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Ring-Opening Polymerization of L-Lactides Catalyzed by Zinc–Sodium/Lithium Heterobimetallic Complexes in the Presence of Water

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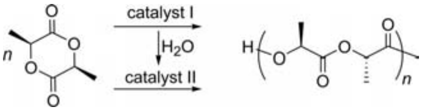
Two heterobimetallic complexes, [(TBBP)$_2$Zn][(Na)$_2$(THF)$_4$] (**3**) and [(TBBP)$_2$Zn][(Li)$_2$(THF)$_4$] (**4**) can initiate the ring-opening polymerization of L-lactide in a controlled fashion. Complex **3** can initiate the ring-opening polymerization of unsublimed L-lactide under moist conditions even in the presence of H_2O, to yield a high conversion and with controllable molecular weight.

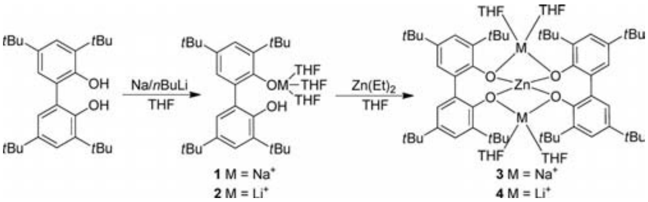
Introduction

Poly(lactide) (PLA)[1] and their copolymers are the most promising biodegradable and biocompatible synthetic macromolecules. Because of their biodegradable, biocompatible, and permeable properties,[2] these materials can be used in a broad range of practical applications such as medicine, pharmaceutics and tissue engineering.[3] Owing to the advantages of well-controlled molecular weight and low polydispersity (PDI), bulky ligand supported metal-based catalytic systems (e.g., Al,[4] Li,[5] Mg,[6] Zn,[7] Ca,[8] Fe,[9] Sn,[10] Ti,[11] or Y[12]) have attracted considerable attention for the ring-opening polymerization (ROP) of cyclic esters. It is necessary to note that most well-defined metal initiators require rigorously anhydrous conditions for their air- and moisture-sensitivity. Therefore, there is an exigent need to develop a practical means for the well-controlled ROP of lactides in laboratories and industry without access to inert-atmosphere facilities or rigorously dried solvents and to reduce costs. ROP of unsublimed *rac*-lactide even in the presence of water or 1 equiv. benzoic acid initiated by a robust zirconium Schiff base alkoxide,[13] a zinc Schiff base complex,[14] and iron alkoxides[15] have been described by Davidson and Gibson and co-workers. Nevertheless, the ROP of lactides in the presence of water still remains relatively unexplored, especially the mechanism of ROP of lactides in the presence of water.

Here, a new strategy was designed to overcome the air-sensitive hindrance (Scheme 1). As a good initiator for the ROP of lactides, catalyst I decomposes to catalyst II in the presence of water, and catalyst II can also initiate the ROP of lactides and can almost compensate for the deactive catalyst I. Two new bulky heterobimetallic aryloxides were synthesized and crystallographically characterized (Scheme 2). The catalytic activities of these complexes toward the ROP of L-lactide (L-LA) are also presented. Preliminary results show that complex **3** catalyzes the ROP of L-LA in the presence of water (50 equiv. with respect to the catalyst) under a controlled model.



Scheme 1. Strategy for the anti-water ROP of the L-lactide system.



Scheme 2. Preparation of compounds **1**–**4**.

