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Porphyrins Fused to N-Heterocyclic Carbenes (NHCs): Modulation of the Electronic and Catalytic Properties of NHCs by the Central Metal of the Porphyrin

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Abstract: We report herein a detailed study of the use of porphyrins fused to imidazolium salts as precursors of N-heterocyclic carbene ligands **1M**. Rhodium(I) complexes **6M**–**9M** were prepared by using **1M** ligands with different metal cations in the inner core of the porphyrin (M = Ni^{II}, Zn^{II}, Mn^{III}, Al^{III}, 2H). The electronic properties of the corresponding N-heterocyclic carbene ligands were investigated by monitoring the spectroscopic changes occurring in the cod and CO ancillary ligands of [(**1M**)Rh(cod)Cl] and [(**1M**)Rh$(CO)_2$Cl] complexes (cod = 1,5-cyclooctadiene). Porphyrin–NHC ligands **1M** with a trivalent metal cation such as Mn^{III} and Al^{III} are overall poorer electron donors than porphyrin–NHC ligands with no metal cation or incorporating a divalent metal cation such as Ni^{II} and Zn^{II}. Imidazolium salts **3M** (M = Ni, Zn, Mn, 2H) have also been used as NHC precursors to catalyze the ring-opening polymerization of L-lactide. The results clearly show that the inner metal of the porphyrin has an important effect on the reactivity of the outer carbene.

Keywords: carbenes • organocatalysis • porphyrinoids • ring-opening polymerization • UV/Vis spectroscopy

Introduction

Over the last 20 years, N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic and coordination chemistry.[1] NHCs are able to catalyze a wide range of chemical transformations, either as ligands of transition-metal catalysts or directly as organocatalysts.[2] Understanding and tuning the electronic and steric properties of NHCs allows the design, selection, and use of tailor-made NHCs for a given catalytic application. Thus, there is a growing interest in developing new NHCs, the electronic properties of which can be finely varied.[3] The modulation of the electronic properties of a given NHC is not trivial, and often requires the synthesis of new NHC precursors from scratch. This explains why switchable NHCs, which allow the reversible and controlled switching of their electronic properties, have attracted so much attention: Redox-active,[4] pH-active,[5] and photoswitchable[6] NHCs are representative examples of such switchable NHCs. The coordination of a metal complex to a distant coordination site attached to the NHC can also dramatically modulate the electronic and steric properties of the NHC moiety. For example, Ganter and co-workers showed that a cationic pentamethylcyclopentadienyl–ruthenium complex ($[RuCp^*]^+$) can be anchored to a benzimidazol-2-ylidene ligand to significantly decrease the overall electron-donating ability of the NHC ligand compared with the parent benzimidazol-2-ylidene ligand.[7] Although this approach cannot be described as a switchable process, it represents an interesting procedure for modulating the electronic properties of NHC ligands.

We have recently developed the chemistry of NHCs fused to porphyrins (**1M**) with the aim of modulating the electronic and catalytic properties of the peripheral carbene unit (Figure 1).[5b] For example, we have shown that NHC ligands annulated to free-base porphyrins can be reversibly switched between electron-poor and -rich states upon protonation and deprotonation of the inner nitrogen atoms of the porphyrin. The porphyrin-NHC ligands thus appear to be interesting candidates for catalytic applications as they should allow the activity of the catalyst to be tuned through simple chemical transformations of the porphyrin, for example, by metalation or protonation of the inner core. Indeed, other

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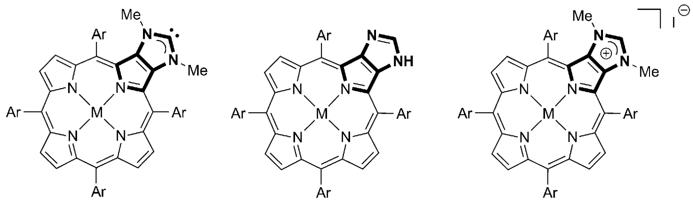


porphyrin-NHC ligand **1M** — porphyrin fused to imidazole ring **2M** — porphyrin fused to imidazolium salt **3M**

Figure 1. Structures of porphyrin-NHC ligand **1M**, a porphyrin fused to the imidazole ring **2M**, and a porphyrin fused to imidazolium salts **3M** (Ar = 4-*t*BuPh).

research groups have synthesized porphyrins incorporating peripheral metal complexes and tuned their catalytic activity by changing the inner metal of the porphyrin. For example, the groups of Osuka-Shinokubo,[8] Klein Gebbink,[9] Imahori,[10] and Liu[11] have independently shown that peripherally anchored palladium complexes exhibit different catalytic activities in Heck reactions depending on the nature of the metal in the porphyrin (Figure 2). Herein we show that NHCs fused to the π system of porphyrins (**1M**) are able to catalyze the ring-opening polymerization (ROP) of L-lactide (L-LA) and that the inner metal of the porphyrin plays a crucial role in the catalytic process.

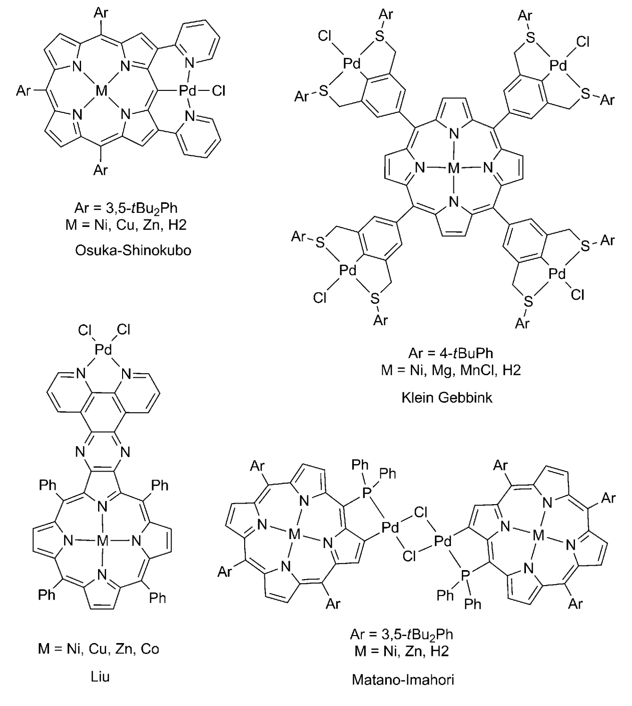
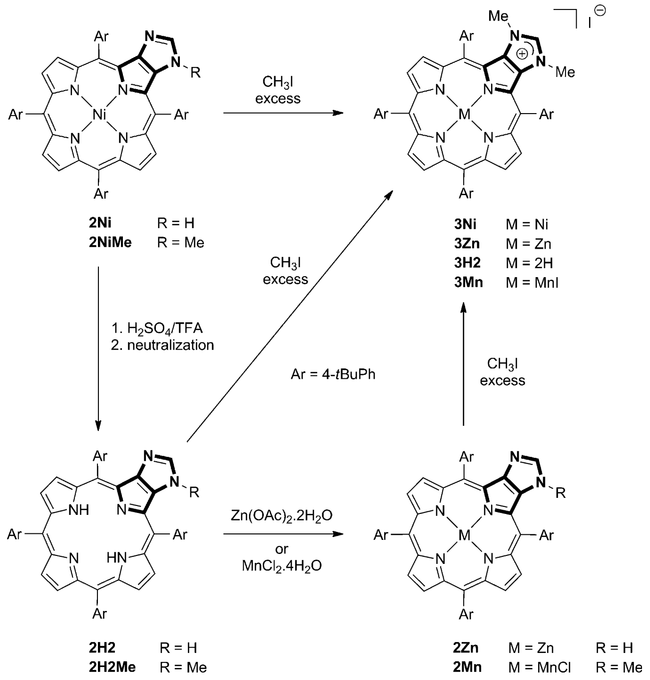


