

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

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Three divalent ytterbium complexes supported by a β -diketiminato ligand were synthesized for the first time. The mixed-ligand ytterbium chlorides $(\text{CH}_3\text{C}_5\text{H}_4)[(\text{DIPPh})_2\text{nacnac}]\text{YbCl}$ (**1**), $(\text{C}_9\text{H}_7)[(\text{DIPPh})_2\text{nacnac}]\text{YbCl}$ (**2**), and $(\text{ArO})[(\text{DIPPh})_2\text{nacnac}]\text{YbCl}(\text{THF})$ (**3**) ($(\text{DIPPh})_2\text{nacnac} = N,N$ -diisopropylphenyl-2, 4-pentanediiimine anion, $\text{ArO} = 2,6$ -di-*tert*-butyl-4-methylphenoxo), which were obtained in high yield by using $[(\text{DIPPh})_2\text{nacnac}]\text{YbCl}_2(\text{THF})_2$ as precursor, were reduced by Na/K alloy in THF to afford the corresponding divalent species $(\text{CH}_3\text{C}_5\text{H}_4)[(\text{DIPPh})_2\text{nacnac}]\text{Yb}(\text{THF})$ (**4**), $(\text{C}_9\text{H}_7)[(\text{DIPPh})_2\text{nacnac}]\text{Yb}(\text{THF})$ (**5**), and $\{(\text{ArO})[(\text{DIPPh})_2\text{nacnac}]\text{Yb}(\text{THF})\}(\text{THF})$ (**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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(1) For reviews, see: (a) Evans, W. J. *Polyhedron* **1987**, *6*, 803. (b) Evans, W. J. *Coord. Chem. Rev.* **2000**, *206*, 263. (c) Evans, W. J. *J. Organomet. Chem.* **2002**, *647*, 2. (d) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119.

(2) (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285. (b) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915. (c) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330. (d) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 4011. (e) Apostolidis, C.; Deacon, G. B.; Dornberger, E.; Edelmann, F. T.; Kanellakopulos, B.; MacKinnon, P.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1997**, 1047. (f) Schultz, M.; Burns, C. J.; Schwartz, D. J.; Andersen, R. A. *Organometallics* **2000**, *19*, 781. (g) Fedushkin, I. L.; Dechert, S.; Schumann, H. *Organometallics* **2000**, *19*, 4066. (h) Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 460.

(3) (a) Evans, W. J.; Gummersheimer, T. S.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1998**, *17*, 284. (b) Khvostov, A. V.; Bulychiev, B. M.; Belsky, V. K.; Sizov, A. I. *J. Organomet. Chem.* **1999**, *584*, 164. (c) Qian, C.; Li, H.; Sun, J.; Nie, W. *J. Organomet. Chem.* **1999**, *585*, 59. (d) Qi, M. H.; Shen, Q.; Gong, X. Q.; Shen, Z. Q.; Weng, L. H. *Chin. J. Chem.* **2002**, *20*, 564. (e) Sheng, E. H.; Wang, S. W.; Yang, G. S.; Zhou, S. L.; Cheng, L.; Zhang, K. H.; Huang, Z. X. *Organometallics* **2003**, *22*, 684.

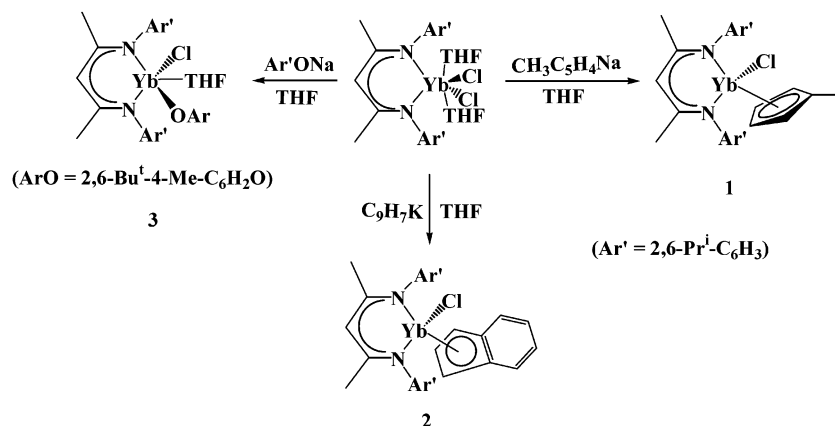
(4) (a) Trifonov, A. A.; Kirillov, E. N.; Fischer, A.; Edelmann, F. T.; Bochkarev, M. N. *J. Chem. Soc., Chem. Commun.* **1999**, 2203. (b) Hou, Z.; Koizumi, T.; Nishiura, M.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 3323. (c) Tardif, O.; Hou, Z.; Nishiura, M.; Koizumi, T.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 4565. (d) Giesbrecht, G. R.; Cui, C. M.; Shafir, A.; Schmidt, J. A. R.; Arnold, J. *Organometallics* **2002**, *21*, 3841. (e) Arndt, S.; Spaniol, T. P.; Okuda, J. *Organometallics* **2003**, *22*, 775.

