ORGANOMETALLICS
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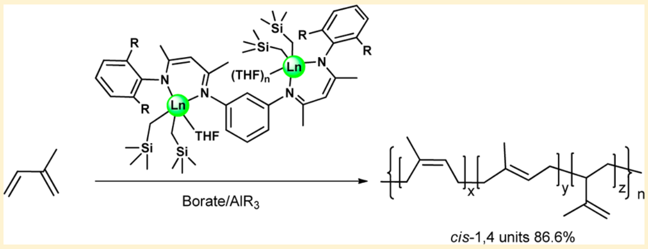
Binuclear Rare-Earth-Metal Alkyl Complexes Ligated by Phenylene-Bridged β-Diketiminate Ligands: Synthesis, Characterization, and Catalysis toward Isoprene Polymerization

Lei Li,[†,‡] Chunji Wu,[†] Dongtao Liu,[†] Shihui Li,*[,†] and Dongmei Cui*[,†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

[‡]Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

S *Supporting Information*



ABSTRACT: Deprotonation of *m*-phenylene-bridged bis(β-diketiminate) ligands ($\mathrm{PBDI}^{i\mathrm{Pr}}$-$\mathrm{H_2}$ = [2,6-$^i\mathrm{Pr_2C_6H_3NHC(Me)C(H)C(Me)N}]_2$-(*m*-phenylene); $\mathrm{PBDI}^{\mathrm{Et}}$-$\mathrm{H_2}$ = $[2,6\text{-}\mathrm{Et_2C_6H_3NHC(Me)C(H)C(Me)N}]_2$-(*m*-phenylene); $\mathrm{PBDI}^{\mathrm{Me}}$-$\mathrm{H_2}$ = $[2,6\text{-}\mathrm{Me_2C_6H_3NHC(Me)C(H)C(Me)N}]_2$-(*m*-phenylene)) by rare-earth-metal tris(alkyls) $\mathrm{Ln(CH_2SiMe_3)_3(THF)_2}$ (Ln = Y, Lu, Sc) gave a series of rare-earth-metal bis(alkyl) complexes: $\mathrm{PBDI}^{i\mathrm{Pr}}$-$\mathrm{[Y(CH_2SiMe_3)_2]_2(THF)_2}$ (**1**), $\mathrm{PBDI}^{\mathrm{Et}}$-$\mathrm{[Ln(CH_2SiMe_3)_2]_2(THF)}_n$ (**2a**, Ln = Y, *n* = 2; **2b**, Ln = Lu, *n* = 2; **2c**, Ln = Sc, *n* = 1), and $\mathrm{PBDI}^{\mathrm{Me}}$-$\mathrm{[Y(CH_2SiMe_3)_2]_2(THF)_2}$ (**3**). All these complexes were fully characterized by NMR spectroscopy, X-ray diffraction, and elemental analyses, adopting binuclear structures with the two rare-earth-metal ions taking *trans* positions versus the phenyl ring. Complexes **1**, **2a**,**b**, and **3** coordinate two solvated THF molecules, while the scandium complex **2c** incorporates only one THF molecule, owing to the steric crowding. Upon activation with 2 equiv of organoborate, the yttrium systems showed higher catalytic activity toward isoprene polymerization in comparison to those based on lutetium, and the scandium system was less active. Addition of aluminum alkyls to the above binary systems accelerated dramatically the polymerization rate irrespective of the central metal type through scavenging impurities in the systems and abstracting the solvated THF molecules in the precursors. The resultant polyisoprene had higher 3,4-regularity (20% vs 5%) as well as higher molecular weights in comparison with the mononuclear systems, which might be attributed to the steric bulky effect of the binuclear systems.

■ INTRODUCTION

Due to the unique reactivities and selectivities of multinuclear metalloenzymes, bi- or oligonuclear organometallic complexes have obtained increasing attention, which are anticipated to lead to unique substrate activation modes and to novel reactivity patterns on the basis of the possible cooperative effects between adjacent active metal centers. Recent years have witnessed an impressive progress in the development of binuclear olefin polymerization catalysts.[1] Marks and coworkers reported that phenylene-, siloxane-, and polymethylene-linked metallocene and half-metallocene early-transition-metal binuclear complexes can provide higher molecular weight and short branch polyolefins and incorporate more comonomer or bulkier α-olefins in the copolymerization with ethylene versus their monometallic counterparts.[2] Salata and Marks reported that the linked phenoxyiminato Ti and Zr complexes gave an activity ~8× that of mononuclear catalysts for ethylene polymerization and enhanced α-olefin enchainment.[3] Solan's group synthesized bis(imino)pyridine Ni(II) complexes as ethylene oligomerization catalysts,[4] while binuclear phenoxyiminato catalysts with different types of linkages have also been reported, albeit with lower activity in comparison with the mononuclear Grubbs catalysts.[5] Baar et al. prepared the linked pyridylimine binuclear Pd(II) complexes, in which the two Pd centers appeared to act essentially independently and exhibited the same activity and stereoregulation as the mononuclear analogues.[6] Pd(II) derivatives bearing pyrazole-based dinucleating ligands with appended imine functions were synthesized by Meyer, displaying performances rather similar to those of the Brookhart α-diimine catalysts.[7] Casalino designed a Pd(II) binuclear complex employing a bis-chelating ligand based on the [1,4]dioxocino[6,5-*b*:7,8-*b*′]dipyridine moiety, which was active for alternating styrene and CO copolymerization.[8] The binuclear phenoxyiminato Ni catalysts generally exhibit higher thermal stability due to the increased steric congestion around the metal centers.[9] Those having electron-withdrawing groups developed by Wehrmann and Mecking[10] gave higher activity, which was attributed to an intrinsically higher rate of propagation rather than a more efficient activation of the catalyst precursor (pyridine dissociation). Agapie reported that the *syn* late-transition-metal nickel binuclear complex bearing