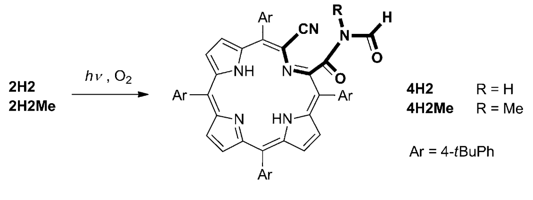
Figure 2. Examples of peripherally metalated porphyrin complexes for catalytic applications[8–11]

Results and Discussion

Synthesis of imidazolium salts fused to porphyrins: Imidazolium salts fused to the π system of a porphyrin macrocycle (**3M**) are the key precursors of the hybrid porphyrin-NHC ligands **1M** (Scheme 1).[12] To exclude steric effects in the following study, only imidazolium salts with *N*-methyl groups were synthesized. The porphyrins fused to an imidazole ring, **2Ni** and **2NiMe**, were obtained by the stepwise functionalization of a Ni^{II} *meso*-tetraarylporphyrin complex (*meso*-aryl = 4-*t*BuPh).[13] Free-base imidazoles **2H2** and **2H2Me** were obtained by treating the corresponding Ni^{II} complexes **2Ni** and **2NiMe** with a mixture of H_2SO_4 and trifluoroacetic acid (TFA). Interestingly, **2H2** and **2H2Me** appeared to be air-sensitive both in solution and in the solid state, and were slowly oxidized to free-base secochlorins **4H2** and **4H2Me** (Scheme 2).[14] Because singlet oxygen ($^1O_2$) generated by free-base macrocycles under ambient light is the dominant oxidant, **2H2** and **2H2Me** should be manipulated under argon in the absence of light to prevent this ring-opening reaction. Metalation of the corresponding free-base **2H2** with $Zn(OAc)_2{\cdot}2H_2O$ afforded Zn^{II} imidazole

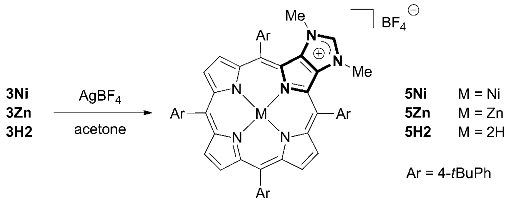


Scheme 1. Preparation of imidazolium salts **3M**.



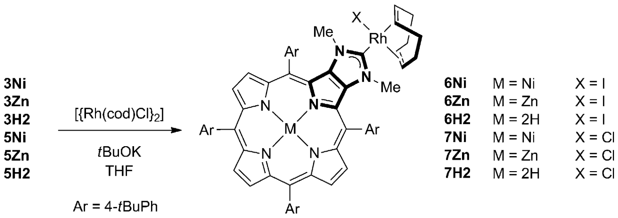
Scheme 2. Formation of free-base secochlorins **4H2** and **4H2Me**.

2Zn in 86 % yield (Scheme 1). Alkylation of imidazoles **2Ni**, **2H2**, and **2Zn** with iodomethane afforded the corresponding imidazolium salts **3Ni**, **3H2**,and **3Zn** in yields of 80–83 % (Scheme 1). The ^{1}H NMR spectra of **3M** (M=Ni, 2H and Zn) recorded in $CDCl_3$ revealed downfield signals at $\delta = 11.01$, 10.77, and 10.17 ppm, respectively, due to hydrogen bonds between the electron-deficient imidazolium rings and iodide.[13a] The corresponding imidazolium salts **5M** (M=Ni, Zn, H2) with tetrafluoroborate as counter anion were then obtained in yields of 90–94 % by treating imidazolium salts **3M** with $AgBF_4$ in acetone (Scheme 3). The imidazolium protons of **5Ni**, **5H2**, and **5Zn** were observed by ^{1}H NMR spectroscopy in $CDCl_3$ at higher fields than the corresponding imidazolium salts **3M**, at $\delta = 9.27$, 9.26, and 9.04 ppm (see Figure S1 in the Supporting Information).



Scheme 3. Preparation of imidazolium salts **5M**.

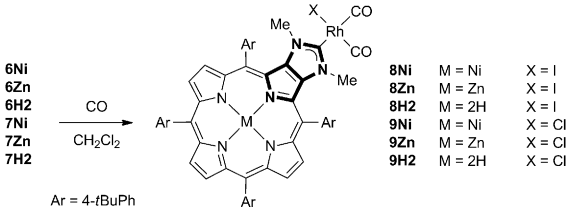
Electronic properties of porphyrin-NHC 1M ligands: Several distinctly different spectroscopic and analytical methods can be used to quantify the electron-donating properties of the NHC ligands. Notably, the Rh^I and Ir^I complexes [(NHC)MCl(cod)] (cod=1,5-cyclooctadiene) and [(NHC)MCl$(CO)_2$] (M=Rh, Ir) are routinely used to evaluate the electron-donating ability of NHCs by monitoring the ^{1}H NMR and IR spectroscopic changes that occur in the cod and CO ancillary ligands, respectively.[15] Rh^I complexes [(**1M**)RhI(cod)] (**6M**; M=Ni, Zn, H2) were obtained in yields of 63–92 % by treating imidazolium salts **3M** with [{RhCl(cod)}$_2$] (0.5 equiv) and *t*BuOK in THF (Scheme 4).



Scheme 4. Preparation of Rh^I complexes **6M** and **7M**.

