Synthesis, Reactivity, and Structure of Mixed-Ligand Ytterbium Complexes Supported by *β*-Diketiminate

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The preparation and reaction chemistry of *β*-diketiminate ytterbium complexes is described. Reaction of [(DIPPh)$_2$nacnac]Li ((DIPPh)$_2$nacnac = *N*,*N*-diisopropylphenyl-2,4-pentanediimine anion) with 1 equiv of anhydrous YbCl$_3$ in THF, followed by crystallization from toluene, affords the monomeric complex [(DIPPh)$_2$nacnac]YbCl$_2$(THF)$_2$ (**1**) in high yield. Recrystallization of complex **1** from toluene gives an unexpected dimeric complex, {[(DIPPh)$_2$nacnac]YbCl(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac](THF)}·1/2MePh (**2**), which has a rare triple chloride bridge. Reaction of complex **1** with CH$_3$C$_5$H$_4$Na in 1:1 molar ratio in THF gives the mixed-ligand ytterbium chloride (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbCl (**3**). Complex **3** readily undergoes metathesis reactions with 1 equiv of LiNPh$_2$ or LiNPr$^i{}_2$ in THF to form the compounds (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbNPh$_2$ (**4**) and (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbNPr$^i{}_2$ (**5**), respectively. The complexes **2**, **3**, and **4** have been characterized by an X-ray diffraction structure determination.

Introduction

In recent years, the use of *β*-diketiminate as supporting ligand systems in both main and transition metal coordination chemistry has attracted considerable attention.[1−19] These ligands have several attractive features; for example, their steric and electronic properties can be easily tuned,[20] and they can coordinate to the metal center in different bonding models ranging from purely σ to a combination of σ and π donation.[7] In particular, some of these *β*-diketiminate complexes are active for olefin polymerization[1,7−10] and lactide "living" polymerization.[12−15] However, the utilization of *β*-diketiminates as ancillary ligands in the synthesis of lanthanide complexes still remains relatively poorly explored. Apart from [(Ph)$_2$nacnac]GdBr$_2$(THF)$_2$, [(Ph)$_2$nacnac]$_3$Ln (Ln = Sm, Gd) ((Ph)$_2$nacnac = *N*,*N*-phenyl-2,4-pentanediimine anion),[21] [(Pr^i)$_2$nacnac)]$_2$LnBr (Ln = Sm, Gd) ((Pr^i)$_2$nacnac = *N*,*N*-isopropyl-2,4-pentanediimine anion),[22] and {[PhC(NSiMe$_3$)]$_2$CH}$_2$Yb,[23] the recently reported [(DIPPh)$_2$nacnac]ScCl$_2$(THF) and [(DIPPh)$_2$nacnac]Sc$^+$CH$_2$Ph[η^6-PhCH$_2$B$^-$(C$_6$F$_5$)$_3$] ((DIPPh)$_2$nacnac = *N*,*N*-diisopropylphenyl-2,4-pentanediimine anion)[24] are the only well-characterized complexes of this type in the literature to our knowledge.

Now, we are interested in the synthesis and reactivity of *β*-diketiminate lanthanide complexes and find that the (DIPPh)$_2$nacnac anion is an ideal ligand for the synthesis of mixed-ligand lanthanide complexes. In this paper, we report the synthesis and characterization of several mono(methylcyclopentadienyl)-*β*-diketiminate ytterbium complexes. The molecular structures of