Received: February 7, 2013

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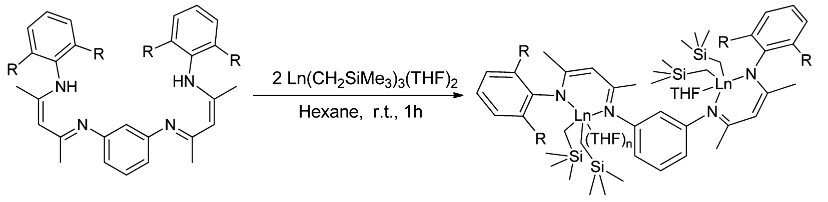
Scheme 1. Syntheses of Bimetallic Complexes 1−3



PBDI^{iPr}-H$_2$: R = ^{i}Pr
PBDI^{Et}-H$_2$: R = Et
PBDI^{Me}-H$_2$: R = Me

R = ^{i}Pr: Ln = Y (**1**, n = 1)
R = Et: Ln = Y (**2a**, n = 1), Ln = Lu (**2b**, n = 1), Ln = Sc (**2c**, n = 0)
R = Me: Ln = Y (**3**, n = 1)

the terphenyl ligand appended with phenoxy and imine donors was more durable to amines than its *anti* isomer and the monomeric counterparts, thus providing solid proof for the cooperative effect of the proximity of the two metal ions.[11] In contrast, reports about rare-earth-metal-based binuclear complexes are scarce and their catalytic behavior has been less explored.[12]

On the other hand, increasing efforts have been devoted to the design of more efficient catalysts for the polymerization of 1,3-conjugated dienes with desired microstructures and properties to afford polyisoprene/polybutadiene, among the most significant and widely used rubbers.[13] The homogeneous rare-earth-metal-based catalytic systems have been demonstrated to be superior by providing high *cis*-1,4, *trans*-1,4 ,or 3,4- (1,2-) regulated polydienes depending on the ancillary ligand frameworks and metal ionic radii; thus, the lanthanocene aluminates and the alkyl-bridged lanthanide carboxylates, monocyclopentadienyl (Cp) rare-earth-metal complexes, and NCN and NPN multidentate non-Cp rare-earth-metal complexes have been reported.[14−18] Despite the significant achievements obtained to date, few reports have been related to employing rare-earth-metal binuclear precursors.[19]

Our group has been pursuing the exploration of new ancillary ligands to support rare-earth-metal cationic active species for specific selective (co)polymerizations of the conjugated dienes to access polydiene materials with tailor-made microstructures.[13e,15f,i,l,n−q] Among these ligands, β-diketiminates can be prepared swiftly and modified easily, although the attached rare-earth-metal complexes are not as stable during the generation of active species.[15m] Herein, we wish to report that *m*-phenylene-bridged bis(β-diketiminates), initially employed by Harder et al. to stabilize zinc bimetallic moieties to initiate expoxide and CO_2 copolymerization,[20] were used for the first time to stabilize rare-earth-metal bis(alkyl) species. Moreover, their catalytic performances under the proper activation of aluminum alkyls and organoborate for isoprene polymerization were also examined.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of β-Diketiminato Binuclear Complexes. To construct the binuclear structure envisioned above, bis(β-diketiminate) ligands with the different substituents PBDI^{iPr}-H$_2$, PBDI^{Et}-H$_2$ and PBDI^{Me}-H$_2$ were prepared by following a modified literature procedure.[20] Metalation of these ligands by a 2-fold molar mass of $Y(CH_2SiMe_3)_3(THF)_2$ was carried out readily at room temperature to afford the corresponding bis(alkyl) complexes PBDI^{iPr}-$[Y(CH_2SiMe_3)_2]_2(THF)_2$ (**1**), PBDI^{Et}-$[Y(CH_2SiMe_3)_2]_2(THF)_2$ (**2a**), and PBDI^{Me}-$[Y(CH_2SiMe_3)_2]_2(THF)_2$ (**3**) in good yields (Scheme 1). Treatment of $Lu(CH_2SiMe_3)_3(THF)_2$ and $Sc(CH_2SiMe_3)_3(THF)_2$ with PBDI^{Et}-H$_2$ gave the lutetium and scandium analogues PBDI^{Et}-$[Lu(CH_2SiMe_3)_2]_2(THF)_2$ (**2b**) and PBDI^{Et}-$[Sc(CH_2SiMe_3)_2]_2(THF)$ (**2c**), respectively. ^{1}H NMR spectroscopic analysis revealed that complexes **1**−**3** show similar resonance topologies. No amino proton resonances (δ 13.19, 12.59, 12.52) from the ligands are observed, suggesting the completeness of the reaction; the yttrium methylene groups $Y{-}CH_2SiMe_3$ appear as a doublet due to yttrium and hydrogen coupling around δ −0.50 ($^2J_{Y-H}$ = 2.8 Hz) for **1**, δ −0.49 ($^2J_{Y-H}$ = 2.0 Hz) for **2a**, and δ −0.48 ($^2J_{Y-H}$ = 2.8 Hz) for **3**; the lutetium methylene groups $Lu{-}CH_2SiMe_3$ in **2b** and the scandium methylene groups $Sc{-}CH_2SiMe_3$ in **2c** give singlet resonances. Meanwhile the phenylene-bridged bis(β-diketiminato) backbones display a similar unitary set of resonances in all these complexes, and the alkyl substituents on the N-aryl rings are nearly indistinguishable, implying rapid rotation and ring flip of the β-diketiminato backbones and the symmetric molecular structures in the solution state. The solid-state structures of complexes **1**−**3** were established by single-crystal X-ray diffraction analysis, as shown in Figures 1 and 2 for complexes **1** and **2c** (Figures S1−S3 (Supporting Information) for **2a**,**b** and **3**, respectively). All of these complexes are analogous, adopting binuclear structures. For the yttrium and lutetium complexes, each metal ion bonds to a N,N-chelating β-