Results and Discussion

Syntheses and Characterization of Zinc–Sodium/Lithium Heterobimetallic Complexes

As shown in Scheme 2, the monosodium/lithium complexes **1** and **2** are obtained by the reaction of 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol(TBBPH$_2$) with sodium/*n*BuLi. These two complexes can be dissolved in toluene, THF, $CHCl_3$ and CH_2Cl_2. Crystals of complex **2** are obtained by cooling the saturated THF solution; the molecular structure of complex **2** is depicted in Figure 1. [(TBBP)$_2$-

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Zn][(Na)$_2$(THF)$_4$] (**3**) or [(TBBP)$_2$Zn][(Li)$_2$(THF)$_4$] (**4**) were obtained as colourless crystalline solids in 50 and 53% yields, respectively, from the reaction of complex **1** or **2** and Zn(Et)$_2$ in a ratio of 2:1 in THF. Complex **3** and **4** are soluble in THF, slightly soluble in toluene, and insoluble in *n*-hexane. The ORTEP drawings of the molecular structures of complexes **3** and **4** are given in Figures 2 and S1. The two molecular structures are similar; the geometries around the zinc atoms are distorted tetrahedral, with coordination by four oxygen atoms from the phenoxy group with an average Zn–O bond length of 1.941(4) Å for Zn1–O and 1.952(3) Å for Zn2–O, respectively. The sodium/lithium atoms are surrounded by two oxygen atoms from THF and two phenyl oxygen atoms from two bulky ligands.

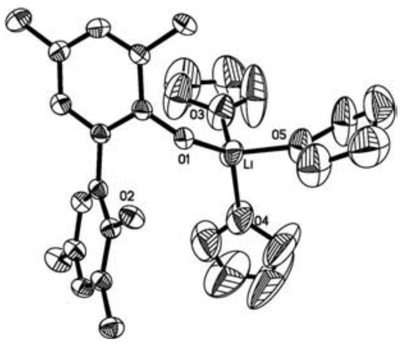

Figure 1. Molecular structure of **2** with ellipsoids given at the 30% probability level (methyl carbon atoms of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: Li–O1 1.877(8), Li–O3 2.013(10), Li–O4 1.996(9), Li–O5 1.962(10).

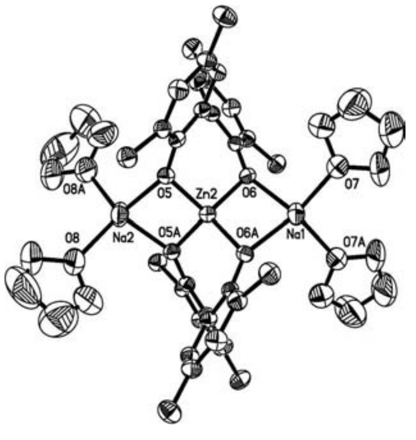

Figure 2. Molecular structure of **3** with ellipsoids given at the 30% probability level (methyl carbon atoms of the *tert*-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: Zn2–O5 1.947(3), Zn2–O5(A) 1.947(3), Zn2–O6 1.957(3), Zn2–O6(A) 1.957(3), Na1–O6 2.225(4), Na1–O6(A) 2.225(4), Na1–O7 2.257(5), Na1–O7(A) 2.257(5), Na2–O5 2.219(4), Na2–O5(A) 2.219(4), Na2–O8 2.256(6), Na2–O8(A) 2.256(6).

After the crystals were exposed to air for several hours, the colour of complex **4** changed from colourless to yellow, which indicates the lability of complex **4**. The crystals of complex **3** are stable in air under moist conditions and can be exposed to air for a few hours without apparent deterioration. After complex **3** is exposed to air for several hours, the ^{1}H NMR spectrum in CDCl$_3$ shows very similar peaks as those in the spectrum of the **3** under a protective nitrogen atmosphere, which also indicates the stabilization of this complex. In order to understand the interaction between complex **3** and water, a ^{1}H NMR titration of the CDCl$_3$ solution of complex **3** with water was performed. The results show that complex **3** hydrolyzes to complex **1** partially and then to the free ligand, as evidenced by the shift in the peak at δ = 6.73 ppm for complex **3** to δ = 7.30 ppm, which can be attributed to the monosodium complex **1**, and by the appearance of a broad peak for the hydroxy group at δ = 5.10 ppm, which indicates the decomposition of complex **3** to the TBBPH$_2$ ligand (Figure S2). The ESI mass spectrum, collected under moist conditions in methanol/acetone, shows a series of peaks for sodium complexes, which also confirms the hydrolysis of complex **3** (Figure S3).

