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Lactide polymerisation by ring-expanded NHC complexes of zinc

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Abstract

The reaction of the ring-expanded N-heterocyclic carbenes (RE-NHCs) with $[\text{ZnMe}_2]$ affords the structurally characterised complexes $[(6\text{-Mes})\text{ZnMe}_2]$ (**1**) and $[(7\text{-Mes})\text{ZnMe}_2]$ (**2**). The activity of the two complexes, along with that of the free carbenes, for the ring-opening polymerisation of *rac*-lactide has been probed. Even for such strongly σ -donating carbenes, dissociation from the metal centre cannot be ruled out.

1. Introduction

In recent years there has been considerable interest in the ring opening polymerisation of lactide.[1-3] This is due to the biodegradable nature of polylactide (PLA) and the fact that the monomer can be prepared from annually renewable raw materials. This has led to it being viewed as a serious, high-volume alternative to plastics derived from petrochemical sources. As a result, intensive efforts have been aimed at developing new, well-defined, sustainable metal initiators that bring about the ring-opening polymerisation of lactide to afford PLA in a well-controlled and stereoselective manner.[4,5] Thus, attempts to find a replacement of the current industrial initiator, tin octanoate, by metals from groups 2[6-10], 3[11-14] and 4[15-19] has been described. Moving to the right of the periodic table, zinc[6, 20-25] has been considered as a very desirable metal centre to use on the grounds of it being cheap, low in toxicity and also biocompatible, which makes it ideal for some of the biomedical applications of PLA, such as stents and scaffolds for tissue engineering applications.[26-28]

In early efforts directed at preparing robust zinc complexes stabilised by N-heterocyclic carbenes (NHCs) as pre-catalysts for the ROP of lactide, the Tolman group[29, 30] demonstrated that NHC dissociation was possible from [(IPr)ZnEt₂] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) upon addition of alcohol initiator, raising the question of whether the subsequent polymerisation was metal or free carbene catalysed.[31,32] The formation of heterotactic enriched PLA from [(IPr)ZnEt₂] in contrast to the formation of isotactic enriched polymer using IPr alone implied that the major catalytically active species present in solution was not the free carbene. In efforts to address this issue further, approaches to help limit the potential for Zn-NHC dissociation have been employed, such as the use of oxygen/nitrogen donor substituents on the carbene in an effort to yield bidentate ligands.[33-35] An alternative approach involves the use of more strongly σ -donating

carbenes, on the basis that they should afford stronger M-C_{NHC} interactions. One such class of these are ring-expanded NHCs, a generic name given to carbenes based on ring-sizes of greater than 5.[36] Herein, we describe our findings on the ROP of *rac*-lactide with [(RE-NHC)Zn(alkyl)₂] pre-catalysts (RE-NHC = 6-Mes, 7-Mes; Scheme 1), as well as the free carbenes for comparison.

2. Experimental

2.1 General Considerations

Manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. Solvents were purified using an MBraun SPS solvent system (toluene, hexane) or under a nitrogen atmosphere from sodium benzophenone ketyl (thf, benzene). C₆D₆ was vacuum transferred from potassium. 6-Mes and 7-Mes were prepared according to the literature.[36b,37] NMR spectra were recorded using a Bruker Avance 500 MHz NMR spectrometer and referenced to solvent signals at δ 7.16 (¹H) and 128.0 (¹³C). Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK.

2.2 Synthesis of [(6-Mes)ZnMe₂] (**1**)

To a stirred benzene (10 mL) solution of 6-Mes (0.252 g, 0.786 mmol) was added a 2.0 M toluene solution of [ZnMe₂] (0.400 mL, 0.800 mmol). After stirring for 20 min, the volatiles were removed under reduced pressure and the product extracted into toluene. This solution was reduced to dryness and the residue washed with hexane, affording a colourless solid, which was dried in vacuo. Yield: 0.145 g (44%). Single crystals suitable for X-ray diffraction studies were grown from toluene/ hexane. Anal. calcd for C₂₄H₃₄N₂Zn (414.90): C 69.31; H 8.24; N 6.74. Found: C 69.19; H 8.23; N 6.80%. ¹H NMR (C₆D₆, 500 MHz, 298 K): δ 6.75 (s, 4H, *m*-ArH), 2.57 (t, *J*_{HH} = 5.9 Hz, 4H, NCH₂), 2.29 (s, 12H, *o*-ArCH₃), 2.00 (s,

6H, *p*-ArCH₃), 1.44 (m, 2H, NCH₂CH₂), -0.67 (s, 6H, ZnCH₃). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K): δ 214.7 (s, NCN), 140.9 (s, *i*-Ar), 138.1 (s, *p*-Ar), 135.5 (s, *o*-Ar), 129.8 (s, *m*-Ar), 43.7 (s, NCH₂), 21.0 (s, *p*-ArCH₃), 20.8 (s, NCH₂CH₂), 18.1 (s, *o*-ArCH₃), -8.8 (ZnCH₃).