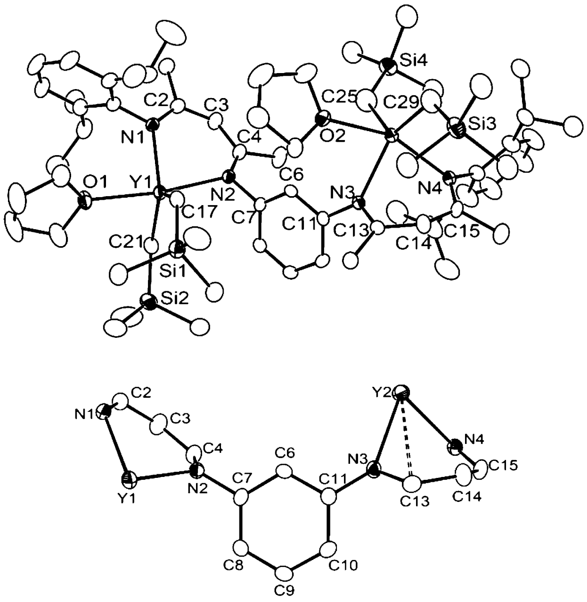


Figure 1. (top) X-ray structure of complex **1** with 30% probability thermal ellipsoids. Hydrogen atoms and solvents are omitted for clarity. (bottom) Asymmetric structure of the two β-diketiminato backbones linked by a phenylene ring in **1**.

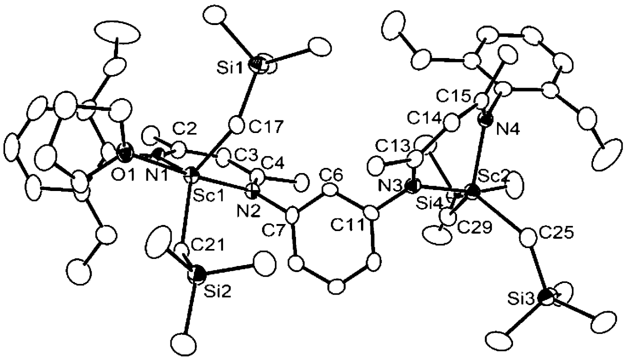


Figure 2. X-ray structure of complex **2c** with 30% probability thermal ellipsoids. Hydrogen atoms and solvents are omitted for clarity.

diketiminate unit, two alkyl moieties, and a THF molecule, generating a trigonal-bipyramidal geometry similar to that in the mononuclear complexes.[15m,21] Thus, typical bond lengths and bond angles around the metal centers in the binuclear complex **3** are comparable to those found in the mononuclear counterpart **4** (Chart 1)[15m] (average Y(1)−N = 2.361 Å and average Y(2)−N = 2.341 Å vs average Y−N = 2.369 Å; average Y(1)−C = 2.398 Å and average Y(2)−C = 2.392 Å vs average Y−C = 2.384 Å; N−Y(1)−N = 79.13(13)° and N−Y(2)−N = 77.50(14)° vs N−Y−N = 77.52(10)°; C−Y(1)−C = 113.89(1)° and C−Y(2)−C = 110.74(1)° vs C−Y−C = 112.59(13)°). The two *β*-diketiminato−metal units take *trans* positions against the phenyl plane due to the steric repulsion of the four alkyl moieties (Figure 1, bottom). Interestingly, the precise coordination geometries around the two metal centers are quite different. For Ln(1) the five atoms on the *β*-diketiminate unit are virtually coplanar (the largest deviations from the NCCCN plane defined by these atoms are 0.069, 0.021, 0.019, and 0.051 Å for **1**, **2a**,**b**, and **3**, respectively), while for Ln(2) the *β*-diketiminato backbone is highly distorted (the largest deviations from the plane are 0.157, 0.101, 0.07, and 0.099 Å for **1**, **2a**,**b**, and **3**, respectively). Furthermore, the metal ions coordinate to the *β*-diketiminate units in different fashions, as evidenced by the fact that Ln(1) sits slightly out of the NCCCN plane (0.685, 0.192, 0.310, and 0.457 Å for **1**, **2a**,**b**, and **3**, respectively), rendering it coordinated edge-on, while Ln(2) is situated significantly out of the plane (1.717, 0.917, 0.985, and 1.045 Å for **1**, **2a**,**b**, and **3**, respectively), resulting in its face-on coordination (Table S1 (Supporting Information)). It deserves special comment that the large displacement off the backbone plane in **1** is rarely seen in *β*-diketiminato lanthanide complexes,[22] which might be attributed to the most sterically encumbered substituents on the ancillary ligand in complex **1** among the series. These geometry characteristics are reflected by the corresponding bond lengths and bond angles. In complex **1**, the N(1)−C(2) (1.336(7) Å), C(2)−C(3) (1.393(7) Å), C(3)−C(4) (1.395(7) Å), and N(2)−C(4)

Chart 1

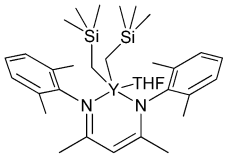


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Table 1. Polymerization of Isoprene by Using Various Catalyst Systems[a]

