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Highly Active Families of Catalysts for the Ring-Opening Polymerization of Lactide: Metal Templated Organic Hydrogen Bond Donors Derived from 2-Guanidinobenzimidazole

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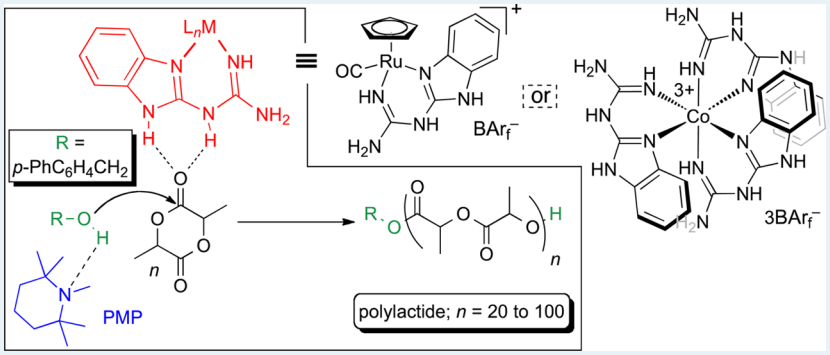
Supporting Information



ABSTRACT: Cobalt and ruthenium chelate complexes of 2-guanidinobenzimidazole (GBI), *mer*-$[Co(GBI)_3](BAr_f)_3 \cdot 14H_2O$ ($\mathbf{1}^{3+}$ $3BAr_f^-$; BAr_f = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$), and $[(\eta^5\text{-}C_5H_5)Ru(CO)(GBI)](BAr_f)$ can serve as hydrogen bond donor catalysts and, together with equimolar quantities of 1,2,2,6,6-pentamethylpiperidene (PMP; hydrogen bond acceptor) and 4-phenylbenzyl alcohol initiator (InOH), effect controlled ring-opening polymerizations of DL-lactide at low loadings (1−3 mol %). These inexpensive systems afford polylactide with narrow dispersities (<1.18) and M_n values of 4000−11 000 g/mol. MALDI-ToF mass spectra show a series of peaks separated by m/z values of 144 and an absence of transesterification side reactions between polymer chains. Runs with multiple charges of monomer establish the living nature of the polymerization, and ^{1}H NMR or UV−visible experiments provide evidence for key hydrogen bonding interactions (InOH/PMP; $\mathbf{1}^{3+}$ $3BAr_f^-$/DL-lactide).

KEYWORDS: *supramolecular, organocatalysis, hydrogen bonding, cobalt, ruthenium, ring-opening polymerization, DL-lactide, polylactide*

The synthesis of biodegradable polymers has attracted much attention recently,[1] and polylactides derived from ring-opening polymerizations of lactide, a monomer readily available from renewable resources, have received particular focus.[2,3] A variety of catalyst systems for lactide polymerization have been developed, and one very promising category involves hydrogen bond donors (HBDs),[3−7] which constitute a major class of what are often termed "organocatalysts".[8] As represented in Scheme 1 (top), these are commonly employed in conjunction with a catalytic amount of a hydrogen bond acceptor (HBA). The donor activates the electrophilic monomer, and the acceptor activates a hydroxylic initiator (InOH) as well as the growing chain end. Some previously utilized hydrogen bond donors are illustrated in Scheme 1 (middle).

We have been developing new types of "organic" chiral HBDs that are templated by metals.[9−11] One series is based upon classical Werner complexes of the type $[Co(en)_3]^{3+}$ $3X^-$ (en = 1,2-ethylenediamine), with X^- being a lipophilic, poorly coordinating anion, such as BAr_f^- ($B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$), to attain sufficient solubilities in organic solvents.[9a] Another involves adducts of the inexpensive and readily available 2-guanidinobenzimidazole ligand (GBI; Scheme 1, bottom).[10,12] This compound has several conformational degrees of freedom that are removed upon chelation, providing a geometrically well-defined array of NH donor groups.

