This paper is published as part of a *Dalton Transactions* themed issue on:

Metal-catalysed Polymerisation

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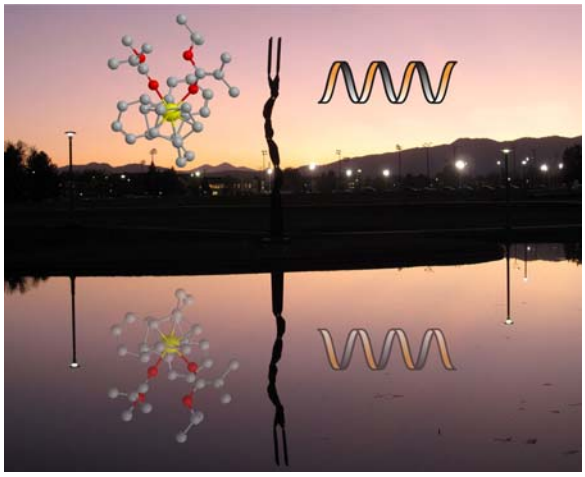
Published in issue 41, 2009 of *Dalton Transactions*



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Supramolecular NHC ligands: on the influence of Zn^{II}-templates on the activity of Rh^{I}(cod) complexes in 'carbene polymerization'†

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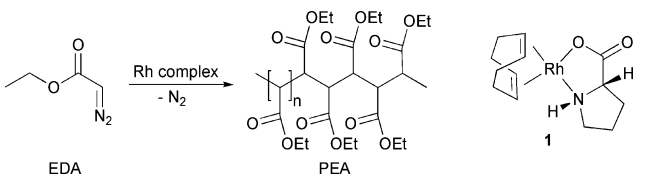
Received 9th June 2009, Accepted 18th August 2009
First published as an Advance Article on the web 7th September 2009
DOI: 10.1039/b911339h

New Rh^{I}(cod) complexes of *N*-heterocyclic carbene ligands containing a pending pyridyl moiety for subsequent binding of Zn^{II}-templates were designed for supramolecular catalyst control in 'carbene polymerization' reactions. Zn^{II}-templates indeed have an influence on the yields and the polymer molecular weights (and weight distributions) produced by these 'supramolecular assemblies'. However, control experiments reveal that the effect of the Zn^{II}-template on the polymerization results is general and not due to the assembly formation.

Introduction

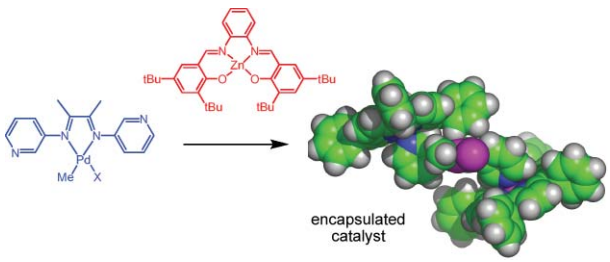
The polymerization of 'carbenes' generated from diazocarbonyl compounds mediated by transition metals (*e.g.* Cu-,[1] and Pd-complexes)[2] generally leads to atactic and low molecular weight oligomers. Recently, however, we described that Rh^{I}(diene)-complexes (*e.g.* **1** in Scheme 1) allow the formation of stereoregular and high molecular weight polymers.[3,4]



Scheme 1 Rhodium-mediated polymerization of ethyl diazoacetate and catalyst precursor [(L-prolinate)Rh^{I}(1,5-cyclooctadiene)] (**1**).

We are currently investigating the effects of ligand modification on the performance of these catalysts in terms of yields, tacticity, and molecular weight (distributions). In this light we wondered if we could use the supramolecular strategies developed in other types of catalysis research in our group to modify the basic catalyst structure in a modular and combinatorial way.

Traditionally, covalent approaches are used to steer the steric and electronic properties of a metal complex.[5] This is a proven method, but usually associated with time consuming synthetic efforts. Recently, supramolecular strategies have been introduced by us,[6–8] and others[9] to make bidentate ligands and to encapsulate metal complexes.[10] One of the advantages is the relative ease with which large catalyst libraries can be prepared as it involves simple mixing of ligand building blocks that form the catalyst. We successfully demonstrated the viability of this approach in the hydroformylation of 1-octene leading to mainly branched aldehydes,[8] in the hydrogenation of challenging enamides[7e] and in the palladium-catalyzed allylic alkylation.[7c] More recently we demonstrated that this novel approach is also valuable in late transition metal mediated copolymerization of CO and 4-*t*-butylstyrene (Scheme 2).[7l] Pyridyl-modified Pd-bian complexes are efficiently encapsulated by Zn^{II}-salphen complexes (salphen = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine dianion), and such supramolecular encapsulated catalysts reveal a higher activity and improved copolymer stereoregularity as compared to the non-encapsulated control catalyst.



Scheme 2 Encapsulation of Pd copolymerization catalysts.

We argued that similar approaches could be useful in Rh-mediated polymerization reactions. As such we decided to study the effect of Zn^{II}-template-based assemblies in the polymerization of carbenes from ethyl diazoacetate (EDA) (Scheme 1).

Results and discussion

Catalyst precursors

We designed new *N*-heterocyclic carbene (NHC) ligands containing a pending pyridyl moiety for subsequent coordination of Zn^{II}-templates (Scheme 3, Fig. 1).[11] Imidazolium salt **2a** was prepared by reacting 2 equiv. of 1-mesitylimidazole and 4-bromopyridine hydrochloride. In a similar manner, NHC precursor **2b** was easily synthesized by the condensation of 1-mesitylimidazole and freshly prepared picolyl chloride in good yield. Subsequent reactions with Ag_2O led to Ag complexes **3a–b**.

