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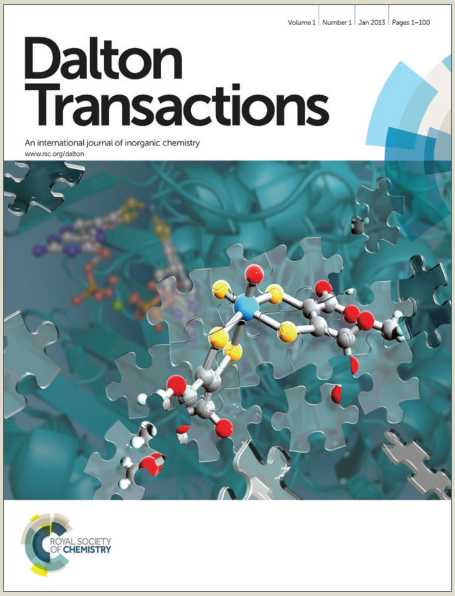

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Group 1 and 2 cyclic (alkyl)(amino)carbene complexes

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

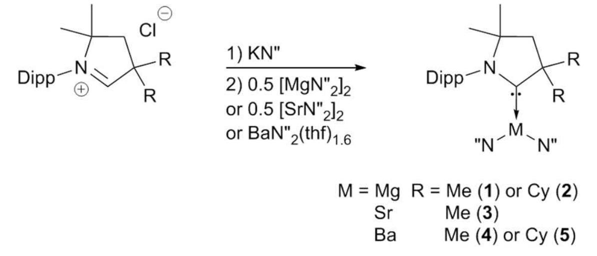
The first examples of cyclic (alkyl)(amino)carbene (CAAC) ligands bound to electropositive metal centres (K, Mg, Sr and Ba) have been isolated and characterised. Preliminary studies demonstrate that all complexes are active for polar monomer polymerisation under ambient conditions affording desirable hydroxyl-terminated telechelic polymers.

Cyclic (alkyl)(amino)carbenes (CAACs) are a more recently developed and less explored class of the ubiquitous *N*-heterocyclic carbenes (NHC),[1] featuring a quaternary carbon α to the carbene centre. This results in unique stereoelectronic properties, being both stronger σ-donors and π-acceptors with respect to NHCs, and demonstrating redox activity.[2] They have already been shown to have the potential for unique reactivity including stabilization of both unusual main group species[3-5] and low valent transition metal complexes,[6, 7] small molecule activation,[8, 9] and homogeneous catalysis.[10, 11] While there remain relatively few examples of electropositive metal NHC complexes,[12, 13] there are no examples of such CAAC complexes to date. CAACs have been largely used as ligands for gold-, palladium- and ruthenium-based catalysts; Bertrand and co-workers very recently reported copper complexes for the catalytic dehydrogenation of ammonia borane.[14]

The alkaline earth metals (Ae; magnesium – barium) are earth abundant and benign in nature, making them attractive targets for homogeneous catalysis.[15] However, on descending the group, the increasingly large coordination sphere of these elements makes them not only highly reactive and the synthesis of well-defined heteroleptic compounds L_nMX_2 (L = neutral ligand, X = monoanionic ligand) challenging. The use of sterically encumbered and multidentate ligands has been most widely demonstrated to prevent ligand scrambling but remains unpredictable. Carpentier and co-workers reported heteroleptic complexes stabilized through β-agostic···H-Si interactions.[16]

We decided to exploit the strong nucleophilic character of CAACs to facilitate the preparation of heteroleptic alkaline earth metal complexes that would be very active for polar monomer polymerisation.[17] Herein we describe the first examples of CAACs bound to both group 1 and 2 metal ions and also their use as efficient catalysts to afford biocompatible polylactide.

