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Zinc Complexes with an Ethylene-Bridged Bis(β-diketiminate) Ligand: Syntheses, Structures, and Applications as Catalysts in the Borylation of Aryl Iodides

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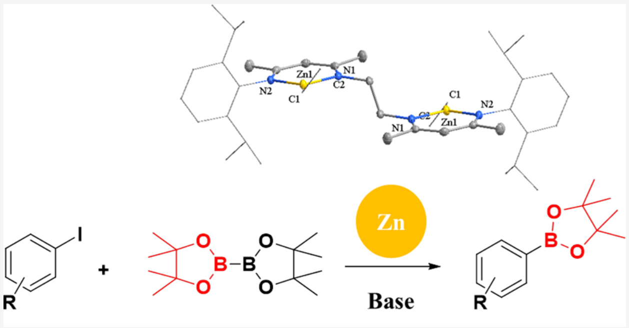

ABSTRACT: A dinucleating bis(β-diketiminate) ligand with a flexible bridge has been employed to synthesize zinc complexes. The ligand, abbreviated H_2L (H_2L = N-(4-((2-((4-((2,6-diisopropylphenyl)imino)pent-2-en-2-yl)amino)ethyl)imino)pent-2-en-2-yl)-2,6-diisopropylaniline), was deprotonated with $ZnEt_2$ to afford $[LZn_2Et_2]$ (**1**). Reactions of **1** with 2 equiv of BnOH and ^{n}BuOH, respectively, gave access to $[LZn_2(OBn)_2]\cdot C_6H_{14}$ (**2**·C_6H_{14}) and $[LZn_2(O^{n}Bu)_2]$ (**3**). Treatment of **1** with 2 equiv of I_2 in THF produced $[LZn_2I_2(THF)_2]\cdot 2THF$ (**4**·2THF). X-ray single-crystal diffraction analyses revealed that they are all heteroleptic bimetallic compounds with two metal centers being chelated by one ligand set. The structurally similar compounds **1** and **4**·2THF possess approximate C_2 symmetry, with two β-diketiminate units being arrayed in head-to-tail antiparallel mode. Thus, the molecular structures of **1** and **4**·2THF exhibit a seesaw-like topology. The structures of **2**·C_6H_{14} and **3** are almost identical, in which two zinc atoms are shared by two ZnN_2C_3 six-membered rings, two $Zn_2ON_2C_2$ seven-membered rings, and one Zn_2O_2 four-membered ring. Therefore, the metal cores of **2**·C_6H_{14} and **3** display a crownlike topology. All complexes are catalytically active for the borylation of aryl iodides with B_2Pin_2 (B_2Pin_2 = 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bis(1,3,2-dioxaborolane). Complex **1** shows higher activity in comparison to **2**, **3**, and **4**·2THF. The borylation reactions catalyzed by **1** could proceed under mild conditions and can be applied to a series of substrates with high functional group generality. This methodology thus represents a novel use of β-diketiminate zinc complexes for C−I borylation.

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INTRODUCTION

The chemistry of zinc complexes has undergone a remarkable renaissance in the past decade.[1−5] The renewed interest toward these compounds has mainly arisen from their attractive reactivities[6−9] and potential applications in a broad range of reactions,[10] including the hydroboration of alkynes,[11,12] the Strecker reaction,[13] the Barbier reaction,[14] the aminophenol oxidation reaction,[15] the C−S cross-coupling reaction,[16] the hydrosilylation of N-heterocycles,[17] the copolymerization of epoxides and CO_2,[18−20] and so forth.[21,22] Zinc is an inexpensive, biocompatible, less toxic and earth-abundant metal, which makes it particularly appealing to replace toxic and/or noble-metal complexes in catalytic transformations. Thus, the synthesis of zinc complexes with high catalytic activity is of great importance.