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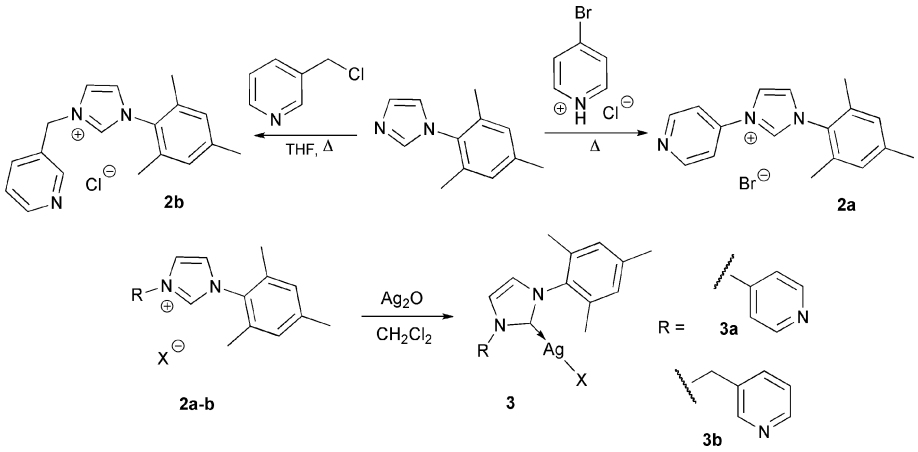
† Electronic supplementary information (ESI) available: UV-vis titration experiments for assemblies **4a**·(**I**) and **4b**·(**I**) and ESI-MS spectrum. CCDC reference numbers 744088 and 744089. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b911339h



Scheme 3 Synthesis of imidazolium salts **2a–b** and silver complexes **3a–b**.

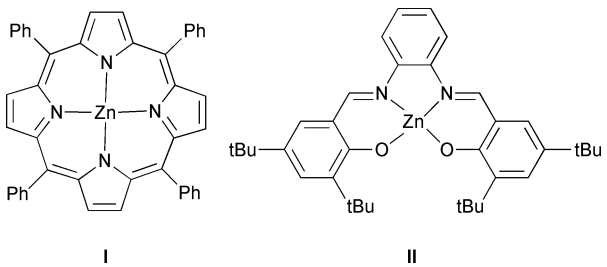
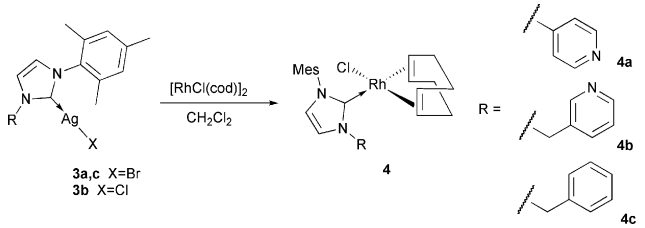


Fig. 1 Zn^{II}-templates tetraphenylporphyrin **I** and salphen **II**.

From these NHC ligands we prepared the [Rh^{I}Cl(NHC)(cod)] complexes **4a–b** following the synthetic routes depicted in Scheme 4, involving transmetallation[12] of the corresponding silver precursor **3a** and **3b** with $[RhCl(cod)]_2$. The analogous complex **4c** was prepared as a control species, using the previously reported silver complex **3c**.[13] NMR reveals axial chirality of complexes **4a–c** due to hindered rotation of the NHC moiety around the Rh–C bond, disclosed by 4 inequivalent olefinic cod signals and an AB pattern for the CH_2Ar moieties of **4b** and **4c**.[14] The X-ray structures‡ of **4a** and **4b** are shown in Fig. 2 (see Table 1 for selected bond lengths and angles). Their coordination geometries



Scheme 4 Synthesis of compounds **4a–c** by transmetallation.

‡ Crystal data for **4a**: $C_{25}H_{29}ClN_3Rh$, $M_r = 509.87$, triclinic, space group $P\bar{1}$, $a = 7.4144(3)$ Å, $b = 11.7114(4)$ Å, $c = 13.4408(6)$ Å, $\alpha = 93.230(2)°$, $\beta = 104.119(2)°$, $\gamma = 93.696(2)°$, $V = 1126.36(8)$ Å^3, $Z = 2$, $T = 110(2)$ K, $D_{calcd} = 1.503$ g cm^{-3}, μ(MoKα) = 8.94 cm^{-1}, MoKα radiation (λ = 0.71073 Å), $F(000) = 524$, $R_1 = 0.0203$, w$R_2 = 0.0479$. Crystal data for **4b**: $C_{26}H_{31}ClN_3Rh$, $M_r = 523.90$, monoclinic, space group $P2_1/c$, $a = 11.1897(3)$ Å, $b = 17.3083(6)$ Å, $c = 13.4145(4)$ Å, $\beta = 115.790(2)°$, $V = 2339.27(13)$ Å^3, $Z = 4$, $T = 150(2)$ K, $D_{calcd} = 1.4876$ g cm^{-3}, μ(MoKα) = 8.64 cm^{-1}, MoKα radiation ($\lambda = 0.71073$ Å), $F(000) = 1080$, $R_1 = 0.0197$, w$R_2 = 0.0504$.

