Synthesis and Structural Characterization of Divalent Ytterbium Complexes Supported by β-Diketiminate Ligands and Their Catalytic Activity for the Polymerization of Methyl Methacrylate

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Three divalent ytterbium complexes supported by a β-diketiminate ligand were synthesized for the first time. The mixed-ligand ytterbium chlorides $(CH_3C_5H_4)[(DIPPh)_2nacnac]YbCl$ (**1**), $(C_9H_7)[(DIPPh)_2nacnac]YbCl$ (**2**), and $(ArO)[(DIPPh)_2nacnac]YbCl(THF)$ (**3**) ($(DIPPh)_2nacnac$ = *N*,*N*-diisopropylphenyl-2, 4-pentanediimine anion, ArO = 2,6-di-*tert*-butyl-4-methylphenoxo), which were obtained in high yield by using $[(DIPPh)_2nacnac]YbCl_2(THF)_2$ as precursor, were reduced by Na/K alloy in THF to afford the corresponding divalent species $(CH_3C_5H_4)[(DIPPh)_2nacnac]Yb(THF)$ (**4**), $(C_9H_7)[(DIPPh)_2nacnac]Yb(THF)$ (**5**), and $\{(ArO)[(DIPPh)_2nacnac]Yb(THF)\}(THF)$ (**6**), respectively. Complexes **2**−**6** were well characterized, and crystal structures of complexes **4**−**6** were determined. These divalent complexes exhibit good catalytic activity for the polymerization of methyl methacrylate.

Introduction

Over the past few decades, great progress has been made in the chemistry of divalent organolanthanide complexes. Divalent organolanthanide complexes exhibit a particularly rich reaction chemistry based on their strong reductive property,[1] and a variety of complexes have been synthesized and widely used in organic synthesis and polymer chemistry.[2−6] The majority of this chemistry has been done utilizing pentamethylcyclopentadienyl or functionalized substituted-cyclopentadienyl as ancillary ligands.

In recent years, the use of β-diketiminates as supporting ligand systems in both main and transition metal coordination chemistry has attracted considerable attention,[7] since their steric and electronic properties can be easily tuned by an appropriate choice of starting

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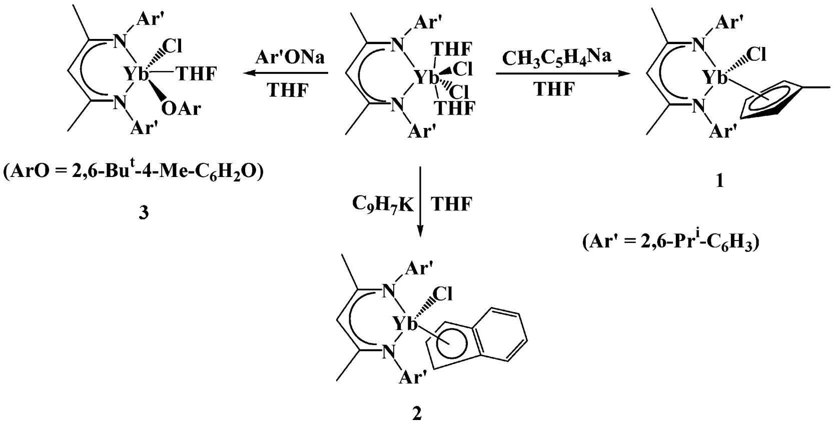
Scheme 1



materials used in their synthesis, and they can coordinate metal centers in different bonding models. Moreover, some of these complexes exhibit exciting reactivity; for example, they show high activity for the polymerization of ethylene[8] and lactide[9] and the copolymerization of carbon dioxide and epoxide.[10] However, the utilization of this ligand system in the synthesis of divalent lanthanide derivatives still remains relatively poorly explored. To our best knowledge, there is only one paper concerning the synthesis and structural characterization of divalent lanthanide complexes utilizing β-diketiminates as ancillary ligands, in which the β-diketiminates act as novel dianionic ligands.[11] Now, we have become interested in studying the synthesis and reactivity of organolanthanide complexes supported by β-diketiminate ligands[12] and find that the bulky β-diketiminate group (DIPPh)$_2$nacnac ((DIPPh)$_2$nacnac = *N*,*N*-2,6-diisopropylphenyl-2,4-pentanediimine anion) is an ideal ligand for the synthesis of mixed-ligand divalent lanthanide complexes. Here, we describe the synthesis and characterization of the divalent ytterbium complexes utilizing this ligand system and the catalytic activities of these complexes for the polymerization of methyl methacrylate (MMA).