Energy-dispersive X-ray (EDX) spectroscopy showed that iodide is coordinated to the rhodium center (Rh/I≈1:1; no Cl detected) in these complexes.[5b] Because the data reported on the electronic properties of NHC–Rh complexes were obtained with chloride coordinated to the rhodium center, the Rh^I complexes [(**1M**)RhCl(cod)] (**7M**; M=Ni, Zn, H2) were obtained in yields of 71–94 % from imidazolium salts **5M** (M=Ni, Zn, H2) as NHC precursors (Scheme 4). For these complexes, EDX spectroscopy confirmed that chloride was coordinated to the rhodium center (Rh/Cl≈1:1; no I detected). The formation of the peripheral [RhX(cod)] complexes (X=I or Cl) in all the complexes **6M** and **7M** was confirmed by 1) the absence of a signal in the ^{1}H NMR spectrum arising from the imidazolium proton due to the formation of the NHC–Rh bond, 2) the four characteristic signals of the coordinated cod ligands in the ^{1}H NMR spectra of the **7M** complexes with M=Ni, Zn, and H2 (see Figure S2 in the Supporting Information), and 3) the molecular mass peaks observed by MALDI-TOF mass spectrometry for these complexes. ^{1}H NMR spectroscopy can be a useful technique for measuring electron densities in Rh–olefin compounds.[16] Olefinic protons, particularly those *trans* to the NHC ligand, are shifted upfield in the presence of electron-donating groups in the 4,5-positions of the NHC. Here, olefinic protons *trans* to the NHC ligand were observed at 5.00, 5.00, and 4.96 ppm for **7Ni**, **7Zn**, and **7H2**, respectively, which indicates that the electron-donating abilities of all the NHC ligands are very similar according to ^{1}H NMR spectroscopy.

A more common method for evaluating the electron-donating properties of NHC ligands involves the synthesis of *cis*-[(NHC)MCl$(CO)_2$] (M=Rh, Ir) complexes and determining their CO stretching vibrations, ν(CO), by IR spectroscopy: lower ν(CO) frequencies are observed with stronger electron-donating NHC ligands.[17,18] Complexes **8M** and **9M** (M=Ni, Zn, H2) were synthesized by bubbling carbon monoxide through a solution of complexes **6M** and **7M**, respectively, in CH_2Cl_2 to quantitatively substitute the cod ligand by two CO ligands (Scheme 5). Two CO stretching frequencies were observed for all complexes **8M** and **9M** by IR spectroscopy and confirmed their *cis* geometry (Table 1). Similar CO stretching vibrations were recorded in CH_2Cl_2 with $\nu^{av}(CO) = 2037$, 2037.5, and 2038 cm^{-1} for **8H2**, **8Zn**, and **8Ni**, respectively (all ν(CO) frequencies are given in Table 1). Higher CO stretching vibrations were recorded in CH_2Cl_2 for **9M** complexes with chloride coordinated to the rhodium center, all with similar ν^{av}(CO) values of 2040.5, 2041, and 2041.5 cm^{-1} for **9Zn**, **9H2**, and **9Ni**, respectively. These IR data are consistent with previously reported ν(CO) data for [(NHC)RhX$(CO)_2$] complexes with X=Cl and I.[15,19] They are also indicative of small differences be-

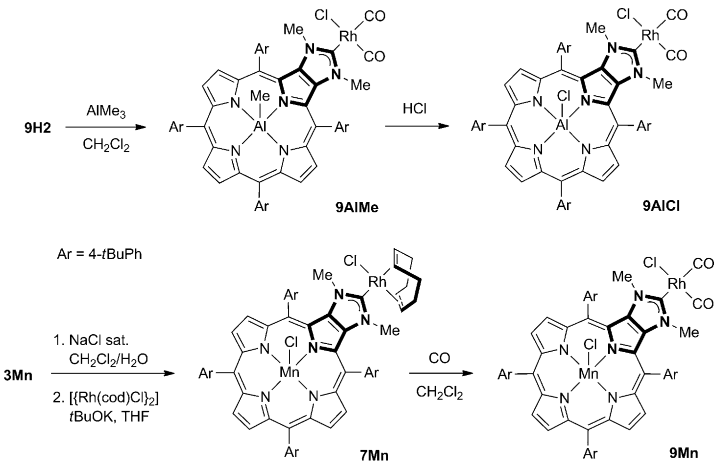


Scheme 5. Preparation of Rh^I complexes **8M** and **9M**.

Table 1. Electrochemical and spectroscopic data for the porphyrin-NHC complexes.

M	E_{ox1}/E_{ox2} for **3M**[a] [V vs. Fc^+/Fc]	δ(**6M**)[b] [ppm]	δ(**7M**)[b] [ppm]	ν(CO, **8M**)[c] [cm^{-1}]	ν(CO; **9M**)[c] [cm^{-1}]
Zn	0.36/0.66	5.22	5.00	2073, 2002	2080, 2001
Ni	0.64/0.64	5.23	5.00	2074, 2002	2081, 2002
H2	0.57/0.75	5.16	4.96	2073, 2001	2080, 2002
Mn					2084, 2004
AlMe					2083, 2003
AlCl					2084, 2005
$H4^{2+}$[d]				2080, 2010	2089, 2010

[a] Measured by cyclic voltammetry in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 (see ref. [13a]). [b] Signal of CH=CH *trans* to the NHC observed in the ^1H NMR spectrum (300 MHz) recorded in $CDCl_3$ at 25 °C. [c] Measured by FTIR spectroscopy in CH_2Cl_2, average values ν^{av}(CO) are given in the text. [d] See ref. [5b]).



Scheme 6. Preparation of Rh^I complexes **9 AlCl** and **9 Mn**.

tween the electron-donating abilities of NHC ligands **1M** with M = H2 and divalent metal cations such as Ni^{II} or Zn^{II}. Porphyrin-NHC ligands **1M** with M = Ni, Zn, and H2 can be seen as intermediate electron-donors in the range of imidazol-2-ylidene and benzimidazol-2-ylidene ligands.[5b, 15, 19]

To detect subtle differences between NHC ligands with similar electron-donating properties, the $Ir^{I/II}$ or $Rh^{I/II}$ redox potentials may serve as a more sensitive measurement.[18] This approach was not straightforward in our case because porphyrins are redox-active molecules with oxidation potentials in the range of those observed for $Rh^{I/II}$. To overcome this problem, the electron-donating abilities of the porphyrin π system of the corresponding NHC precursors **3M** were evaluated by cyclic voltammetry measurements of their electrochemical oxidation processes. The first oxidation potentials of the porphyrins (E_{OX1} vs. Fc^+/Fc) are shifted anodically in the order **3 Zn** < **3 H2** < **3 Ni** (Table 1). Based on these results, the electron-donating ability of the porphyrin π system fused to the imidazolium unit depends, as expected, on the nature of the metal in the porphyrin and increases in the order Ni < 2H < Zn.[10] This order is in agreement with the small differences observed by IR spectroscopy for **9M**, but electrochemical measurements of the NHC precursors **3M** may be seen as a more informative technique in our case compared with IR spectroscopy.