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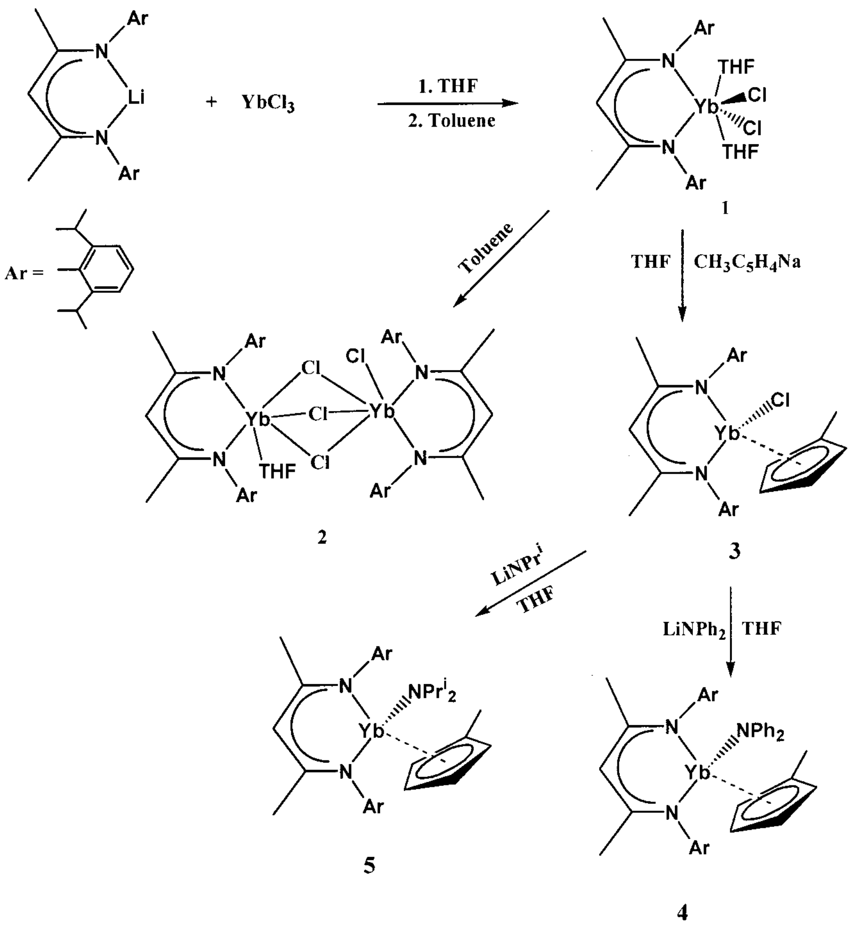
Scheme 1



{[(DIPPh)$_2$nacnac]YbCl(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac](THF)}·1/2MePh (**2**), (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbCl (**3**), and (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbNPh$_2$ (**4**) are described.

Results and Discussion

Synthesis of Ytterbium β-Diketiminate Complexes. [(DIPPh)$_2$nacnac]Li reacted with 1 equiv of anhydrous YbCl$_3$ in THF to afford the β-diketiminate ytterbium dichloride which was identified by elemental analysis as [(DIPPh)$_2$nacnac]YbCl$_2$(THF)$_2$ (**1**) in 72% yield as red microcrystals after crystallization from toluene (Scheme 1). To obtain crystals suitable for X-ray analysis, complex **1** was recrystallized from toluene. The unexpected complex **2**, which was characterized to be part of coordinated THF lost, was obtained as violet crystals. Structural analysis of complex **2** reveals that it has a rare triple chloride bridge, {[(DIPPh)$_2$nacnac]YbCl(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac](THF)}·1/2MePh (vide infra). Attempts to prepare bis(β-diketiminate) ytterbium complex [(DIPPh)$_2$nacnac]$_2$YbCl by the metathesis reaction of complex **1** with additional [(DIPPh)$_2$nacnac]Li or YbCl$_3$ with 2 equiv of [(DIPPh)$_2$nacnac]Li in THF were unsuccessful; even under more drastic conditions, the isolated products were complex **1** and [(DIPPh)$_2$nacnac]Li, respectively. Therefore, the (DIPPh)$_2$nacnac anion seems to be an ideal ligand for synthesis of the mixed-ligand lanthanide derivatives.

When complex **1** was treated with 1 equiv of CH$_3$C$_5$H$_4$Na in THF, the desired mixed-ligand ytterbium chloride (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbCl (**3**) was isolated as red crystals in high yield. The reaction of complex **1** with other anionic ligands, such as aryloxo, indenyl, and amido, is currently being studied.

We notice that the mixed-ligand pentamethylcyclopentadienyl-benzamidinate yttrium chloride {Cp*[PhC(NSiMe$_3$)$_2$]YCl}$_2$ is inert for substitution of the chloride with aryloxides, amides, or some alkyls.[25] We wonder whether this is a special case. Therefore, the reaction chemistry of complex **3** with selected nucleophiles has been further studied. Treatment of complex **3** with 1 equiv of LiNPh$_2$ or LiNPr$^i_2$ in THF smoothly allowed for the replacement of chloride and the production of the complexes (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbNPh$_2$ (**4**) and (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbNPr$^i_2$ (**5**) in good yields (65−77%) after crystallization from toluene, respectively. These results show complex **3** is a useful precursor for the synthesis of mono(methylcyclopentadienyl) lanthanide derivatives. Comparison of the reactivity between complex **3** and complex {Cp*[PhC(NSiMe$_3$)$_2$]YCl}$_2$ indicates that the effect of a π ancillary ligand on the reactivity of the complex should be crucial.