Table 1 Selected bond lengths (Å) and angles (°)

	4a	**4b**
Rh(1)–Cl(1)	2.3674(4)	2.3858(4)
Rh(1)–$C_{carbene}$	2.0349(15)	2.0373(15)
Rh(1)–C(1)	2.1018(16)	2.0953(16)
Rh(1)–C(8)	2.1244(16)	2.1041(18)
Rh(1)–C(5)	2.1770(16)	2.1919(17)
Rh(1)–C(4)	2.2177(16)	2.2228(17)
C(1)–C(8)	1.400(2)	1.398(3)
C(4)–C(5)	1.372(3)	1.361(3)
C(14)–Rh(1)–Cl(1)	86.42(4)	90.77(4)
C(5)–Rh(1)–Cl(1)	89.01(5)	88.15(6)
C(14)–Rh(1)–C(8)	95.11(6)	92.22(6)
C(5)–Rh(1)–C(8)	82.21(7)	82.03(8)

are similar to those observed for related Rh^{I}(Cl)(cod)(NHC) complexes.[14,15] The NHC ligand is oriented parallel with the cod double bonds, presumably to allow optimal π-interactions of both the cod ligand and the NHC ligand with the metal d-orbitals. The cod double bonds *trans* to the NHC ligands (C4–C5) are shorter and at a larger distance from the metal than the cod double bonds *trans* to the chlorine atom (C1–C8), reflecting the stronger *trans* influence of the NHC ligands compared to Cl^-, perhaps suggesting some metal-to-ligand back-bonding to the NHC ligand.[16] The structures reveal non-coordinating pyridine groups and the presence of both enantiomers in the unit cell. In the particular case of **4a**, the orientation of the dangling pyridine in the solid state is determined by intermolecular π–π stacking interactions between the 4-pyridyl rings (separated by a distance of 2.57 Å) of two enantiomeric molecules.

The formation of the supramolecular assemblies **4b**·(**I**) and **4b**·(**II**) by encapsulation of Rh complex **4b** with the Zn^{II}-templates tetraphenylporphyrin (**I**) and salphen (**II**) (Fig. 1) was studied by NMR and UV-vis.[17]

UV-vis titration experiments revealed binding constants $K_{as} = 4.6 \times 10^3$ M^{-1} for **4b**·(**I**); and $K_{as} = 3.0 \times 10^5$ M^{-1} for **4b**·(**II**), which are similar Py–Zn bond strengths as reported for analogous phosphine derivatives.[8,18] To get a rough feeling for their 3D structure, we modelled the assemblies **4a**·(**I**) and **4b**·(**I**) with semi-empirical methods (PM3), which reveal (as expected) in complex **4a** the biggest steric crowding around the metal imposed by the template (Fig. 3).

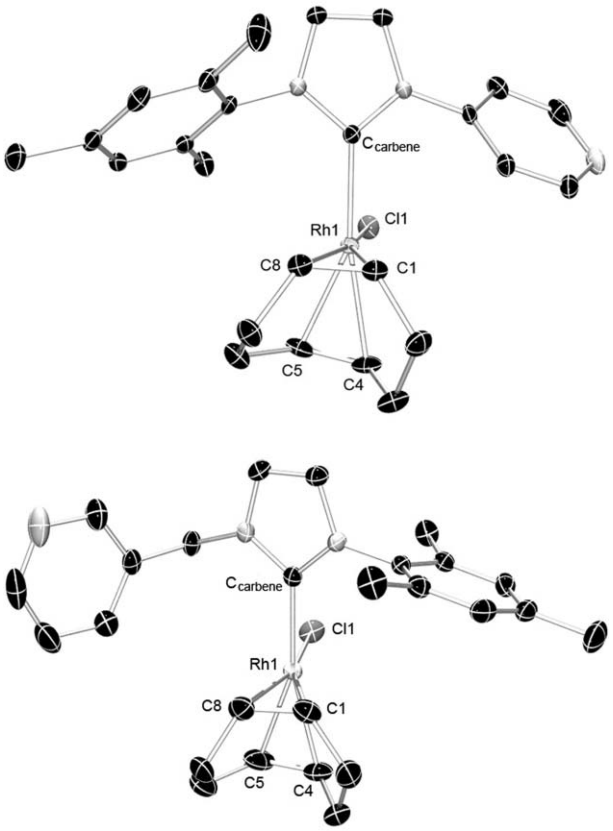


Fig. 2 ORTEP drawing of the molecular structures of **4a** (top) and **4b** (bottom) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

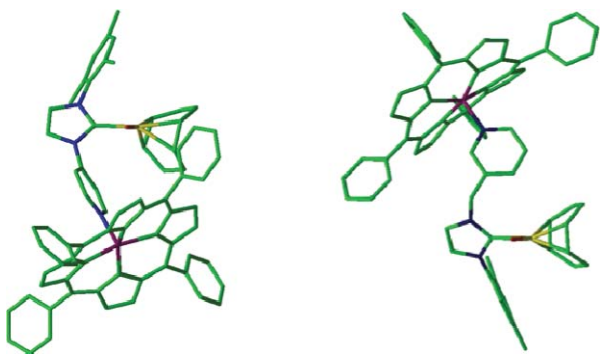


Fig. 3 Spartan (semi-empirical PM3) optimized geometries of the assemblies **4a**·(**I**) (left) and **4b**·(**I**) (right).

Polymerization of carbenes from ethyl diazoacetate

There are no previous reports on the use of NHC ligands in 'carbene polymerization' from diazocompounds. Since NHC-complexes are known to mediate other carbene transfer reactions (copper, silver and gold complexes of NHC ligands are active in C–H bond functionalization with diazo compounds),[19] we expected at least some activity of the complexes **4a–c** in 'carbene polymerization' (Scheme 1). As such we applied complexes **4a–c** in the polymerization of EDA to poly(ethyl 2-ylidene-acetate) (PEA).