Free cyclic (alkyl)(amino) carbenes (CAACs) were generated *in situ* by reaction of the cyclic iminium salts with one equivalent of KN" (N" = $N(SiMe_3)_2$).[10] Subsequent reaction with group 2 metal amides ($[MgN"_2]_2$, $[SrN"_2]_2$, $BaN"_2(thf)_{1.6}$) afforded the corresponding highly air- and moisture-sensitive CAAC complexes **1**-**5** ($(^{R}CAAC)MN"_2$; R = Me_2, M = Mg (**1**), Sr (**3**), Ba (**4**) or R = Cy, M = Mg (**2**), Ba (**5**)) in moderate isolated yields (Scheme 1). Reactions carried out in sealed NMR tubes demonstrated that the formation of the **1**-**5** was essentially quantitative as judged by ^{1}H NMR spectroscopy. Attempts to prepare analogous calcium complexes have proved unsuccessful to date, resulting in intractable mixtures of products.



Scheme 1. Syntheses of group 2 CAAC complexes **1-5**

Complexes **1**, **2**, **4** and **5** were characterised in the solid state by single crystal X-ray diffraction studies (Figure 1 and S9-14). Complexes **1** and **2** are mononuclear with the coordination geometry about magnesium being distorted trigonal planar (C(1)-Mg(1)-N(2) = 112.28(8)° (**1**) and 111.65(4)° (**2**), C(1)-Mg(1)-N(3) = 120.85(5)° (**1**) and 123.11(4)° (**2**), N(2)-Mg(1)-N(3) = 125.47(5)° (**1**) and 123.30(4)° (**2**)); the widest angles

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† Electronic Supplementary Information (ESI) available: Full experimental details and characterising data of all complexes, computational details and polymerisation data. See DOI: 10.1039/x0xx00000x

reflecting the steric demands of the silyl amide ligands and also of the bulky diisopropyl substituent of the CAAC ligands. The Mg(1)-C(1) distances of 2.2931(12) Å (**1**) and 2.2989(12) Å (**2**) compare with the longest reported values for Mg-NHC bond lengths (2.153-2.288 Å).[18, 19] Both CAAC ligands are twisted about the C(3)-C(4) backbone and are asymmetrically bound to the magnesium centre (Table S2 and S3). Complexes **4** and **5** were isolated as base-free CAAC adducts but single crystals suitable for an X-ray diffraction study were grown with bound thf. They are mononuclear with the coordination geometry around barium being distorted tetrahedral. The Ba(1)-C(1) distances of 3.108(3) Å (**4**) and 3.1209(17) Å (**5**) are long compared with the three structurally characterised barium NHC adducts (2.915-3.002 Å) but display similar evidence of asymmetric coordination.[20-22]