Because similar ν(CO) frequencies were measured for Rh^I complexes **9M** with divalent metal cations Ni^{II} and Zn^{II}, trivalent metal cations such as Al^{III} and Mn^{III} were also included in the inner core of the porphyrin to study the influence of the valence of the metal on the electronic properties of the peripheral NHC ligand. Al^{III} complexes **9 AlX** (X = Me, Cl) were prepared by using **9 H2** as the starting material. We first synthesized **9 H2** by bubbling CO through a solution of **7 H2** in CH_2Cl_2 (Scheme 5). Then $AlMe_3$ (2 M solution in *n*-heptane) was added to the freshly prepared solution of **9 H2** (Scheme 6). At this stage, the fifth coordination site of the Al^{III} is coordinated by CH_3^- in **9 AlMe** and CO stretching frequencies were observed at $\nu^{av}(CO) = 2043\ cm^{-1}$ (Table 1).[20] Then a vial of a solution of **9 AlMe** in CH_2Cl_2 was placed under an atmosphere of HCl for 30 min to substitute CH_3^- by chloride (Scheme 6). The stretching vibrations of the resulting **9 AlCl** were observed at $\nu^{av}(CO) = 2044.5\ cm^{-1}$ (Table 1). These stretching frequencies are in good agreement with previously reported data for $[(NHC)RhCl(CO)_2]$ complexes.[15] Here, the slightly higher ν(CO) frequencies observed for **9 AlCl** ($\Delta\nu(CO) = 4\ cm^{-1}$ between the Zn^{II} and Al^{III} complexes, Table 1) show that the corresponding **1 AlCl** ligand is a weaker NHC electron-donor than **1M** ligands with M = Ni, Zn, or H2. These data show that the electronic properties of the outer NHC can be finely modulated by 1) the nature of the inner metal of the porphyrin and its valence, and 2) the nature of the axial ligands, which are more or less able to compensate the positive charge of the inner metal. It is also interesting to note that the stretching frequencies of **9 AlCl** ($\nu^{av}(CO) = 2044.5\ cm^{-1}$) are intermediate between those of **9 Zn** ($\nu^{av}(CO) = 2040.5\ cm^{-1}$), which incorporates the most electron-donating zinc porphyrin, and those of **9 H4^{2+}** ($\nu^{av}(CO) = 2049.5\ cm^{-1}$), which incorporates the least electron-donating protonated porphyrin (Table 1).[5b]

Another trivalent metal cation such as Mn^{III} was also included in the inner core of the porphyrin to confirm that the donating ability of the peripheral NHC is weaker in the presence of a trivalent metal cation in the porphyrin. The synthesis of Mn^{III} complexes performed with **2 H2** as the starting material proved to be tedious. However, imidazole **2 Mn** was obtained in a yield of 91 % by metalation of **2 H2Me** with $MnCl_2{\cdot}4H_2O$ in air to oxidize the initially formed Mn^{II} porphyrin (Scheme 1). The MALDI-TOF mass spectrum of **2 Mn** is in agreement with the metalation of the inner core of the porphyrin by Mn^{III} and showed the molecular ion peak at $m/z = 945.4$ $[M-Cl]^+$. The chloride anion was evidenced by EDX spectroscopy (Mn/Cl ≈ 1:1). Magnetic measurements showed that the χT value at 300 K is equal to 3.04 emu K mol^{-1}, which corresponds to the value calculated for a magnetically isolated high-spin Mn^{III} ion with $S = 2$ and $g = 2.0$. Imidazolium salt **3 Mn** was obtained by alkylating the corresponding imidazole **2 Mn** with excess iodomethane (Scheme 1). The molecular mass ion peak expected for the imidazolium cation **3Mn** was observed by ESI-TOF MS ($m/z = 480.2$ $[M-2I]^{2+}$). Iodide was also detected by ESI-TOF MS ($m/z = 127.0$ $[I]^-$). EDX spectroscopy showed a Mn/I ratio of around 1:2, and therefore we concluded that chloride was exchanged by iodide as the axial ligand. We presume that chloride reacts with CH_3I to form iodide as the axial ligand and CH_3Cl gas. The results of a UV/Vis spectroscopic analysis are also in agreement with the metalation of the inner core of the porphyrins **2Mn** and **3Mn** by Mn^{III} (see Figures S3 and S4 in the Supporting Information).[21] Imidazolium salt **3Mn** was then treated with a saturated aqueous solution of NaCl. The crude dry residue was subsequently treated with $[\{RhCl(cod)\}_2]$ (0.5 equiv) and *t*BuOK in THF (Scheme 6) to give the Rh^I complex **7Mn** in a yield of 58%. The classical absorption bands of Mn^{III}–porphyrin complexes were observed by UV/Vis spectroscopy in ethanol, with one intense Soret band at $\lambda = 474$ nm and two Q bands at $\lambda = 572$ and 609 nm (Figure 3).[21] EDX spectroscopy showed a Mn/Rh/Cl ratio of approximately 1:1:2, and iodide was detected in only trace amounts. Carbon monoxide was then bubbled through a solution of **7Mn** to afford **9Mn** with $\nu^{av}(CO) = 2044\ cm^{-1}$ (Table 1). These stretching frequencies are in excellent agreement with those obtained for **9AlCl**, and also show that porphyrin-NHC ligands incorporating trivalent metal cations are weaker electron-donors than those with divalent metal cations.

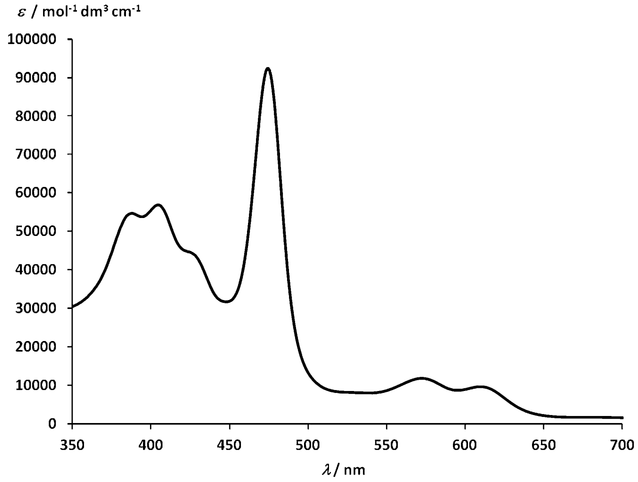
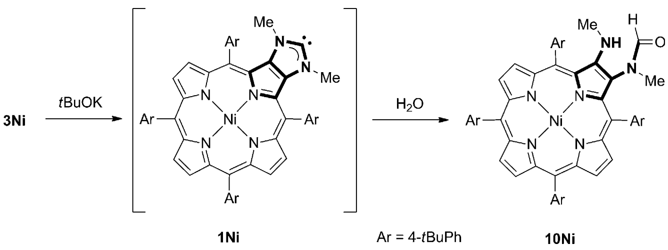


Figure 3. UV/Vis spectrum of Rh^I complex **7Mn** in ethanol.