run	cat.	[AlR$_3$]/ [cat.]	[B]/ [cat.][b]	time (min)	yield (%)	microstructure[c] (%) *cis*-1,4	*trans*-1,4	3,4-	M_n(th)[d] (×10^4)	M_n(exp)[e] (×10^4)	M_w/M_n[e]
1	**1**−**3**[f]	10 (^{i}Bu)	0	600	trace						
2	**1**−**3**[f]	0	1 (TB)	600	trace						
3	**1**	0	2 (TB)	200	100	86.6	0.3	13.1	3.4	21.3	1.3
4	**2a**	0	2 (TB)	200	100	83.5	2.6	13.9	3.4	19.9	1.3
5	**2b**	0	2 (TB)	200	88.6	76.5	2.4	21.1	3.0	41.3	1.8
6	**2c**	0	2 (TB)	200	41.1	70.6	4.7	24.7	1.4	4.7	1.2
7	**3**	0	2 (TB)	200	100	83.2	1.3	15.5	3.4	22.3	1.3
8	**1**	10 (^{i}Bu)	1 (TB)	10	100	84.1	1.1	14.8	6.8	17.5	1.9
9	**1**	10 (^{i}Bu)	2 (TB)	5	100	83.5	0.8	15.7	3.4	13.1	1.4
10	**1**	10 (^{i}Bu)	3 (TB)	10	100	82.3	1.0	16.7	6.8	23.1	2.0
11[g]	**1**	10 (^{i}Bu)	2 (TB)	5	100	83.1	1.0	15.9	3.4	10.8	1.6
12	**2a**	10 (^{i}Bu)	2 (TB)	5	100	78.3	1.1	20.6	3.4	15.1	1.5
13	**2b**	10 (^{i}Bu)	2 (TB)	5	100	71.6	2.9	25.5	3.4	15.2	1.6
14	**2c**	10 (^{i}Bu)	2 (TB)	5	100	70.1	3.0	26.9	3.4	12.9	1.6
15	**3**	10 (^{i}Bu)	2 (TB)	5	100	79.7	1.1	19.2	3.4	14.1	2.2
16[h]	**4**	5 (^{i}Bu)	1 (TB)	5	100	94.1	2.2	3.7	3.4	6.4	1.4
17[h]	**4**	10 (^{i}Bu)	1 (HNB)	5	60	96.3	0.5	3.2	2.0	4.2	2.1
18	**1**	20 (^{i}Bu)	2 (TB)	5	100	83.5	1.0	15.5	3.4	9.9	1.6
19	**1**	40 (^{i}Bu)	2 (TB)	5	100	83.2	1.1	15.7	3.4	9.4	1.7
20	**1**	10 (Me)	2 (TB)	5	10.4	83.9	3.5	12.6	0.35	14.5	2.0
21	**1**	10 (Et)	2 (TB)	5	100	83.3	1.8	14.9	3.4	11.4	1.6
22	**1**	10 (^{i}Bu)	2 (HNB)	5	100	82.8	1.1	16.1	3.4	34.3	1.6

[a]Polymerization conditions: 10 °C; toluene (5.0 mL); cat. (10 μmol); [IP]/[cat.] = 1000. [b]Abbreviations: TB, $[Ph_3C][B(C_6F_5)_4]$; HNB, $[PhNHMe_2][B(C_6F_5)_4]$. [c]Determined by ^{1}H NMR and ^{13}C NMR spectroscopy in $CDCl_3$. [d]M_n(th) = 1000 × ([cat.]/[B]) × yield × 68. [e]Determined by GPC in THF at 40 °C against a polystyrene standard. [f]Polymerization performed at 60 °C. [g]Polymerization performed in 10 mL of toluene. [h]Conditions: cat. (20 μmol); [IP]/[cat.] = 500.

bond distances (1.334(7) Å) are intermediate between the corresponding single-bond and double-bond distances, indicating that the electrons are largely delocalized over the NCCCN backbone attached to Y(1); in contrast, N(4)−C(15) (1.288(7) Å) and C(13)−C(14) (1.402(7) Å) are shorter than N(3)−C(13) (1.335(7) Å) and C(14)−C(15) (1.445(8) Å), respectively, suggesting a more localized distribution of electrons within the NCCCN backbone attached to Y(2). Moreover, the face-on coordination in **1** drags the Y(2) ion closer to the backbone carbon atom C(13), rendering a Y(2)−C(13) distance of 2.909(5) Å, indicative of a weak interaction, which might also contribute to the shortest distance between the two yttrium ions among its yttrium congeners (Y(1)−Y(2) = 7.735 Å for **1** vs 8.127 Å for **2a** vs 8.104 Å for **3**). In the smallest scandium complex **2c**, the more twisted Sc(2) metal center is four-coordinate, remaining free of a THF base, while the slightly twisted Sc(1) metal center is additionally coordinated with a THF molecule (as in the case of the above yttrium and lutetium complexes). The variance in coordination mode renders the N(3)−Sc(2)−N(4) (86.03(16)°) angle larger than N(1)−Sc(1)−N(2) (83.79(15)°) by 2.24° (the largest variation among the series), probably compensating for the coordination-number degeneration. The Sc−N, Sc−C, and Sc−O bond distances fall in the normal single-bond regions in the literature,[23] while a slightly closer proximity of the two scandium ions (Sc(1)−Sc(2) = 7.955 Å) in **2c** is mainly ascribed to the smaller metal ionic size.

According to previous reports,[2] metal−metal spatial proximity and the steric bulk in a binuclear complex may incur notable concerted effects of the two metal centers and influence its catalytic behavior. Thus, the polymerization of isoprene (IP) by using these bimetallic precursors was tentatively investigated.