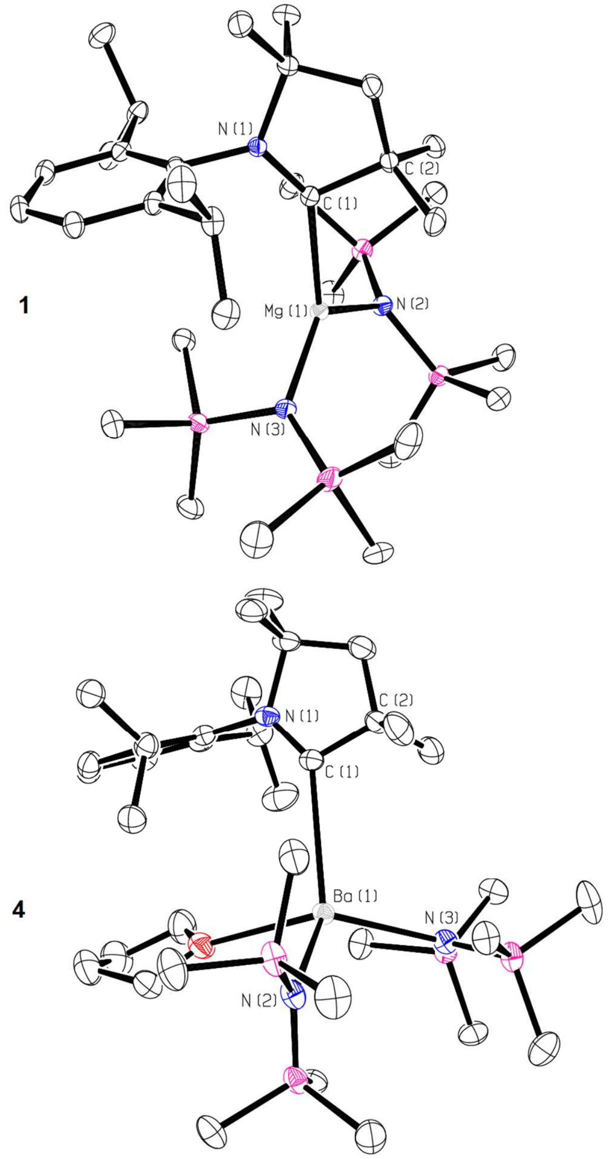
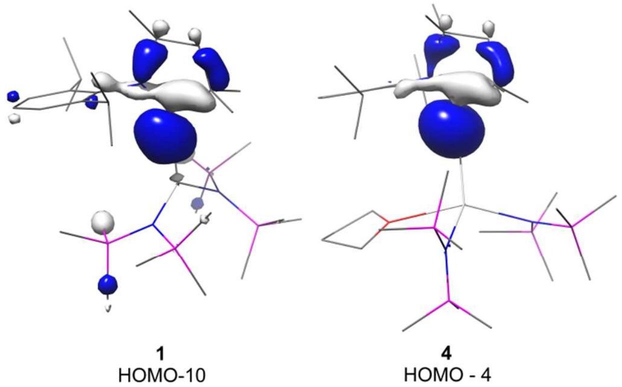


Figure 1. Thermal displacement ellipsoid drawings (30% probability) of complexes **1** and **4**. Hydrogen atoms are omitted for clarity.

Complexes **1**-**5** feature similar characteristic resonances in their ^{1}H NMR spectra (See ESI). For example in **1**; a septet at 2.61 ppm ($^3J_{HH}$ = 6.6 Hz) coupling to doublets at 1.41 and 1.01 ppm represents the isopropyl substituents on the aromatic ring, two singlets at 1.58 and 0.91 ppm account for the $C(CH_3)_2$ groups, a singlet at 1.27 ppm corresponds to the methylene backbone protons and a singlet at 0.34 ppm for the silylamide protons. In the $^{13}C\{^1H\}$ spectra, diagnostic high frequency resonances accounting for $C_{carbene}$ were identified at 266.6, 283.8 and 303.0 ppm in complexes **1**, **3** and **4** respectively which follows the decreasing Lewis acidity of the metal ions descending the group (Mg > Ca > Sr > Ba) and reflects the smaller singlet-triplet gap with respect to NHCs. Similar trends were found for NHC adducts of group 2 metallocenes reported by Arduengo and co-workers (Mg: 185.7 ppm, Ca: 196.2 ppm, Sr: 198.2 ppm, Ba: 203.5 ppm).[20] It is noted that the $C_{carbene}$ resonance of free ^{Me2}CAAC was reported to be 304.2 ppm (thf-d_8).[23] The extremely high frequency $C_{carbene}$ resonance in **4** (303.0 ppm) correlates well with the long metal-ligand bond length; it implies that there is significant electron density on the carbene carbon, and that the interaction with the metal centre is highly ionic.[24]

In order to further investigate the nature of the s-block M-CAAC bond, density functional theory (DFT) calculations were performed at the BP86 or B3LYP level for complexes **1**, **2** and **4**. Geometry optimizations were found to reproduce the metrical data established experimentally well. In all cases, the LUMO was found to be based on the CAAC ligand (p_x and p_y orbitals on C(1) and N(1)) and the HOMO based on the silylamide ligand. The metal-ligand interaction is primarily composed of CAAC $C_{carbene}$ p_z character as would be anticipated from dative σ donation to a highly electropositive metal centre. The contribution of the metal centre to this bonding interaction (Mg > Ba) follows on from the observed trends in solid state M-CAAC bond lengths and the solution $C_{carbene}$ $^{13}C\{^1H\}$ NMR spectroscopic resonances and implies that the ionic contribution to bonding increases down the group and that Ae-$C_{carbene}$ bond strength decreases. (Figure 2 and ESI).[25]