Results and Discussion

Synthesis of Trivalent Ytterbium β-Diketiminate Complexes. We previously reported that the bulky β-diketiminate [(DIPPh)$_2$nacnac]$^-$ is an ideal ligand for synthesis of the mixed-ligand trivalent lanthanide derivatives, and (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbCl (**1**) can be conveniently synthesized in high yield using [(DIPPh)$_2$nacnac]YbCl$_2$(THF)$_2$ as precursor.[12a] Thus, freshly prepared [(DIPPh)$_2$nacnac]YbCl$_2$(THF)$_2$ in situ was used to synthesize the β-diketiminate ytterbium derivatives. [(DIPPh)$_2$nacnac]YbCl$_2$ reacted with 1 equiv of C$_9$H$_7$K in THF; after workup, the black microcrystals were obtained as final products which were identified to be (C$_9$H$_7$)[(DIPPh)$_2$nacnac]YbCl (**2**) by elemental analyses and IR spectrum. We propose that complex **2** exists as a monomer according to the structure of the analogous complex **1**, which was identified by structure determination. When [(DIPPh)$_2$nacnac]YbCl$_2$ was treated with 1 equiv of ArONa (ArO = 2,6-di-*tert*-butyl-4-methylphenoxo) in THF, the desired mixed-ligand aryloxo ytterbium complex (ArO)[(DIPPh)$_2$nacnac]-YbCl(THF) (**3**) was isolated as red microcrystals in high yield (Scheme 1). In the IR spectra of complexes **2** and **3**, there are strong absorptions near 1550 and 1530 cm^{-1}, which were consistent with partial C=N double bond character. These complexes are well soluble in THF and DME.

Synthesis of Divalent Ytterbium β-Diketiminate Complexes. Reduction of trivalent lanthanide complexes by alkali metals is a popular method to synthesize divalent lanthanide complexes. The reactions of complexes **1**−**3** with a slight excess of Na/K alloy in THF smoothly produce the divalent β-diketiminate ytterbium complexes (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]Yb(THF) (**4**), (C$_9$H$_7$)[(DIPPh)$_2$nacnac]Yb(THF) (**5**), and {(ArO)[(DIPPh)$_2$nacnac]Yb(THF)}(THF) (**6**), respectively (Scheme 2). Recrystallization from concentrated toluene solution gave **4**−**6** as black crystals in good yield. Usually, the synthesis of monomethylcyclopentadienyl or mono-unsubstituted indenyl divalent lanthanide complexes was difficult due to disproportionation. Complex **4** is the first example of a monomethylcyclopentadienyl heteroleptic divalent lanthanide complex. Up to now, there has been only one example of an indenyl-containing heteroleptic divalent lanthanide complex, [(C$_9$H$_7$)YbI(DME)$_2$], in the literature,[13] and complex **5** is the second one.

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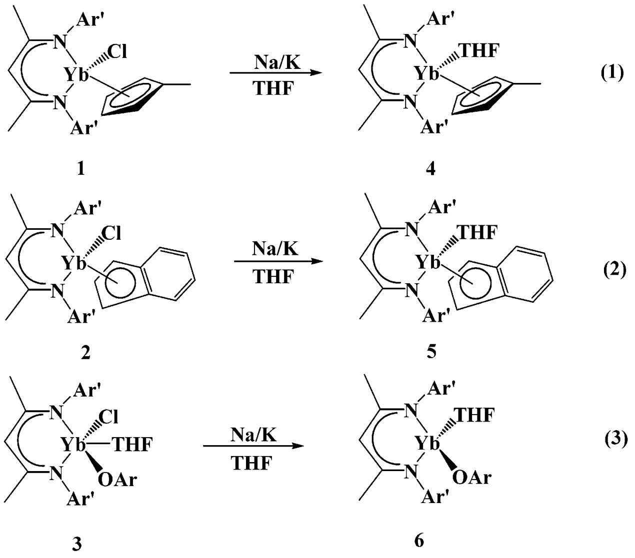
Scheme 2



Complexes **4**−**6** are all very sensitive to air and moisture. They have good solubility in THF and DME and moderate solubility in toluene. These complexes gave satisfactory elemental analyses, and their infrared spectra showed absorptions characteristic of the β-diketininate ligand. The diamagnetic nature of divalent Yb allowed characterization of these complexes by NMR spectroscopy. The structural analyses reveal that the β-diketininate acts as a monoanionic spectator ligand in these divalent ytterbium complexes (see below). This is quite different from those in {Yb[$Me_3SiNC(C_6H_4Ph$-4)$CHC(C_6H_4Ph$-4)$NSiMe_3$(μ-Li(THF))]$_2$}(THF) and {Yb[$Me_3SiNC(Ph)CHC(Ph)NSiMe_3$(μ-Li(THF))]$_2$}, in which the β-diketininates act as dianionic ligands, although they are also obtained by the reduction of trivalent β-diketininate ytterbium complexes.[11]

Molecular Structures. The molecular structures of complexes **4**−**6** were characterized by X-ray diffraction. All of them have solvated monomeric structure. Figures 1−3 show their ORTEP drawings, and their selected bond parameters are listed in Tables 1−3, respectively.