(5) (a) Deacon, G. B.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; MacKinnon, P.; Newnham, R. H. *J. Chem. Soc., Chem. Commun.* **1989**, 935. (b) Hou, Z.; Yamazaki, H.; Kobayashi, K.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1992**, 722. (c) Evans, W. J.; Anwender, R.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5. (d) Evans, W. J.; Greci, M. A.; Ziller, J. W. *J. Chem. Soc., Dalton Trans.* **1997**, 3035. (e) Nishiura, M.; Hou, Z.; Koizumi, T.; Imamoto, T.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 8245. (f) Yao, Y. M.; Shen, Q.; Zhang, Y.; Xue, M. Q.; Sun, J. *Polyhedron* **2001**, *20*, 3201.

(6) (a) Corradi, M. M.; Frankland, A. D.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2323. (b) Hou, Z.; Zhang, Y.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963. (c) Hou, Z.; Tezuka, H.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Macromolecules* **1998**, *31*, 8650. (d) Hou, Z.; Zhang, Y.; Tezuka, H.; Xie, P.; Tardif, O.; Koizumi, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10533. (e) Hou, Z.; Zhang, Y.; Tardif, O.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9216. (f) Evans, W. J.; Zucchi, G.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 10. (g) Hou, Z.; Zhang, Y.; Nishiura, M.; Wakatsuki, Y. *Organometallics* **2003**, *22*, 129.

(7) (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031. (b) Panda, A.; Stender, M.; Wright, R.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909. (c) Harder, S. *Organometallics* **2002**, *21*, 3782. (d) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307. (e) Yu, R. C.; Hung, C. H.; Huang, J. H.; Lee, H. Y.; Chen, J. T. *Inorg. Chem.* **2002**, *41*, 6450. (f) Rieth, L. R.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 15239.

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 ethylene⁸ and lactide⁹ 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 -diketimate ligands¹² and find that the bulky β -diketimate group (DIPPh)₂nacnac ((DIPPh)₂nacnac = *N,N*-2,6-diisopropylphenyl-2,4-pentanedimine 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 -Diketimate Complexes. We previously reported that the bulky β -diketimate [(DIPPh)₂nacnac][−] is an ideal ligand for synthesis of the mixed-ligand trivalent lanthanide derivatives, and (CH₃C₅H₄)[(DIPPh)₂nacnac]YbCl (**1**) can be conveniently synthesized in high yield using [(DIPPh)₂nacnac]YbCl₂(THF)₂ as precursor.^{12a} Thus, freshly prepared [(DIPPh)₂nacnac]YbCl₂(THF)₂ in situ was used to synthesize the β -diketimate ytterbium derivatives. [(DIPPh)₂nacnac]YbCl₂ reacted with 1 equiv of C₉H₇K in THF; after workup, the black microcrystals were obtained as final products which were identified to be (C₉H₇)[(DIPPh)₂nacnac]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)₂nacnac]YbCl₂ 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)₂nacnac]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 -Diketimate 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 -diketimate ytterbium complexes (CH₃C₅H₄)[(DIPPh)₂nacnac]Yb(THF) (**4**), (C₉H₇)[(DIPPh)₂nacnac]Yb(THF) (**5**), and {(ArO)[(DIPPh)₂nacnac]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, [(C₉H₇)YbI(DME)₂], in the literature,¹³ and complex **5** is the second one.

(8) (a) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514. (b) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161. (c) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895. (d) MacAdams, L. A.; Kim, W. K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952. (e) Hayes, P. G.; Piers, W. E.; McDonald, R. J. *Am. Chem. Chem.* **2002**, *124*, 2132.