Ring-Opening Polymerization of L-Lactides

The ROP of L-lactide that employs **3**/**4** (0.02 mmol) as catalyst was systematically examined in toluene at 90 °C, as shown in Table 1. The catalytic experimental results show that complexes **3** and **4** are efficient catalysts for the ROP of L-lactide, and the polymerization occurs to about 90% conversion within 48 h with the ratio 100:1 to 250:1 for [monomer]/[complex]. By taking into account the lower solution state volume of PLA relative to polystyrene standards used for the GPC measurements, and on the basis of conversions from ^{1}H NMR analysis, the observed polymer molecular weights are consistent with the propagation of only one PLA chain from each complex. Further, a good polymerization control is demonstrated by the linear relationship between the number-average molecular weight (M_n) and the monomer-to complex ratio ($[M]_0/[\text{complex}]_0$) and polymers with PDIs ranging from 1.26 to 1.46 (Figure 3). Furthermore, epimerization of the chiral centres in PLLA does not occur as observed by the homonuclear decoupled ^{1}H NMR studies in the methine region.[16] End-group analysis of the polymer reveals the existence of a terminal hydroxy group, evidenced by the peak at 4.36 ppm in

Table 1. Ring-opening polymerization of L-LA with complexes **3** and **4**.[a]

Entry	Catalyst	$[M]_0/[\text{complex}]_0$	Conv. [%]	M_n (obsd.)[b]	M_n (calcd.)[c]	PDI
1	**3**	125	90.6	18800	16400	1.36
2	**3**	150	89.5	19300	19300	1.40
3	**3**	200	91.0	25500	26200	1.42
4	**3**	250	91.6	29000	33000	1.45
5	**4**	100	89.0	12800	12300	1.40
6	**4**	150	91.3	22200	19700	1.46
7	**4**	175	87.0	23900	22200	1.40
8	**4**	200	95.0	27400	27360	1.26

[a] Conditions: All manipulations were carried out under a dry nitrogen atmosphere, 0.02 mmol of complex, 10 mL of toluene, 90 °C, reaction time 48 h. [b] Obtained from GPC analysis times 0.58[18] and calibrated by polystyrene standard. [c] M_n (calcd.) = $([M]_0/[\text{complex}]_0) \times 144.13 \times$ conv.

^{1}H NMR spectrum, which indicates that the polymer is linear chain. The existence of a terminal hydroxy group as the end group on isolated polylactide samples and no epimerization possibly suggests that lactide polymerization is initiated by deprotonation of the monomer and propagation occurs through a coordination–insertion mechanism.[3c,17]

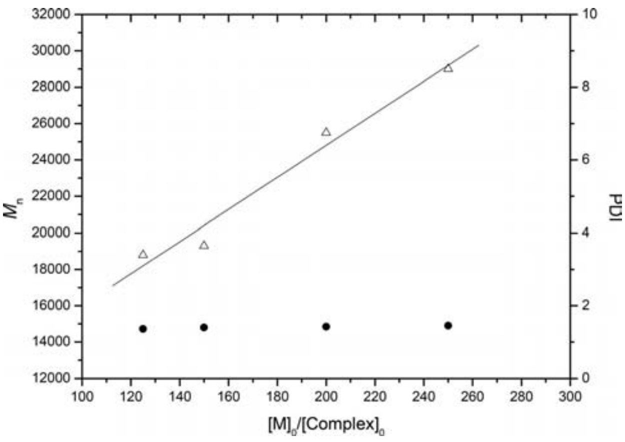

Figure 3. Polymerization of L-LA catalyzed by **3** in toluene at 90 °C. The relationship between M_n (△) [PDI (●)] of the polymer and the initial mol ratio [M]$_0$/[complex]$_0$ is shown.