The coordination geometries around ytterbium atoms in complexes **4** and **5** are similar, which resemble that in complex **1**.[12a] The coordination sphere of the Yb center is composed of the two nitrogen atoms of the chelating β-diketiminate anion, a methylcyclopentadienyl (indenyl) group, and an oxygen atom of the THF molecule; the formal coordination number of the central metal is six. The coordination geometry of the ytterbium atom can be described as slightly distorted pseudo-tetrahedral if the methylcyclopentadienyl (indenyl) group is regarded to occupy one coordination site with the ring center. However, the coordination mode of the β-diketiminate ligand in complexes **4** and **5** is different from that in complex **1**. In complexes **4** and **5**, the Yb−C(13, 14, 15) (Yb−C(11, 12, 13) for **5**) distances are quite long, which are well beyond values considered indicative of π bonding. Thus, there is only purely σ bond between ytterbium and the β-diketiminate ligand, and the β-diketiminate ligand adopts an η^2-coordination mode, while the β-diketiminate ligand adopts an η^4-coordination mode in complex **1**.[12a] This is also different from those in {Yb[$Me_3SiNC(C_6H_4Ph$-4)$CHC(C_6H_4Ph$-4)$NSiMe_3$-(μ-Li(THF))]$_2$}(THF) and {Yb[$Me_3SiNC(Ph)CHC(Ph)$-$NSiMe_3$(μ-Li(THF))]$_2$}, in which the β-diketiminate ligands can be regarded as being η^5-bonded to the central metal.[11] The bond distances within the backbone of the β-diketiminate ligand fall in the range of corresponding distances of single and double bonds, which

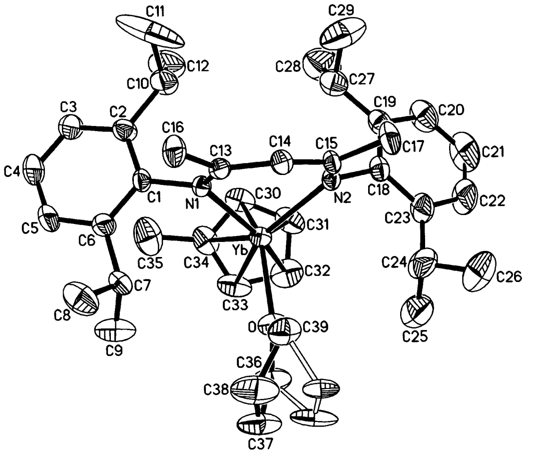


Figure 1. Molecular structure of complex **4** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clarity). Each disordered THF ligand is shown in two possible orientations.

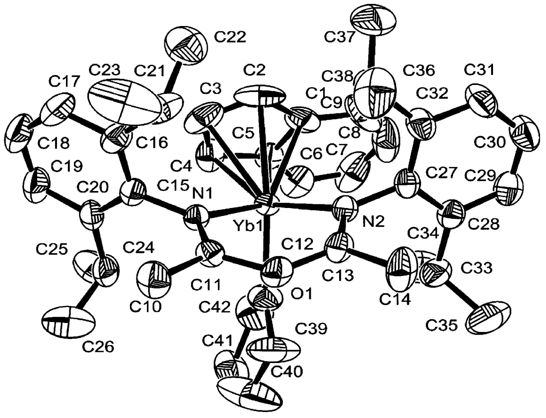


Figure 2. Molecular structure of complex **5** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clarity).

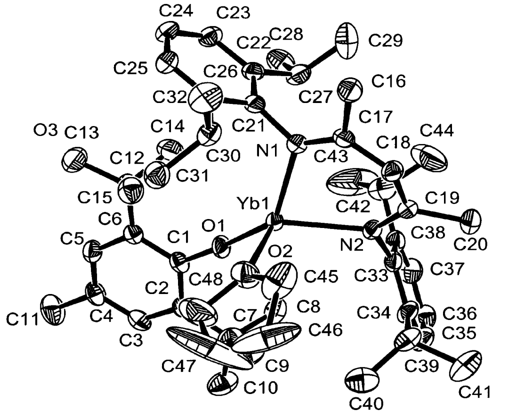


Figure 3. Molecular structure of complex **6** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clarity).

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Yb-N(1)	2.380(4)	Yb−C(34)	2.701(6)
Yb−N(2)	2.362(4)	Yb−C(av)	2.688(6)
Yb−O	2.382(4)	N(1)−C(13)	1.305(6)
Yb−C(30)	2.679(6)	N(2)−C(15)	1.321(6)
Yb−C(31)	2.689(7)	C(13)−C(14)	1.420(7)
Yb−C(32)	2.683(7)	C(14)−C(15)	1.401(7)
Yb−C(33)	2.688(6)		
N(1)−Yb−N(2)	81.25(15)	N(1)−C(13)−C(14)	124.3(5)
N(1)−Yb−O	101.27(14)	N(2)−C(15)−C(14)	125.1(5)
N(2)−Yb−O	102.68(15)	C(13)−C(14)−C(15)	132.0(5)

reflects substantial electron delocalization. This resembles those in trivalent β-diketiminate lanthanide complexes.