Catalysis on Isoprene Polymerization. All of the bimetallic complexes activated with 10 equiv of Al^iBu_3 or 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ alone did not induce visible polymerization, even at elevated temperature (Table 1, runs 1 and 2). When the amount of $[Ph_3C][B(C_6F_5)_4]$ was increased to 2 equiv, so that both metal centers were cationized, gradual consumption of isoprene could be observed (Table 1, runs 3−7). The yttrium- and lutetium-based systems showed similar activities, while the scandium complex **2a** was less active, probably due to the crowded environment around the smaller Sc^{3+} center providing fewer chances for isoprene monomer coordination. This might explain to some degree why the larger yttrium (ionic radius 1.040 Å) complexes **1**, **2a**, and **3** exhibited higher *cis*-1,4 selectivity (84%−87%, runs 3, 4, and 7) in comparison with their lutetium and scandium counterparts (Lu^{3+} at 0.977 Å, 77%; Sc^{3+} at 0.885 Å, 71%; runs 5 and 6), as the *cis*-η^4 coordination of isoprene monomer that incurs *cis*-1,4 regularity favors a large coordination environment.[15g,24] In particular, the scandium complex **2c** provided much higher 3,4-selectivity, ~25% (run 6), in accord with the crowding environment around the smallest Sc^{3+} ion center and its lower coordination number that allowed isoprene η^2 coordination. When both aluminum alkyls and organoborate cocatalysts were employed, the polymerization activity was accelerated significantly. In the presence of 10 equiv of Al^iBu_3 when 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ was added to abstract the alkyl group in complex **1**, that is, only one of the two yttrium centers was cationized to become an active site (Y^+) while the other center remained neutral (Y) and inert, the polymerization could be completed in 10 min in comparison with 600 min without Al^iBu_3 (run 2 vs 8); when the borate loading was increased to an equimolar amount of the metal, both yttrium centers became cationic ($2Y^+$),[25] resulting in more rapid polymerization (run 9); on further increase in borate loading, which might arouse a dicationic Y^{2+} (no metal−carbon σ bond for the monomer insertion) and a cationic yttrium center Y^+, no obvious change in activity was observed, as shown in run 10 in comparison with run 8. Correspondingly, the molecular weight of polyisoprene obtained from the $2Y^+$ system was smaller with narrow polydispersity in comparison with those from $Y + Y^+$ and $Y^{2+} + Y^+$ systems. Addition of aluminum alkyls to the catalyst systems significantly increasing activity has been well documented, as they play the role of impurity scavenger, transform (alkylating) active species, and adjust the molecular weight of the product as a chain transfer agent. In this system, we believed that aluminum alkyls first acted as an impurity scavenger. This can be proved by the fact that the catalytic efficiency increased upon addition of aluminum alkyls, as evidenced by the decrease in the molecular weight of the resultant polyisoprene in comparison with those of binary systems without aluminum alkyls, in which some active species were consumed by impurities (runs 8−15 vs 3−7). Second, the aluminum alkyls abstracted the coordinated THF molecule in precursors to give unsaturated THF-free active species, allowing coordination and insertion of monomers, which was the main reason for the aluminum alkyls accelerating the polymerization rate.[15h,i,n,17e,26] Third, aluminum alkyl might participate in polymerization, since changing the type of aluminum alkyl affected the activity in the order $Al^iBu_3 = AlEt_3 \gg AlMe_3$ (Table 1, runs 9, 21, and 20), which might be attributed to the formation of a less active aluminate species between the sterically less demanding $AlMe_3$ and the cationic rare-earth-metal moiety.[27] In the meantime, slight drops of 1,4-regularity and molecular weight of the resultant polyisoprene and broadening of the molecular weight distributions were observed. Adding an excess amount of Al^iBu_3, such as 20 and 40 equiv, respectively, led to further decrease of the molecular weight with a negligible change of regularity (Table 1, runs 18 and 19), albeit not inverse to the amount of Al^iBu_3,[15n] suggesting that it induced chain transfer polymerization but in a nonliving fashion.[28] The possible cooperative binuclear effects of these systems were reflected by their different selectivities in comparison to the mononuclear β-diketiminato yttrium system reported by us previously, which gave high *cis*-1,4 polyisoprene (94.1%, 96.3%) under the same conditions (runs 16 and 17).[15m] This could be attributed to the steric bulkiness of binuclear complexes, which provided more chances for η^2 coordination of polyisoprene, resulting in higher 3,4-regulated polyisoprene. The binuclear catalytic systems usually show steric influences, as reported in systems of ethylene polymerization.[2] This steric effect might also contribute to higher molecular weight polyisoprene, as the active metal centers were wrapped.[2b,5,10,29] Thus, when the polymerization was performed at dilute catalyst and monomer concentrations, the molecular weight of the isolated polyisoprene decreased significantly (run 11).

■ CONCLUSION

The series of binuclear rare-earth-metal bis(alkyl) complexes **1**−**3** have been successfully synthesized and well-defined by introducing bis(β-diketiminate) ligands bridged by the rigid *m*-phenylene group, $[2,6\text{-}R_2C_6H_3NHC(Me)C(H)C(Me)N]_2$-(*m*-phenylene). Due to the steric repulsion of the Ln−alkyl moieties, in the solid state, two β-diketiminato−metal units of all binuclear complexes take *trans* positions against the phenyl ring. In solution, both the Ln−alkyl groups and the β-diketiminate ligands are fluxional and indistinguishable on the NMR time scale at room temperature. Upon activation with 2 equiv of organoborate, these binuclear rare-earth-metal alkyl complexes exhibit moderate catalytic activity for isoprene polymerization, while further addition of aluminum alkyls accelerates the polymerization rate significantly and arouses an increment of catalytic efficiency by excluding the coordinated THF molecules and impurities in the system. The binuclear active species show relatively lower *cis*-1,4-selectivity and increased 3,4-selectivity and give polyisoprene with much higher molecular weight in comparison with the mononuclear analogue, which might be attributed to the steric effect of the two adjacent active metal centers. The copolymerization of conjugated dienes and α-olefins catalyzed by binuclear rare-earth-metal alkyl complexes are in progress.

■ EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. All solvents were purified from an MBraun SPS system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer. The molecular weight and molecular weight distribution of the polymers were measured by TOSOH HLC 8220 GPC at 40 °C using THF as eluent (the flow rate was 0.35 mL/min) against polystyrene standards. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). Isoprene was dried over CaH_2 with stirring for 48 h and distilled under vacuum before use. $Ln(CH_2SiMe_3)_3(THF)_2$[30] was prepared according to the literature. $[Ph_3C][B(C_6F_5)_4]$ and $[PhNHMe_2][B(C_6F_5)_4]$ were synthesized following the literature procedures.[31] The microstructure of polyisoprene was determined by ^{1}H NMR and ^{13}C NMR spectra.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at calculated positions and were included in the structure calculations without further refinement of the parameters. The crystallographic data and structure refinement details of complexes **1**−**3** are summarized in Table S2 (Supporting Information).