By comparing with other zinc alkoxides, these two complexes show a low activity for the ROP of L-LA. However, it is interesting that complex **3** was found to be an active catalyst for ROP of LA under moist conditions without the protection of nitrogen. To systematically examine its sensitivity to water, unsublimed L-LA was used as a monomer and the weighing of the catalyst and the ROP reaction were performed in air. The results are summarized in Table 2. As expected, the higher conversion (more than 85%) was achieved at various monomer-to complex ratios. Further, a linear relationship between M_n and [M]$_0$/[complex]$_0$ was obtained (Table 2, Entries 1–4, Figure 4). Surprisingly, when an additional amount (18 µL) of water (50 equiv. with respect to complex **3**) was introduced into the ROP reaction with complex **3** as the catalyst, a high conversion and a controllable molecular weight were also obtained (Table 2, Entry 5). Catalyst **4** can also catalyze the polymerization of L-lactide with the addition of 3.6 µL water, but with low conversion (Table 2, Entry 6). Complex **1** was also systematically examined as a catalyst for the ROP of LA; the results are summarized in Table 3. The results show that complex **1** catalyzes the ROP reaction; experimental average molecular number weights based on the propagation of one PLA chain from two molecules of complex **1** were slightly higher than expected. Therefore, complex **3** can catalyze the ROP of LA in the presence of water; this outstanding feature possibly arises because the hydrolysis product complex **1** is also an efficient catalyst for the ROP of LA. The strategy mentioned in Scheme 1 was therefore achieved. Complex **1** can almost compensate for the decomposed complex **3**.

Table 2. Ring-opening polymerization of L-LA with complexes **3** and **4** under moist conditions.[a]

Entry	Catalyst	[M]$_0$/[complex]$_0$	Conv. [%]	M_n (obsd.)[b]	M_n (calcd.)[c]	PDI
1	**3**[d]	100	87.0	17300	12500	1.47
2	**3**[d]	125	90.0	21700	19400	1.49
3	**3**[d]	150	92.0	24700	23200	1.50
4	**3**[d]	175	93.7	27300	26900	1.36
5	**3**[e]	100	85.0	13000	12200	1.33
6	**4**[f]	100	25.4	n.d.	n.d.	n.d.

[a] Conditions: 0.02 mmol of complex, 10 mL of toluene, 90 °C, reaction time 48 h. [b] Obtained from GPC analysis times 0.58[18] and calibrated by polystyrene standard. [c] M_n (calcd.) = ([M]$_0$/[complex]$_0$) × 144.13 × conv. [d] The lactide was not recrystallized, the polymerization reactions were exposed to air. [e] 18 µL of H_2O added. [f] 3.6 µL of H_2O added.

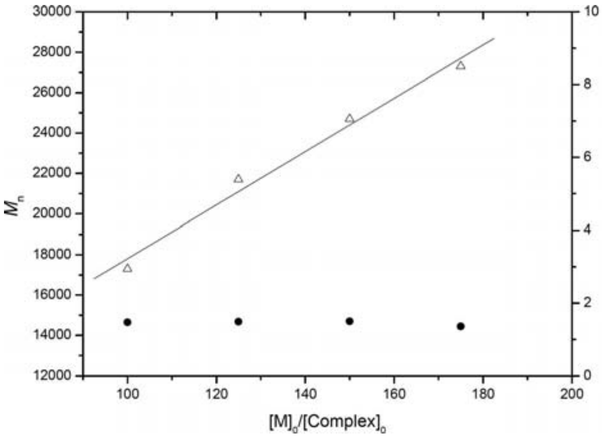

Figure 4. Polymerization of unsublimed L-LA catalyzed by **3** in toluene at 90 °C. The relationship between M_n (△) [PDI (●)] of the polymer and the initial mol ratio [M]$_0$/[complex]$_0$ is shown.