These complexes have proven to be highly active as well as enantioselective catalysts (when enantiopure) for a variety of condensation reactions of small molecules.[9b,10c] We set out to probe their suitability as catalysts for lactide polymerization. Although a variety of hydrogen bonding motifs would be possible, a mechanism along the lines of Scheme 2 would be expected for the GBI adducts. This sequence is illustrated with the HBA 1,2,2,6,6-tetramethylpipyridene (PMP) and the initiator 4-phenylbenzyl alcohol (p-$PhC_6H_4CH_2OH$), both of which have proved particularly effective in earlier studies.[6b,13] In this communication, we disclose two architecturally distinct HBD catalysts that represent a substantial conceptual departure

Received: January 30, 2014
Revised: February 26, 2014
Published: February 28, 2014

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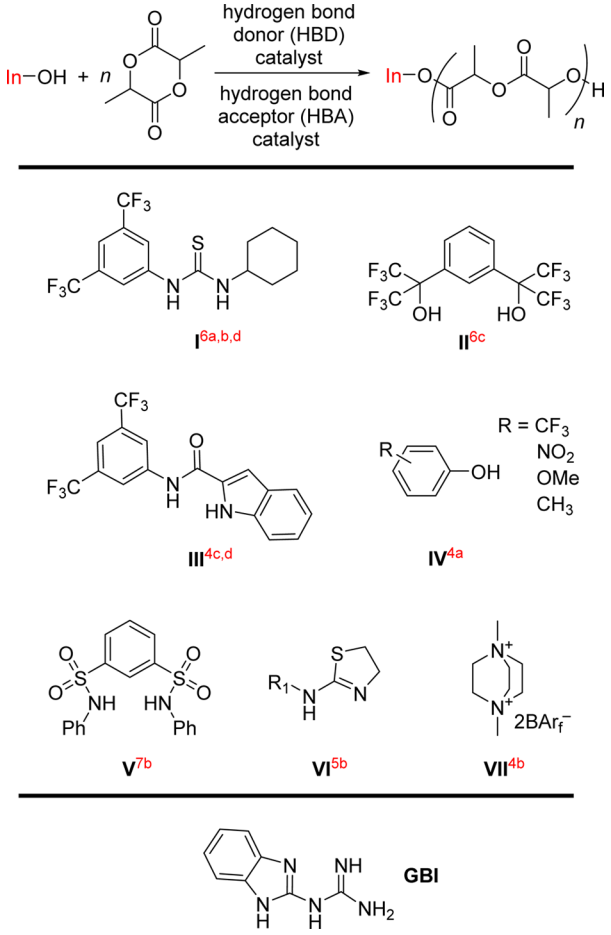
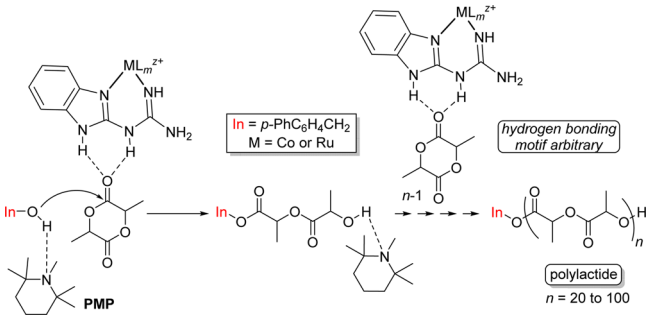
Scheme 1. Ring-Opening Polymerization of Lactide Using Hydrogen Bond Donor/Acceptor Catalyst Systems (top), Typical Hydrogen Bond Donors Employed Previously (middle), and the New Catalyst Component 2-Guanidinobenzimidazole (GBI, bottom)