One fertile route for the preparation of zinc complexes is to employ β-diketiminate ligands.[23] These ligands could be easily synthesized, and their steric demands can be readily tuned by varying the organic substituents attached to the imine groups. Consequently, a number of zinc complexes have been synthesized by the utilization of a large variety of β-diketiminate ligands.[24−33] They behaved as highly active catalysts for the ring-opening polymerization (ROMP) of lactides.[24−33] Particularly, Harder and co-workers reported a series of dinuclear zinc complexes supported by bridged β-diketiminate ligands.[34] In studies of the copolymerization of epoxides and CO_2, they found that there existed an equilibrium between the active dimer and inactive monomer (both are adducts of a catalyst, CO_2, and epoxide), and the coexistence of the dimer and monomer decreased the efficiency of polymerization reactions. They solved this problem by using zinc complexes with bridged β-diketiminate ligands. The rigid *p*-phenylene, *m*-phenylene, and 2,6-pyridylene were employed as bridges. Inspired by the works of Harder, we anticipated that the rigid bridges may be replaced by flexible ones, affording a

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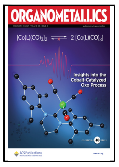

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plethora of zinc complexes with interesting structures and properties.

In this work, we employed an ethylene-bridged *β*-diketiminate *N*-(4-((2-((4-((2,6-diisopropylphenyl)imino)-pent-2-en-2-yl)amino)ethyl)imino)pent-2-en-2-yl)-2,6-diisopropylaniline (H_2L) as a ligand to synthesize zinc complexes. Four complexes of the compositions [LZn_2Et_2] (**1**), [$LZn_2(OBn)_2$]·C_6H_{14} (**2**·C_6H_{14}), [$LZn_2(O^nBu)_2$] (**3**), and [$LZn_2I_2(THF)_2$]·2THF (**4**·2THF) were prepared. They are catalytically active for the borylation of aryl iodides with bis(pinacolato)diboron. Complex **1** shows higher activity in comparison to **2**, **3**, and **4**·2THF, giving a series of arylboronic acid derivatives.

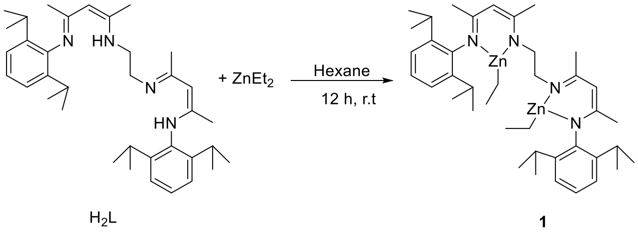
Arylboronic acid derivatives are highly valuable synthetic precursors that are widely used as intriguing building blocks in organic synthesis, particularly as substrates for transition-metal-catalyzed C−C, C−O, and C−N bond-forming reactions.[35] Recent advances in the preparation of arylboronic acid derivatives revealed that these compounds can be generated by the borylation of aryl halides with diborons.[36−39] Several metal complexes, including Pd,[40−43] Rh,[44] Fe,[45] W,[46] Zn,[47−50] Co,[51,52] Cu,[53−56] and Ni,[57−60] have been proven to be able to catalyze the borylation of aryl halides. It is found that visible light[61,62] and free radicals[63,64] are also effective in this transformation. However, there has beeh no report about this borylation reaction catalyzed by *β*-diketiminate complexes. Herein, we report the synthesis and structures of complexes **1**, **2**·C_6H_{14}, **3**, and **4**·2THF and the first efficient borylation of aryl iodides with bis(pinacolato)diboron catalyzed by zinc *β*-diketiminate complexes.

■ RESULTS AND DISCUSSION

Dinucleating Ligand H_2L. The ethylene-bridged *β*-diketiminate ligand H_2L (H_2L = N-(−4-((2-((4-((2,6-diisopropylphenyl)imino)pent-2-en-2-yl)amino)ethyl)imino)-pent-2-en-2-yl)-2,6-diiso-propylaniline) has been synthesized according to the literature procedure.[65−68] The H_2L ligand was characterized by $^1H/^{13}C$ NMR spectroscopy and X-ray single crystal diffraction. An ORTEP drawing of the molecular structure of the H_2L ligand is shown in Figure S1. The ^1H NMR spectrum of the H_2L ligand in $CDCl_3$ is fully consistent with its structure (Figure S6).