1
HOMO-10

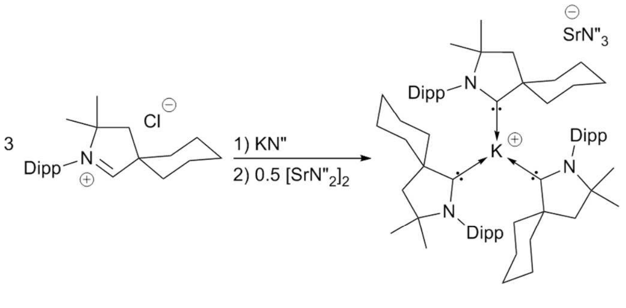
4
HOMO - 4

Figure 2. DFT-computed HOMO-10 and HOMO-4 of complex **1** (left) and **4** (right) respectively.

Attempts to isolate $(^{Cy}CAAC)SrN''_2$ proved to be unsuccessful with this method. However, it did reliably (albeit in low yield) result in the formation of charge-separated heterobimetallic complex **6** (Scheme 2), where three CAAC ligands are ligated to a central potassium cation with a strontiate counterion (SrN''_3^-). The reaction was found to proceed quantitatively when 3 equivalents of [^{Cy}CAACH]Cl, 1 equivalent of KN" and 0.5 equivalents of $[SrN''_2]_2$ were combined. Though group 1 metal complexes bound to NHCs with anionic tethers have been reported, examples of neutral NHC group 1 metal complexes are extremely limited.[12, 26] Furthermore, the only homoleptic complexes are those reported by Hill and co-workers, $[(IPr)_2M][AeN''_3]$ (IPr = $C(NDippCH_2)_2$, M = Li, Na, K)[27].

Complex **6** was structurally characterised in a single crystal X-ray diffraction study (Figure 3). The potassium ion sits on a C_3 axis rendering all ^{Cy}CAAC ligands equivalent ($C_{carbene}$-K-$C_{carbene}$ = 118.00(8) °). The K(1)-C(1) distance of 2.998(2) Å is long compared to the homoleptic NHC complexes of Hill and co-workers (2.810(2)-2.8720(17) Å).

The ^{1}H NMR spectrum of complex **6** features a single set of ^{Cy}CAAC resonances indicating that the ligand environments are also equivalent in solution at 298 K. In the $^{13}C\{^1H\}$ NMR spectrum, there is a high frequency resonance at 270.6 ppm for $C_{carbene}$.



(**6**)

Scheme 2. Synthesis of homoleptic group 1 CAAC complex **6**.