The β-diketiminate ligand in complex **4** is symmetrically coordinated to the ytterbium atom, with a variation in Yb−N bond lengths of 0.018 Å (2.380(4) and 2.362(4) Å, respectively) and an average Yb−N bond length of 2.371(4) Å. The Yb−C(ring) distances range from 2.679(6) to 2.701(6) Å, giving the average Yb−C(ring) distance of 2.688(6) Å. These values are ca. 0.13 Å longer than those in complex **1**,[12a] which is in accordance with the difference in ionic radii between Yb(II) and Yb(III) species.[14] The Yb−C(ring) distance is still comparable to the average Yb−C(ring) distances in divalent ytterbocene complexes such as $(CH_3C_5H_4)_2$-Yb(DME)[15] and $[(CH_3C_5H_4)_2Yb(THF)]_n$.[16] The THF molecule in complex **4** exhibits disorder between C37 and C38 atoms; however, the Yb−O bond length of 2.382(4) Å is still observed. The N1−Yb−N2 angle of 81.25(15)° is comparable to that in complex **1**.[12a]

In complex **5**, the average Yb−N bond distance of 2.360(3) Å is comparable with that in complex **4**. The Yb−C(ring) distances range from 2.669(5) to 2.762(3) Å. Indenyl hapticities can be determined conveniently by calculating the slip value ΔM−C,[17] which is found to be 0.026 Å in complex **5**. Thus, the bonding mode of the metal atom with the indenyl ligand might be described as η^5-mode. This coordination mode resembles those in some divalent indenyl lanthanide complexes,[3d,e] but it is different from that in *rac*-$[O(CH_2CH_2C_9H_6)_2]$-$YbN(SiMe_3)_2$, which is partially slipped toward η^3- from η^5-mode.[18] The average Yb−C(ring) distance of 2.713(4) Å is comparable with the corresponding values in complex **4** and other divalent indenyl lanthanide complexes if the difference in ionic radii is considered.[3]

An X-ray analysis has revealed that complex **6** is a solvated monomeric divalent ytterbium complex, which bears mixed ArO and β-diketiminate ligands. This complex has a low coordination number, and the central ytterbium atom is four-coordinated by two nitrogen atoms from the β-diketiminate ligand and two oxygen atoms from ArO group and a THF molecule, respectively. This may be attributed to the steric repulsion among the bulky substituents on the arene rings of the ArO group and the β-diketiminate ligand. The coordinate geometry can be best described as a distorted tetrahedron.

The average Yb−N bond distance of 2.388(4) Å is comparable with the corresponding values in complexes **4** and **5**. But these distances are apparently longer than those in $\{Yb[Me_3SiNC(C_6H_4Ph\text{-}4)CHC(C_6H_4Ph\text{-}4)NSiMe_3$-$(\mu\text{-}Li(THF))]_2\}(THF)$ and $\{Yb[Me_3SiNC(Ph)CHC(Ph)$-$NSiMe_3(\mu\text{-}Li(THF))]_2\}$, although there are two bulky β-diketiminate ligands coordinated to the central metal in the latter.[11] The β-diketiminate ligand in complex **6** is an *N*,*N′*-bonded chelate, and as expected, there is electron delocalization within the backbone of the β-diketiminate ligand. The bond distance of Yb−O(Ar) (2.179(3) Å) is slightly longer than those values found in $(ArO)_2Yb(THF)_2$ (2.137(9) Å) and $(ArO)_2Yb(Et_2O)_2$ (2.154(8) Å),[5a] and it is also slightly longer than the terminal Yb−O(Ar) bonds found in $[(ArO)Yb(\mu\text{-}OAr)]_2$ (2.10(2) and 2.08(2) Å)[19] if the effect of coordination number on ionic radii is considered.[14] It is reasonable to ascribe the difference in bond parameters among these complexes to the increased steric congestion in the former due to the replacement of one ArO group by a bulky β-diketiminate ligand. Also reflecting the sterically congested feature in complex **6**, the angle of Yb(1)−O(1)−C(1) (163.0(3)°) is smaller than those of Yb−O−C (168−171°) found for the terminal ArO ligands in $[(ArO)Yb(\mu\text{-}OAr)]_2$[19] and in $(ArO)_2Yb(Et_2O)_2$.[5a] The bond distance of O(1)−C(1) (1.343(5) Å) is apparently shorter than the single C−O bond length, reflecting substantial electron delocalization from oxygen into the aromatic ring.