Ring-opening polymerization of L-lactide: The imidazolium salts **3M** were used as NHC precursors to catalyze the ROP of L-lactide (L-LA). Recent studies have shown that the NHC structure (i.e., its steric and electronic properties) can dramatically modulate the polymerization rates, polydispersity ($Đ_M = M_w/M_n$), and molecular weights of the obtained polymers.[22] As expected, free carbenes **1M** prepared by deprotonating **3M** with *t*BuOK are too unstable to be isolated. For example, **1Ni** is readily hydrolyzed in humid air to the ring-opened amine formamide derivative **10Ni** (Scheme 7 and Figure S5 in the Supporting Information). The polymerization reactions were therefore conducted in a glovebox at ambient temperature by using an alcohol initiator, such as benzyl alcohol (BnOH), with porphyrin-NHCs **1M** as catalysts generated in situ ($[\mathbf{3M}]_0/[tBuOK]_0 = 1$). The ROPs of L-LA were evaluated in THF for a $[L\text{-}LA]_0/[BnOH]_0/[\mathbf{1M}]_0$ ratio of 100:1:1 ($[L\text{-}LA]_0 \approx 2\,M$) and followed by size exclusion chromatography (SEC; Table 2). The number-averaged molecular weights (M_n) obtained for each catalyst vary linearly with conversion (Figure 4). The linearity of this plot demonstrates the controlled nature of each polymerization reaction and indicates that little chain transfer occurs. Moreover, differential scanning calorimetry (DSC) analyses confirmed that no racemization occurred in the course of the ROP of L-LA.[23] In comparison with the polymerization reaction catalyzed by *N*,*N*-dimethylbenzimidazol-2-ylidene (Benz), **1M** catalysts are less active. Nevertheless, the reactions appeared to be more controlled in the studied polymerization because narrower $Đ_M$ values were observed for **1M** compared with Benz (ca. 2.4, Table 2). It has been shown that benzimidazol-2-ylidene with small nitrogen substituents, such as Benz, can dimerize to form enetetra-



Scheme 7. Hydrolytic cleavage of **1Ni**.

Table 2. Properties of poly(L-lactide)s obtained from Benz and **1M** carbenes.[a]

Cat.[b]	*t* [h]	Conv. [%]	M_n[c] [g mol⁻¹]	$Đ_M$[c]
Benz[d]	0.33	99	14500	2.40
1Zn	0.33	83	15500	1.17
	0.58	93	17000	1.12
1H2	0.83	86	16000	1.20
1Ni	0.83	23	4100	1.20
	3.33	93	17000	1.60
1Mn	0.33	6	1000	1.03
	1.00	10	1900	1.04
	3.17	18	3350	1.14
	6.00	27	4200	1.16

[a] The reactions were performed in THF with BnOH as initiator. L-LA = 2 M, $[L\text{-}LA]_0/[BnOH]_0/[carbene]_0 = 100:1:1$. [b] The NHC was generated in situ by deprotonating the imidazolium salts **3M** with *t*BuOK. [c] Determined by SEC in $CHCl_3$ at 35 °C by using polystyrenes standards. [d] **Benz** = *N*,*N*-dimethylbenzimidazol-2-ylidene generated in situ by deprotonating *N*,*N*-dimethylbenzimidazolium iodide.

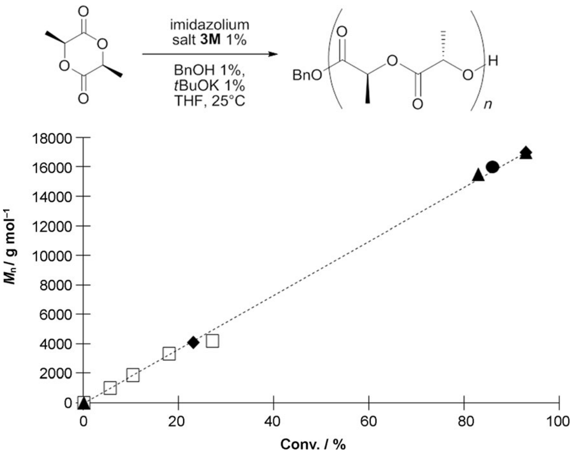


Figure 4. Plot of M_n (estimated by SEC) versus L-LA conversion: ▲) **1Zn**, ●) **1H2**, ◆) **1Ni**, and □) **1Mn**.

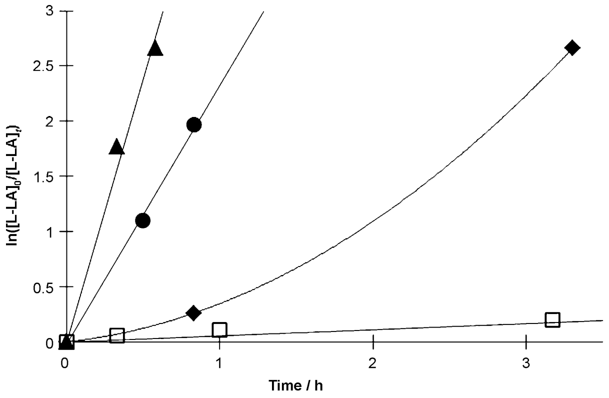


Figure 5. Plot of $\ln([\text{L-LA}]_0/[\text{L-LA}]_t)$ versus time for $[\text{L-LA}]_0 = 2\,\text{M}$ and a targeted DP of 100: ▲) **1Zn**, ●) **1H2**, ◆) **1Ni**, and □) **1Mn**.

mines,[24] and Wanzlick showed that these enetetramines have the reactivity of nucleophilic carbenes.[25] Such "Wanzlick" carbenes were used by Hedrick and co-workers as nucleophilic catalysts for the ROP of lactide.[22b] Their results showed that controlled polymerizations are difficult to achieve and that the obtained polymers had a broad PDI. Similar reactivity was observed in this work with Benz as catalyst. In contrast, the much smaller values of PDI observed for **1M** suggest that porphyrin-NHC ligands are not prone to dimerize due to the presence of the porphyrin backbone and the two sterically demanding *meso* 4-*t*BuPh groups close to the NHC moiety.

Despite identical steric properties and small differences between the electron-donating capacities of **1M**, the results of this work show striking differences in their reactivity, increasing in the order **1Mn** ≪ **1Ni** < **1H2** < **1Zn**. Although 83 % conversion was achieved within 20 min with **1Zn** as catalyst, only 6 % conversion was observed with **1Mn** under identical conditions. This clearly shows the important effect of the inner metal of the porphyrin on the outer carbene reactivity (Table 2): the more electron-rich the NHCs are (i.e., the porphyrin π system is electron-rich), the faster the ROP reactions. Polymers with $M_n = 16\,000$–$17\,000\ \text{g mol}^{-1}$ and $Đ_M = 1.1$–1.2 were obtained with the most active catalysts **1Zn** and **1H2**. Interestingly, the polymerizations of L-LA initiated by BnOH/**1M** (M = Zn, Ni, H2) mixtures are also living processes, the semi-logarithmic dependence of $\ln([\text{L-LA}]_0/[\text{L-LA}]_t)$ on time being linear (Figure 5). A marked autoacceleration was observed only when **1Ni** was used, but this did not influence the final properties of the poly(L-LA), with $M_n = 17\,000\ \text{g mol}^{-1}$ and $Đ_M = 1.6$ (Table 2). This might be due to a change in the proportion between aggregated and nonaggregated species,[26] the aggregation of porphyrin derivatives being a commonly observed phenomenon.[27] During the course of the ROP of L-LA, the electronic spectra of the reaction mixtures did not undergo substantial changes, which confirms that the porphyrin remained intact and that demetalation did not occur. Control experiments performed with *meso*-tetrakis(4-*t*BuPh)porphyrin derivatives (i.e., **1M** (M = Zn, H2, Ni) without the fused NHC ligand) showed that they are unable to catalyze the ROP of L-LA alone without the NHC in the reaction mixture. Moreover, we also verified that the Lewis acidic core of the porphyrin does not activate the L-LA: In the polymerization reaction, upon combining the less active **1Mn** catalyst with 1 equiv of the free base or the Zn complex of *meso*-tetrakis(4-*t*BuPh)-porphyrin, the observed rate remained unchanged. This shows that the Lewis acidic core of the porphyrin is not able to co-catalyze the polymerization reaction.