Synthesis and Structure of [LZn_2Et_2] (1). Compound **1** was obtained by reacting the dinucleating ligand H_2L with 2 equiv of diethylzinc in hexane through an alkyl elimination reaction (Scheme 1), generating the corresponding zinc ethyl complex **1** in 81% yield. The structure of **1** was determined by X-ray single-crystal diffraction. In the solid state, compound **1** exhibits an approximate C_2 symmetry (Figure 1). Two zinc atoms are chelated by one ligand set. Each zinc atom is tricoordinated by two N atoms of one *β*-diketiminate moiety and one C atom of the ethyl group. Thus, compound **1** shows a trigonal geometry (Figure 1). The C1−Zn1−N2, C1−Zn1−N1, and N1−Zn1−N2 angles are 132.44, 132.69, and 96.7°, respectively. The sum of these angles is 361.86°, indicating that these four atoms are perfectly planar. The two N_2C_3Zn chelating rings for the bidentate ligands are arranged in a head-to-tail antiparallel fashion. The two *N*-phenyl substituents of two *β*-diketiminate groups are also arrayed in an antiparallel mode and are vertical to the planes formed by N_2C_3Zn chelating rings. Thus, compound **1** displays a seesaw-like topology.

Scheme 1. Synthesis of [LZn_2Et_2] (1)



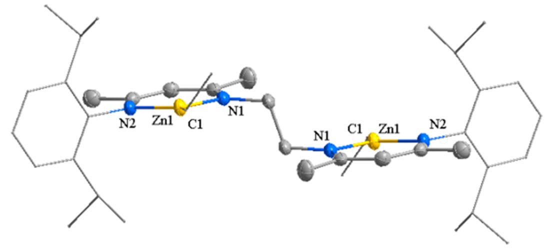
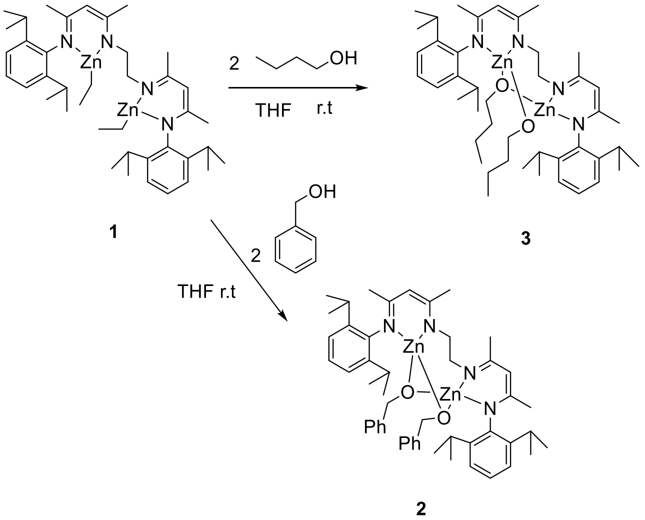
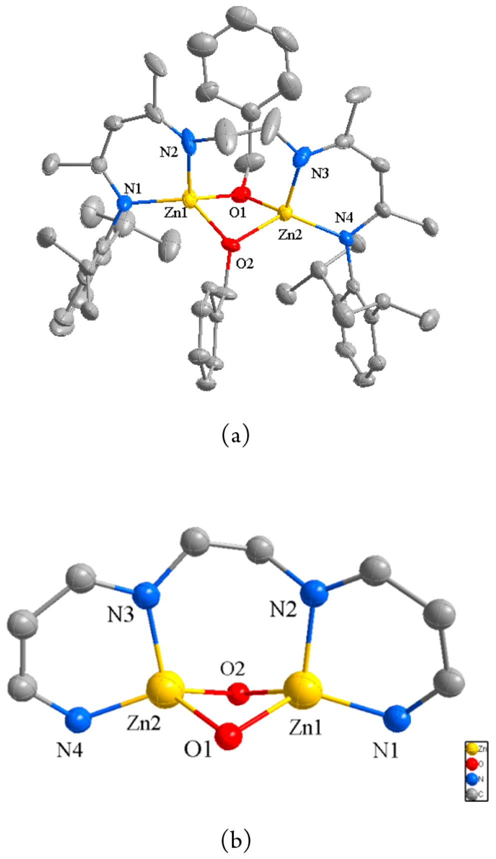