Complexes **1**−**5** were characterized by elemental analyses, IR spectra, and X-ray structural analysis (complexes **2**−**4**). These complexes have good thermal stability. Complexes **1**−**3** are moderately sensitive to air and moisture and are well soluble in THF and DME, moderately in aromatic solvents, and insoluble in ali-

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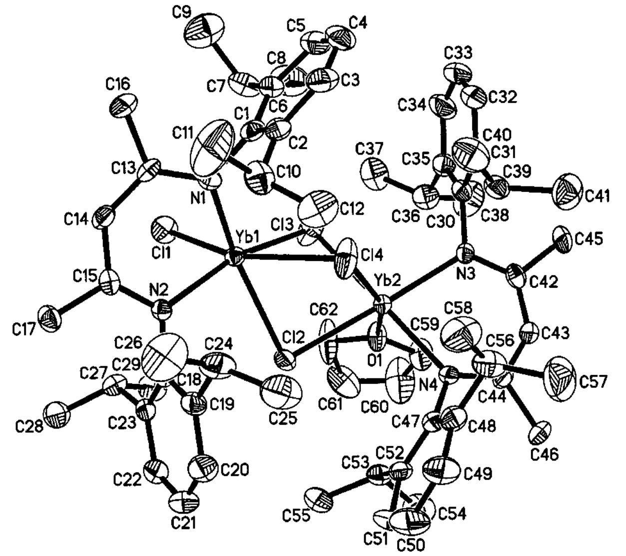

Figure 1. Molecular structure of complex **2** (hydrogen atoms omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Yb(1)−N(1)	2.253(5)	Yb(2)−N(3)	2.295(5)
Yb(1)−N(2)	2.282(5)	Yb(2)−N(4)	2.298(5)
Yb(1)−Cl(1)	2.505(2)	Yb(2)−O(1)	2.299(4)
Yb(1)−Cl(2)	2.710(2)	Yb(2)−Cl(2)	2.612(2)
Yb(1)−Cl(3)	2.663(2)	Yb(2)−Cl(3)	2.593(2)
Yb(1)−Cl(4)	2.752(2)	Yb(2)−Cl(4)	2.610(2)
Yb(1)−C(13)	3.105(7)	Yb(1)−Yb(2)	3.692(6)
Yb(1)−C(15)	3.144(6)	N(3)−C(42)	1.339(8)
N(1)−C(13)	1.335(7)	C(42)−C(43)	1.382(8)
C(13)−C(14)	1.410(8)	C(43)−C(44)	1.379(8)
C(14)−C(15)	1.403(8)	C(44)−N(4)	1.350(7)
C(15)−N(2)	1.325(7)		

N(1)−Yb(1)−N(2)	84.19(18)	N(3)−Yb(2)−N(4)	81.92(18)
N(1)−Yb(1)−Cl(2)	153.03(14)	N(3)−Yb(2)−Cl(2)	177.85(14)
N(2)−Yb(1)−Cl(2)	87.25(13)	N(4)−Yb(2)−Cl(2)	100.23(13)
N(1)−Yb(1)−Cl(3)	114.65(14)	N(3)−Yb(2)−Cl(3)	97.60(14)
N(2)−Yb(1)−Cl(3)	160.83(14)	N(4)−Yb(2)−Cl(3)	176.59(14)
N(1)−Yb(1)−Cl(4)	86.13(14)	N(3)−Yb(2)−Cl(4)	102.22(14)

phatic hydrocarbons, and complexes **4** and **5** have good solubility even in aromatic solvents.