2.3 Synthesis of [(7-Mes)ZnMe₂] (**2**)

To a stirred benzene (10 mL) solution of 7-Mes (0.310 g, 0.927 mmol) was added a 1.0 M hexane solution of [ZnMe₂] (1.300 mL, 1.300 mmol). After stirring for 30 min, the volatiles were removed under reduced pressure and the colourless residue dried in vacuo. The product was re-precipitated from benzene/hexane and dried in vacuo. Yield: 0.230 g (54%). Single crystals suitable for X-ray diffraction studies were grown from toluene/hexane. Anal. calcd for C₂₅H₃₆N₂Zn (429.92): C 69.84; H 8.44; N 6.52. Found: C 69.87; H 8.30; N 6.36%. ¹H NMR (C₆D₆, 500 MHz, 298 K): δ 6.76 (s, 4H, *m*-ArH), 3.11 (m, 4H, NCH₂), 2.36 (s, 12H, *o*-ArCH₃), 2.00 (s, 6H, *p*-ArCH₃), 1.59 (m, 4H, NCH₂CH₂), -0.75 (s, 6H, ZnCH₃). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K): δ 225.8 (s, NCN), 143.2 (s, *i*-Ar), 137.8 (s, *p*-Ar), 135.1 (s, *o*-Ar), 129.9 (s, *m*-Ar), 52.4 (s, NCH₂), 25.9 (s, NCH₂CH₂), 20.9 (s, *p*-ArCH₃), 18.8 (s, *o*-ArCH₃), -8.6 (s, ZnCH₃).

2.4. Crystallography

Data for **1** and **2** were collected on Agilent Excalibur and Supernova diffractometers respectively. Relevant details are summarised in Table 1. There were several pertinent issues in relation to refinement of these structures. In particular, the asymmetric unit in **1** comprises one full molecule plus a half of one molecule of the zinc complex. In the latter, the zinc centre (Zn2) and the carbene carbon (C25) are coincident with a crystallographic 2-fold rotation axis about which some disorder was prevalent. This was modelled by treating all atoms in the half carbene ligand as being located over two proximate sites in equal ratio.

Additional disorder was evident for the apical carbon (C27) of the NHC ring which was also modelled. Ultimately, separation of these two fractional-occupancy, half-ligand moieties into separate 'parts' precluded addition of the hydrogens to the heterocyclic ring at chemically correct positions. Hence, the hydrogen atoms attached to C26, C27, C26A and C27A were omitted from this refinement. Fractional occupancy carbon and nitrogen atoms were refined subject to some ADP restraints during the final least-squares in order to assist convergence.

In **2**, the asymmetric unit comprises of two crystallographically independent molecules of zinc complex and an additional half molecule of the same material. Of these, one of the full molecules is completely ordered and the atoms therein have been labelled with suffix A. Atom labels with suffix B belong to the half molecule present in the asymmetric unit. Atoms Zn1B and C1B, therein, are located on a crystallographic 2-fold rotation axis which serves to generate the remainder of this moiety. N1B, C2B and C3B in this fragment exhibited 50:50 disorder (the corresponding fractional occupancy atoms are labelled with suffix C). Some ADP restraints were included in the model for these disordered atoms to assist convergence. Finally, the second full molecule present in the motif exhibited considerable disorder. Labelling in this molecule is denoted by suffix D and, where disorder is present, a comparative fractional occupancy atom is present labelled with suffix E. The disorder itself extended to all atoms present (with the exception of the mesityl group based on C15D) in a 55:45 ratio. A significant number of restraints were added to assist convergence in this latter molecule and these included treating the disordered phenyl rings of the mesityl group based on C6D/C6E as rigid hexagons. C_{carbene}-N distances were also restrained to being similar, as were N-C_{mesityl} distances. ADP restraints were also included for all fractional occupancy atoms to assist convergence. The structure of **2** falls into the category of *crystallographer-tormenter*. Initially, prejudice resulted in not accepting the credibility of a *c* axis length greater than 76 Å, for a compound of this type. In fact, it took screening of well in

excess of a dozen samples before it was accepted that the diffraction pattern did not arise from a twinned sample and that the crystals were predominantly single. It is worthy of mention that crystals were also examined at room temperature, as well as at 150 K, the temperature at which the data were collected. These ambient temperature analyses afforded the same space group and unit cell metrics to those reported here, precluding the fact that the long c axis arises from a crystal that is undergoing a phase transition.