Figure 1. Molecular structure of **1** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Syntheses and Structures of [$LZn_2(OBn)_2$]·C_6H_{14} (2·C_6H_{14}) and [$LZn_2(O^nBu)_2$] (3). Intrigued by the successful preparation of zinc alkyl complex **1**, we next attempted to study the reactivity of **1** with alcoholic reagents. Two metathesis reactions with the zinc alkyl starting material **1** were explored. The reaction of **1** with 2 equiv of BnOH in THF gives a crude product. The recrystallization of the crude product in hexane generated the zinc alkoxide complex [$LZn_2(OBn)_2$]·C_6H_{14} (**2**·C_6H_{14}). Treatment of **1** with 2 equiv s of ^{n}BuOH afforded another zinc alkoxide compound, [$LZn_2(O^nBu)_2$] (**3**) (Scheme 2). The structures of **2**·C_6H_{14} and **3** were determined by X-ray single-crystal diffraction, and ORTEP drawings of the molecular structures of **2**·C_6H_{14} and **3** are given in Figures 2 and 3, respectively. The structures of **2**·C_6H_{14} and **3** are quite similar; therefore, only the structure of **2**·C_6H_{14} is discussed in detail. As expected, the ethyl groups binding to Zn atoms are replaced by two OBn groups. The

Scheme 2. Syntheses and Structures of [$LZn_2(OBn)_2$] (2) and [$LZn_2(O^nBu)_2$] (3)





(a)

(b)

Figure 2. (a) Molecular structure of **2** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) The crownlike topology of the core structure of **2**.

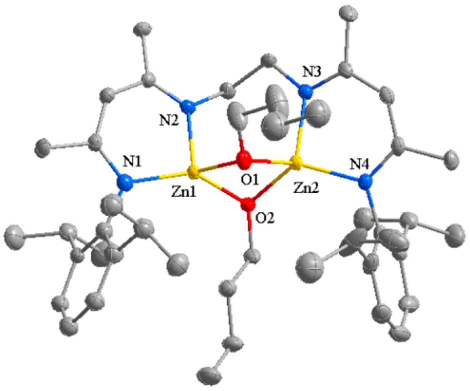
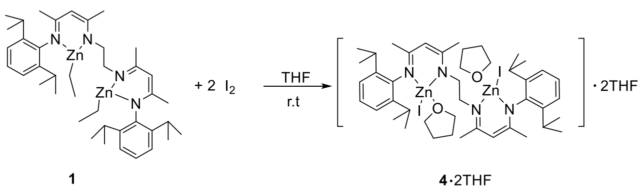


Figure 3. Molecular structure of **3** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

oxygen atom of the OBn moiety coordinates with metal centers in a η^2 mode. As a consequence, the two zinc atoms are doubly bridged by two oxygen atoms of two OBn groups, forming a four-membered Zn_2O_2 core. Each zinc atom is four-coordinated by two nitrogen atoms and two oxygen atoms to give a tetrahedral geometry. Two zinc atoms are shared by two ZnN_2C_3 six-membered rings, two $Zn_2ON_2C_2$ seven-membered rings, and one Zn_2O_2 four-membered ring to form a crownlike topology (Figure 2b).

Synthesis and Structure of [$LZn_2I_2(THF)_2$]·2THF (4·2THF). The iodine-coordinated metal complexes continue to attract intense attention because they are necessary precursors for the synthesis of complexes with low-valence metal centers by reducing iodine-coordinated metal complexes utilizing alkali metals.[69] With the successful preparation of zinc alkoxide complexes by employing the zinc alkyl compound **1** as the starting material, we endeavored to prepare iodine-coordinated metal complexes by using **1** as the reagent as well. Addition of 2 equiv of I_2 to a THF solution of **1** gave [$LZn_2I_2(THF)_2$]·2THF (**4**·2THF) in moderate yield (Scheme 3). An X-ray single-crystal diffraction analysis reveals that complex **4**·2THF crystallizes in the monoclinic space group $P2_1/c$. As can be seen in Figure 4, complex **4**·2THF is a bimetallic compound, and each β-diketiminate unit chelates one Zn^{II} ion. The ethyl group of **1** is replaced by an iodine atom to form a zinc−iodide bond. In addition, there is one tetrahydrofuran molecule coordinating to the Zn^{II} center. Each four-coordinated zinc center exhibits a tetrahedral geometry.