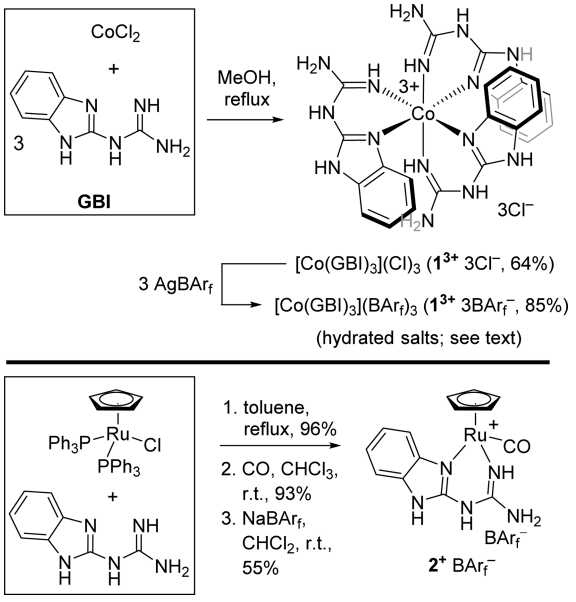
Scheme 2. Possible Mechanism for the Ring-Opening Polymerization of Lactide Using GBI Complex Catalysts



from those depicted in Scheme 1, with activities that match or exceed common literature benchmarks.

In screening experiments with Werner complexes, polymerization of DL-lactide indeed occurred; however, the GBI adducts selected gave more promising results. Two lead compounds were accessed, as shown in Scheme 3. First, $CoCl_2$ and GBI (3.0 equiv) were reacted in methanol to give the previously reported cobalt tris(GBI) trihydrate *mer*-$[Co(GBI)_3](Cl)_3 \cdot 3H_2O$ ($\mathbf{1}^{3+}$ $3Cl^-$) as a red solid in 64% yield after workup.[14] The crystal structure of a mixed chloride/nitrate salt showed

Scheme 3. Syntheses of Cobalt and Ruthenium GBI Complexes



the trication to have the meridional (mer) geometry,[14] which is furthermore chiral. This complex readily dissolved in water, DMF, DMSO, and acetone, but not in CH_2Cl_2 or ether; hence, a more lipophilic salt was sought.

Thus, an aqueous solution of $\mathbf{1}^{3+}$ $3Cl^-$ was treated with a CH_2Cl_2 solution of $AgBAr_f$ (3.0 equiv). The red aqueous layer decolorized, and workup of the CH_2Cl_2 phase afforded the desired salt *mer*-$[Co(GBI)_3](BAr_f)_3 \cdot 14H_2O$ ($\mathbf{1}^{3+}$ $3BAr_f^-$) as a tetradecahydrate in 85% yield. This new complex was characterized by microanalysis and NMR (^1H, ^{13}C), IR, and UV–visible spectroscopy, as detailed in the Supporting Information. The ^1H and ^{13}C NMR spectra showed three sets of signals in a 1:1:1 ratio, diagnostic of a mer isomer with inequivalent GBI ligands. The hydration level, which was reproducible (±1), was established by ^1H NMR and microanalysis.

Second, the cyclopentadienyl ruthenium complex $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)$ was converted in a previously described three-step procedure involving (1) substitution of the chloride and one PPh_3 ligand by GBI, (2) substitution of the remaining PPh_3 ligand by CO, and (3) exchange of the chloride anion by BAr_f^- to give the racemic chiral salt $[(\eta^5\text{-}C_5H_5)Ru(CO)(GBI)](BAr_f) \cdot 1.5H_2O$ ($\mathbf{2}^+$ BAr_f^-) as a slightly hydrated yellow powder in 49% overall yield.[10]

The ring-opening polymerization of DL-lactide was investigated under the conditions indicated in Table 1 and Schemes 2 and 4. Reactions were carried out in 1.0 M CH_2Cl_2 solutions of DL-lactide in the presence of activated 4 Å molecular sieves to reduce the concentration of water, which can independently initiate polymerization[15] or bind to the catalysts. In most experiments, equimolar quantities of the HBD, HBA, and initiator 4-phenylbenzyl alcohol were employed.