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	1	2
Empirical formula	C ₃₆ H ₅₁ N ₃ Zn _{1.50}	C _{62.5} H ₉₀ N ₅ Zn _{2.5}
Formula weight	623.85	1074.825
Temperature/K	150(2)	150(2)
Radiation	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)
Crystal system	Orthorhombic	Monoclinic
Space group	C222 ₁	C2/c
<i>a</i> /Å	15.6941(6)	9.1036(3)
<i>b</i> /Å	9.3009(3)	17.0628(5)
<i>c</i> /Å	47.6563(16)	76.881(2)
α /°	90	90
β /°	90	92.036(3)
γ /°	90	90
Volume	6956.4(4)	11934.6(6)
<i>Z</i>	8	8
ρ_{calc} /cm ³	1.191	1.196
μ /mm ⁻¹	1.069	1.493
F(000)	2664	4600.0
Crystal size/mm ³	0.2675 × 0.2122 × 0.1245	0.1308 × 0.0692 × 0.0463
Theta range for data collection	3.32 to 27.48	9.208 to 136.492
Index ranges	-19 ≤ <i>h</i> ≤ 19 -12 ≤ <i>k</i> ≤ 12 -61 ≤ <i>l</i> ≤ 59	-10 ≤ <i>h</i> ≤ 10 -20 ≤ <i>k</i> ≤ 20 -92 ≤ <i>l</i> ≤ 91
Reflections collected	24942	17282
Independent reflections	7682 [<i>R</i> _{int} = 0.0456]	10684 [<i>R</i> _{int} = 0.0355]
Data / restraints / parameters	7682 / 120 / 492	10684/218/822
Goodness-of-fit on <i>F</i> ²	1.039	1.239
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0461, <i>wR</i> ₂ = 0.0901	<i>R</i> ₁ = 0.0947, <i>wR</i> ₂ = 0.2213
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0590, <i>wR</i> ₂ = 0.0956	<i>R</i> ₁ = 0.1084, <i>wR</i> ₂ = 0.2263
Largest diff. peak/hole / e Å ⁻³	0.372, -0.402	0.68, -1.20
Absolute structure parameter	0.015(12)	—

2.5 Ring-opening polymerization (ROP) studies

For polymerizations, the monomer:Zn/RE-NHC:BnOH ratio employed was 100:1:1 at room temperature; in all cases 0.72 g of *rac*-lactide were used. After the appropriate reaction time, the vessel was opened to air to quench the reaction, the resulting solid then dissolved in CH₂Cl₂ and all solvents then removed in vacuo. ¹H NMR spectroscopy (CDCl₃) and GPC (THF) were used to determine tacticity and molecular weights (*M_n* and *M_w*) of the polymers produced; *P_m* (the probability of isotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ¹H NMR spectra. GPC were recorded on a Polymer Labs 50 instrument and referenced to polystyrene standards.

3. Results and Discussion

3.1. Synthesis and Characterisation of [(6-Mes)ZnMe₂] (**1**) and [(7-Mes)ZnMe₂] (**2**)

The N-aryl substituted carbene complexes of [ZnMe₂], **1** and **2** (Scheme 1), were prepared by reaction of equimolar amounts of the free 6- and 7-membered ring carbenes 6-Mes and 7-Mes with [ZnMe₂] in benzene solution. Colourless crystalline samples of both species were isolated in moderate yields of 44 and 54% respectively after work up.