Our previous work has shown that bis(methylcyclopentadienyl) lanthanide amides are highly active initiators in the syndiotactic polymerization of methyl methacrylate (MMA).[26−29] To understand the effect of the ancillary ligand on the activity of amide complexes, we tested the catalytic activity of complexes **4** and **5** in MMA polymerization. Preliminary studies show that both complexes have no catalytic activity at all. It is really unexpected that replacing one methylcyclopentadienyl group by a β-diketiminate ligand results in such a dramatic decrease of its activity, although a decrease of catalytic reactivity has been observed by replacing the bis(pentamethylcyclopentadienyl) ligand system with two *N*,*N*′-bis(trimethylsilyl)benzamidinate ligands.[30] Considering the great difference in activity between $(CH_3C_5H_4)_2YbNPh_2$ and sterically crowded complex $(C_5Me_5)_2YbNPh_2$ in MMA polymerization (the former very high, the latter no activity at all),[28] we ascribe this failure mainly to the steric congestion around the metal center brought about by the bulky $(DIPPh)_2$nacnac ligand, although this difference in activity could also be ascribed to electronic changes caused by the nitrogen ligation of the ytterbium ion. We are currently investigating the activity of these complexes with other monomers.

Molecular Structure of {[(DIPPh)$_2$nacnac]YbCl-(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac](THF)}·1/2MePh (2). The molecular structure of complex **2** is shown in Figure 1, and the selected bond lengths and angles are listed in Table 1. The molecule is dinuclear in the solid state. The most interesting feature of the structure is that the two ytterbium centers are triply chloride-bridged. Generally, the central metals in dimeric lanthanide halides are connected by one or two halogen bridge(s). Only a few examples of crystallographically characterized multiple halogen bridges between two lanthanide atoms are those found in lanthanide clusters.[31] Moreover, the coordination environment around the two ytterbium centers in complex **2** is inequivalent, although the coordination geometry around two ytterbium centers is similar (six-coordinate distorted octahedral). The Yb(1) atom is coordinated by two nitrogen atoms of the β-diketiminate ligand and one terminal chlorine atom and three bridged chlorine atoms; the Yb(2) center is coordinated by two nitrogen atoms and three bridged chlorine atoms and one oxygen atom of THF molecule. The reason for the formation of a triple chloride bridge and the coordination of only one THF molecule may be attributed to the increased steric demand of the bulky β-diketiminate ligands.

Two β-diketiminate ligands are symmetrically coordinated to Yb(1) and Yb(2), respectively, but the Yb(1)−N(1,2) bond lengths (2.253(5), 2.282(5) Å) are slightly shorter than those of Yb(2)−N(3,4) (2.295(5), 2.298(5) Å). The bond distances of C(13)−C(14), C(14)−C(15), N(1)−C(13), and N(2)−C(15) (see Table 1) suggest significant delocalization within the π-system of the β-diketiminate ligand. The Yb−C(13,14,15) distances are quite long, suggesting a negligible π contribution to the β-deketiminate−Yb bonding in this compound.

Molecular Structures of $(CH_3C_5H_4)[(DIPPh)_2$nacnac]YbR (3, R = Cl; 4, R = NPh$_2$). A drawing of complex **3** is shown in Figure 2, and selected bond distances and angles are listed in Table 2. The structure analysis reveals complex **3** to be a solvent-free monomeric species formed by ytterbium, methylcyclopentadienyl, $(DIPPh)_2$nacnac, and chlorine. The unsolvated monomeric structure is rare in lanthanide monochloride derivatives. Normally, they have solvated monomeric structures or solvent-free bridging structures in the solid state.[31−33] The coordination geometry about the ytter-

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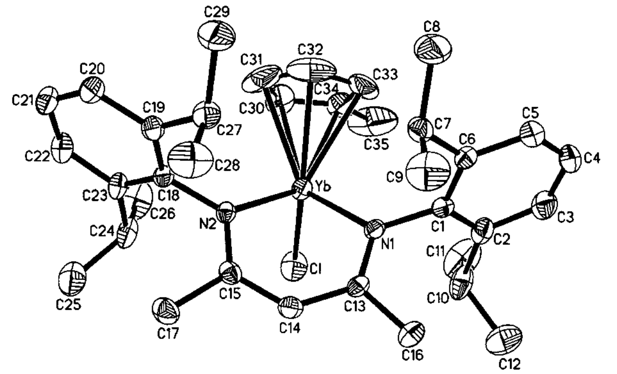

Figure 2. Molecular structure of complex **3** (hydrogen atoms omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 3