Conclusion

We have described herein the electronic and catalytic properties of NHC ligands fused to porphyrins. In this study, the porphyrin moiety was modified to tune the properties of the NHC ligands. We have largely investigated how the inner metal of the porphyrin is able to modulate the properties of the outer NHC. We have shown that fine modulation of the electronic properties of the outer NHC ligand can be achieved by varying the nature of the inner metal of the porphyrin. Porphyrin-NHC ligands **1M** with divalent metal cations such as Ni^{II} and Zn^{II} are intermediate electron donors and display similar electronic properties to the NHC ligand fused to the corresponding free-base porphyrin. Porphyrin-NHC ligands **1M** with trivalent metal cations, such as Al^{III} and Mn^{III}, are weaker NHC electron donors than those with divalent metal cations. These data show that the valence, and as a consequence the charge of the porphyrin backbone, is responsible for the electronic properties of the outer NHC ligand. To study if the inner metal of the porphyrin plays a significant role in the catalytic properties of the outer NHC ligands, we used these porphyrin-NHC ligands to organocatalyze the ring-opening polymerization of L-lactide. Surprisingly, huge differences in reactivity were observed between the **1M** catalysts despite the small differences in their electron-donating capacities. Such differences in reactivity may thus only be partly related to the small variations in the electron-donating properties of **1M**, and other phenomena should also be taken into consideration. Indeed, in our systems (and probably also in other reported systems dealing with the use of a porphyrin backbone to tune the catalytic activity of a peripheral catalytic site), the aggregation of the porphyrin catalyst (e.g., for **1Ni**) or the coordination of additional innocent or non-innocent ligands on the inner metal of the porphyrin, could also have a significant effect on the properties of the peripheral catalytic site. Further developments are now in progress to use these highly tunable NHC ligands for other catalytic applications with or without a metal anchored to the periphery of the porphyrin.

Experimental Section

General: Reactions were performed under argon using oven-dried glassware. Dry THF was obtained by distillation over CaH_2 and then Na/benzophenone. Preparative separations were performed by silica gel flash column chromatography (Baeckeroot-Labo 60M). Chemicals were obtained from Alfa-Aesar, Sigma–Aldrich, and Acros and used as received. Reactions were monitored by thin-layer chromatography using Merck© TLC silica gel 60 F_{254} plates. NMR spectra were recorded in $CDCl_3$ on either a Bruker 300 MHz or 200 MHz Fourier-transform spectrometer. Chemical shifts are reported in ppm referenced to the $CHCl_3$ solvent residual peak at 7.26 ppm for ^{1}H. Abbreviations for ^{1}H NMR spectra are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 35 spectrophotometer in quartz cells. IR spectra were recorded in CH_2Cl_2 solutions in a CaF_2 cell with a Nicolet Avatar 320 FT-IR spectrometer. ESI mass spectra were recorded on a Q-Tof Waters 2001 MS spectrometer. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III MS spectrometer with anthracene-1,8,9-triol as matrix. The electrochemical studies and the syntheses of the imidazole derivatives **2M** and the imidazolium salts **3M** are described in ref. [13a].

Syntheses of the imidazole and imidazolium salts

Imidazole 2Mn: Nickel(II) *N*-methylimidazole **2NiMe** (380 mg, 4.00×10^{-4} mol) was dissolved in a TFA/H_2SO_4 mixture (20 mL/5 mL) and the solution was stirred at room temperature for 30 min. It was then poured onto ice, diluted with chloroform (200 mL), neutralized with saturated K_2CO_3, washed with water, dried (Na_2SO_4), and evaporated. Crystallization from CH_2Cl_2/MeOH afforded the free-base imidazole **2H2Me** in a yield of 98 % (350 mg). A solution of **2H2Me** (350 mg, 3.92×10^{-4} mol) in a $CHCl_3$/MeOH mixture (80 mL/20 mL) was prepared and $MnCl_2\bullet4H_2O$ (800 mg, 4.04×10^{-3} mol) was added. The mixture was heated at 50 °C for 12 h. After evaporation of the solvents, the crude product was purified by column chromatography on alumina (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH 95:5), and crystallization from CH_2Cl_2/*n*-pentane afforded **2Mn** in a yield of 91 % (348 mg). UV/Vis (EtOH): λ_{max} (ε) = 383 (62000), 403 (64000), 472 (100000), 566 (12000), 603 nm (9000 $mol^{-1}dm^3cm^{-1}$); MS (ESI-TOF$^+$): *m/z* calcd for $C_{62}H_{62}N_6Mn^+$: 945.44 $[M-Cl]^+$; found: 945.5.

Imidazolium salt 3Mn: Manganese(III) *N*-methylimidazole **2Mn** (132 mg, 1.35×10^{-4} mol) was dissolved in acetone (10 mL). Iodomethane (5 mL) was added and the solution was stirred at 40 °C under argon for 48 h. The completion of the alkylation was verified by silica gel TLC and the solvent was evaporated. Then the solvent was evaporated and crystallization from CH_2Cl_2/*n*-pentane afforded **3Mn** in a yield of 82 % (133 mg). UV/Vis (EtOH) = λ_{max} (ε): 387 (51000), 404 (51000), 426 (43000), 473 (89000), 574 (12000), 614 nm (10000 $mol^{-1}dm^3cm^{-1}$); MS (ESI-TOF$^+$): *m/z* calcd for $C_{63}H_{65}N_6Mn^{2+}$: 480.23 $[M-2I]^{2+}$; found: 480.2; MS (ESI-TOF$^-$): *m/z* calcd for I^-: 126.90 $[M^-]$; found: 127.0.