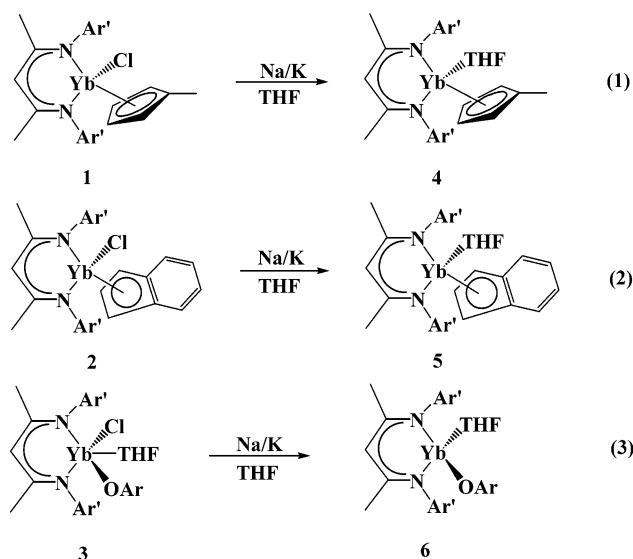
(9) (a) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583. (b) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 283. (c) Chisholm, M. H.; Huffman, J. C.; Phomphrai, K. *J. Chem. Soc., Dalton Trans.* **2001**, 222. (d) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Oviatt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (e) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785.

(10) (a) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018. (b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738. (c) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284. (d) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599. (e) Eberhardt, R.; Allmendinger, M.; Luinstra, G. A.; Rieger, B. *Organometallics* **2003**, *22*, 211.

(11) Avent, A. G.; Khvostov, A. V.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **2002**, 1410.

(12) (a) Yao, Y. M.; Zhang, Y.; Shen, Q.; Yu, K. B. *Organometallics* **2002**, *21*, 819. (b) Yao, Y. M.; Luo, Y. J.; Jiao, R.; Shen, Q.; Yu, K. B.; Weng, L. H. *Polyhedron* **2003**, *22*, 441.

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 -diketiminato ligand. The diamagnetic nature of divalent Yb allowed characterization of these complexes by NMR spectroscopy. The structural analyses reveal that the β -diketiminato acts as a monoanionic spectator ligand in these divalent ytterbium complexes (see below). This is quite different from those in $\{\text{Yb}[\text{Me}_3\text{SiNC}(\text{C}_6\text{H}_4\text{Ph}-4)\text{CHC}(\text{C}_6\text{H}_4\text{Ph}-4)\text{NSiMe}_3(\mu\text{-Li}(\text{THF}))_2](\text{THF})\}$ and $\{\text{Yb}[\text{Me}_3\text{SiNC}(\text{Ph})\text{CHC}(\text{Ph})\text{NSiMe}_3(\mu\text{-Li}(\text{THF}))_2]\}$, in which the β -diketiminates act as dianionic ligands, although they are also obtained by the reduction of trivalent β -diketiminato 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 -diketiminato 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 -diketiminato 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 -diketiminato ligand, and the β -diketiminato ligand adopts an η^2 -coordination mode, while the β -diketiminato ligand adopts an η^4 -coordina-

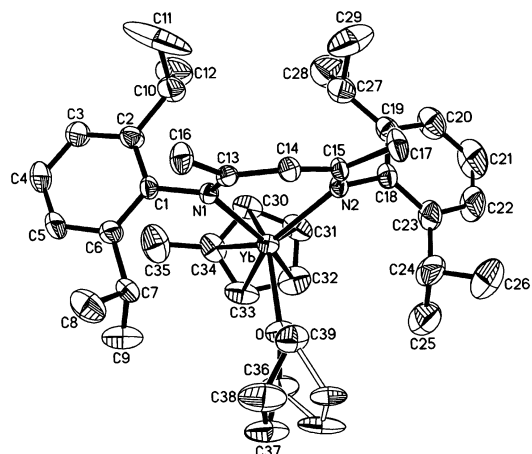


Figure 1. Molecular structure of complex **4** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clarity). Each disordered THF ligand is shown in two possible orientations.

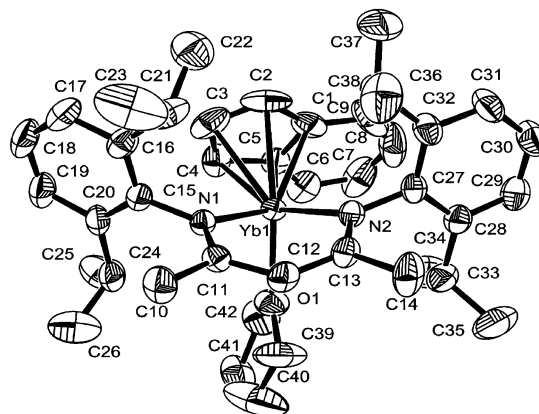


Figure 2. Molecular structure of complex **5** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clarity).