Yb−N(1)	2.247(3)	Yb−C(34)	2.610(5)
Yb−N(2)	2.239(3)	Yb−C(13)	3.086(4)
Yb−Cl	2.4704(14)	Yb−C(15)	3.049(5)
Yb−C(30)	2.584(6)	N(1)−C(13)	1.330(5)
Yb−C(31)	2.554(7)	N(2)−C(15)	1.322(5)
Yb−C(32)	2.557(8)	C(13)−C(14)	1.409(6)
Yb−C(33)	2.588(6)	C(14)−C(15)	1.396(6)
N(1)−Yb−N(2)	85.43(13)	C(13)−N(1)−Yb	116.9(3)
N(1)−Yb−Cl	105.07(10)	C(15)−N(2)−Yb	115.4(3)
N(2)−Yb−Cl	107.48(10)	C(13)−C(14)−C(15)	132.3(5)

bium center approximates a three-legged piano stool with the two nitrogen atoms of the chelating β-diketiminate anion and a chlorine atom constituting the "legs" of the molecule, and the formal coordination number of the central metal is six.

Interestingly, the Yb−C(13) and Yb−C(15) distances are 3.086(4) and 3.049(5) Å, respectively, which are comparable with those of 2.986(6) and 3.180(9) Å for bridging η^2-C_5H_5 bonding in $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$[34] and 2.814(4)−3.148(6) Å for chelating η^6-, η^1-Ph−Yb bonding in $[Yb(Odpp)_3]_2$ (Odpp = 2,6-diphenylphenolate),[35] respectively. This indicates that the complex may be considered to involve π coordination of the β-diketiminate ligand to the ytterbium atom. Therefore, the β-diketiminate ligand appears to be relatively more π bound in complex **3** than in complex **2**. There is the expected pattern of delocalization within the β-diketiminate ligand. The backbone of the ligand (NC_3N) and ytterbium atom form a stable six-membered ring which adopts a boat conformation with C(14) and Yb lying 0.13 and 1.03 Å out of the N(1), C(13), C(15), N(2) plane, respectively. The β-diketiminate ligand is symmetrically coordinated to the ytterbium atom with variation in Yb−N bond lengths of 0.008 Å (2.247(3) and 2.239(3) Å, respectively). The Yb−C(ring) distances range from 2.554(7) to 2.610(5) Å, giving the average Yb−C(ring) distance of 2.579(6) Å. The N(1)−Yb−N(2) angle is 85.43(13)°, which is comparable with that in complex **2**.

Complex **4** crystallizes with two crystallographically independent but chemically similar molecules (**4a** and **4b**) in the unit cell; the selected bond lengths and angles are provided in Table 3 for both molecules. The methylcyclopentadienyl ring of **4b** is disordered due to strong thermal motion. An ORTEP of molecule **4a** is depicted in Figure 3. The coordination geometry around the ytterbium atom resembles that in complex **3**, and the six-membered chelating ring also adopts a boat conformation, with C(14) and Yb lying 0.11 and 0.91 Å out of the NC_2N plane, respectively. The Yb−C(13), Yb−C(14), and Yb−C(15) distances are quite long (3.184(7), 3.419(7), and 3.156(7) Å, respectively), which indicates that there is only purely σ bonding.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

4a		4b	
Yb(1)−N(1)	2.298(6)	Yb(2)−N(4)	2.281(5)
Yb(1)−N(2)	2.257(5)	Yb(2)−N(5)	2.310(6)
Yb(1)−N(3)	2.259(6)	Yb(2)−N(6)	2.214(6)
Yb(1)−C(13)	3.184(7)	Yb(2)−C(60)	3.192(6)
Yb(1)−C(15)	3.156(7)	Yb(2)−C(62)	3.221(7)
Yb(1)−C(42)	2.592(7)	Yb(2)−C(89)	2.583(14)
Yb(1)−C(43)	2.570(8)	Yb(2)−C(90)	2.584(14)
Yb(1)−C(44)	2.554(8)	Yb(2)−C(91)	2.596(17)
Yb(1)−C(45)	2.590(7)	Yb(2)−C(92)	2.602(18)
Yb(1)−C(46)	2.607(7)	Yb(2)−C(93)	2.594(10)
N(1)−C(13)	1.346(8)	N(4)−C(60)	1.339(8)
N(2)−C(15)	1.341(8)	N(5)−C(62)	1.313(9)
C(13)−C(14)	1.385(9)	C(60)−C(61)	1.393(9)
C(14)−C(15)	1.387(9)	C(61)−C(62)	1.414(10)
N(1)−Yb(1)−N(2)	82.9(2)	N(4)−Yb(2)−N(5)	82.2(2)
N(1)−Yb(1)−N(3)	113.9(2)	N(4)−Yb(2)−N(6)	114.9(2)
N(2)−Yb(1)−N(3)	110.9(2)	N(5)−Yb(2)−N(6)	113.5(2)

