.2, 126.6, 126.4, 125.9, 123.4 (aromatic C) 120.5 (q, $^1J_{\text{CF}} = 284$ Hz, CF_3), 90.4 ($\beta\text{-CH}$), 28.8, 25.1, 24.7, 22.8, 20.5, 14.5 ($\alpha\text{-Me} + \text{Et} + ^i\text{Pr}$).

3.3.6. (BODDI-1)H₂

The preparation of this compound was accomplished using a modified literature procedure [14]. Diacetylacetone [21] (2.32 g, 16.3 mmol) and 2,6-diisopropylaniline (6.36 g, 35.8 mmol) were combined and heated until the neat solution was homogeneous, then stirred overnight at r.t. The light brown solution was dissolved in CH₂Cl₂ and dried with Na₂SO₄, filtered, and the volatiles were removed in vacuo. The product was crystallized from EtOH at –20 °C (5.26 g, 70%). ¹H-NMR (C₆D₆, 300 MHz): δ 12.32 (2H, b, NH), 7.04 (6H, m, ArH), 5.24 (2H, s, β-CH), 3.30 (4H, m, *J* = 6.5 Hz, CHMe₂), 1.49 (6H, s, α-Me), 1.10 (12H, d, *J* = 6.5 Hz, CHMeMe), 1.08 (12H, d, *J* = 6.4 Hz, CHMeMe). ¹³C{¹H}-NMR (C₆D₆, 75 MHz) δ 191.4, 159.0 (C–N + C=O), 147.2, 135.3, 128.1, 123.6 (aromatic C), 96.9 (β-CH), 28.8, 24.8, 22.7, 19.4 (α-Me + ^{*i*}Pr).

3.4. Complex synthesis

3.4.1. Synthesis of [(BDI)ZnR]

[(BDI-1)ZnMe], [(BDI-1)ZnEt] and [(BDI-2)ZnEt] were prepared via literature procedures [6c] and correlated with known ¹H-NMR [6c,9c]. General procedure for (BDI)ZnR: (BDI-2)H (1.0 g, 2.8 mmol) was dissolved in 20 ml toluene in a Schlenk tube in a drybox. ZnMe₂ (2.1 ml of a 2.0 M solution in toluene, 4.14 mmol) was added and the mixture was heated to 75 °C for 18 h. After cooling to room temperature the volatiles were removed in vacuo resulting in quantitative conversion to [(BDI)ZnR]. These complexes were used without further purification unless otherwise noted.

3.4.2. [(BDI-2)ZnMe]

Light yellow waxy solid. ¹H-NMR (C₆D₆, 300 MHz): δ 7.03 (6H, b, ArH), 4.93 (1H, s, β-CH), 2.54 (8H, m, *J* = 7.2 Hz, CH₂CH₃), 2.52 (6H, s, α-CH₃), 2.45 (12H, t, *J* = 7.2 Hz, CH₂CH₃), –0.67 (3H, s, CH₃). ¹³C{¹H}-NMR (C₆D₆, 75 MHz): δ 167.2 (iminate C–N), 146.6, 137.0, 126.8, 125.4 (aromatic C), 95.6 (β-CH), 25.2, 23.2 (α-Me + Et), 14.7 (Zn–Me).

3.4.3. [(BDI-3)ZnEt]_∞

Light yellow powder. Slowly cooling a toluene solution of the complex yielded light yellow prisms suitable for X-ray analysis. ¹H-NMR (C₆D₆, 300 MHz): δ 7.00 (6H, b, ArH), 2.88 (4H, m, *J* = 7.0 Hz, CHMe₂), 2.14 (6H, s, α-Me), 1.14 (12H, d, *J* = 7.0 Hz, CHMeMe), 1.00 (12H, d, *J* = 7.0 Hz, CHMeMe), 0.71 (3H, t, *J* = 8.0 Hz, CH₂CH₃), 0.11 (2H, q, *J* = 8.0 Hz, CH₂CH₃). X-ray analysis revealed a coordination polymer as shown in Fig. 1.