Synthesis and Characterization of Ligands. The synthesis of $PBDI^{iPr}$-H_2 was carried out according to the procedure by Harder et al.[20b] The syntheses of $PBDI^{Et}$-H_2 and $PBDI^{Me}$-H_2 were carried out following a similar procedure, but $2,6\text{-}Et_2C_6H_3NH_2$ and $2,6\text{-}Me_2C_6H_3NH_2$ were used, respectively, instead of $2,6\text{-}{}^iPr_2C_6H_3NH_2$. The yields of these ligands were moderate ($PBDI^{Et}$-H_2, 44%; $PBDI^{Me}$-H_2, 39%).

$PBDI^{Et}$-H_2. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.15 (t, $^3J_{H-H}$ = 7.5 Hz, 12H, CH_2CH_3),, 1.68 (s, 6H, CH_3CN), 2.05 (s, 6H, CH_3CN), 2.38−2.58 (m, 8H, CH_2CH_3), 4.85 (s, 2H, CH_3CNCH), 6.56 (t, $^4J_{H-H}$ = 1.9 Hz, 1H, $CH_{\text{N-aryl}}$), 6.61 (dd, $^3J_{H-H}$ = 7.9 Hz, $^4J_{H-H}$ = 1.9 Hz, 2H, $CH_{\text{N-aryl}}$), 7.01−7.09 (m, 6H, $CH_{\text{N-aryl}}$), 7.14 (t, $^3J_{H-H}$ = 7.9 Hz, 1H, $CH_{\text{N-aryl}}$), 12.59 (s, 2H, NH). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ 14.49 (CH_2CH_3), 20.96 (CH_3CN), 20.99 (CH_3CN), 25.05 (CH_2CH_3), 96.12 (CH_3CNCH), 116.76 ($CH_{\text{N-aryl}}$), 117.53 ($CH_{\text{N-aryl}}$), 124.31 ($CH_{\text{N-aryl}}$), 126.09 ($CH_{\text{N-aryl}}$), 128.47 ($CH_{\text{N-aryl}}$), 129.12 ($CH_{\text{N-aryl}}$), 136.67 ($CH_{\text{N-aryl}}$), 144.09 (C═N), 145.27 (C═N), 157.16 (C═N), 162.63 (C═N). Anal. Calcd for $C_{36}H_{46}N_4$: C, 80.85; H, 8.67; N, 10.48. Found: C, 80.91; H, 8.82; N, 10.27.

$PBDI^{Me}$-H_2. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.66 (s, 6H, CH_3CN), 2.05 (s, 6H, CH_3CN), 2.12 (s, 12H, CH_3), 4.86 (s, 2H, CH_3CNCH), 6.58 (t, $^4J_{H-H}$ = 1.8 Hz, 1H, $CH_{\text{N-aryl}}$), 6.63 (dd, $^3J_{H-H}$ = 7.9 Hz, $^4J_{H-H}$ = 1.8 Hz, 2H, $CH_{\text{N-aryl}}$), 6.90 (t, $^3J_{H-H}$ = 7.9 Hz, 2H, $CH_{\text{N-aryl}}$), 7.02 (d, $^3J_{H-H}$ = 7.9 Hz, 4H, $CH_{\text{N-aryl}}$), 7.14 (t, $^3J_{H-H}$ = 7.9 Hz, 1H, $CH_{\text{N-aryl}}$), 12.52 (s, 2H, NH). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ 18.54 (CH_3), 20.85 (CH_3CN), 20.93 (CH_3CN), 96.27 (CH_3CNCH), 117.13 ($CH_{\text{N-aryl}}$), 117.78 ($CH_{\text{N-aryl}}$), 123.76 ($CH_{\text{N-aryl}}$), 127.88 ($CH_{\text{N-aryl}}$), 128.47 ($CH_{\text{N-aryl}}$), 129.10 ($CH_{\text{N-aryl}}$), 130.66 ($CH_{\text{N-aryl}}$), 144.94 (C═N), 145.69 (C═N), 156.78 (C═N), 162.84 (C═N). Anal. Calcd for $C_{32}H_{38}N_4$: C, 80.29; H, 8.00; N, 11.70. Found: C, 80.43; H, 8.06; N, 11.51.

Synthesis and Characterization of Binuclear Complexes. *$PBDI^{iPr}$-$[Y(CH_2SiMe_3)_2]_2(THF)_2$ (**1**).* To a stirred solution of the ligand $PBDI^{iPr}$-H_2 (0.590 g, 1.0 mmol) in hexane (10 mL) was added $Y(CH_2SiMe_3)_3(THF)_2$ (0.990 g, 2.0 mmol) in hexane (5 mL) at 25 °C, and the mixture was stirred for 0.5 h. Then the solution was concentrated to half volume and cooled to −30 °C. Yellow single crystals of complex **1** were isolated after 1 day (0.791 g, 70%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.50 (d, $^2J_{Y-H}$ = 2.8 Hz, 8H, CH_2SiMe_3), 0.22 (s, 36H, CH_2SiMe_3), 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.31 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.33 (br s, 8H, THF-β-CH_2), 1.65(s, 6H, CH_3CN), 2.18 (s, 6H, CH_3CN), 3.23 (sept, $^3J_{H-H}$ = 6.8 Hz, 4H, $CH(CH_3)_2$), 3.64 (br s, 8H, THF-α-CH_2), 5.16 (s, 2H, CH_3CNCH), 6.58 (t, $^4J_{H-H}$ = 1.9 Hz, 1H, $CH_{\text{N-aryl}}$), 7.02 (dd, $^3J_{H-H}$ = 7.9 Hz, $^4J_{H-H}$ = 1.9 Hz, 2H, $CH_{\text{N-aryl}}$), 7.09 (s, 6H, $CH_{\text{N-aryl}}$), 7.14 (t, $^3J_{H-H}$ = 7.9 Hz, 1H, $CH_{\text{N-aryl}}$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 4.55 (CH_2SiMe_3), 24.15 (CH_3CN), 24.59 ($CH(CH_3)_2$), 24.71 (CH_3CN), 25.05 (THF-β-CH_2), 25.34 ($CH(CH_3)_2$), 34.94 (CH_2SiMe_3), 35.34 (CH_2SiMe_3), 70.08 (THF-α-CH_2), 96.80 (CH_3CNCH), 119.43 ($CH_{\text{N-aryl}}$), 119.95 ($CH_{\text{N-aryl}}$), 124.35 ($CH_{\text{N-aryl}}$), 126.22 ($CH_{\text{N-aryl}}$), 127.94 ($CH_{\text{N-aryl}}$), 128.18 ($CH_{\text{N-aryl}}$), 130.00 ($CH_{\text{N-aryl}}$), 142.32 ($CH_{\text{N-aryl}}$), 144.43 (C═N), 151.09 (C═N), 160.81 (C═N), 167.22 (C═N). Anal. Calcd for $C_{64}H_{112}N_4O_2Si_4Y_2$: C, 61.02; H, 8.96; N, 4.45. Found: C, 59.95; H, 8.86; N, 4.29.