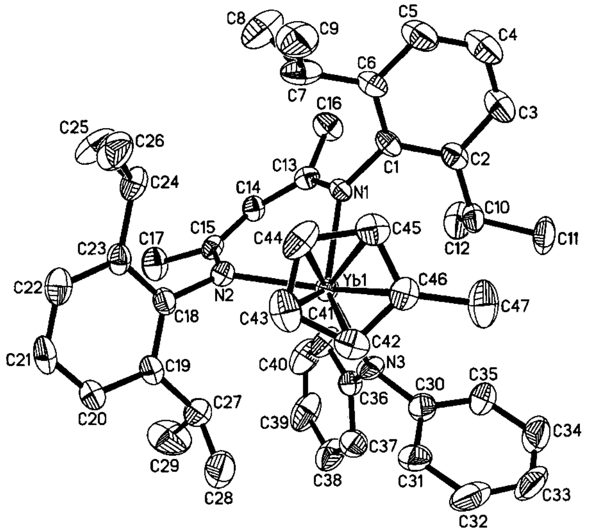

Figure 3. Molecular structure of complex **4** (hydrogen atoms omitted for clarity). Only one of the two independent molecules is presented.

The N(1)−Yb(1)−N(2) angle is 82.9(2)°, which is more acute than the corresponding angle in complex **3**, and the Yb(1)−N(1) and Yb(1)−N(2) bond lengths of 2.257(5) and 2.298(6) Å are slightly longer than those in complex **3**, respectively. Considering the elongated Yb(1)−C(13), −C(14), and −C(15) distances in complex **4**, it is reasonable to ascribe the difference in bond parameters of complexes **3** and **4** to the increased steric congestion in the latter due to the replacement of chlorine by a diphenylamido group.

Conclusions

We have shown that the $(DIPPh)_2$nacnac anion should be a useful ancillary ligand for preparing soluble, well-

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Table 4. Crystallographic Data for Complexes 2, 3, and 4

	2	3	4
formula	$C_{65.5}H_{94}Cl_4N_4OYb_2$	$C_{35}H_{48}ClN_2Yb$	$C_{47}H_{58}N_3Yb$
fw	1441.33	705.24	838.00
T (K)	299(2)	297(2)	290(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/n$	$P2(1)/n$
unit cell			
a (Å)	19.951(4)	10.422(2)	12.420(2)
b (Å)	13.918(2)	26.247(5)	16.469(3)
c (Å)	24.257(5)	12.653(2)	40.264(7)
β (deg)	98.710(10)	106.050(10)	93.530(10)
V (Å^3)	6658(2)	3326.3(10)	8220(2)
Z	4	4	8
D_{calcd} (g cm^{-3})	1.438	1.408	1.354
μ (mm^{-1})	2.994	2.916	2.310
F(000)	2924	1436	3448
cryst size (mm)	0.40 × 0.32 × 0.20	0.52 × 0.34 × 0.34	0.52 × 0.42 × 0.22
θ_{max} (deg)	25.0	25.0	25.0
no. of collected reflns	13 060	6579	16 305
no. of unique reflns	11 734	5846	14 493
no. of obsd reflns [$I > 2.0\sigma(I)$]	6754	3902	7451
no. of variables	715	353	937
GOF	0.790	0.841	0.816
R	0.0405	0.0316	0.0478
R_w	0.0561	0.0571	0.0703

defined ytterbium(III) complexes. The mixed-ligand complexes $(CH_3C_5H_4)$[(DIPPh)$_2$nacnac]YbX are accessible through stepwise ligand introduction, starting from anhydrous $YbCl_3$ by first introducing a β-diketiminate ligand to the metal's coordinate sphere. In these complexes, β-diketiminates show different coordination modes depending on the steric environment. The chloride $(CH_3C_5H_4)$[(DIPPh)$_2$nacnac]YbCl shows a similar reactivity with its bis(methylcyclopentadienyl)ytterbium analogues, it readily undergoes metathesis reactions with $LiNPh_2$ or $LiNPr^i{}_2$ in THF to form the corresponding ytterbium amides. However, these ytterbium amides show notably different reactivity compared to those seen in related $(CH_3C_5H_4)_2YbNPr^i{}_2$ and $(CH_3C_5H_4)_2YbNPh_2$, and they cannot efficiently initiate MMA polymerization.