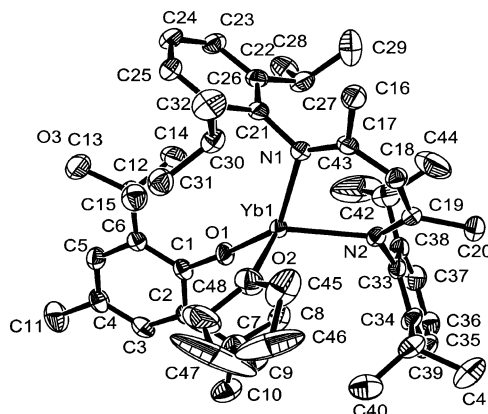


Figure 3. Molecular structure of complex **6** drawn with 50% probability ellipsoids (hydrogen atoms omitted for clarity).

tion mode in complex **1**.^{12a} This is also different from those in $\{\text{Yb}[\text{Me}_3\text{SiNC}(\text{C}_6\text{H}_4\text{Ph}-4)\text{CHC}(\text{C}_6\text{H}_4\text{Ph}-4)\text{NSiMe}_3(\mu\text{-Li}(\text{THF}))_2](\text{THF})\}$ and $\{\text{Yb}[\text{Me}_3\text{SiNC}(\text{Ph})\text{CHC}(\text{Ph})\text{NSiMe}_3(\mu\text{-Li}(\text{THF}))_2]\}$, in which the β -diketiminato ligands can be regarded as being η^5 -bonded to the central metal.¹¹ The bond distances within the backbone of the β -diketiminato ligand fall in the range of corresponding distances of single and double bonds, which

(13) Trifonov, A. A.; Kirillov, E. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2001**, 3055.

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 -diketiminato lanthanide complexes.

The β -diketiminato 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 (CH₃C₅H₄)₂Yb(DME)¹⁵ and [(CH₃C₅H₄)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 $\Delta M-C$,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(CH₂CH₂C₉H₆)₂]-YbN(SiMe₃)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 -diketiminato ligands. This complex has a low coordination number, and the central ytterbium atom is four-coordinated by two nitrogen atoms from the β -diketiminato 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 -diketiminato ligand. The coordination 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[Me₃SiNC(C₆H₄Ph-4)CHC(C₆H₄Ph-4)NSiMe₃(μ -Li(THF))]₂}(THF) and {Yb[Me₃SiNC(Ph)CHC(Ph)NSiMe₃(μ -Li(THF))]₂}, although there are two bulky β -diketiminato ligands coordinated to the central metal in the latter.¹¹ The β -diketiminato ligand in complex **6** is an *N,N*-bonded chelate, and as expected, there is electron delocalization within the backbone of the β -diketiminato 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(Et₂O)₂ (2.154(8) Å),^{5a} and it is also slightly longer than the terminal Yb–O(Ar) bonds found in [(ArO)Yb(μ -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 -diketiminato 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(μ -OAr)]₂¹⁹ and in (ArO)₂Yb(Et₂O)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 -diketiminato ligand. Lappert et al. previously mentioned that YbI₂ reacted with 2 equiv of [(Me₃Si)NC(Ph)CHC(Ph)N(SiMe₃)]K to give a homoleptic divalent complex, but no structure was reported.²⁰ Recently, two ionic β -diketiminato ytterbium(II) complexes, {Yb[Me₃SiNC(C₆H₄Ph-4)CHC(C₆H₄Ph-4)NSiMe₃(μ -Li(THF))]₂}(THF) and {Yb[Me₃SiNC(Ph)CHC(Ph)NSiMe₃(μ -Li(THF))]₂}, were reported, in which only β -diketiminato ligands coordinated to the central metal.¹¹

Polymerization of MMA by Divalent Ytterbium Complexes. It has been reported that divalent lanthanocene 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

(14) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, 32, 751.

(15) Jiang, T.; Shen, Q.; Lin, Y. H.; Jin, S. C. *J. Organomet. Chem.* **1993**, 450, 121.

(16) Zinnen, H. A.; Pluth, J. T.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810.

(17) (a) $\Delta M-C = 1/2[(Yb-C1 + Yb-C5) - (Yb-C2 + Yb-C4)]$; $\Delta M-C$ values close to zero indicate little distortion from η^5 hapticity, whereas values above ca. 0.5 Å indicate nearly η^3 hapticity (ref 17b). (b) Westcott, S. A.; Kakkar, A.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, 394, 777.

(18) Qian, C. T.; Zou, G.; Chen, Y. F.; Sun, J. *Organometallics* **2001**, 20, 3106.

(19) van den Hende, J.; Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1995**, 1435.

(20) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2691.