First, to confirm the operation of a dual HBD/HBA catalyst system, three experiments were conducted with the initiator but without *either* the HBD ($\mathbf{1}^{3+}$ $3BAr_f^-$ or $\mathbf{2}^+$ BAr_f^-) or HBA (PMP) component. As summarized in entries 1, 2, and 8 of Table 1, no reactions of DL-lactide were observed after 24 h using either 1 or 3 mol % loadings.

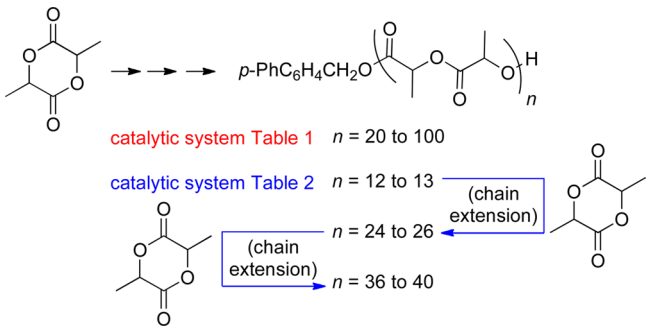
dx.doi.org/10.1021/cs500134z | ACS Catal. 2014, 4, 1134–1138

Table 1. Ring-Opening Polymerization of DL-Lactide.[a]

entry	catalyst system (HBD/HBA)[b]	DL-lactide/HBD: HBA/InOH[b]	conv (%)[c]	$M_{n,TH}$ (g/mol)[d]	$M_{n,SEC}$ (g/mol)[e]	$Đ^c$
1	−/PMP	100:0:1:1[f]	0	0		
2	$\mathbf{1}^{3+}$ $3BAr_f^-$/−	100:1:0:1[f]	0	0		
3	$\mathbf{1}^{3+}$ $3BAr_f^-$/PMP	100:1:1:1	100	14500	4440	1.11
4	$\mathbf{1}^{3+}$ $3BAr_f^-$/PMP	100:3:3:3	99	4930	4270	1.16
5	$\mathbf{1}^{3+}$ $3BAr_f^-$/PMDETA	100:1:1:1	50	7290	4360	1.18
6	$\mathbf{1}^{3+}$ $3BAr_f^-$/$CyNMe_2$	100:1:1:1	46	6710	4190	1.15
7	$\mathbf{1}^{3+}$ $3BAr_f^-$/NEt_3	100:1:1:1	32	4670		
8	$\mathbf{2}^{+}$ BAr_f^-/−	100:1:0:1[f]	0	0		
9	$\mathbf{2}^{+}$ BAr_f^-/PMP	100:1:1:1	100	14500	11000	1.05
10	$\mathbf{2}^{+}$ BAr_f^-/PMP	100:3:3:3	100	4940	4680	1.07
11	$\mathbf{2}^{+}$ BAr_f^-/PMDETA	100:1:1:1	44	6420	6160	1.10
12	$\mathbf{2}^{+}$ BAr_f^-/$CyNMe_2$	100:1:1:1	35	5100		
13	$\mathbf{2}^{+}$ BAr_f^-/NEt_3	100:1:1:1	23	3350		
14	GBI/PMP	100:1:1:1	30	4375		

[a]Conditions: [DL-lactide] = 1.0 M in CH_2Cl_2, 4 Å molecular sieves, room temperature, 24 h reaction time. [b]PMP = 1,2,2,6,6-tetramethylpipyridene, PMDETA = $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$, InOH = 4-phenylbenzyl alcohol. [c]Monomer conversion was determined by ^1H NMR. [d]Calculated from $\{[\text{DL-lactide}]_0/[\text{In}]_0 \times \text{DL-lactide conversion} \times M_{\text{DL-lactide}}\} + M_{\text{In}}$, with $M_{\text{DL-lactide}}$ = 144 g/mol and M_{In} = 184 g/mol. [e]M_w/M_n, determined by SEC using a refractive index detector vs polystyrene standards for conversions of >40%. [f]Results were identical when the HBD or HBA and InOH loadings were increased to 3 mol %.