Scheme 3. Synthesis of [$LZn_2I_2(THF)_2$]·2THF (4·2THF)



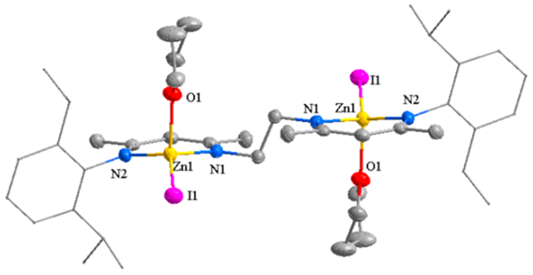
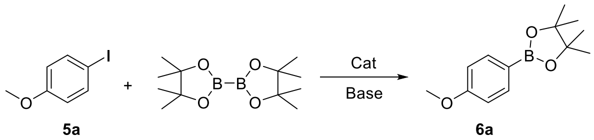


Figure 4. Molecular structure of **4** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Borylation of Aryl Iodides. Inspired by the discoveries that the ZnX_2-dtbpy,[47] $ZnCl_2$-NHC,[48,49] and $ZnEt_2$[50] systems could effectively catalyze the borylation of aryl halides with diboron reagents, we envisioned that the synthesized complexes **1**−**3** and **4**·2THF may be also feasible catalysts for the borylation of aryl halides in the presence of strong alkaline alkoxide bases. To examine this proposal, the possible borylation of 1-iodo-4-methoxybenzene (**5a**) by B_2Pin_2, using **1**−**3** and **4**·2THF, respectively, as catalysts was tested (Table 1). The reactions were initially conducted by employing KOEt as the base, in THF solution at 75 °C. To our delight, all four complexes could catalyze this borylation transformation. It was found that the yield was the highest by employing **1** as the catalyst, affording **6a** in 81% yield (entry 1). The employment of **2**, **3**, and **4**·2THF as catalysts under the same conditions as those of **1** produced **6a** in 45%, 55%, and 50% yields, respectively (entries 2−4). To compare the catalytic activities of the dinuclear compound **1** with its mononuclear analogue, the mononuclear complex **L^{2}ZnEt** (HL^2 = *N*-(4-((2,6-diisopropylphenyl)imino)pent-2-en-2-yl)-2,6-diisopropylaniline) was prepared (Figure S16).[70] To our surprise, the

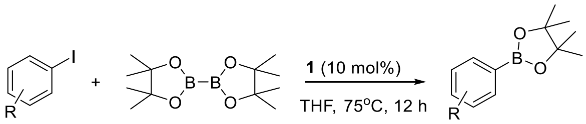
Table 1. Optimization of the Conditions for Borylation of 1-Iodo-4-methoxybenzene (**5a**) with B_2pin_2[a]

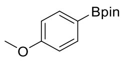
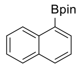
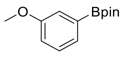
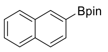
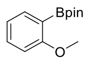
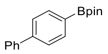
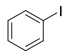
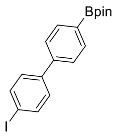
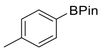
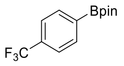
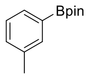
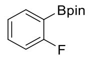
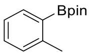
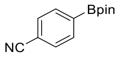
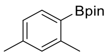
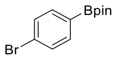
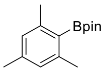
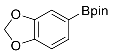


entry	cat. (10 mol %)	base	time (h)	solvent	yield[b] (%)
1	**1**	KOEt	12	THF	81
2	**2**	KOEt	12	THF	45[d]
3	**3**	KOEt	12	THF	55[d]
4	**4**·2THF	KOEt	12	THF	50[d]
5	$\mathbf{L^2ZnEt}$	KOEt	12	THF	0
6	**1**	NaOEt	12	THF	57
7	**1**	NaOAc	12	THF	0
8	**1**	NaO^tBu	12	THF	trace
9	**1**	KO^tBu	12	THF	trace
10	**1**	KOMe	12	THF	74[d]
11	**1**	NaOMe	12	THF	41[d]
12	**1**	KOEt	24	THF	>99[d]
13	**1**		12	THF	0
14		KOEt	12	THF	trace
15	**1**	KOEt	12	MTBE	>99[d]
16	**1**	KOEt	12	toluene	trace
17	**1**	KOEt	12	THF	64[c]