(21) (a) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyaki, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, 26, 7134. (b) Boffa, L. S.; Novak, B. M. *Macromolecules* **1994**, 27, 6993.

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 $(MeC_5H_4)_2Yb(DME)$ as an initiator at $-40^\circ C$, and the conversion is still 70% even when the polymerization temperature is decreased to $-78^\circ C$.¹⁵ However, complexes **4–6** are inactive for MMA polymerization when the polymerization temperature decreases to $-40^\circ C$ 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 $(C_5Me_5)_2Yb(THF)_2$ ^{21a} or $(MeC_5H_4)_2Yb(DME)$ 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 1H 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 $30^\circ C$.

$(C_9H_7)[(DIPPh)_2nacnac]YbCl$ (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 $-20^\circ C$ for 4 days (3.34 g, 77.3%). Mp: $245–247^\circ C$. 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. 1H 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}): $3062(w)$, $2962(vs)$, $2928(s)$, $2868(s)$, $1622(vs)$, $1552(vs)$, $1528(vs)$, $1461(s)$, $1437(s)$, $1388(s)$, $1363-$

(22) Ferugusan, R. C.; Overnall, D. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, 26, 182.

(23) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, 24, 387.

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 ₂ OYb	C ₄₂ H ₅₆ N ₂ OYb	C ₅₂ H ₈₀ N ₂ O ₃ Yb
fw	741.90	777.96	954.26
<i>T</i> (K)	290(2)	193(2)	193(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.198(2)	17.683(2)	9.510(4)
<i>b</i> (Å)	17.576(3)	11.130(1)	12.673(6)
<i>c</i> (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)
<i>V</i> (Å ³)	3710.0(12)	3817.5(7)	2451.5(19)
<i>Z</i>	4	4	2
<i>D</i> _{calcd} (g cm ⁻³)	1.328	1.353	1.293
μ (mm ⁻¹)	2.550	2.482	1.949
<i>F</i> (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 (<i>R</i> _{int} = 0.042)	9070 (<i>R</i> _{int} = 0.034)	11 009 (<i>R</i> _{int} = 0.039)
no. of obsd reflns	3939 [<i>I</i> > 2.0σ(<i>I</i>)]	7010 [<i>I</i> > 2.0σ(<i>I</i>)]	8924 [<i>I</i> > 2.0σ(<i>I</i>)]
no. of variables	408	471	603
GOF	0.842	0.97	0.99
<i>R</i>	0.0354	0.036	0.037
<i>R</i> _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)₂nacnac]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 C₉H₇K. Red crystals were obtained from a toluene solution (1.16 g, 81.2%). Mp: 153–156 °C (dec). Anal. Calcd for C₄₈H₇₂ClN₂O₂Yb: 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. ¹H NMR (C₆D₆, 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).

(CH₃C₅H₄)[(DIPPh)₂nacnac]Yb(THF) (4). To a THF solution of (CH₃C₅H₄)[(DIPPh)₂nacnac]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 C₃₉H₅₆N₂OYb: 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. ¹H NMR (C₆D₆, ppm): 1.23 (d, 24H, CH₃), 1.53–1.70 (m, 10H, CH₃ and THF), 2.64 (s, 3H, CH₃),

3.07–3.54 (m, 8H, THF and CH₃CHCH₃), 4.52 (s, 1H, CH=C(CH₃)N), 5.95–6.21 (m, 4H, CH₃C₅H₄), 6.52–7.31 (m, 6H, Ph). ¹³C NMR (C₆D₆, 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.

(C₉H₇)[(DIPPh)₂nacnac]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 C₄₂H₅₆N₂OYb: 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. ¹H NMR (C₆D₆, ppm): 1.24 (d, 24H, CH₃), 1.53–1.70 (m, 10H, CH₃ and THF), 3.07–3.54 (m, 8H, THF and CH₃CHCH₃), 4.56 (s, 1H, CH=C(CH₃)N), 6.45–7.20 (m, 13H, Ph and C₉H₇). ¹³C NMR (C₆D₆, 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)₂nacnac]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 $-20\text{ }^{\circ}\text{C}$ for 3 days (2.18 g, 84.1%). Mp: $141\text{ }^{\circ}\text{C}$ (dec). Anal. Calcd for $\text{C}_{52}\text{H}_{80}\text{N}_2\text{O}_3\text{Yb}$: 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_3CHCH_3), 4.55 (s, 1H, $\text{CH}=\text{C}(\text{CH}_3)\text{N}$), 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 $-5\text{ }^{\circ}\text{C}$ 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 $30\text{ }^{\circ}\text{C}$ 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 $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). 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 \AA), 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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