The polymerization reactions were carried out by addition of 50 equiv. of EDA to a solution of the catalyst precursor at room temperature. The NHC complexes are active, but perform only moderately. The reactions were not complete after 24 h, after which catalyst decomposition had occurred, leading to low PEA polymer yields (< 25%; MeOH insoluble fraction) and oligomer yields between 15 and 30% (entries 1–4, Table 2; MeOH soluble fraction). However, in all cases, high molecular mass polymers were obtained (M_w typically in the range 70–150 kDa) and their polydispersity values (M_w/M_n) are typically around 2.5 for the reactions in dichloromethane.

Catalysts **4b** and **4c**, containing $-CH_2Ph$ and $-CH_2Py$ substituents, give lower yields and lower molecular weight PEA than catalyst **4a** in which a 4-pyridyl fragment is directly attached to the NHC ligand (entries 1–4). However, overall the results obtained with **4a–c** are roughly comparable to the catalytic activity of the known [Rh^I(cod)(prolinate)] catalyst **1** (entries 13 and 14). Lower PEA yields, and PEA with somewhat lower molecular weights were obtained with **4a–c**, and the PDI values are somewhat smaller with **4a–c**, but in all cases highly stereoregular (syndiotactic) PEA was obtained.[3,4]

Albeit small, the differences between **1** and **4a–c** could mean that the NHC ligands influence the catalytic results as auxiliary ligands bonded to the active species responsible for the polymerization event. We thus considered it worthwhile to study the effect of encapsulating **4a** and **4b** with the Zn^{II}-templates **I** and **II** (Fig. 1) on the catalytic results. Indeed, in the presence of 1 equiv. of the corresponding Zn^{II}-template polymers with higher molecular weights (260–310 kDa), but in even lower yields and with higher PDI values (3.5–4.7) were obtained (entries 5, 6 and 9). Initially we interpreted these results being the result of the envisaged supramolecular encapsulation. However, in control experiments performed with complex **4c** (which does not contain a pyridyl group suitable for binding the Zn^{II}-templates) we observed exactly the same effect of adding template **II** (entries 4 and 12). Another control experiment was performed in which we investigated the effect of template **I** and **II** on the activity of the previously reported catalyst **1**,[3] in which we observed a similar effect of the Zn^{II}-template (entries 13, 14, 16 and 17); lower yields of PEA with somewhat higher molecular weights and broader PDI values. Finally, to rule out the possibility of the Zn^{II}-template acting directly as a Lewis acid catalyst, templates **I** and **II** were tested in the absence of any rhodium species. As expected, no reaction with EDA occurred (entries 18 and 19).

Although the initial supramolecular transition metal complex is formed and the new NHC ligand functions as such, the explanation of the effect of the Zn^{II}-templates cannot be sought in the initially expected supramolecular encapsulation. Nevertheless, the templates do influence the polymerization results, and apparently we can steer the reaction to produce longer polymers by simply adding Lewis acidic Zn^{II}-complexes. The simplest explanation for all above observations is the following: All the different precursor complexes (**1** and **4a–c**) produce the same active species under catalytic conditions (most likely a species derived from a Rh^I(cod) fragment),[4] but the efficiency by which this species is formed depends on the ligands attached to the precursor. Possibly, the addition of the Zn^{II}-templates somehow decreases the initiation efficiency, with less active species leading to higher weight polymers, although at this point we cannot completely exclude a more active

Table 2 Polymerization experiments with EDA[a]

Entry	Catalyst	Solvent	Template	PEA yield (%)[b]	Oligomer yield (%)[c]	M_w/kDa	M_w/M_n
1	**4a**	CH_2Cl_2	—	25	15	110	2.7
2	**4b**	$CHCl_3$	—	20	30	150	4.7
3	**4b**	CH_2Cl_2	—	5	15	80	2.5
4	**4c**	CH_2Cl_2	—	5	20	70	2.5
5	**4a**	CH_2Cl_2	**I**	10	20	260	3.7
6	**4b**	CH_2Cl_2	**I**	15	15	310	3.5
7	**4b**	THF	**I**	10	5	150	2.8
8[d]	**4b**	MeOH	**I**	0	40	—	—
9	**4b**	CH_2Cl_2	**II**	10	10	265	4.7
10	**4b**	THF	**II**	5	20	140	2.7
11	**4b**	MeOH	**II**	5	10	60	2.3
12	**4c**	CH_2Cl_2	**II**	5	20	225	4.2
13	**1**	CH_2Cl_2	—	30	50	190	4.1
14	**1**	$CHCl_3$	—	50	30	150	3.6
15	**1**	MeOH	—	10	40	50	2.2
16	**1**	CH_2Cl_2	**I**	25	40	320	4.7
17	**1**	CH_2Cl_2	**II**	25	35	220	4.7
18	—	CH_2Cl_2	**I**	0	0	—	—
19	—	CH_2Cl_2	**II**	0	0	—	—
20[e]	**2b**	CH_2Cl_2	—	0	0	—	—

[a] Conditions: 0.04 mmol catalyst, 0.04 mmol template, 2 mmol EDA, 5 mL solvent, room temperature, 24 h reaction time. [b] MeOH insoluble fraction. [c] MeOH soluble fraction, excluding diethyl maleate and fumarate. [d] Template **I** is only scarcely soluble in MeOH. [e] Deprotonated *in situ* with *t*BuOK.

role of the Lewis acidic Zn^{II}-complexes on the polymerization event (*e.g.* Zn · · · O=C interactions with the carbonyl groups of the Rh-bound growing polymer chain, which might facilitate opening of a vacant site and/or slow down termination reactions). As far as we know, such an effect of Zn^{II} Lewis acids on the polymerization of polar monomers has not been observed previously. Active Lewis-acid participation of the Zn-templates should be weaker in polar solvents, and for that reason we investigated the influence of more polar solvents on the polymerization reactions in the presence of **I** and **II**. Indeed the effect of the templates is lowered (*i.e.* lower molecular weights of the polymer) when using more polar solvents (THF, MeOH, entries 7, 8, 10, 11). The effect of MeOH is general and larger than expected. Also in absence of any Zn-templates, MeOH causes the formation of substantially lower polymer molecular weights than in any of the other solvents (entry 15). Most likely MeOH facilitates chain termination (or chain transfer).