Experimental Section

The chemistry described below was performed under pure argon with exclusion of air and moisture by Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over Na or sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous $YbCl_3$[36] and [(DIPPh)$_2$nacnac]Li[1] were prepared according to the literature methods. $CH_3C_5H_4Na$ was prepared by the reaction of $CH_3C_5H_5$ with sodium in THF. $LiNPh_2$ and $LiNPr^i{}_2$ were obtained by the reaction of $HNPh_2$ or $HNPr^i{}_2$ with n-BuLi in a solution of toluene and hexane.

Melting points were determined in sealed argon-filled capillaries and are uncorrected. Metal analyses were carried out using complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion; quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets.

[(DIPPh)$_2$nacnac]YbCl$_2$(THF)$_2$ (1). A solution of [(DIPPh)$_2$nacnac]Li (25 mL, 7.73 mmol) in toluene/hexane was slowly added to a suspension of $YbCl_3$ (2.16 g, 7.73 mmol) in 40 mL of THF at room temperature. The color of the solution gradually changed to red. The reaction mixture was stirred overnight at room temperature. Solvent was completely removed under vacuum, and the red residue was extracted with toluene. The dissolved portion was removed by centrifugation. The filtrate was concentrated to 30 mL and cooled at −20 °C, and red microcrystals were collected in two crops by filtration (4.29 g, 72.1%), mp 132−133 °C (dec). Anal. Calcd for $C_{37}H_{57}Cl_2N_2O_2Yb$: C, 55.15; H, 7.13; N, 3.48; Yb, 21.47. Found: C, 55.62; H, 7.38; N, 3.35; Yb, 21.58. IR (KBr, cm^{-1}): 3060(w), 2960(vs), 2926(s), 2867(s), 1621(vs), 1550(vs), 1483(m), 1462(s), 1439(s), 1387(m), 1362(s), 1325(s), 1276(s), 1254(m), 1174(m), 1108(w), 1075(m), 1034(m), 930(w), 789(s), 758(s), 728(w).

[(DIPPh)$_2$nacnac]YbCl(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac(THF)]·1/2MePh (2). Complex **1** (0.98 g, 1.22 mmol) was recrystallized from toluene, and violet crystals suitable for X-ray analysis were obtained at room temperature. The products were collected by filtration (0.71 g, 81.3%), mp 140 °C (dec). Anal. Calcd for $C_{65.5}H_{94}Cl_4N_4OYb_2$: C, 54.58; H, 6.57; N, 3.88; Yb, 24.01. Found: C, 53.85; H, 6.35; N, 3.68; Yb, 24.32. IR (KBr, cm^{-1}): 3160(w), 2961(vs), 2927(s), 2867(s), 1622(vs), 1593(s), 1552(vs), 1481(s), 1462(s), 1439(s), 1383(s), 1361(s), 1326(s), 1275(vs), 1175(m), 1102(w), 1075(m), 1024(m), 933(w), 798(s), 758(s), 729(m), 700(m).

$(CH_3C_5H_4)$[(DIPPh)$_2$nacnac]YbCl (3). Method a. To a THF solution (30 mL) of compound **1** (3.29 g, 4.57 mmol) was slowly added a solution of $CH_3C_5H_4Na$ (7.2 mL, 4.57 mmol) in THF at room temperature. After being stirred for 24 h, the precipitate was separated by centrifugation and the solvent was evaporated completely under reduced pressure. Then toluene was added to extract the product, and the dissolved portion was separated by centrifugation. The red crystals were obtained from concentrated toluene solution at −10 °C for 3 days (2.73 g, 84.1%), mp 222−224 °C. Anal. Calcd for $C_{35}H_{48}ClN_2Yb$: C, 59.61; H, 6.86; N, 3.97; Yb, 24.54. Found: C, 59.31; H, 6.68; N, 3.92; Yb, 24.47. IR (KBr, cm^{-1}): 3058(w), 2963(vs), 2927(s), 2867(s), 1622(vs), 1552(vs), 1519(vs), 1462(s), 1435(s), 1386(s), 1363(s), 1317(s), 1263(s), 1173(m), 1101(m), 1072(w), 1022(m), 927(m), 853(w), 834(m), 789(s), 782(s), 757(s), 688(w). Crystals suitable for single-crystal structure studies were obtained by recrystallization from toluene solution at −10 °C for a week.