Imidazolium salt 5Ni: Imidazolium salt **3Ni** (84 mg, 7.69×10^{-5} mol) was dissolved in acetone (20 mL). Then a solution of silver tetrafluoroborate (16 mg, 8.22×10^{-5} mol) in acetone (1 mL) was slowly added and the reaction mixture was stirred in the dark for 1 h. After evaporation of solvent, the imidazolium salt **5Ni** was purified by column chromatography on silica gel (eluent: from CH_2Cl_2 to CH_2Cl_2/EtOH 95:5). Evaporation of the solvent afforded the imidazolium salt **5Ni** as a purple solid in a yield of 92 % (74 mg). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 9.27 (s, 1H; C*H* iminium), 8.75 (s, 2H; pyrrole), 8.72 (d, *J* = 5.0 Hz, 2H; pyrrole), 8.68 (d, *J* = 5.0 Hz, 2H; pyrrole), 8.06 (d, *J* = 8.2 Hz, 4H; Ar *meso*), 7.95 (d, *J* = 8.2 Hz, 4H; Ar *meso*), 7.80 (d, *J* = 8.2 Hz, 4H; Ar *meso*), 7.73 (d, *J* = 8.2 Hz, 4H; Ar *meso*), 3.16 (s, 6H; N-CH_3), 1.56 (s, 18H; *t*Bu), 1.54 ppm (s, 18H; *t*Bu); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 426 (222000), 537 (16000), 575 nm (sh 4000 $mol^{-1}dm^3cm^{-1}$); MS (ESI-TOF$^+$): *m/z* calcd for $C_{63}H_{65}N_6Ni^+$: 963.46 $[M]^+$; found: 963.3; MS (ESI-TOF$^-$): *m/z* calcd for BF_4^-: 87.0 $[M]^-$; found: 87.0.

Imidazolium salt 5Zn: The imidazolium salt **5Zn** was obtained in a yield of 94 % from **3Zn** following the same procedure as described for **5Ni**. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 9.04 (s, 1H; C*H* iminium), 8.93 (s, 2H; pyrrole), 8.92 (d, *J* = 4.8 Hz 2H; pyrrole), 8.80 (d, *J* = 4.8 Hz 2H; pyrrole), 8.27 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 8.12 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 7.84 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 7.77 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 3.20 (s, 6H; N-CH_3), 1.62 (s, 18H; *t*Bu), 1.59 ppm (s, 18H; *t*Bu); UV/Vis (CH_2Cl_2) = λ_{max} (ε): 428 (540000), 556 (25000), 600 nm (8000 $mol^{-1}dm^3cm^{-1}$); MS (ESI-TOF$^+$): *m/z* calcd for $C_{63}H_{65}N_6Zn^+$: 969.46 $[M]^+$; found: 969.5; MS (ESI-TOF$^-$): *m/z* calcd for BF_4^-: 87.0 $[M]^-$; found: 87.0.

Imidazolium salt 5H2: The imidazolium salt **5H2** was obtained in a yield of 90 % from **3H2** following the same procedure as described for **5Ni**. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 9.26 (s, 1H; C*H* iminium), 8.95 (s, 4H; pyrrole), 8.75 (s, 2H; pyrrole), 8.39 (d, ^3J(H,H) = 7.8 Hz, 4H; Ar *meso*), 8.20 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 7.93 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 7.82 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 3.16 (s, 6H; N-CH_3), 1.62 (s, 18H; *t*Bu), 1.61 (s, 18H; *t*Bu), −2.97 ppm (s, 2H; N*H*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 428 (353000), 528 (13000), 567 (8000), 597 (5000), 657 nm (7000 $mol^{-1}dm^3cm^{-1}$); MS (ESI-TOF$^+$): *m/z* calcd for $C_{63}H_{67}N_6^+$: 907.54 $[M]^+$; found: 907.5; MS (ESI-TOF$^-$): *m/z* calcd for BF_4^-: 87.0 $[M]^-$; found: 87.0.

Rh^I complex 7Ni: A 25 mL flask was charged with imidazolium salt **5Ni** (35 mg, 3.33×10^{-5} mol), [{RhCl(cod)}$_2$] (10 mg, 2.02×10^{-5} mol), and *t*BuOK (4,1 mg, 3.65×10^{-5} mol) in THF (10 mL). The reaction mixture was stirred under an atmosphere of argon for 2 h at ambient temperature. Completion of the reaction was verified by TLC analysis. THF was removed under reduced pressure leaving a crude product that was purified by silica gel column chromatography with dichloromethane as eluent. Evaporation of the solvent afforded rhodium(I) complex **7Ni** in a yield of 94 % (37.7 mg) as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.69 (s, 2H; pyrrole), 8.65 (s, 4H; pyrrole), 8.31–8.19 (br d, 2H; Ar *meso*), 7.97 (d, *J* = 7.8 Hz, 4H; Ar *meso*), 7.90–7.77 (br d, 4H; Ar *meso*), 7.70 (d, *J* = 7.8 Hz, 6H; Ar *meso*), 5.00 (br s, 2H; C*H* cod), 3.44 (s, 6H; N-CH_3), 3.35 (br s, 2H; C*H* cod), 2.46–2.28 (br m, 4H; CH_2 cod), 2.07–1.87 (br m, 4H; CH_2 cod), 1.58 (m, 18H; *t*Bu), 1.55 ppm (m, 18H; *t*Bu); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 426 (296000), 538 (22000), 572 nm (sh 7000 $mol^{-1}dm^3cm^{-1}$); MS (MALDI-TOF$^+$): *m/z* calcd for $C_{71}H_{76}N_6ClNiRh_{\bullet}^{+}$: 1208.42 $[M]_{\bullet}^{+}$; found: 1208.4.

Rh^I complex 7Zn: Rhodium(I) complex **7Zn** was obtained in a yield of 71 % from **5Zn** following the same procedure as described for **7Ni**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.93 (s, 2H; pyrrole), 8.92 (d, *J* = 4.8 Hz, 2H; pyrrole), 8.86 (d, *J* = 4.8 Hz, 2H; pyrrole), 8.58 (dd, *J* = 7.5, 2.3 Hz, 2H; Ar *meso*), 8.21–8.10 (m, 4H; Ar *meso*), 7.99 (dd, *J* = 7.5, 2.3 Hz, 2H; Ar *meso*), 7.93 (dd, *J* = 7.5, 2.3 Hz, 2H; Ar *meso*), 7.83–7.69 (m, 6H; Ar *meso*), 5.00 (br s, 2H; C*H* cod), 3.63 (s, 6H; N-CH_3), 3.50 (br s, 2H; C*H* cod), 2.52–2.31 (br m, 4H; CH_2 cod), 2.11–1.92 (br m, 4H; CH_2 cod), 1.65 (s, 18H; *t*Bu), 1.62 ppm (s, 18H; *t*Bu); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 428 (561000), 555 (31000), 596 nm (9000 $mol^{-1}dm^3cm^{-1}$); MS (MALDI-TOF$^+$): *m/z* calcd for $C_{71}H_{76}N_6ClRhZn_{\bullet}^{+}$: 1214.42 $[M]_{\bullet}^{+}$; found: 1214.5.