Additional information about this reaction was obtained with NMR and ESI-MS experiments. As mentioned above, the studied reactions proceeded rather slowly (less than 50% overall yield in 24 h) which allowed us to perform "*in situ*" NMR studies. Thus, ^{1}H-NMR spectra of a d_2-dichloromethane solution of **4b** in the presence of 3 equiv. of EDA showed that the pre-catalyst signals remained unaltered for a long period of time (24 h) while signals of oligomers and PEA started appearing during the first hour. Subsequent additions of EDA produced an increase in PEA yields. These results, together with a final control experiment where the free NHC (generated in situ by the addition of *t*-BuOK to **2b**) showed no activity in the EDA polymerization (entry 20), confirm that the true active species is rhodium-based. Furthermore, the active species must be present in very small amounts compared to the precursor **4b**, since polymers are obtained even when using only 3 equiv. of EDA. Initiation is slow compared to chain-growth.

Interestingly, ESI-MS analyses of the oligomeric fraction indicated loss of the NHC ligand from the metal, with possibly partial incorporation of the NHC moiety into the oligomeric chains.[17] Analyzed samples contained the fragmentation peaks corresponding to species **A** and **B** (Fig. 4). Additional higher mass peaks increased by 86 mass units ($CHCO_2Et$) were also observed but with very low relative intensities (**C**). These species are probably formed in the initiation steps *via* a reductive elimination process from Rh-alkyl-carbene species leading to incorporation of the NHC moiety in the oligomeric fraction. The proposed reductive elimination of an imidazolium cation from the NHC and a TM alkyl is in analogy to findings of others with palladium[20] and nickel[21] complexes.

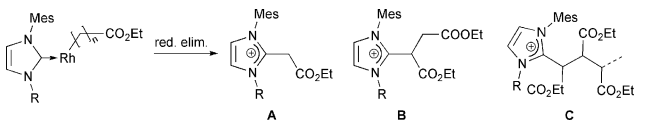


Fig. 4 Proposed formation of NHC-based oligomeric and polymeric species.

Conclusions

In summary, the envisaged supramolecular encapsulation method to steer and control 'carbene polymerization' does not work as expected. Zn^{II}-templates do influence the outcome of the polymerization reaction somehow, but control experiments reveal that the effect of the Zn^{II}-template on the polymerization results is general and not due to the expected assembly formation. The templates do influence the polymerization results though, and apparently we can steer the reaction to produce longer polymers by simply adding Lewis acidic Zn^{II}-complexes. The Zn^{II}-effect seems to be mostly based on its influence on the initiation efficiency

towards the active species. The 'true' active species are probably based on $[Rh(cod)]^+$ (or its derivatives) formed when the NHC ligand has dissociated from the metal. The exact role of Zn^{II} is poorly understood and further investigations are in progress.

Experimental

General procedures

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Dichloromethane distilled from calcium hydride, hexane distilled from sodium and tetrahydrofuran distilled from sodium benzophenone ketyl, were used for metal complex synthesis. NMR spectroscopy experiments were carried out on a Varian Inova 500 spectrometer or a Bruker AV400 spectrometer. Abbreviations used are: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad, cod = 1,5-cyclooctadiene. IR solid state measurements were performed on a Shimadzu FTIR 8400S spectrometer equipped with a Specac MKII Golden Gate Single Reflection ATR system. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. UV-vIS spectroscopy experiments were performed on a HP 8453 UV-vis System. Elemental analyses (CHN) were performed by the Kolbe analytical laboratory in Mülheim an der Ruhr (Germany). [(L-prolinate)Rh^I(1,5-cyclooctadiene)] (**1**),[3] 1-mesitylimidazole,[22] Zn^{II}-templates **I**[23] and **II**[24] were synthesized according to published procedures. All other chemicals are commercially available and were used without further purification.

Synthesis of compounds 2–4

***N*-mesityl-*N*′-(4-pyridyl)imidazolium bromide (2a).** 1-Mesitylimidazole (600 mg, 3.22 mmol) and 4-bromopyridine hydrochloride (290 mg, 1.5 mmol) were heated at 120 °C overnight. The reaction mixture was washed with THF and Et_2O and dried under vacuum. The product was re-crystallized from ethanol–hexane. White solid. Yield: 400 mg, 75%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 2.13 (s, 6 H, 2 CH_3), 2.36 (s, 3 H, CH_3), 7.20 (s, 2 H, 2 H arom), 8.10 (d, J_{HH} = 5 Hz, 2 H, 2 H arom), 8.27 (s, 1 H, =CH), 8.87 (s, 1 H, =CH), 8.96 (d, J_{HH} = 5 Hz, 2 H, 2 H arom), 10.37 (s, 1 H, NC*H*N) ppm. ^{13}C-NMR (DMSO-d_6, 100.6 MHz): δ 17.1 (2 Me), 20.6 (Me), 116.2 (2 CH arom), 121.0 (=CH), 125.2 (=CH), 129.3 (2 CH arom), 130.9 (C_q arom), 134.4 (2 C_q arom), 137.5 (N*C*N), 140.6 (C_q arom), 142.8 (C_q arom), 150.0 (2 CH arom) ppm. IR: ν 3165, 3138, 2995, 2961, 1636, 1605, 1537, 1518, 1485, 1383, 1331, 1312, 1248, 1229, 1150, 1072, 997, 957, 932, 855, 737, 692, 662 cm^{-1}. HRMS (FAB): *m*/*z*, 264.1499, $[M - Br]^+$ (exact mass calculated for $C_{17}H_{18}N_3$: 264.1501).