To our best knowledge, complexes **4**−**6** represent the first examples of a structurally characterized mixed-ligand lanthanide(II) species containing a β-diketiminate ligand. Lappert et al. previously mentioned that YbI_2 reacted with 2 equiv of $[(Me_3Si)NC(Ph)CHC(Ph)N$-$(SiMe_3)]K$ to give a homoleptic divalent complex, but no structure was reported.[20] Recently, two ionic β-diketiminate ytterbium(II) complexes, $\{Yb[Me_3SiNC(C_6H_4Ph\text{-}4)$-$CHC(C_6H_4Ph\text{-}4)NSiMe_3(\mu\text{-}Li(THF))]_2\}(THF)$ and $\{Yb$-$[Me_3SiNC(Ph)CHC(Ph)NSiMe_3(\mu\text{-}Li(THF))]_2\}$, were reported, in which only β-diketiminate ligands coordinated to the central metal.[11]

Polymerization of MMA by Divalent Ytterbium Complexes. It has been reported that divalent lanthanocece complexes are effective single-component initiators for MMA polymerization.[15,21] To elucidate the effect of ancillary ligands on the activity of divalent lanthanide complexes, we tested the catalytic activity of complexes **4**−**6** for MMA polymerization. Preliminary results reveal that these complexes as single-component catalysts can initiate the polymerization of MMA in toluene as shown in Table 4. The conversions are in the range 78−100% at −20 °C for 0.5 h in the case of 0.5 mol % initiator concentration ([M]/[I] = 200). The polymerization of MMA with complex **4** or **6** gives a relatively high

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

Yb−N(1)	2.363(3)	Yb−C(5)	2.762(3)
Yb−N(2)	2.358(3)	Yb−C(av)	2.713(4)
Yb−O(1)	2.383(3)	N(1)−C(11)	1.319(5)
Yb−C(1)	2.731(4)	N(2)−C(13)	1.332(5)
Yb−C(2)	2.669(5)	C(11)−C(12)	1.412(5)
Yb−C(3)	2.687(5)	C(12)−C(13)	1.416(5)
Yb−C(4)	2.719(4)		
N(1)−Yb−N(2)	80.9(1)	N(1)−C(11)−C(12)	124.4(3)
N(1)−Yb−O(1)	97.6(1)	N(2)−C(13)−C(12)	124.5(3)
N(2)−Yb−O(1)	102.58(11)	C(11)−C(12)−C(13)	131.0(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 6

Yb(1)−N(1)	2.374(4)	N(1)−C(17)	1.333(6)
Yb(1)−N(2)	2.402(4)	N(2)−C(19)	1.332(5)
Yb(1)−O(1)	2.179(3)	C(17)−C(18)	1.406(6)
Yb(1)−O(2)	2.321(3)	C(18)−C(19)	1.407(6)
O(1)−C(1)	1.343(5)		
N(1)−Yb(1)−N(2)	80.97(13)	N(2)−Yb(1)−O(2)	98.94(14)
O(1)−Yb(1)−N(1)	127.24(12)	Yb(1)−O(1)−C(1)	163.0(3)
O(1)−Yb(1)−N(2)	140.30(12)	N(1)−C(17)−C(18)	125.1(4)
O(1)−Yb(1)−O(2)	100.51(13)	N(2)−C(19)−C(18)	124.7(4)
N(1)−Yb(1)−O(2)	102.39(13)	C(17)−C(18)−C(19)	131.9(4)

conversion even when using 0.2 mol % initiator concentration ([M]/[I] = 500). However, for complex **5**, the conversion is still very low even when the polymerization time is prolonged to 3 h under the same polymerization conditions. This may be attributed to the destruction of the extremely sensitive indenyl lanthanide complex by the contaminating H_2O and/or oxygen in the system.[21a] The living polymerization of MMA via divalent lanthanocenes as an initiator was previously reported.[21a] However, the polymerization in the present case is not well controlled. The polydispersity of the resultant polymers is rather broad.

The ancillary ligand has great effect on the activity of divalent lanthanide complexes for MMA polymerization. Replacing one cyclopentadienyl group by a β-diketiminate ligand results in a decrease of its activity. The conversion is as high as 95% using $(MeC_5H_4)_2$Yb(DME) as an initiator at −40 °C, and the conversion is still 70% even when the polymerization temperature is decreased to −78 °C.[15] However, complexes **4**−**6** are inactive for MMA polymerization when the polymerization temperature decreases to −40 °C under the same polymerization conditions. The tacticity of the resultant poly(MMA) was determined with reference to the reported triad.[22] The coordination environment of the catalyst also has influence on the tacticity of the resultant polymers. The atactic poly(MMA) is obtained for complexes **4**−**6**. But the highly syndiotactic poly(MMA) can be obtained using $(C_5Me_5)_2$Yb$(THF)_2$[21a] or $(MeC_5H_4)_2$Yb(DME)[15] as an initiator under the same polymerization temperature.