Rh^I complex 7H2: Rhodium(I) complex **7H2** was obtained in a yield of 92 % from **5H2** following the same procedure as described for **7Ni**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.90 (d, *J* = 5.1 Hz, 2H; pyrrole), 8.86 (d, *J* = 5.1 Hz, 2H; pyrrole), 8.72 (s, 2H; pyrrole), 8.65 (br d,

$J=7.8$ Hz, 2H; Ar *meso*), 8.33–8.05 (br m, 4H; Ar *meso*), 8.11 (br d, $J=7.8$ Hz, 2H; Ar *meso*), 7.98 (br d, $J=7.8$ Hz, 2H; Ar *meso*), 7.72–7.89 (br m, 6H; Ar *meso*), 4.96 (br s, 2H; C*H* cod), 3.46 (s, 6H; N-CH_3), 3.43 (br s, 2H; C*H* cod), 2.50–2.27 (br m, 4H; CH_2 cod), 2.08–1.89 (br m, 4H; CH_2 cod), 1.64 (s, 18H; *t*Bu), 1.61 (s, 18H; *t*Bu), −2.92 ppm (s, 2H; N*H*); UV/Vis (CH_2Cl_2): λ_{max} (ε)=430 (322000), 528 (16000), 564 (11000), 599 (5000), 661 nm (4000 $mol^{-1}dm^3cm^{-1}$); MS (MALDI-TOF$^+$): *m*/*z* calcd for $C_{71}H_{79}N_6ClRh^+$: 1153.51 $[M+H]^+$; found: 1153.5.

Rh^I complex 7Mn: Imidazolium salt **3Mn** (65 mg, 5.34×10^{-5} mol) was dissolved in CH_2Cl_2 (15 mL) and a saturated aqueous solution of NaCl (50 mL) was added. The mixture was vigorously stirred for 24 h. Then the organic layer was separated, washed with water, and dried with Na_2SO_4. After drying under vacuum, the crude product was dissolved in THF (10 mL). Then [{RhCl(cod)}$_2$] (16 mg, 3.24×10^{-5} mol) and *t*BuOK (7.2 mg, 6.42×10^{-5} mol) was added and the reaction mixture was stirred under an atmosphere of argon for 2 h at ambient temperature. THF was removed under reduced pressure to leave the crude product that was purified by silica gel column chromatography (eluent: from CH_2Cl_2 to CH_2Cl_2/acetone 9:1). Evaporation of the solvent and crystallization from CH_2Cl_2/*n*-pentane afforded **7Mn** in a yield of 58% (38 mg). UV/Vis (EtOH): λ_{max} (ε)=387 (54000), 405 (57000), 474 (92000), 572 (12000) 609 nm (10000 $mol^{-1}dm^3cm^{-1}$); MS (MALDI-TOF$^+$): *m*/*z* calcd for $C_{71}H_{76}N_6MnClRh^+$: 1205.43 $[M-Cl]^+$; found: 1205.5.

General procedure for the preparation of carbonyl Rh^I complexes 8M and 9M: Rhodium(I) complex **6M** or **7M** (20 mg) was dissolved and stirred in CH_2Cl_2 (20 mL). Then carbon monoxide was bubbled through the solution for 1 h and the corresponding carbonyl Rh^I complex **8M** or **9M** was obtained. Aliquots of the reaction mixture were sampled for IR spectroscopy analyses. Complex **9AlMe** was synthesized by adding 2 M $AlMe_3$ in *n*-heptane (1.2 equiv, 21 µL) to a solution of **9H2** in CH_2Cl_2. A vial of **9AlMe** was placed under an atmosphere of HCl for 30 min to generate **9AlCl**. Rh^I complexes **8M** and **9M** were stable for hours in solution but decomposed upon evaporation of dichloromethane. The CO stretching frequencies measured by IR spectroscopy are presented in Table 1.

Ring-opened amine formamide derivative 10Ni: A solution of imidazolium salt **3Ni** (60 mg, 5.50×10^{-5} mol) and *t*BuOK (20 mg, 1.78×10^{-4} mol) in non-distilled THF (20 mL) was stirred for 24 h at room temperature under air. The completion of the reaction was verified by silica gel TLC analysis (one brown spot). After solvent evaporation, the compound was purified by silica gel column chromatography (eluent: from CH_2Cl_2/*n*-pentane 1/1 to CH_2Cl_2). After solvent evaporation, **10Ni** was dried under vacuum for one night and obtained in a yield of 96% (52 mg). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta=8.70$ (s, 2H; pyrrole), 8.69 (d, $J=5.0$ Hz, 1H; pyrrole), 8.64 (d, $J=5.0$ Hz, 1H; pyrrole), 8.61 (d, $J=5.0$ Hz, 1H; pyrrole), 8.52 (d, $J=5.0$ Hz, 1H; pyrrole), 8.30 (s, 1H; C*H*O), 7.95–7.61 (m, 16H; Ar *meso*), 4.25 (q, $J=5.5$ Hz, 1H; N*H*-CH_3), 2.81 (d, $J=5.5$ Hz, 3H; NH-CH_3), 2.78 (s, 3H; CH_3), 1.57 (s, 18H; *t*Bu), 1.56 (s, 9H; *t*Bu), 1.57 ppm (s, 9H; *t*Bu); IR (CH_2Cl_2): $\nu=1682$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε)=420 (150000), 542 (11000), 597 nm (6000 $mol^{-1}dm^3cm^{-1}$); MS (ESI-TOF$^+$): *m*/*z* calcd for $C_{63}H_{67}N_6NiO^+$: 981.47 $[M+H]^+$; found: 981.3.

Polymerization reactions

Materials: L-Lactide (GALACTIC, Belgium) was recrystallized from dried toluene and stored in a glovebox under dry nitrogen before use. Benzyl alcohol (Sigma–Aldrich, 97%) was dried over calcium hydride for 48 h, distilled under reduced pressure, and stored in a glovebox under dry nitrogen before use. Imidazolium salts **3M** and *t*BuOK (Sigma–Aldrich, 98%) were dried overnight or for 48 h under vacuum at 100°C and stored in a glovebox under dry nitrogen before use. THF solvent was dried by using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

Characterization: Size exclusion chromatography (SEC) was performed in chloroform at 35°C by using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic LC 1120 HPLC pump (flow rate = 1 mL min^{-1}), a triple detector (refractive index (ERMA 7517), capillary viscometry, and light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC-RI/CV/RALS)), an automatic injector (Polymer Laboratories GPC-RI/UV), and four columns (a PL gel 10 µm guard column and three PL gel Mixed-B 10 µm columns). Polystyrene standards were used for calibration. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q200 apparatus from T.A. Instruments under a flow of nitrogen (heating and cooling rate 5°C min^{-1}).

General polymerization procedure illustrated with 3Ni as catalyst: In a glovebox, a dried vial equipped with a stirrer was charged with L-lactide (0.13 g, 9.0×10^{-4} mol), **3Ni** (10 mg, 9.17×10^{-6} mol), and *t*BuOK (1 mg, 9.17×10^{-6} mol) in dry THF (0.3 mL). Benzyl alcohol (1 mg, 9.0×10^{-6} mol) was added to the solution. The sealed vial was then maintained under agitation and several withdrawals were realized to follow the kinetics by SEC.

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