[a] Reaction conditions unless specified otherwise: **1** (0.025 mmol, 10 mol %), B_2Pin_2 (0.375 mmol, 1.5 equiv), base (0.0375 mmol, 1.5 equiv), and **5a** (0.25 mmol, 1 equiv) in 1 mL of solvent, 75 °C, 12 h. [b] Isolated yield. [c] **1** (0.0125 mmol, 5 mol %) and B_2Pin_2 (0.375 mmol, 1.5 equiv). [d] Yield determined by ^1H NMR using 1,2-dichloroethane as the internal standard.

Table 2. Scope of Cross-Coupling of B_2Pin_2 with Aryl Iodides[a]



Entry	Product	Yield[b] (%)	Entry	Product	Yield[b] (%)
1	 **6a**	>99[c,e] 82[d]	10	 **6j**	91[e]
2	 **6b**	73	11	 **6k**	75
3	 **6c**	>99[c]	12	 **6l**	93[e]
4	 **6d**	73	13	 **6m**	43 52[f]
5	 **6e**	80	14	 **6n**	40
6	 **6f**	81	15	 **6o**	82[c]
7	 **6g**	84	16	 **6p**	65[c]
8	 **6h**	88	17	 **6q**	43
9	 **6i**	43[f]	18	 **6r**	>99

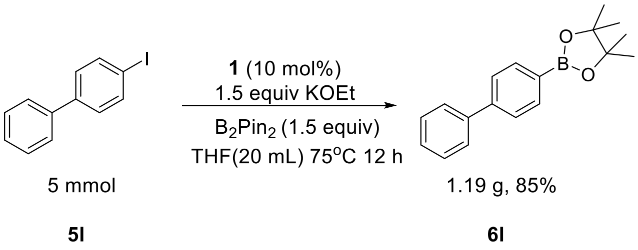
[a] Reaction conditions unless specified otherwise: **1** (0.025 mmol, 10 mol %), B_2Pin_2 (0.375 mmol, 1.5 equiv), base (0.0375 mmol, 1.5 equiv), and aryl iodides (0.25 mmol, 1 equiv). in 1 mL of solvent, 75 °C, 12 h. [b] Isolated yield unless otherwise noticed. [c] Yield determined by ^1H NMR using 1,2-dichloroethane as internal standard. [d] 75 °C, 15 min. [e] 75 °C, 3 h. [f] 75 °C, 24 h.

mononuclear compound $\mathbf{L^2ZnEt}$ did not catalyze the borylation reaction of **5a** by B_2Pin_2 (entry 5, Figure S35). We reasoned that the steric hindrance of the mononuclear complex $\mathbf{L^2ZnEt}$ is greater than that of the dinuclear compound **1**. It is easier for the substrates to combine with the more open zinc centers of **1**. Next, the reaction conditions catalyzed by **1** were optimized. The borylation product **6a** was not obtained by using NaOAc as a base (entry 6). Trace amounts of products were obtained by employing NaO^tBu (entry 7) and KO^tBu (entry 8) as bases, although 57% (entry 5), 41% (entry 10), and 74% (entry 9) yields were obtained by utilizing NaOEt, NaOMe, and KOMe as bases, respectively. Heating of **5a** and B_2pin_2 in THF at 75 °C without base did not give any product (entry 13). Similarly, a trace amount of product (entry 14) was detected without adding **1** as the catalyst. When the solvent was switched to MTBE, we obtained a yield similar to that of in tetrahydrofuran (entry 15). However, when the solvent was changed to toluene (entry 16), a trace amount of the desired product was afforded. Decreasing the amount of catalyst from 10 mol % to 5 mol % caused a marked drop in the yield, generating **6a** in 64% yield (entry 17).