*$PBDI^{Et}$-$[Y(CH_2SiMe_3)_2]_2(THF)_2$ (**2a**).* Following the procedure described for **1**, the reaction of $PBDI^{Et}$-H_2 (0.427 g, 0.8 mmol) with 2 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ (0.792 g, 1.6 mmol) afforded **2a** as yellow crystals (0.654 g, 68%) after crystallization from hexane at −30 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.49 (d, $^2J_{Y-H}$ = 2.0 Hz, 8H, CH_2SiMe_3), 0.22 (s, 36H, CH_2SiMe_3), 1.20 (t, $^3J_{H-H}$ = 7.5 Hz, 12H, CH_2CH_3), 1.25 (br s, 8H, THF-β-CH_2), 1.52 (s, 6H, CH_3CN), 2.20 (s, 6H, CH_3CN), 2.52−2.67 (m, 8H, CH_2CH_3), 3.44 (br s, 8H, THF-α-CH_2), 5.11 (s, 2H, CH_3CNCH), 6.92 (s, 1H, $CH_{\text{N-aryl}}$), 6.99 (s, 6H, $CH_{\text{N-aryl}}$), 7.29−7.31 (m, 2H, $CH_{\text{N-aryl}}$), 7.36−7.40 (m, 1H, $CH_{\text{N-aryl}}$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 4.55 (CH_2SiMe_3), 13.92 (CH_2CH_3), 23.53 (CH_3CN), 25.12 (CH_2CH_3), 25.22 (THF-β-CH_2), 25.78 (CH_3CN), 35.59 (CH_2SiMe_3), 35.99 (CH_2SiMe_3), 70.53 (THF-α-CH_2), 98.93 (CH_3CNCH), 122.62 ($CH_{\text{N-aryl}}$), 123.58 ($CH_{\text{N-aryl}}$), 125.40 ($CH_{\text{N-aryl}}$), 126.06 ($CH_{\text{N-aryl}}$), 127.94 ($CH_{\text{N-aryl}}$), 128.18 ($CH_{\text{N-aryl}}$), 130.62 ($CH_{\text{N-aryl}}$), 138.08 ($CH_{\text{N-aryl}}$), 146.28 (C═N), 151.30 (C═N), 165.26 (C═N), 165.90 (C═N). Anal. Calcd for $C_{60}H_{104}N_4O_2Si_4Y_2$: C, 59.87; H, 8.71; N, 4.65. Found: C, 59.47; H, 8.52; N, 4.51.

*$PBDI^{Et}$-$[Lu(CH_2SiMe_3)_2]_2(THF)_2$ (**2b**).* Following the procedure described for **1**, the reaction of $PBDI^{Et}$-H_2 (0.427 g, 0.8 mmol) with 2 equiv of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.929 g, 1.6 mmol) afforded **2b** as yellow crystals (0.744 g, 67%) after crystallization from hexane at −30 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.65 (s, 8H, CH_2SiMe_3), 0.22 (s, 36H, CH_2SiMe_3), 1.18 (br s, 8H, THF-β-CH_2), 1.20 (t, $^3J_{H-H}$ = 7.5 Hz, 12H, CH_2CH_3), 1.51 (s, 6H, CH_3CN), 2.18 (s, 6H, CH_3CN), 2.55−2.69 (m, 8H, CH_2CH_3), 3.39 (br s, 8H, THF-α-CH_2), 5.10 (s, 2H, CH_3CNCH), 6.92 (s, 1H, $CH_{\text{N-aryl}}$), 6.99 (s, 6H, $CH_{\text{N-aryl}}$), 7.28−7.30 (m, 2H, $CH_{\text{N-aryl}}$), 7.35−7.39 (m, 1H, $CH_{\text{N-aryl}}$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 4.73 (CH_2SiMe_3), 13.83 (CH_2CH_3), 23.80 (CH_3CN), 25.02 (CH_2CH_3), 25.21 (THF-β-CH_2), 26.14 (CH_3CN), 42.57 (CH_2SiMe_3), 70.82 (THF-α-CH_2), 99.32 (CH_3CNCH), 122.96 ($CH_{\text{N-aryl}}$), 124.11 ($CH_{\text{N-aryl}}$), 125.41 ($CH_{\text{N-aryl}}$), 125.98 ($CH_{\text{N-aryl}}$),

127.94 ($CH_{\text{N-aryl}}$), 128.18 ($CH_{\text{N-aryl}}$), 130.46 ($CH_{\text{N-aryl}}$), 138.09 ($CH_{\text{N-aryl}}$), 146.76 ($C{=}N$), 151.51 ($C{=}N$), 165.99 ($C{=}N$), 166.63 ($C{=}N$). Anal. Calcd for $C_{60}H_{104}N_4O_2Si_4Lu_2$: C, 52.38; H, 7.62; N, 4.07. Found: C, 51.99; H, 7.42; N, 3.99.