Table 3. Ring-opening polymerization of L-LA with complex **1**.[a]

Entry	Catalyst	[M]$_0$/[complex]$_0$	Conv. [%]	M_n (obsd.)[b]	M_n (calcd.)[c]	PDI
1	1	150	92.3	38600	20000	1.33
2	1	200	90.0	34800	26000	1.40
3	1	225	92.0	48400	30000	1.44
4	1	250	93.7	50600	34000	1.43

[a] Conditions: 0.02 mmol of complex, 10 mL of toluene, 80 °C, reaction time 24 h. [b] Obtained from GPC analysis times 0.58[18] and calibrated by polystyrene standard. [c] M_n (calcd.) = ([M]$_0$/[complex]$_0$) × 144.13 × conv.

Conclusions

Two new heterometallic aryloxides were synthesized as catalysts for the ring-opening polymerization of L-lactide. Compounds **3** and **4** have been demonstrated to be efficient catalysts for the "controlled" ROP of L-lactide. Complex **3** can even catalyze the ROP of unsublimed L-lactide in the presence of water, with a high conversion and a controllable molecular weight. A new strategy for the ROP of lactide under moist conditions was presented.

Experimental Section

General Considerations: All manipulations were carried out under a dry nitrogen atmosphere. Solvents, L-lactide and benzyl alcohol were purified before use. *n*BuLi (1.6 M in hexane) and $Zn(Et)_2$ (1.0 M in hexane) were purchased from Aldrich and used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-300 (300 MHz, 200 MHz) spectrometer with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed by using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Hitachi L-700 system equipped with a differential Bischoff 8120 RI detector by using THF (HPLC grade) as an eluent running at 1 mL/min. Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

(TBBP)Na(THF)$_3$ (1): A solution of 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol ($TBBPH_2$) (0.820 g, 2.0 mmol) and sodium (0.050 g, 2.2 mmol) was stirred in THF (20 mL) overnight at 50 °C under a N_2 atmosphere. The solvent was removed under vacuum to afford a white solid. Yield: 0.79 g (61%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.30, 7.12 (s, 4 H, Ph), 3.69 (s, 12 H, $-OCH_2CH_2-$), 1.83 (s, 12 H, $-OCH_2CH_2-$), 1.34, 1.30 [s, 36 H, $C(CH_3)_3$] ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 136.64, 129.03, 128.22, 126.05, 125.29, 123.04 (Ph), 67.96 ($-OCH_2CH_2-$), 34.79, 34.16, 31.78, 29.88 (*t*Bu), 25.52 ($-OCH_2CH_2-$) ppm. $C_{40}H_{65}NaO_5$ (645.91): calcd. C 74.03, H 10.10; found C 74.86, H 9.63.

(TBBP)Li(THF)$_3$ (2): A solution of 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol (0.820 g, 2.0 mmol) and *n*BuLi (1.4 mL, 2.2 mmol, 1.6 M in pentane) was stirred in THF (20 mL) at 0 °C under a N_2 atmosphere for 3 h. The solvent was removed under vacuum to afford a white solid. The white solid was dissolved in THF (5 mL). The THF solution was then filtered through Celite. After the filtrate was left for several hours at room temperature, colourless crystals were obtained. Yield: 0.66 g (52%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.31, 7.10 (s, 4 H, Ph), 3.65 (s, 12 H, $-OCH_2CH_2-$), 1.82 (s, 12 H, $-OCH_2CH_2-$), 1.41, 1.31 [s, 36 H, $C(CH_3)_3$] ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 136.45, 128.93, 128.04, 126.17, 125.09, 122.85 (Ph), 67.96 ($-OCH_2CH_2-$), 34.96, 34.20, 31.72, 29.90 (*t*Bu), 25.45 ($-OCH_2CH_2-$) ppm. $C_{40}H_{65}LiO_5$ (629.86): calcd. C 75.91, H 10.35; found C 76.70, H 9.85.