Scheme 4. Polymerizations in Tables 1 and 2



Next, analogous experiments were conducted with $\mathbf{1}^{3+}$ $3BAr_f^-$ or $\mathbf{2}^{+}$ BAr_f^- *and* PMP. As shown by entries 4 and 10, both HBD/HBA systems were effective catalysts when employed together with the initiator at 3 mol % loadings. The monomer was consumed over the course of 24 h, and the number average molecular weights of the polylactides determined by size exclusion chromatography (SEC; M_n 4270 and 4680 g/mol, respectively) were close to the theoretical maximum (~4900 g/mol). Importantly, the dispersities ($Đ$) were narrow (1.16−1.07), and MALDI-ToF mass spectra showed only a single family of ions separated by m/z values of 144. These data establish the operation of a controlled polymerization[16] in both cases. Separate experiments (2 mol % loadings) showed that the cobalt complex $\mathbf{1}^{3+}$ $3BAr_f^-$ gave a slightly more active catalyst system than the ruthenium complex $\mathbf{2}^{+}$ BAr_f^- (14 vs 17 h completion).

When analogous experiments were conducted at 1% loadings (entries 3 and 9), all monomer was again consumed, and the M_n value of the polylactide derived from $\mathbf{2}^{+}$ BAr_f^- and PMP was close to the theoretical maximum (11 000 vs 14 500 g/mol). Together with the low dispersity (1.05) and MALDI-ToF data, a controlled polymerization was again evident; however, the M_n value of the polylactide derived from $\mathbf{1}^{3+}$ $3BAr_f^-$ was much lower than the theoretical maximum (4440 vs 14 500 g/mol), although the dispersity remained low (1.11) and no other families of polymers were detected by mass spectrometry. To our knowledge, this profile of properties has not previously been reported for any polylactide sample, and efforts to develop a rationale remain in progress.

Additional experiments were conducted at 1% loadings, but with (a) free GBI in place of the complexes $\mathbf{1}^{3+}$ $3BAr_f^-$ or $\mathbf{2}^{+}$ BAr_f^-, or (b) other tertiary amine HBA additives in place of PMP. As shown by entry 14 of Table 1, GBI was much less active than either of the complexes, which is consistent with the poorer HBD properties that would be expected. As summarized in entries 5−7 and 11−13, the amines PMDETA (Me_2N-$(CH_2)_2NMe(CH_2)_2NMe_2$),[6d] $CyNMe_2$ and NEt_3 showed progressively diminishing conversions (50−44%, 46−35%, 32−23%), with $\mathbf{1}^{3+}$ $3BAr_f^-$ giving slightly more reactive systems than $\mathbf{2}^{+}$ BAr_f^-. Together with a previous study,[4a] there appears to be a rough correlation between activity and the pK_a value of the conjugate acid of the HBA, at least for the monoamines.[17]

Table 2. Stepwise Chain Extension of Polylactide[a]

entry	catalyst system (HBD/HBA)	DL-lactide/HBD HBA/InOH	time (h)	conv (%)	$M_{n,TH}$ (g/mol)	$M_{n,SEC}$ (g/mol)	$Đ^c$
15	$\mathbf{1}^{3+}$ $3BAr_f^-$/PMP	50:4:4:4	24	100	1990	2550	1.22
16[b]	$\mathbf{1}^{3+}$ $3BAr_f^-$/PMP	100[b]:4:4:4	48[b]	100	3790	5090	1.10
17[b]	$\mathbf{1}^{3+}$ $3BAr_f^-$/PMP	150[b]:4:4:4	72[b]	100	5590	9530	1.17
18	$\mathbf{2}^{+}$ BAr_f^-/PMP	50:2:2:2	24	100	3790	5600	1.28
19[b]	$\mathbf{2}^{+}$ BAr_f^-/PMP	100[b]:2:2:2	48[b]	98	7240	9290	1.22
20[b]	$\mathbf{2}^{+}$ BAr_f^-/PMP	150[b]:2:2:2	72[b]	92	10110	13530	1.15