*$PBDI^{Et}$-$[Sc(CH_2SiMe_3)_2]_2(THF)$ (**2c**).* Following the procedure described for **1**, the reaction of $PBDI^{Et}$-H_2 (0.534g, 1.0 mmol) with 2 equiv of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.902 g, 2.0 mmol) afforded **2c** as a yellow powder (0.762 g, 73%). Pale yellow crystals suitable for X-ray analysis were grown from a mixture of hexane and toluene (5/1 v/v) at −30 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.10 (br s, 8H, CH_2SiMe_3), 0.14 (s, 36H, CH_2SiMe_3), 1.21 (t, $^3J_{H-H}$ = 7.5 Hz, 12H, CH_2CH_3), 1.32 (m, 4H, THF-β-CH_2), 1.50 (s, 6H, CH_3CN), 2.05 (s, 6H, CH_3CN), 2.54−2.71(m, 8H, CH_2CH_3), 3.54 (m, 4H, THF-α-CH_2), 5.08 (s, 2H, CH_3CNCH), 7.01 (s, 1H, $CH_{\text{N-aryl}}$), 7.05 (s, 6H, $CH_{\text{N-aryl}}$), 7.25−7.27 (m, 2H, $CH_{\text{N-aryl}}$), 7.28−7.31 (m, 1H, $CH_{\text{N-aryl}}$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 3.82 (CH_2SiMe_3), 14.26 (CH_2CH_3), 23.26 (CH_3CN), 24.64 (CH_3CN), 25.16 (CH_2CH_3), 25.48 (THF-β-CH_2), 43.91 (CH_2SiMe_3), 69.74 (THF-α-CH_2), 99.54 (CH_3CNCH), 122.94 ($CH_{\text{N-aryl}}$), 123.10 ($CH_{\text{N-aryl}}$), 126.34 ($CH_{\text{N-aryl}}$), 126.57 ($CH_{\text{N-aryl}}$), 127.94 ($CH_{\text{N-aryl}}$), 128.18 ($CH_{\text{N-aryl}}$), 130.84 ($CH_{\text{N-aryl}}$), 137.98 ($CH_{\text{N-aryl}}$), 144.41($C{=}N$), 149.75 ($C{=}N$), 165.35 ($C{=}N$), 167.29 ($C{=}N$). Anal. Calcd for $C_{56}H_{96}N_4OSi_4Sc_2$: C, 64.45; H, 9.27; N, 5.37. Found: C, 64.01; H, 9.04; N, 5.25.

*$PBDI^{Me}$-$[Y(CH_2SiMe_3)_2]_2(THF)_2$ (**3**).* Following the procedure described for **1**, the reaction of $PBDI^{Me}$-H_2 (0.478 g, 1.0 mmol) with 2 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ (0.990 g, 2.0 mmol) afforded **3** as yellow crystals (0.809 g, 71%) after crystallization from hexane at −30 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ −0.48 (d, $^2J_{Y-H}$ = 2.0 Hz, 8H, CH_2SiMe_3), 0.22 (s, 36H, CH_2SiMe_3), 1.20 (br s, 8H, THF-β-CH_2), 1.48 (s, 6H, CH_3CN), 2.15 (s, 12H, CH_3), 2.19 (s, 6H, CH_3CN), 3.39 (br s, 8H, THF-α-CH_2), 5.10 (s, 2H, CH_3CNCH), 6.78−6.82 (m, 2H, $CH_{\text{N-aryl}}$), 6.86−6.88 (m, 4H, $CH_{\text{N-aryl}}$), 6.97 (s, 1H, $CH_{\text{N-aryl}}$),7.30−7.32 (m, 2H, $CH_{\text{N-aryl}}$), 7.37−7.41 (m, H, $CH_{\text{N-aryl}}$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 4.55 (CH_2SiMe_3), 19.37 (CH_3), 23.20 (CH_3CN), 25.25 (THF-β-CH_2), 25.83 (CH_3CN), 35.59 (CH_2SiMe_3), 35.72 (CH_2SiMe_3), 36.12 (CH_2SiMe_3), 70.33 (THF-α-CH_2), 99.07 (CH_3CNCH), 122.90 ($CH_{\text{N-aryl}}$), 124.13 ($CH_{\text{N-aryl}}$), 124.88 ($CH_{\text{N-aryl}}$), 127.94 ($CH_{\text{N-aryl}}$), 128.17 ($CH_{\text{N-aryl}}$), 128.84 ($CH_{\text{N-aryl}}$), 130.68 ($CH_{\text{N-aryl}}$), 133.01 ($CH_{\text{N-aryl}}$), 147.27 ($C{=}N$), 151.12 ($C{=}N$), 165.42 ($C{=}N$), 165.72 ($C{=}N$). Anal. Calcd for $C_{56}H_{96}N_4O_2Si_4Y_2$: C, 58.61; H, 8.43; N, 4.88. Found: C, 58.19; H, 8.33; N, 4.61.

Isoprene Polymerization. A detailed polymerization procedure is described as follows (Table 1, run 9). Under a nitrogen atmosphere, a toluene solution (2 mL) of $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg, 20 μmol) was added to a toluene solution (3 mL) of complex **1** (12.6 mg, 10 μmol) in a 25 mL flask. Then 10 equiv of Al^iBu_3 (0.1 mL, 100 μmol, 1.0 M in toluene) was added with stirring after a few minutes. Upon the addition of 1000 equiv of isoprene (1 mL, 0.01 mol), polymerization was initiated and carried out for 5 min. The reaction mixture was poured into a large quantity of methanol and then dried under vacuum at 50 °C to a constant weight (0.68 g, 100%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving crystallographic data and structure refinement details for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dmcui@ciac.jl.cn (D.C.); shihui-li@ciac.jl.cn (S.L.). Fax: (+86) 431 85262774. Tel: +86 431 85262773.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the National Natural Science Foundation of China for projects No. 20934006, 51073148, 51021003, 201104074, and 201104072 and the Ministry of Science and Technology of China for projects No. 2009AA03Z501 and 2011DF50650.

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