Having the optimized conditions in hand, we investigated the scope of this transformation, and the results are summarized in Table 2. Aryl iodides with different electronic properties as well as different steric hindrances were examined. It was found that iodobenzene (**5d**) and its derivatives with electron-donating groups underwent borylation smoothly to afford the corresponding arylboronates in high yields (Table 2, entries 1−8). Remarkably, the substituent position of the methyl and methoxy groups had no remarkable effect on the present borylation reactions, giving the corresponding products in 73% to 84% yields (Table 2, entries 1−3 and 5−7). Electron-withdrawing substituents, including Br, F, CF_3, and CN groups, are well tolerated (Table 2, entries 14−17). However, the yields are lower than those of the substrates with electron-donating groups. Naphthyl iodides with the iodide in the 1- or 2-position are effective in the borylation reactions, giving naphthyl borates in high yields of 91% and 75%, respectively (Table 2, entries 10 and 11). Substrates with larger sterically congested substituents, such as 1-iodo-2,4-dimethylbenzene (**5h**) and 2-iodo-1,3,5-trimethyl-benzene (**5i**), are compatible with this borylation transformation, whereas the yields were decreased from 88% to 43% with an increase in steric hindrance. The heterocycle-containing substrate 5-iodobenzo[*d*][1,3]dioxole (**5r**) gives a very good yield. To the best of our knowledge, this is the first time that the *β*-diketiminate compounds have been used as catalysts for the borylation of aryl iodides.

On consideration that the borylation of 1-iodo-4-phenylbenzene (**5l**) could give a 93% yield, the borylation reaction of **5l** with B_2Pin_2 was then conducted on a large scale (Scheme 4). The borylation of 5 mmol of **5l** afforded 1.19 g (85%) of **6l**, revealing that high efficiency was maintained even in the large-scale reaction.

Scheme 4. Gram-Scale Reaction



Mechanistic studies on the borylation of aryl iodides catalyzed by zinc *β*-diketiminate complexes are ongoing. On consideration that the borylation of 1-iodo-4-methoxybenzene (**5a**) by B_2Pin_2 proceeded extremely quickly, affording **6a** in 82% yield within 15 min, and the reaction was completed in 3 h (>99% NMR yield; Table 2, entry 1), we speculated that the radical mechanism is plausible for this transformation.[47] Thus, we conducted several reactions by adding radical scavengers.

For the borylation reaction of **5a**, under the conditions given in Table 2, entry 1, the yield of **6a** decreased from 82% to 50% when ethene-1,1-diyldibenzene (2 equiv) was added as a radical scavenger (Figure S36). The products **6a,f,l** were not afforded (0% yields) when TEMPO (2 equiv) was added to the borylation reaction systems of **5a,f,l** (Figures S37−S39), respectively. These results revealed the involvement of the radicals in the borylation transformation.

Another pathway is that the metathesis between borylzincate and aryl iodides[50] might occur independently. We have endeavored to synthesize a borylzincate by the stoichiometric reaction of complex **1**, KOEt, and B_2Pin_2. A mixture with black precipitates was obtained. Unfortunately, our many attempts to characterize the black precipitates failed, due to their poor solubility or the instability of a Zn−B bond.[50] Studies on this pathway are underway.

■ CONCLUSIONS

The use of a flexible dinucleating bis(*β*-diketiminate) ligand with an ethylene bridge allowed the synthesis of the series of zinc diketiminate complexes $[LZn_2Et_2]$ (**1**), $[LZn_2(OBn)_2]\cdot C_6H_{14}$ (**2**$\cdot C_6H_{14}$), $[LZn_2(O^nBu)_2]$ (**3**), and $[LZn_2I_2(THF)_2]\cdot 2THF$ (**4**·2THF), which were facile catalysts for the borylation of aryl iodides with B_2Pin_2. Borylation reactions catalyzed by **1** were thoroughly investigated. Electronically and sterically challenging substrates are well tolerated. Thus, this method provides a cost-effective alternative to the widely utilized palladium catalysts. As far as the substrate scope and activities of the simple Zn system of Marder and co-workers[48] and our system are concerned, the activity of their system is higher than ours and the substrate scope of their system is broader than that of this work. In comparison with the pyrophoric $ZnEt_2$, complex **1** is much easier to handle. The successful preparation of arylborate on a large scale makes such a paradigm much more attractive.