3.4.4. [(BDI-4)ZnEt]_∞

Light yellow powder. Slowly cooling a toluene solution of the complex yielded light yellow prisms suitable

for X-ray analysis. ¹H-NMR (C₆D₆, 300 MHz, 50 °C): δ 6.90 (6H, br s, Ar–H), 2.48–2.20 (8H, m, *J* = 7.2 Hz, CH₂CH₃), 2.05 (6H, s, α-Me), 1.1 (12H, t, *J* = 7.2 Hz, CH₂CH₃), 0.68 (3H, t, *J* = 7.0 Hz, CH₂CH₃), 0.05 (2H, q, *J* = 7.0 Hz, CH₂CH₃). ¹³C{¹H}-NMR (C₆D₆, 75 MHz, 50 °C): δ 171.34 (iminate C–N), 145.26, 136.06, 127.60, 126.41, 123.00 (aromatic C + CN), 24.70, 22.00, 14.17, (Et + α-Me) 11.40, –2.18 (Zn–Et). X-ray analysis revealed a coordination polymer as shown in Fig. 2.

3.4.5. [(BDI-5)ZnEt]

Bright yellow waxy solid. ¹H-NMR (C₆D₆, 300 MHz): δ 7.09 (3H, s, ArH), 6.97 (3H, s, ArH), 5.52 (1H, s, β-CH), 3.20 (2H, m, *J* = 6.7 Hz), 2.33 (4H, m, *J* = 7.5 Hz, CH₂CH₃), 1.44 (3H, s, α-CH₃), 1.28 (6H, d, *J* = 6.7 Hz, CHMeMe), 1.20 (6H, d, *J* = 6.7 Hz, CHMeMe), 1.08 (6H, t, *J* = 7.5 Hz, CH₂CH₃), 0.78 (3H, t, *J* = 8.1 Hz, CH₂CH₃), 0.17 (2H, q, *J* = 8.1 Hz, CH₂CH₃). ¹³C{¹H}-NMR (C₆D₆, 75 MHz): δ 171.2 (iminate C–N), 145.6, 142.3, 135.7, 127.9, 126.8, 126.4, 126.1, 123.5 (aromatic C + CF₃), 91.2 (β-CH), 28.7, 25.0, 24.9, 23.0, 22.8 (α-Me + ^{*i*}Pr + Et), 14.2, 11.5 (Zn–Et).

3.4.6. [(BODDI-1)(ZnEt)₂]

This complex was prepared as described for the (BDI)ZnEt complexes. Crystallized from hexanes at –20 °C (54% yield). ¹H-NMR (C₆D₆, 300 MHz): δ 7.05 (6H, m, ArH), 5.04 (2H, s, β-CH), 3.16 (4H, septet, *J* = 7.0 Hz, CHMe₂), 1.53 (6H, s, α-Me), 1.18 (6H, t, *J* = 8.0 Hz, CH₂CH₃), 1.12 (12H, d, *J* = 7.0 Hz, CHMeMe), 1.09 (12H, d, *J* = 7.0 Hz, CHMeMe), 0.16 (4H, q, *J* = 8.0 Hz, CH₂CH₃). X-ray analysis revealed that the complex exists as a monomeric complex with two Zn–Et moieties as shown in Fig. 4.

3.4.7. Synthesis of [(BDI)Zn(μ-OAc)]₂

[(BDI-5)Zn(μ-OAc)]₂ was previously reported [6e]. [(BDI)Zn(μ-OAc)] for BDI ligands 1–4 were synthesized with the following general procedure. [(BDI)ZnEt] was dissolved in the appropriate solvent (hexanes for (BDI-1) and (BDI-2); CH₂Cl₂ for (BDI-3) and (BDI-4)), the solution was cooled to 0 °C, and acetic acid (1 equiv.) was added dropwise. The solution was stirred overnight, allowing gradual warming to r.t. then the volatiles were removed in vacuo.

3.4.8. [(BDI-1)Zn(μ-OAc)]₂

The white solid was crystallized from CH₂Cl₂ at –20 °C (87% yield). ¹H and ¹³C{¹H}-NMR correlate to known spectra [6c].

3.4.9. [(BDI-2)Zn(μ-OAc)]₂

The white solid was crystallized from toluene at –20 °C (85% yield). ¹H and ¹³C{¹H}-NMR correlate to known spectra [6c].