***N*-mesityl-*N*′-(3-pyridylmethyl)imidazolium chloride (2b).** 3-(Chloromethyl)pyridine hydrobromide (1.76 g, 10.75 mmol) was neutralized using a saturated aqueous solution of sodium carbonate. The liberated 3-chloromethylpyridine was extracted into diethyl ether (3 × 50 cm^3) at 0 °C, dried with magnesium sulfate and filtered. The filtrate was concentrated until a volume of 75 mL approximately. 1-Mesitylimidazole (1 g, 5.37 mmol) in THF (50 cm^3) at 0 °C was added, the ether removed under reduced pressure and the solution was warmed to room temperature and then refluxed for seven days. After cooling, the solid precipitate was filtered, washed with diethyl ether and dried under vacuum. White solid. Yield: 1.095 g, 65%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.07 (s, 6 H, 2 CH_3), 2.35 (s, 3 H, CH_3), 6.25 (s, 2 H, CH_2), 7.01 (s, 2 H, 2 H arom), 7.14 (s, 1 H, =CH), 7.54 (dd, J_{HH} = 8, 5 Hz, 1 H, py), 8.05 (m, 1 H, =CH), 8.66 (dd, J_{HH} = 5, 2 Hz, 1 H, py), 8.70 (dt, J_{HH} = 8, 2 Hz, 1 H, py), 9.16 (d, J_{HH} = 2 Hz, 1 H, py), 10.95 (s, 1 H, NCHN) ppm. ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ 17.4 (2 Me), 20.9 (Me), 50.4 (CH_2), 122.9 (=CH), 123.3 (=CH), 124.1 (CH arom), 129.7 (2 CH arom), 130.0 (C_q arom), 130.5 (C_q arom), 133.9 (2 C_q arom), 137.2 (CH arom), 138.3 (NCN), 141.1 (C_q arom), 149.8 (CH arom), 150.4 (CH arom) ppm. IR: ν 3171, 3119, 3082, 3026, 2960, 1672, 1637, 1597, 1545, 1485, 1456, 1433, 1375, 1201, 1163, 1109, 1032, 937, 873, 802, 746, 733, 710, 671, 654 cm^{-1}. HRMS (FAB): *m*/*z*, 278.1653, $[M]^+$ (exact mass calculated for $C_{18}H_{20}N_3$: 278.1657).

[*N*-mesityl-*N*′-(4-pyridyl)imidazol-2-ylidene] silver bromide (3a). *N*-mesityl-*N*′-(4-pyridyl)imidazolium bromide (2a) (800 mg, 2.32 mmol) and Ag_2O (270 mg, 1.16 mmol) were mixed in CH_2Cl_2 (100 mL) and heated to 40 °C for 3 h. After cooling, the reaction mixture was filtered through Celite and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the solid product was washed with diethyl ether and dried *in vacuo*. Yellow solid. Yield: 690 mg, 65%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.07 (s, 6 H, 2 CH_3), 2.37 (s, 3 H, CH_3), 7.02 (s, 2 H, 2 H arom), 7.21 (d, J_{HH}= 2 Hz, 1 H, =CH), 7.60 (d, J_{HH}= 2 Hz, 1 H, =CH), 7.73 (dd, J_{HH}= 5, 2 Hz, 2 H, 2 H arom), 8.85 (bs, 2 H, 2 H arom) ppm. ^{13}C-NMR (CD_2Cl_2, 400 MHz): δ 17.8 (2 Me), 21.1 (Me), 117.6 (2 CH arom), 120.7 (=CH), 124.3 (=CH), 129.7 (2 CH arom), 134.3 (2 C_q arom), 135.0 (C_q arom), 140.2 (C_q arom), 146.0 (C_q arom), 151.9 (2 CH arom) ppm. N*C*N not observable. IR: ν 3080, 3034, 2916, 2855, 1661, 1589, 1543, 1489, 1408, 1379, 1308, 1273, 1248, 1217, 1089, 1034, 993, 933, 852, 823, 737, 700, 665 cm^{-1}. HRMS (FAB): *m*/*z*, 372.0471, $[M - Br]^+$ (exact mass calculated for $C_{17}H_{17}N_3Ag$: 372.0471).