[(TBBP)$_2$Zn][(Na)$_2$(THF)$_4$] (3): A solution of 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol (0.820 g, 2.0 mmol) and sodium (0.050 g, 2.2 mmol) was stirred in THF (20 mL) overnight at 50 °C under a N_2 atmosphere. $Zn(Et)_2$ (1.2 mL, 1.2 mmol, 1.0 M in hexane) was then slowly added to the solution. After stirring for 6 h, the solvent was removed under vacuum to afford a white solid. The white solid was dissolved in THF (5 mL), and the solution was then filtered through Celite. After the filtrate was left for several hours at room temperature, colourless crystals were obtained. Yield: 0.60 g (50%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 136.64, 129.03, 128.22, 126.05, 125.29, 123.04(Ph), 67.96 ($-OCH_2CH_2-$), 34.79, 34.16, 31.78, 29.88 (*t*Bu), 25.52 ($-OCH_2CH_2-$).: δ = 7.09, 6.73 (s, 8 H, Ph), 3.57 (s, 16 H, $-OCH_2CH_2-$), 1.72 (s, 16 H, $-OCH_2CH_2-$), 1.25, 1.18 [s, 72 H, $C(CH_3)_3$] ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 160.81, 135.30, 135.15, 134.69, 128.23, 121.58 (Ph), 67.91 ($-OCH_2CH_2-$), 34.66, 33.98, 31.90, 31.59 (*t*Bu), 25.31 ($-OCH_2CH_2-$) ppm. $C_{72}H_{108}Na_2O_8Zn$ (1213.01): calcd. C 71.29, H8.97; found C, 71.60; H, 8.86.

[(TBBP)$_2$Zn][(Li)$_2$(THF)$_4$] (4): A solution of 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol (0.820 g, 2.0 mmol) and *n*BuLi (1.4 mL, 2.2 mmol, 1.6 M in pentane) was stirred in THF (20 mL) at 0 °C under a N_2 atmosphere for 3 h. $Zn(Et)_2$ (1.2 mL, 1.2 mmol, 1.0 M in hexane) was then slowly added to the solution. After stirring for 4 h, the solvent was removed under vacuum to afford a white solid. The white solid was dissolved in toluene (7 mL). The toluene solution was then filtered through Celite. After the filtrate was left overnight at room temperature, colourless crystals were obtained. Yield: 0.63 g (53%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.11, 6.72 (s, 8 H, Ph), 3.57 (s, 16 H, $-OCH_2CH_2-$), 1.67 (s, 16 H, $-OCH_2CH_2-$), 1.21, 1.18 [s, 72 H, $C(CH_3)_3$] ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 158.88, 136.13, 135.74, 134.07, 128.22, 122.00 (Ph), 68.08 ($-OCH_2CH_2-$), 34.85, 33.98, 32.10, 31.50 (*t*Bu), 25.30 ($-OCH_2CH_2-$) ppm. $C_{72}H_{108}Li_2O_8Zn$ (1180.92): calcd. C 73.23, H 9.22; found C 73.53, H 9.16.

Typical Polymerization Procedures: A typical polymerization procedure is exemplified by the synthesis of PLLA-150 (the number 150 indicates the designed $[M]_0/[complex]_0$) at 90 °C (Table 1, Entry 2). The polymerization conversion was analyzed by ^1H NMR spectroscopy. L-Lactide (0.432 g, 3.0 mmol) was added to a solution of complex **3** (0.027 g, 0.02 mmol) in toluene (10 mL). After the solution was stirred at 90 °C for 48 h, the reaction was quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL). Hexane (40 mL) was then added to the above mixture to give a white crystalline solid. The resulting solid was washed with water twice and then dried under vacuum.

X-Ray Crystallographic Studies: A summary of the crystallographic data is given in Table S1. Suitable crystals of **2**, **3** and **4** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and were mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.3° per frame). The absorption correction was based on the symmetry-equivalent reflections by using the program SADABS. The space group determination was based on a check of the Laue symmetry, and systematic absence and was confirmed by using the structure solution. The structures were solved by direct methods by using the SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined by using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. CCDC-777036, -777037 and -777038 (for complexes **1**–**3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic and structure refinement data, results from the ^1H NMR titration of the $CDCl_3$ solution, electrospray-ionization mass spectra, and ^1H NMR spectra are presented.

Acknowledgments

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