[a]All conditions, methods, and abbreviations are the same as Table 1, unless noted. [b]This entry is a continuation of the previous experiment after charging with additional DL-lactide (cumulative total or time indicated).

dx.doi.org/10.1021/cs500134z | ACS Catal. 2014, 4, 1134−1138

The feasibility of generating higher molecular weight polylactides and the living nature of the catalyst systems were probed. As shown in Scheme 4 and Table 2, three chain extension cycles were performed with each dual HBD/PMP system (entries 15−17 and 18−20). Higher loadings were employed with $\mathbf{1}^{3+}$ $3BAr_f^-$ than with $\mathbf{2}^+$ BAr_f^- (4 vs 2 mol %) in the hope that this might bring the M_n values of the polylactides more in line with the theoretical maxima. In both series, the reactions were charged with the same quantities of DL-lactide at the start (initial entry), after 24 h (second entry), and after 48 h (final entry).

For all entries, conversions were essentially complete. At each chain extension stage, the molar masses of the polylactides were in good agreement with the theoretical maxima, and the dispersities remained low (1.28−1.10). MALDI-ToF mass spectra (Supporting Information) showed small amounts of a second polylactide family with ions that differed from the "main family" ($\Delta m/z$ 144) by m/z 72. These are known to be derived from transesterifications in which the hydroxyl terminus of one growing polymer chain attacks an interior ester linkage of another,[4,6a] a process favored by the higher catalyst loadings and, hence, polymer concentrations in these experiments. However, the quantities of these anomalous polymers are not high enough to influence the data in Table 2, which establish the controlled and living character of these polymerizations.[16]

Finally, additional experiments were conducted bearing on the HBD/HBA interactions proposed in Scheme 2. First, the neat HBA PMP (20 equiv) was gradually added to a 0.050 M $CDCl_3$ solution of 4-phenylbenzyl alcohol (InOH). The hydroxyl ^{1}H NMR signal progressively shifted downfield from 1.71 to 2.76 ppm. Given the pK_a values of 4-phenylbenzyl alcohol and the conjugate acid of PMP (~16,[18] 11.25[17a]), proton transfer must be insignificant, and the downfield shift is ascribed to hydrogen bonding per Scheme 2. Second, a 0.010 M CH_2Cl_2 solution of $\mathbf{1}^{3+}$ $3BAr_f^-$ was titrated with neat DL-lactide and monitored by UV−visible spectroscopy. The λ_{max} gradually shifted from 504.5 to 509.0 nm as the first equivalent of lactide was added and then remained constant as additional equivalents were added. A variety of types of experiments with other guests described elsewhere support the efficacy of $\mathbf{2}^+$ BAr_f^- as a HBD.[10]

In summary, the GBI complexes $\mathbf{1}^{3+}$ $3BAr_f^-$ and $\mathbf{2}^+$ BAr_f^- have significantly expanded the range of HBD catalysts that can be applied to the ring-opening polymerization of DL-lactide. They are representatives of a large, conceptually new family of organic HBDs that are templated by metal fragments and offer innumerable diversity elements. They are also effective at loadings, temperatures, and reaction times that are among the lowest in the literature.[3−7] Spectroscopic experiments support the general mode of HBD and HBA interactions shown in Scheme 2. In terms of future work, it should be noted that both HBDs are chiral, and close relatives of $\mathbf{2}^+$ BAr_f^- are easily rendered enantiopure,[10c] thereby providing candidates for stereocontrolled lactide polymerizations. Furthermore, it might prove possible to incorporate the HBA function into the counteranion. These and other themes will receive attention in future reports from this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Details of syntheses, MALDI-ToF mass specrtra, SEC data, rate experiments, NMR spectra, and titrimetric experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Welch Foundation (Grant A-1656) for support.

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