[*N*-mesityl-*N*′-(3-pyridylmethyl)imidazol-2-ylidene] silver chloride (3b). *N*-mesityl-*N*′-(3-pyridylmethyl)imidazolium chloride (2b) (200 mg, 0.64 mmol) and Ag_2O (74 mg, 0.32 mmol) were mixed in DCM (30 mL) and heated to 40 °C for 3 h. After cooling, the reaction mixture was filtered through Celite and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the solid product was washed with diethyl ether and dried *in vacuo*. Yellow solid. Yield: 240 mg, 90%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 2.06 (s, 6 H, 2 CH_3), 2.40 (s, 3 H, CH_3), 5.49 (s, 2 H, CH_2), 7.07 (s, 2 H, 2 H arom), 7.08 (d, J_{HH}= 4 Hz, 1 H, =CH), 7.20 (d, J_{HH}= 4 Hz, 1 H, =CH), 7.39 (dd, J_{HH}= 8, 4 Hz, 1 H, H arom), 7.67 (bd, J_{HH}= 8 Hz, 1 H, H arom), 8.61 (d, J_{HH}= 8, 2 Hz, 1 H, H arom), 8.64 (dd, J_{HH}= 4, 2 Hz, 1 H, H arom) ppm. ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 17.3 (2 Me), 20.7 (Me), 53.0 (CH_2), 121.0 (CH arom), 123.6 (CH arom), 123.8 (CH arom), 129.2 (2 CH arom), 131.4 (C_q arom), 134.7 (2 C_q arom), 135.0 (CH arom), 135.3 (C_q arom), 139.6 (C_q arom), 148.7 (CH arom), 149.9 (CH arom), 181.7 (N*C*N) ppm. IR: ν 3150, 3107, 3075, 3034, 2944, 2914, 1593, 1558, 1551, 1477, 1431, 1377, 1354, 1329, 1231, 1188, 1092, 1042, 1030, 966, 933, 856, 827, 806, 731, 704, 675 cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{18}H_{19}N_3Ag$: 384.0630; found: 384.0638 $[M - Cl]^+$. Elemental Analysis: $C_{18}H_{19}N_3AgCl$ (420.68): calcd C 51.4, H 4.5, N 10.0; found C 51.3, H 4.5, N 10.1.

Chloro(1,5-cyclooctadiene)(*N*-mesityl-*N*′-4-pyridyl-imidazol-2-ylidene) rhodium(I) (4a). To a solution of [*N*-mesityl-*N*′-4-pyridyl-imidazol-2-ylidene] silver bromide (3a) (150 mg, 0.33 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[RhCl(cod)]_2$ (82 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred during 24 h. The reaction mixture was then filtered through a Celite plug and the solvent was removed under vacuum. The compound was purified by precipitation from CH_2Cl_2–hexane. Yellow solid. Yield: 150 mg, 90%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 1.60–1.80 (m, 5 H, C*H*H COD), 1.92 (s, 3 H, CH_3), 1.95–2.10 (m, 3 H, C*H*H COD), 2.40 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.13 (m, 1 H, =CH COD), 3.18 (m, 1 H, =CH COD), 4.64 (m, 1 H, =CH COD), 4.79 (m, 1 H, =CH COD), 7.01 (s, 1 H, H arom), 7.01 (d, J_{HH}= 2 Hz, 1 H, =CH), 7.13 (s, 1 H, H arom), 7.48 (d, J_{HH}= 2 Hz, 1 H, =CH), 8.51 (d, J_{HH}= 5 Hz, 2 H, H arom), 8.82 (d, J_{HH}= 5 Hz, 2 H, H arom) ppm. ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 18.3 (Me), 20.0 (Me), 21.4 (Me), 28.5 (CH_2 COD), 29.3 (CH_2 COD), 32.1 (CH_2 COD), 33.8 (CH_2 COD), 68.6 (d, J_{RhC}= 14 Hz, CH COD), 69.2 (d, J_{RhC}= 14 Hz, CH COD), 97.4 (d, J_{RhC}= 8 Hz, CH COD), 97.8 (d, J_{RhC}= 8 Hz, CH COD), 119.9 (2 CH arom), 121.5 (CH arom), 125.5 (CH arom), 128.9 (CH arom), 130.1 (CH arom), 134.2 (C_q arom), 135.7 (C_q arom), 136.8 (C_q arom), 139.1 (C_q arom), 147.4 (C_q arom), 151.2 (2 CH arom), 185.5 (d, J_{CRh}= 51 Hz, N*C*N) ppm. Elemental analysis for $C_{25}H_{29}ClN_3Rh{\cdot}0.5H_2O$: calcd C 57.87, H 5.83, N 8.10; found C 58.19, H 5.96, N 8.00.

Chloro(1,5-cyclooctadiene)(*N*-mesityl-*N*′-(3-pyridylmethyl)-imidazol-2-ylidene) rhodium(I) (4b). To a solution of [*N*-mesityl-*N*′-(3-pyridylmethyl)imidazol-2-ylidene] silver chloride (**3b**) (63 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $[RhCl(cod)]_2$ (37 mg, 0.075 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 24 h. The reaction mixture was then filtered through a Celite plug and the solvent was removed under vacuum. The compound was purified by precipitation from CH_2Cl_2–hexane. Yellow solid. Yield: 75 mg, 90%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 1.40–1.80 (m, 5 H, C*H*H COD), 1.86 (s, 3 H, CH_3), 1.90–2.20 (m, 3 H, C*H*H COD), 2.38 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.99 (m, 1 H, =CH COD), 3.23 (m, 1 H, =CH COD), 4.72 (m, 1 H, =CH COD), 4.82 (m, 1 H, =CH COD), 5.86 (d, J_{HH}= 15 Hz, 1 H, C*H*H), 6.26 (d, J_{HH}= 15 Hz, 1 H, CH*H*), 6.84 (d, J_{HH}= 2 Hz, 1 H, =CH), 6.96 (s, 1 H, H arom), 6.98 (d, J_{HH}= 2 Hz, 1 H, =CH), 7.12 (s, 1 H, H arom), 7.36 (dd, J_{HH}= 8, 5 Hz, 1 H, py), 7.86 (dt, J_{HH}= 8, 2 Hz, 1 H, py), 8.60 (dd, J_{HH}= 5, 1.5 Hz, 1 H, py), 8.71 (d, J_{HH}= 1.5 Hz, 1 H, H arom) ppm. ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 18.1 (Me), 20.0 (Me), 21.4 (Me), 28.5 (CH_2 COD), 29.5 (CH_2 COD), 32.1 (CH_2 COD), 34.3 (CH_2 COD), 53.2 (CH_2), 68.4 (d, J_{RhC}= 14 Hz, CH COD), 69.2 (d, J_{RhC}= 15 Hz, CH COD), 97.6 (d, J_{RhC}= 8 Hz, CH COD), 97.8 (d, J_{RhC}= 8 Hz, CH COD), 121.5 (CH arom), 124.3 (CH arom), 124.4 (CH arom), 128.8 (CH arom), 130.0 (CH arom), 133.7 (C_q arom), 134.9 (C_q arom), 136.5 (CH arom), 136.6 (C_q arom), 137.3 (C_q arom), 139.4 (C_q arom), 150.1 (CH arom), 150.2 (CH arom), 184.1 (d, J_{CRh}= 51 Hz, N*C*N-Rh) ppm. Elemental analysis for $C_{26}H_{31}ClN_3Rh{\cdot}H_2O$: calcd C 57.62, H 6.14, N 7.75; found C 57.81, H 5.96, N 7.69.