Diagnostic proton resonances for the backbone positions at $\delta = 2.57$ ppm (**1**) and $\delta = 3.11$ ppm (**2**) integrated in a ratio of 4:6 with zinc bound methyl signals at $\delta = -0.67$ ppm and $\delta = -0.75$ ppm respectively. The ¹³C{¹H} PENDANT spectra revealed high frequency resonances at $\delta = 215$ ppm (**1**) and $\delta = 226$ ppm (**2**), diagnostic of coordinated RE-NHC ligands.[38]

Scheme 1

The X-ray crystal structures of the two compounds are shown in Figs 1 and 2. Both displayed the expected trigonal planar structures, with the sum of the bond angles around Zn adding up to 360° in both instances. Interestingly, the Zn-C_{NHC} distances of 2.099(3) and 2.100(5) Å in **1** and **2**, respectively, are the same as those in [(IPr)ZnR₂] (R = Et: 2.1000(18) Å;[30] R= Me: 2.112(2) Å[39]) and [(IAd)ZnEt₂] (2.096(3) Å).[40] Thus, despite being stronger donors, the greater steric demand of the larger ring carbenes, evidenced by widening

of the N-C_{carbene}-N angle (**1**: 117.7(3)°; **2**: 119.6(5)°; c.f. 103.3(2)° in [(IPr)ZnMe₂]) results in the bulkier 6-Mes and 7-Mes ligands being pushed away from the metal centre. It is worth noting that for a system where a more donating carbene is accommodated, but where steric clash is largely negated, namely the C4 or ‘abnormally’ bound carbene complex [(abNHC)Zn(Et)(N{SiMe₃}₂)], the Zn-C_{carbene} distance is not shortened that dramatically (2.061(2) Å).[41]

Fig 1. Structure of the ordered molecule in the asymmetric unit of [(6-Mes)ZnMe₂] (**1**).

Thermal ellipsoids are shown at 30% with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)-C(1) 2.099(3), Zn(1)-C(23) 2.005(4), Zn(1)-C(24) 2.001(4), C(1)-Zn(1)-C(23) 115.51(14), C(1)-Zn(1)-C(24) 115.98(14), C(23)-Zn(1)-C(24) 128.51(16), N(1)-C(1)-N(2) 117.7(3).

Fig 2. Structure of the ordered molecule in the asymmetric unit of [(7-Mes)ZnMe₂] (**2**).

Thermal ellipsoids are shown at 30% with all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1a)-C(1a) 2.100(5), Zn(1a)-C(24a) 2.014(7), Zn(1a)-C(25a) 1.995(7), C(1a)-Zn(1a)-C(24a) 117.1(3), C(1a)-Zn(1a)-C(25a) 115.7(3), C(24a)-Zn(1a)-C(25a) 127.1(3), N(1a)-C(1a)-N(2a) 119.6(5).

3.2. Polymerization of *rac*-lactide by **1**, **2** and free RE-NHCs

To assess the applicability of the complexes for the ROP of *rac*-lactide, **1** and **2**, as well as the free carbenes, were trialled in solution at a 100:1:1 ratio of LA:Zn(or free carbene):BnOH for 2 h at room temperature in either THF or toluene. The results are summarised in Table 2.

Table 2. ROP results for the complexes and free carbenes.

Catalyst	[LA]:[Cat]:[BnOH]	Conversion ^b	Solvent	M_n^c	PDI ^c	P_m^d
1	100:1:1	98	Toluene	21300	1.51	0.65
1^a	100:1:1	99	Toluene	23200	1.18	0.70
1	100:1:2	99	Toluene	11100	1.30	0.60
1	100:1:1	44	THF	5700	1.11	n/d
6-Mes	100:1:1	98	Toluene	19100	1.21	0.65
6-Mes	100:1:1	77	THF	7750	1.15	0.65
2	100:1:1	98	Toluene	17550	1.10	0.65
2	100:1:1	33	THF	5800	1.11	0.50
7-Mes	100:1:1	99	Toluene	13250	1.46	0.60
7-Mes	100:1:1	60	THF	6450	1.18	0.60

^a 0 °C. ^b determined from ¹H NMR. ^c determined from GPC analysis. ^d determined from analysis of the ¹H{¹H} NMR.

Both the zinc complexes and the free carbenes were able to afford PLA under the conditions tested. As expected, polymerization was slower in THF. Narrow molecular weight distributions were observed for all systems indicating a degree of control in the molecular weight with these systems, particularly when run at 0 °C. End group analysis (by MALDI-ToF MS) for the PLA produced in THF with 6-Mes indicated an H- and –OCH₂Ph end group were present. When two equivalents of BnOH were used, the molecular weight of the PLA reduced by a half, indicative of a good degree of control in the polymerization process. Furthermore, there is a suggestion of very slight isotactic bias as indicated by an enhanced *iii* tetrad in the ¹H{¹H} NMR spectra of the polymers obtained. In toluene, there does not appear to be a major difference between the Zn complexes and the free carbenes in their ability to polymerise *rac*-lactide, both affording PLA with a M_n of ca. 20,000 after 2 h. However, in

THF, the yields of PLA were significantly lower for the Zn complexes compared to the free carbenes, 44% vs 77% for the 6-NHC systems and 33% vs 60% for the 7-NHC cases. This suggests that the Zn centre is playing a role in the polymerization in THF. However, as noted above for other Zn-NHC cases, the similarity of the data between the Zn complexes and the free carbenes in toluene implies that even with such strongly donating NHCs, dissociation of carbene from Zn being responsible for the activity cannot be ruled out.