Method b. To a slurry of anhydrous $YbCl_3$ (1.75 g, 6.26 mmol) in about 40 mL of THF was slowly added a solution of [(DIPPh)$_2$nacnac]Li (20 mL, 6.26 mmol) in toluene/hexane at room temperature. After $YbCl_3$ disappeared completely, the THF solution of $CH_3C_5H_4Na$ (9.8 mL, 6.26 mmol) was added

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[36] Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.

slowly. The mixture was stirred at room temperature for another 48 h, then the precipitate was removed from the reaction mixture by centrifugation. THF was completely removed in a vacuum, and toluene was added to extract the product. The precipitate was removed again by centrifugation. The red microcrystals were obtained from the concentrated toluene solution at −10 °C (3.35 g, 75.8%).

$(CH_3C_5H_4)[(DIPPh)_2nacnac]YbNPh_2$ (4). A toluene/hexane solution of $LiNPh_2$ (15 mL, 2.17 mmol) was slowly added to the THF solution (30 mL) of compound **3** (1.53 g, 2.17 mmol) at 0 °C. The mixture was stirred for 2 h at 0 °C, and then for another 48 h at room temperature. The solvent was evaporated completely under reduced pressure. Then toluene was added to extract the product, and the dissolved portion was separated by centrifugation. Black crystals suitable for single-crystal structure studies were obtained from concentrated toluene solution at −20 °C for 2 days (1.41 g, 77.3%), mp 161−162 °C. Anal. Calcd for $C_{47}H_{58}N_3Yb$: C, 67.36; H, 6.98; N, 5.01; Yb, 20.65. Found: C, 67.45; H, 6.83; N, 4.92; Yb, 20.54. IR (KBr, cm^{-1}): 3059(w), 2961(vs), 2927(s), 2867(s), 1659(m), 1622(vs), 1592(vs), 1551(vs), 1494(vs), 1460(s), 1432(s), 1385(s), 1363(s), 1312(s), 1255(s), 1174(m), 1112(m), 1073(w), 1030(m), 932(m), 853(w), 786(s), 749(vs), 692(s), 615(m), 507(m).

$(CH_3C_5H_4)[(DIPPh)_2nacnac]YbNPr^i_2$ (5). The synthesis of compound **5** was carried out as described for **4**, but $LiNPr^i_2$ (1.56 mmol) was used in place of $LiNPh_2$. Black microcrystals were obtained from toluene solution (0.78 g, 65.2%), mp 156−158 °C. Anal. Calcd for $C_{41}H_{62}N_3Yb$: C, 63.95; H, 8.11; N, 5.46; Yb, 22.47. Found: C, 63.67; H, 7.93; N, 5.52; Yb, 22.58. IR (KBr, cm^{-1}): 3059(w), 2961(vs), 2927(s), 2867(s), 1659(m), 1622(vs), 1592(vs), 1551(vs), 1494(vs), 1460(s), 1432(s), 1385(s), 1363(s), 1312(s), 1255(s), 1174(m), 1112(m), 1073(w), 1030(m), 932(m), 853(w), 786(s), 749(vs), 692(s), 615(m), 507(m).

X-ray Structure Determination. Suitable single crystals of complexes **2**, **3**, and **4** were sealed in a thin-walled glass capillary for single-crystal structure determination. Intensity data were collected on a Siemens P4 diffractometer in ω scan mode using Mo Kα radiation ($\lambda = 0.71073$ Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 4.

The crystal structures of these complexes were solved by direct methods using the SHELXS-97 program and expanded by Fourier techniques. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C−H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement.

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Supporting Information Available: Tables of X-ray diffraction data for complexes **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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