Chloro(1,5-cyclooctadiene)(*N*-mesityl-*N*′-benzylimidazol-2-ylidene) rhodium(I) (4c). To a solution of *N*-mesityl-*N*′-benzylimidazolium bromide (286 mg, 0.8 mmol) in CH_2Cl_2 (30 mL) was added silver(I) oxide (93 mg, 0.4 mmol) and the mixture was stirred in the darkness for 3 h at 40 °C. After cooling down, the reaction mixture was filtered over Celite onto a solution of $[RhCl(cod)]_2$ (197 mg, 0.4 mmol) in CH_2Cl_2 (5 mL) and stirred for 24 h. The solvent was removed under vacuum and the residue was purified by flash chromatography (AcOEt–hexane 1 : 1). Yellow solid. Yield: 310 mg, 75%. ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ 1.40–1.80 (m, 5 H, C*H*H COD), 1.87 (s, 3 H, CH_3), 1.90–2.20 (m, 3 H, C*H*H COD), 2.39 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.00 (m, 1 H, =CH COD), 3.31 (m, 1 H, =CH COD), 4.70 (m, 1 H, =CH COD), 4.82 (m, 1 H, =CH COD), 5.69 (d, J_{HH}= 15 Hz, 1 H, C*H*H), 6.35 (d, J_{HH}= 15 Hz, 1 H, CH*H*), 6.81 (d, J_{HH}= 2 Hz, 1 H, =CH), 6.96 (bs, 2 H, 2 H arom), 7.12 (bs, 1 H, H arom), 7.33–7.48 (m, 5 H, 5 H arom) ppm. ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 17.4 (Me), 19.3 (Me), 20.7 (Me), 27.8 (CH_2 COD), 28.8 (CH_2 COD), 31.5 (CH_2 COD), 33.6 (CH_2 COD), 55.1 (CH_2), 67.4 (d, J_{RhC}= 14 Hz, CH COD), 68.5 (d, J_{RhC}= 14 Hz, CH COD), 96.4 (d, J_{RhC}= 8 Hz, CH COD), 96.8 (d, J_{RhC}= 7 Hz, CH COD), 121.0 (CH arom), 123.3 (CH arom), 127.7 (CH arom), 128.0 (2 CH arom), 128.1 (CH arom), 128.7 (2CH arom), 129.3 (CH arom), 134.4 (C_q arom), 136.1 (C_q arom), 136.7 (C_q arom), 137.4 (C_q arom), 138.6 (C_q arom), 182.9 (d, J_{CRh}= 51 Hz, N*C*N-Rh) ppm. Elemental analysis for $C_{27}H_{32}ClN_2Rh$: calcd C 62.02, H 6.17, N 5.36; found C 61.96, H 6.21, N 5.40.

Polymerization of carbenes from EDA to poly(ethyl-2-ylidene-acetate)

Ethyl diazoacetate (EDA) (2 mmol) was added to a solution (5 mL) of catalyst precursor (0.04 mmol) either with or without the Zn^{II}-template added (0.04 mmol). Upon addition, gas evolution was visible, and the colour of the reaction mixture became slightly darker. The mixture was stirred for 24 h at room temperature. Subsequently, the solvent was removed in vacuo, and methanol was added to the oily residue. The precipitate was centrifuged and washed with methanol until the washings were colourless (in case of using template **I**, which is scarcely soluble in methanol, a small amount of toluene was added to wash away **I**). The resulting white powder was dried *in vacuo* and identified as poly(ethyl-2-ylidene-acetate) (PEA). The methanol soluble oligomeric fraction was analyzed separately after evaporation of the solvent.

Polymer and oligomer characterization

Molecular mass distributions were measured using size exclusion chromatography (SEC) on a Shimadzu LC-20AD system with two PLgel 5 μm MIXED-C columns (Polymer Laboratories) in series and a Shimadzu RID-10A refractive index detector, using dichloromethane as mobile phase at 1 mL min^{-1} and T = 35 °C. Polystyrene standards in the range of 760–1 880 000 g mol^{-1} (Aldrich) were used for calibration.

Acknowledgements

This research was supported by the Netherlands Organization for Scientific Research (NWO-CW, VIDI project 700.55.426), the European Research Council (ERC, EU 7th framework program, Grant Agreement 202886-CatCIR), and the University of Amsterdam. The Spanish Ministerio de Ciencia e Innovación and FECYT are acknowledged for a postdoctoral fellowship of M. R. We thank J. W. H. Peters for performing HRMS analyses.

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