3. Conclusions

Two new zinc complexes containing strongly σ -donating ring-expanded N-heterocyclic carbenes have been prepared and investigated as pre-catalysts for the ring-opening polymerisation of *rac*-lactide. A comparison of their activity with that of the free carbenes 6-Mes and 7-Mes suggests that both metal species and free ligands play a role in catalysis, depending on the solvent. Given this complication, further experiments are in order to elucidate the nature of the zinc species formed under the catalytic conditions and show whether it is these which dissociate NHC rather than **1** and **2**. Overall, our findings imply that even the most donating monodentate carbenes still appear to be prone to dissociation from zinc during lactide polymerisation.

Appendix A. Supplementary material

CCDC 1416189 and 1416190 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

- [1] R. Auras, B. Harte, S. Selke, *Macromol. Biosci.*, 4 (2004) 835-864.
- [2] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.*, 104 (2004) 6147-6176.
- [3] Y. Ikada, H. Tsuji, *Macromol. Rapid Commun.*, 21 (2000) 117-132.
- [4] K. Majerska, A. Duda, *J. Am. Chem. Soc.*, 126 (2004) 1026-1027.
- [5] M. J. Stanford, A. P. Dove, *Chem. Soc. Rev.*, 39 (2010) 486-494.
- [6] B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.*, 123 (2001) 3229-3238.
- [7] M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.*, 122 (2000) 11845-11854.
- [8] M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.*, 41 (2002) 2785-2794.
- [9] M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.*, (2003) 48-49.
- [10] M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.*, 43 (2004) 6717-6725.
- [11] A. Amgoune, C. M. Thomas, T. Roisnel, J. F. Carpentier, *Chem. Eur. J.*, 12 (2006) 169-179.
- [12] C. Bakewell, A. J. P. White, N. J. Long, C. K. Williams, *Angew. Chem. Int. Ed.*, 53 (2014) 9226-9230.
- [13] J. L. Brosmer, P. L. Diaconescu, *Organometallics*, 34 (2015) 2567-2572.
- [14] W. Gu, P. Xu, Y. Wang, Y. Yao, D. Yuan, Q. Shen, *Organometallics*, 34 (2015) 2907-2916.

- [15] S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt, M. Kol, *Inorg. Chem.*, 45 (2006) 4783-4790.
- [16] D. J. Gilmour, R. L. Webster, M. R. Perry, L. L. Schafer, *Dalton Trans.*, 44 (2015) 12411-12419.
- [17] S. L. Hancock, M. F. Mahon, M. D. Jones, *Dalton Trans.*, 40 (2011) 2033-2037.
- [18] M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schaefer, A. Buchard, L. H. Thomas, M. F. Mahon, J. P. Lowe, *Chem. Commun.*, 50 (2014) 15967-15970.
- [19] Y. Kim, G.K. Jnaneshwara, J. G. Verkade, *Inorg. Chem.*, 42 (2003) 1437-1447.
- [20] C. Bakewell, G. Fateh-Iravani, D.W. Beh, D. Myers, S. Tabthong, P. Hormnirun, A. J. P. White, N. Long, C. K. Williams, *Dalton Trans.*, 44 (2015) 12326-12337.
- [21] J. Boerner, I.d.S. Vieira, M. D. Jones, A. Doering, D. Kuckling, U. Floerke, S. Herres-Pawlis, *Eur. J. Inorg. Chem.*, (2011) 4441-4456.
- [22] C. Di Iulio, M. D. Jones, M. F. Mahon, D. C. Apperley, *Inorg. Chem.*, 49 (2010) 10232-10234.
- [23] C. Fliedel, V. Rosa, F. M. Alves, A. M. Martins, T. Aviles, S. Dagorne, *Dalton Trans.*, 44 (2015) 12376-12387.
- [24] C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.*, 125 (2003) 11350-11359.
- [25] Y. Yang, H. Wang, H. Ma, *Inorg. Chem.*, 54 (2015) 5839-5854.
- [26] L. T. Lim, R. Auras, M. Rubino, *Prog. Polym. Sci.*, 33 (2008) 820-852.
- [27] R. M. Rasal, A. V. Janorkar, D. E. Hirt, *Prog. Polym. Sci.*, 35 (2010) 338-356.
- [28] B. D. Ulery, L. S. Nair, C. T. Laurencin, *J. Polym. Sci., Part B: Polym. Phys.*, 49 (2011) 832-864.
- [29] T. R. Jensen, L. E. Breyfogle, M. A. Hillmyer, W. B. Tolman, *Chem. Commun.*, (2004) 2504-2505.