3.4.10. $[(BDI-3)Zn(\mu-OAc)]_2$

The product was isolated as a microcrystalline powder from CH_2Cl_2 solution at $-20^\circ C$ (50% yield). 1H -NMR (THF- d_8 , 400 MHz): δ 7.12 (6H, b, ArH), 3.26 (4H, septet, $J=7.0$ Hz, $CHMe_2$), 2.00 (6H, s, α -Me), 1.63 (3H, s, OAc), 1.21 (12H, d, $J=7.0$ Hz, $CHMeMe$), 1.13 (12H, d, $J=7.0$ Hz, $CHMeMe$).

3.4.11. $[(BDI-4)Zn(\mu-OAc)]_2$

The crude material was crystallized from toluene at r.t. to give colorless blocks (84% yield). 1H -NMR (60 $^\circ C$, C_6D_6 , 300 MHz): δ 6.99 (3H, m, ArH), 6.88 (3H, m, ArH), 2.27 (8H, quartet, $J=7.5$ Hz, CH_2CH_3), 1.96 (6H, s, α -Me), 1.46 (3H, b, OAc), 1.00 (12H, t, $J=7.5$ Hz, CH_2CH_3). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 75 MHz), δ 180.52 (iminate C–N), 172.48, 144.47, 136.52, 125.95, 125.77, 123.60 (aromatic C+CN), 80.87 (β -CH), 23.38, 22.10, 13.55 (α -Me+Et+OAc).

3.4.12. $[(BODDI-1)Zn_2(\mu-OAc)_2]$

To a solution of $[(BODDI-1)(ZnEt)_2]$ in a minimal amount of hexanes was added one equivalent of acetic acid at $0^\circ C$. After stirring overnight allowing a gradual temperature increase to r.t., the clear solution was dried in vacuo to leave a yellow solid. The product was crystallized from hexanes at r.t. to give brilliant fluorescent yellow blocks (82% yield). 1H -NMR (C_6D_6 , 400 MHz): δ 7.12 (6H, m, ArH), 4.95 (2H, s, β -CH), 3.43 (4H, septet, $J=6.8$ Hz, $CHMe_2$), 1.73 (6H, s, OAc), 1.58 (6H, s, α -Me), 1.30 (12H, d, $J=6.8$ Hz, $CHMeMe$), 1.19 (12H, d, $J=6.8$ Hz, $CHMeMe$). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 75 MHz), δ 181.23, 176.69 (C–N+C=O), 169.28, 143.95, 143.38, 126.24, 124.20 (aromatic C), 93.18 (β -CH), 27.93, 24.48, 24.24, 24.01, 23.54 (α -Me+ i Pr). X-ray analysis revealed that this molecule exists as a monomer with two μ -OAc ligands bridging the Zn atoms as shown in Fig. 5.

3.4.13. $[\{(BDI-3)Zn(\mu-OAc)\}_2Zn(\mu-OAc)_2]$

One equivalent of MeOH (0.052 ml, 1.28 mmol) was added to a solution of $[(BDI-3)ZnEt]_\infty$ (0.66 g, 1.16 mmol) in CH_2Cl_2 (30 ml) at r.t. The reaction was stirred for 24 h and the volatiles were removed in vacuo. 1H -NMR analysis showed only 25% conversion (based on ZnEt peaks). Additional MeOH was added (about five equivalents) in excess and the reaction was allowed to proceed until all ZnEt peaks were reacted (about 2 days). The volatiles were removed in vacuo and the crude white solid was crystallized from hexanes to give white microcrystals (0.32 g, 34% based on Zn). 1H -NMR (C_6D_6 , 300 MHz): δ 7.03 (6H, m, ArH), 6.94 (6H, m, ArH), 3.00 (12H, s, OMe), 2.96 (10H, m, $CHMe_2$ + α -Me), 2.07 (6H, s, α -Me), 1.15 (12H, d, $J=7.0$ Hz, $CHMeMe$), 1.02 (12H, m, $CHMeMe$). The molecular structure of this complex was determined using X-ray analysis and is shown in Fig. 6.