■ EXPERIMENTAL SECTION

General Methods. All of the reactions were performed in a N_2-filled Vigor glovebox. THF, hexane, and toluene were dried over purple sodium benzophenone ketyl and stored with 4 Å molecular sieves. $ZnEt_2$ was purchased from J&K and Macklin Chemical and directly used as received. Deuterochloroform was dried over CaH_2 before it was distilled under vacuum and stored with 4 Å molecular sieves. ^1H NMR spectra were recorded at ambient temperature on Bruker Avance-III 400 MHz and Aglient 400 MHz instruments and the spectra were referenced to the TMS signal (0 ppm). ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Avance-III 600 MHz NMR spectrometer. Elemental analyses for C, H, and N were carried out on a PerkinElmer 2400 analyzer. Crystal determination was performed with a Bruker SMART APEX II CCDC diffractometer equipped with graphite-monochromated Mo K*α* radiation (λ = 0.71073 Å).

Synthesis of $[LZn_2Et_2]$ (1). H_2L (0.542 g, 1 mmol) was dissolved in hexane (2 mL), and then a solution of $ZnEt_2$ (3 mL, 1 M in hexane, 3 mmol) was added. The mixture was stirred at room temperature for 15 h. Volatiles were removed under vacuum to give a white powder. Yield: 0.589 g (80.7%). Block-shaped colorless crystals were obtained in toluene at −35 °C after 1 day. Anal. Calcd for $C_{40}H_{62}N_4Zn_2$ (**1**): C, 65.84; H, 8.56; N, 7.68. Found: C, 66.03; H, 8.73; N, 7.71.

Synthesis of $[LZn_2(OBn)_2]\cdot C_6H_{14}$ (2·C_6H_{14}). Compound **1** (0.589 g, 0.81 mmol) was dissolved in THF (2 mL), and then BnOH (0.18 g 1.66 mmol) was added. The mixture was stirred at room temperature for 12 h. Volatiles were removed under vacuum to give a white powder. Yield: 0.687 g (96.0%). Block-shaped colorless crystals were obtained in hexane at −35 °C overnight. Anal. Calcd for $C_{50}H_{66}N_4O_2Zn_2$ (**2**): C, 67.79; H, 7.51; N, 6.32. Found: C, 67.74; H, 7.58; N, 6.23.

Synthesis of $[LZn_2(O^nBu)_2]$ (3). Compound **1** (0.124 g, 0.17 mmol) was dissolved in THF (2 mL), and then ^{n}BuOH (0.0375 g, 0.51 mmol) was added. The mixture was stirred at room temperature for 12 h. Volatiles were removed under vacuum to give a white powder. Yield: 0.133 (97%). Block-shaped colorless crystals were obtained in hexane at −35 °C overnight. Anal. Calcd for $C_{44}H_{70}N_4O_2Zn_2$ (**3**): C, 64.62; H, 8.63; N, 6.85. Found: C, 64.58; H, 8.81; N, 6.85.

Synthesis of $[LZn_2I_2(THF)_2]\cdot 2THF$ (4·2THF). Compound **1** (0.125 g, 0.17 mmol) was dissolved in THF (2 mL), and then a solution of I_2 (0.104 g, 0.41 mmol) in THF was added. The mixture was stirred at room temperature for 15 h. The solvent and excess iodine were removed under vacuum to give an orange powder. Orange crystals were obtained in THF at −35 °C overnight. Yield: 0.117 g (63.9%). Anal. Calcd for $C_{44}H_{68}N_4O_2I_2Zn_2$ (**4**): C, 49.41; H, 6.41; N, 5.24. Found: C, 49.28; H, 6.38; N, 5.21.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00733.

> Crystal data and data collection details for compounds **1**, **2**·C_6H_{14}, **3**, and **4**·2THF, details of experimental procedures, and ^1H and ^{13}C NMR spectra of the compounds and products (PDF)

Accession Codes

CCDC 2009130–2009131, 2009146, and 2042443–2042444 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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