GPC analyses showed that the molecular weights for the polymers obtained are at least twice the values calculated depending on the molar ratio of monomer to initiator. These results support the supposition that the polymerization mechanism by divalent lanthanide complexes proceeds via the formation of a trivalent bisinitiator. The Yb(II) complex acts as a reductant and undergoes one-electron transfer to a molecule of MMA, forming a trivalent radical anion. Subsequent dimerization of the radical anions gives the final actual bisinitiator.[21b]

Conclusion

In summary, three new soluble mixed-ligand divalent ytterbium complexes supported by β-diketiminate ligands were successfully synthesized by direct reduction of the corresponding mixed-ligand trivalent ytterbium chlorides with Na/K alloy without ligand redistribution, and their crystal structures were determined. These complexes represent the first examples of a structurally characterized mixed-ligand lanthanide(II) species containing a β-diketiminate ligand. Moreover, these divalent ytterbium complexes can serve as single-component catalysts for the polymerizations of MMA.

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. Methyl methacrylate was dried over CaH_2 for 4 days and stored over 3 Å molecular sieves under argon after distillation. Anhydrous $YbCl_3$[23] and $[(DIPPh)_2nacnac]Li$[8a] were prepared according to the literature methods. $(CH_3C_5H_4)[(DIPPh)_2nacnac]YbCl$ (**1**) was prepared as previously reported.[12a] ArONa was obtained by the reaction of ArOH with sodium in THF. C_9H_7K was prepared by the reaction of C_9H_8 with potassium in THF.

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 on a Carlo Erba-1110 instrument; quoted data are the average of at least two independent determinations. The ^{1}H NMR spectra were obtained in C_6D_6 solution for lanthanide complexes and in $CDCl_3$ for polymers on a Unity Varian-400 spectrometer, and the ^{13}C NMR spectra were obtained in C_6D_6 solution on a Bruker APX-300 spectrometer. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. Molecular weight and molecular weight distributions were determined against a polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4). THF was used as an eluent at 30 °C.

$(C_9H_7)[(DIPPh)_2nacnac]YbCl$ (2). To a slurry of anhydrous $YbCl_3$ (1.63 g, 5.83 mmol) in about 40 mL of THF was slowly added a solution of $[(DIPPh)_2nacnac]Li$ (18.6 mL, 5.83 mmol) in toluene/hexane at room temperature. After $YbCl_3$ disappeared completely, a THF solution of C_9H_7K (1.14 mL, 5.83 mmol) was added slowly. The mixture was stirred at room temperature for another 48 h, and 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. Black crystals were obtained from a concentrated toluene solution at −20 °C for 4 days (3.34 g, 77.3%). Mp: 245−247 °C. Anal. Calcd for $C_{38}H_{48}ClN_2Yb$: C, 61.57; H, 6.53; N, 3.78; Yb, 23.34. Found: C, 61.33; H, 6.24; N, 3.58; Yb, 23.51. ^{1}H NMR (C_6D_6, ppm): −49.80 (s, 2H), −17.29 (t, 8H), −15.19 (d, 5H), 1.73 (m, 5H), 4.94 (s, 6H), 15.01 (s, 2H), 22.02 (d, 4H), 23.65 (s, 2H), 25.50 (t, 6H), 39.45 (d, 2H), 40.82 (s, 6H). IR (KBr, cm^{-1}): 3062(w), 2962(vs), 2928(s), 2868(s), 1622(vs), 1552(vs), 1528(vs), 1461(s), 1437(s), 1388(s), 1363-

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Table 4. Polymerization of MMA Initiated by Complexes 4, 5, and 6[a]

entry	initiator	[M]/[I]	conv (%)	$M_n \times 10^{-4}$[c]	M_w/M_n[b]	tacticity (%)		
						mm	mr	rr
1	**4**	200	78.9	6.26	3.08	24.9	41.7	33.4
2	**4**	500	74.1	6.09	3.15	31.2	47.1	21.7
3	**5**	200	78.5	5.16	2.96	12.7	27.5	59.8
4	**5**	500	0					
5[c]	**5**	500	12.7	2.39	4.42	21.5	30.9	47.6
6	**6**	200	100	5.99	2.08	12.5	23.3	64.2
7	**6**	500	63.8	3.99	2.94	14.8	26.0	59.2
8	[(DIPPh)$_2$nacnac]Li	200	0					

[a] Polymerization conditions: in toluene; −20 °C; 0.5 h; solvent/monomer = 2 (v/v). [b] Measured by GPC calibrated with standard polystyrene samples. [c] 3 h, solvent/monomer = 1 (v/v).