3.4.14. $[\{(BDI-5)Zn(\mu-OAc)\}_2Zn(\mu-OAc)_2]$

$ZnEt_2$ (0.77 ml of a 1.1 M toluene, 0.84 mmol) was added to a solution of (BDI-5)H (0.25 g, 0.56 mmol) in toluene (5 ml) in the drybox at r.t. The solution was heated to $75^\circ C$ for 16 h and the volatiles were removed in vacuo to leave a waxy yellow solid, $[(BDI-5)ZnEt]$, which was used without further purification. The complex was dissolved in 5 ml hexanes and MeOH (23 μ l, 0.56 mmol) was added dropwise and stirred for 18 h at r.t. The volatiles were removed in vacuo and the crude yellow material was crystallized from hexanes to give light yellow blocks, (0.26 g, 57% based on Zn). 1H -NMR (C_6D_6 , 300 MHz): δ 7.06 (3H, s, ArH) 6.99 (3H, s, ArH), 5.30 (2H, s, β -CH), 3.42 (4H, m, $CHMe_2$), 3.09 (12H, br, OCH₃), 2.52 (8H, m, $J=7.5$ Hz, CH_2CH_3), 1.37 (15H, m, $CHMeMe$ + α -CH₃) 1.28 (12H, d, $J=6.0$ Hz, $CHMeMe$), 1.13 (12H, t, $J=7.5$ Hz, CH_2CH_3). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 75 MHz): δ 172.4 (iminate C–N), 143.1, 136.0, 127.4, 127.3, 127.2, 126.8, 126.5 (aromatic C+CF₃), 91.2 (β -CH), 55.2 (OMe), 28.3, 25.6, 24.0, 23.90, 22.8, 13.7 (α -Me+Et+ i Pr).

3.5. Reaction of $[(BDI)ZnR]$ with benzaldehyde

$[(BDI-n)ZnR]$ ($n=1, 2$; R=Me, Et) (20 mg) was dissolved in 1 ml C_6D_6 . To the solution was added 1 equivalent of benzaldehyde. The solution was transferred to an NMR tube fitted with a Teflon stopcock, and was allowed to react for 24 h at $50^\circ C$. The reaction was monitored via 1H -NMR and in all instances the formation of benzylbenzoate was observed with no change to the $[(BDI)ZnR]$ complex. The polymerization of 1,4-dicarboxaldehyde was accomplished using this procedure.

References

- [1] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.
- [2] (a) M. Cheng, A.B. Attygalle, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 121 (1999) 11583; (b) B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 3229.
- [3] A.P. Dove, V.C. Gibson, E.L. Marshall, A.J.P. White, D.J. Williams, Chem. Commun. (2001) 283.
- [4] (a) M.H. Chisholm, D. Navarro-Llobet, W.J. Simonsick, Macromolecules 34 (2001) 8851; (b) M.H. Chisholm, J. Gallucci, K. Phomphrai, Inorg. Chem. 41 (2002) 2785; (c) M.H. Chisholm, J. Gallucci, K. Phomphrai, Chem. Commun. (2003) 48.
- [5] L.R. Rieth, D.R. Moore, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 15239.
- [6] (a) M. Cheng, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 120 (1998) 11018; (b) M. Cheng, N.A. Darling, E.B. Lobkovsky, G.W. Coates, Chem. Commun. (2000) 2007; (c) M. Cheng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B.