- [30] T. R. Jensen, C. P. Schaller, M. A. Hillmyer, W. B. Tolman, *J. Organomet. Chem.*, 690 (2005) 5881-5891.
- [31] For comprehensive reviews of NHCs as organocatalysts in polymerisation reactions, see:
- (a) M. K. Kieswetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules*, 43 (2010) 2093-2107.
- (b) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.*, 42 (2013) 2142-2172.
- (c) S. Naumann, A. P. Dove, *Polym. Chem.*, 6 (2015) 3185-3200.
- [32] For pertinent primary literature citations, see:
- (a) F. Connor, G. W. Nyce, M. Myers, A. Möck, J. L. Hedrick, *J. Am. Chem. Soc.*, 124 (2002) 914-915.
- (b) A. P. Dove, H. Li, R. C. Pratt, B. G. G. Lohmeijer, D. A. Culkin, R. M. Waymouth, J. L. Hedrick, *Chem. Commun.*, (2006) 2881-2883.
- (c) D. A. Culkin, W. Jeong, S. Csihony, E. D. Gomez, N. P. Balsara, J. L. Hedrick, R. M. Waymouth, *Angew. Chem. Int. Ed.*, 46 (2007) 2627-2630.
- (d) T. K. Sen, S. C. Sau, A. Mukherjee, A. Modak, S. K. Mandak, D. Koley, *Chem. Commun.*, 47 (2011) 11972-11974.
- [33] P. L. Arnold, I. J. Casely, Z. R. Turner, R. Bellabarba, R. B. Tooze, *Dalton Trans.*, (2009) 7236-7247.
- [34] C. Fliedel, S. Mameri, S. Dagorne, T. Avilés, *Appl. Organomet. Chem.*, 28 (2014) 504-511.
- [35] C. Fliedel, D. Vila-Viçosa, M. J. Calhorda, S. Dagorne, T. Avilés, *ChemCatChem*, 6 (2014) 1357-1367.
- [36] (a) A. M. Magill, K. J. Cavell, B. F. Yates, *J. Am. Chem. Soc.*, 126 (2004) 8717-8724.

- (b) M. Iglesias, D. J. Beetstra, J. C. Knight, L. L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi, I. A. Fallis, *Organometallics*, 27 (2008) 3279-3289.
- (c) P. Hauwert, J. J. Dunsford, D. S. Tromp, J. J. Weigand, M. Lutz, K. J. Cavell, C. J. Elsevier, *Organometallics*, 32 (2013) 131-140.
- (d) E. L. Kolychev, A. F. Asachenko, P. B. Dzhevakov, A. A. Bush, V. V. Shuntikov, V. N. Khrusalev, M. S. Nechaev, *Dalton. Trans.*, 42 (2013) 6859-6866.
- [37] O. S. Morozov, A. V. Lunchev, A. A. Bush, A. A. Tukov, A. F. Asachenko, V. N. Khrustalev, S. S. Zalesskiy, V. P. Ananikov, M. S. Nechaev, *Chem. Eur. J.*, 20 (2014) 6162-6170
- [38] D. Tapu, D. A. Dixon, C. Roe, *Chem. Rev.*, 109 (2009) 3385-3407.
- [39] G. Schnee, C. Fliedel, T. Avilés, S. Dagorne, *Eur. J. Inorg. Chem.*, (2013) 3699-3709.
- [40] A. J. Arduengo, III, H. V. R. Dias, F. Davidson, R. L. Harlow, *J. Organomet. Chem.*, 462 (1993) 13-18.
- [41] T. K. Sen, S. C. Sau, A. Mukherjee, P. K. Hota, S. K. Mandal, B. Maity, D. Koley, *Dalton Trans.*, 42 (2013) 14253-14260.