Table 5. Crystallographic Data for Complexes 4, 5, and 6

	4	5	6
formula	$C_{39}H_{56}N_2OYb$	$C_{42}H_{56}N_2OYb$	$C_{52}H_{80}N_2O_3Yb$
fw	741.90	777.96	954.26
T (K)	290(2)	193(2)	193(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P2_1/c$	$P\bar{1}$
a (Å)	10.198(2)	17.683(2)	9.510(4)
b (Å)	17.576(3)	11.130(1)	12.673(6)
c (Å)	20.701(4)	20.150(2)	20.547(9)
α (deg)	90	90	93.348(10)
β (deg)	90.84(2)	105.698(2)	92.645(11)
γ (deg)	90	90	96.75(2)
V (Å^3)	3710.0(12)	3817.5(7)	2451.5(19)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.328	1.353	1.293
μ (mm^{-1})	2.550	2.482	1.949
F(000)	1528	1600	1000
cryst size (mm)	0.58 × 0.48 × 0.12	0.65 × 0.45 × 0.30	0.60 × 0.30 × 0.30
θ_{max} (deg)	25.0	27.5	27.5
no. of collected reflns	7432	41 442	27 264
no. of unique reflns	6234 (R_{int} = 0.042)	9070 (R_{int} = 0.034)	11 009 (R_{int} = 0.039)
no. of obsd reflns	3939 [$I > 2.0\sigma(I)$]	7010 [$I > 2.0\sigma(I)$]	8924 [$I > 2.0\sigma(I)$]
no. of variables	408	471	603
GOF	0.842	0.97	0.99
R	0.0354	0.036	0.037
R_w	0.0698	0.051	0.047

(s), 1325(s), 1276(s), 1178(s), 1096(m), 1068(w), 1019(m), 933(m), 786(m), 759(s), 692(m).

(ArO)[(DIPPh)$_2$nacnac]YbCl(THF) (3). The synthesis of complex **3** was carried out as described for complex **2**, but a THF solution of ArONa (1.56 mmol) was used in place of the solution of C_9H_7K. Red crystals were obtained from a toluene solution (1.16 g, 81.2%). Mp: 153−156 °C (dec). Anal. Calcd for $C_{48}H_{72}ClN_2O_2Yb$: C, 62.83; H, 7.91; N, 3.05; Yb, 18.86. Found: C, 62.52; H, 7.92; N, 3.07; Yb, 18.72. ^{1}H NMR (C_6D_6, ppm): −24.67 (br, 4H), −9.96 (s, 3H), −0.82 (br, 3H), 0.93 (d, 2H), 1.25 (d, 21H), 1.42 (s, 16H), 1.59 (d, 3H), 1.71 (s, 4H), 2.29 (s, 4H), 3.03 (s, 3H), 3.35 (s, 4H), 4.92 (d, 4H), 12.54 (s, 1H). IR (KBr, cm^{-1}): 3061(w), 2960(vs), 2927(s), 2867(s), 1635(s), 1621(vs), 1550(vs), 1531(vs), 1463(s), 1439(s), 1396(m), 1362(s), 1325(s), 1277(s), 1225(m), 1175(s), 1152(m), 1120(w), 1073(w), 932(m), 865(m), 789(s), 759(s), 685(w), 642(w).

($CH_3C_5H_4$)[(DIPPh)$_2$nacnac]Yb(THF) (4). To a THF solution of ($CH_3C_5H_4$)[(DIPPh)$_2$nacnac]YbCl (2.1 g, 2.98 mmol) was added Na/K alloy in 1.2 molar ratio. The mixture was stirred at room temperature, and the color of the solution gradually changed to black. After stirring for 48 h, 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. Black crystals were obtained from a concentrated THF solution at −20 °C for a week (1.88 g, 85.0%). Mp: 188−189 °C (dec). Anal. Calcd for $C_{39}H_{56}N_2OYb$: C, 63.13; H, 7.62; N, 3.78; Yb, 23.32. Found: C, 63.05; H, 7.56; N, 3.73; Yb, 23.52. ^{1}H NMR (C_6D_6, ppm): 1.23 (d, 24H, CH_3), 1.53−1.70 (m, 10H, CH_3 and THF), 2.64 (s, 3H, CH_3), 3.07−3.54 (m, 8H, THF and CH_3CHCH_3), 4.52 (s, 1H, $CH{=}C(CH_3)N$), 5.95∼6.21 (m, 4H, $CH_3C_5H_4$), 6.52∼7.31 (m, 6H, Ph). ^{13}C NMR (C_6D_6, ppm): 23.05, 24.35, 25.01, 28.14, 32.03, 38.97, 68.56, 92.88, 94.36, 109.37, 120.05, 123.55, 124.64, 126.56, 140.94. IR (KBr, cm^{-1}): 3063(m), 2962(vs), 2868(s), 1660(m), 1623(s), 1551(s), 1515(m), 1461(s), 1436(s), 1394(s), 1363(s), 1312(m), 1256(m), 1173(m), 1107(m), 1044(m), 938(w), 784(m), 758(s). Crystals suitable for X-ray crystal structure studies were obtained by recrystallization from THF/toluene solution at −5 °C for a week.