- Lobkovsky, G.W. Coates, *J. Am. Chem. Soc.* 123 (1993) 8738;
- (d) D.R. Moore, M. Cheng, E.B. Lobkovsky, G.W. Coates, *Angew. Chem. Int. Ed. Engl.* 41 (2002) 2599;
- (e) S.D. Allen, D.R. Moore, E.B. Lobkovsky, G.W. Coates, *J. Am. Chem. Soc.* 124 (2002) 14284;
- (f) D.R. Moore, PhD thesis, Cornell University, May 2003.
- [7] For a historical perspective on the origins of Zn alkyl chemistry see: D. Seyferth, *Organometallics* 20 (2001) 2940.
- [8] (a) G. Parkin, A. Looney, R. Han, I. Gorrell, M. Cornebise, K. Yoon, *Organometallics* 14 (1995) 274;
- (b) C.M. Dowling, G. Parkin, *Polyhedron* 20 (2001) 285.
- [9] (a) For other recent reports of the synthesis and reactivity of [(BDI)ZnR] complexes see: R. Eberhardt, M. Allmendinger, G.A. Luinstra, B. Rieger, *Organometallics* 22 (2003) 211;
- (b) J. Prust, H. Hohmeister, A. Stasch, H.W. Roesky, J. Magull, E. Alexopoulos, I. Uson, H.G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* (2002) 2156;
- (c) J. Prust, A. Stasch, W.J. Zheng, H.W. Roesky, E. Alexopoulos, I. Uson, D. Bohler, T. Schuchardt, *Organometallics* 20 (2001) 3825;
- (d) J. Prust, K. Most, I. Muller, A. Stasch, H.W. Roesky, I. Uson, *Eur. J. Inorg. Chem.* (2001) 1613.
- [10] (a) H. Zhao, R.A. Heintz, X. Ouyang, K.R. Dunbar, C.F. Campana, R.D. Rogers, *Chem. Mater.* 11 (1999) 736;
- (b) M.J. Gunter, T.P. Jeynes, M.R. Johnston, P. Turner, Z. Chen, *J. Chem. Soc. Perkins Trans.* (1998) 1945;
- (c) E.K. Woller, S.G. DiMagno, *J. Org. Chem.* 62 (1997) 1588.
- [11] (a) S. Iguchi, A. Inoue, *Chem. Pharm. Bull.* 11 (1963) 390;
- (b) S. Garratt, *J. Org. Chem.* 28 (1963) 1886;
- (c) A.I. Meyers, J. Schneller, N.K. Ralhan, *J. Org. Chem.* 28 (1963) 2944;
- (d) J.D. Edwards, J.E. Page, M. Pianka, *J. Chem. Soc.* (1964) 5200.
- [12] (a) S. Goto, A. Kono, S. Iguchi, *J. Pharm. Sci.* 57 (1968) 791;
- (b) A.K. Kiang, S.F. Tan, W.S. Wong, *J. Chem. Soc. C Org.* (1971) 2721;
- (c) J.A. Van Allan, G.A. Reynolds, J.T. Alessi, S.C. Chang, R.C. Joines, *J. Heterocyclic Chem.* 8 (1971) 919;
- (d) F. Millich, M.T. El-Shoubary, *Org. Prep. Proc. Int.* 28 (1996) 366.
- [13] (a) M. Himmelsbach, R.L. Lintvedt, J.K. Zehetmair, M. Nanny, M.J. Heeg, *J. Am. Chem. Soc.* 109 (1987) 8003;
- (b) H. Adams, N.A. Bailey, D.E. Fenton, M.S.L. Gonzalez, C.A. Phillips, *J. Chem. Soc. Dalton Trans.* (1983) 371;
- (c) D.E. Fenton, S.E. Gayda, *J. Chem. Soc. Dalton Trans.* (1977) 2095;
- (d) D.E. Fenton, S.E. Gayda, R.S.Z. Kowalski, *Transition Met. Chem.* 1 (1976) 95;
- (e) D.E. Fenton, S.E. Gayda, *J. Chem. Soc. Chem. Commun.* (1974) 960.
- [14] A.K. Kiang, S.F. Tan, W.S. Wong, *J. Chem. Soc. C Org.* (1971) 2721.
- [15] L. Pu, H.B. Yu, *Chem. Rev.* 101 (2001) 757.
- [16] M.R. Burgstein, H. Berberich, P.W. Roesky, *Chem. Eur. J.* 7 (2001) 3078.
- [17] (a) I. Yamaguchi, T. Kimishima, K. Osakada, T. Yamamoto, *J. Polym. Sci. Polym. Chem.* 35 (1997) 1265;
- (b) S. Onozawa, T. Sakakura, M. Tanaka, M. Shiro, *Tetrahedron* 52 (1996) 4291;
- (c) S.-H. Choi, E. Yashima, Y. Okamoto, *Polym. J.* 29 (1996) 261.
- [18] E.J. Corey, Z. Wang, *Tetrahedron Lett.* 34 (1993) 4001.
- [19] K. Tamura, H. Mizukami, K. Maeda, H. Watanabe, K. Uneyama, *J. Org. Chem.* 58 (1993) 32.
- [20] S.K. Bertilsson, L. Tedenborg, D.A. Alonso, P.G. Andersson, *Organometallics* 18 (1999) 1281.
- [21] J.R. Bethell, P. Maitland, *J. Chem. Soc.* (1962) 3751.