(C_9H_7)[(DIPPh)$_2$nacnac]Yb(THF) (5). The synthesis of complex **5** was carried out as described for complex **4**, but a THF solution of **2** (1.23 g, 1.66 mmol) was used in place of the solution of **1**. Black crystals were obtained from a concentrated toluene solution at −20 °C for 4 days (1.00 g, 78.0%). Mp: 220−222 °C (dec). Anal. Calcd for $C_{42}H_{56}N_2OYb$: C, 64.83; H, 7.27; N, 3.60; Yb, 22.24. Found: C, 64.53; H, 7.19; N, 3.85; Yb, 22.45. ^{1}H NMR (C_6D_6, ppm): 1.24 (d, 24H, CH_3), 1.53−1.70 (m, 10H, CH_3 and THF), 3.07−3.54 (m, 8H, THF and CH_3CHCH_3), 4.56 (s, 1H, $CH{=}C(CH_3)N$), 6.45−7.20 (m, 13H, Ph and C_9H_7). ^{13}C NMR (C_6D_6, ppm): 20.71, 23.04, 24.45, 25.07, 28.64, 53.09, 69.75, 93.58, 94.35, 96.71, 118.09, 119.56, 120.63, 123.55, 124.73, 125.81. IR (KBr, cm^{-1}): 3061(w), 2961(vs), 2926(s), 2867(s), 1624(vs), 1552(vs), 1461(s), 1438(s), 1380(m), 1363(s), 1325(s), 1276(s), 1175(s), 1102(w), 1057(w), 1035(w), 935(m), 786(m), 757(s), 702(m). Crystals suitable for X-ray crystal structure studies were obtained by recrystallization from a toluene solution at room temperature for 3 days.

{(ArO)[(DIPPh)nacnac]Yb(THF)}(THF) (6). The synthesis of complex **6** was carried out as described for complex **4**, but a THF solution of **3** (2.50 g, 2.72 mmol) was used in place of the solution of **1**. Black crystals were obtained from a concentrated toluene solution at −20 °C for 3 days (2.18 g, 84.1%). Mp: 141 °C (dec). Anal. Calcd for $C_{52}H_{80}N_2O_3Yb$: C, 65.44; H, 8.47; N, 2.94; Yb, 18.13. Found: C, 65.28; H, 8.36; N, 2.98; Yb, 18.24. ^1H NMR (C_6D_6, ppm): 1.08−1.24 (m, 42H, CH_3), 1.53−1.70 (m, 14H, CH_3 and THF), 2.59 (s, 3H, CH_3), 3.07−3.35 (m, 12H, THF and CH_3*CH*CH_3), 4.55 (s, 1H, *CH*═C(CH_3)N), 6.00 (s, 2H, Ph), 6.82−7.31 (m, 6H, Ph).^{13}C NMR (C_6D_6, ppm): 20.73, 23.72, 24.47, 25.33, 28.39, 69.51, 93.60, 94.37, 96.71, 118.12, 119.55, 120.65, 123.36, 123.88, 124.75, 125.83. IR (KBr, cm^{-1}): 3060(w), 2961(vs), 2925(s), 2869(s), 1623(s), 1552(vs), 1531(s), 1462(s), 1437(s), 1395(m), 1363(s), 1326(s), 1275(s), 1175(m), 1065(w), 1044(m), 861(w), 789(m), 758(s). Crystals suitable for X-ray crystal structure studies were obtained by recrystallization from a THF/toluene solution at −5 °C for a few days.

Polymerization of Methyl Methacrylate Initiated by Divalent Lanthanide Complexes. A typical example of polymerization is given. To a toluene solution (1 mL) of methyl methacrylate (1 mL, 9.35 mmol) was added at once a toluene solution (1 mL) of complex **4**, **5**, or **6** (0.0467 mmol) with vigorous magnetic stirring at the desired temperature. After the polymerization was carried out for a fixed time, 5 mL of ethanol containing 2% HCl solution was added to terminate the reaction, and then the viscous solution mixture was poured into a large excess of petroleum ether to induce the precipitation of the polymer. The polymer was washed with petroleum ether three times and dried at 30 °C in a vacuum.

X-ray Structure Determination. Suitable single crystals of complexes **4**, **5**, and **6** were each 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 (for **4**) or a Rigaku Mercury CCD in $\omega-2\theta$ (for **5** and **6**) using Mo Kα radiation (λ = 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 5.

The crystal structures of these complexes were solved by direct methods 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 **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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