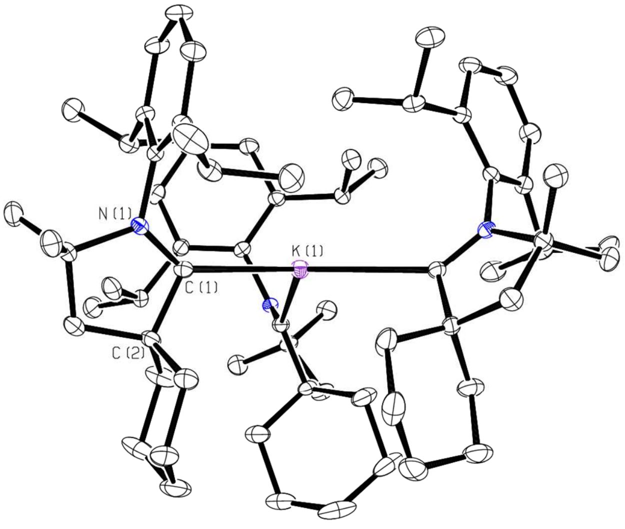
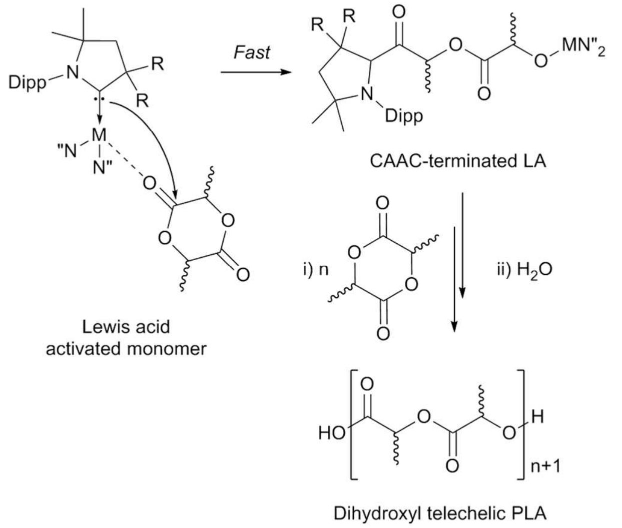


Figure 3. Thermal displacement ellipsoid drawing (30% probability) of complex **6**. SrN''_3^- counterion and hydrogen atoms have been omitted for clarity.

We postulated that use of these new Ae-CAAC complexes should highly active, and potentially controlled, catalysts for ring-opening polymerisation (ROP) of L- and *rac*-lactide (LA). Polymerisation data using complexes **1**, **3** and **4** at 296 K in benzene-d_6 are collated in Table S26 and S27.

The polymerisation kinetics have a second order dependence on LA monomer. The apparent rate constant of L-LA consumption (k_{app}) increases with increasing size and electropositivity of the metal ion and decreasing strength of the Ae-$C_{carbene}$ bond (0.024(2), 0.556(40) and 0.839(25) $M^{-1}h^{-1}$ for **1**, **3** and **4** respectively). This trend compares well to Ae-based catalysts reported by Carpentier and co-workers.[28] When *rac*-LA was polymerised using complexes **3** and **4**, the rates were four times slower than with its L- isomer (0.134(5) $M^{-1}h^{-1}$ for **3** and 0.171(3) $M^{-1}h^{-1}$ for **4**. Negligible epimerization and promisingly isotactic-biased PLA (P_i = 0.68-0.74) were observed when L- and *rac*-LA monomers were used respectively (Figures S24-28). MALDI-TOF spectrometry demonstrated the formation of dihydroxyl telechelic lactide units (*e.g.* HO-$(LA)_4$-OH, *m/z* = 610.52; Figures S60 and S62); the presence of two reactive end groups is particularly desirable for block co-polymer synthesis.[29] With $[LA]_0/[M]_0$ of 200, the experimental molecular weights are similar to those calculated for strontium (**3**) and barium (**4**) initiators, though broad molecular weight distributions are observed which is indicative of a lack of control. However, when **4** was used in $[LA]_0/[M]_0$ of 100, the experimental M_n were 50% higher than the theoretical ones demonstrating that not all of the initiator was active in the catalytic cycle. The amide starting materials MN''_2 demonstrated poor activity and kinetics that were first order in [LA] (Tables S17-21, Figures S47-58), whilst the free carbene ^{Me2}CAAC showed negligible conversion after 72 h (Tables S22 and S23), in line with the expectation that, unlike NHCs, CAACs are not able to act as organocatalysts. Kinetic data using heterobimetallic complex **6** do not show straightforward first- or second-order dependence on [LA] (Figures S41-44).



Scheme 3. Postulated mechanism for ROP using Ae-CAAC complexes.

We propose that the polymerisation proceeds by initial activation of the monomer by the Lewis acidic metal centre. Crucially, ring-opening of LA by the carbene is then required, followed by ROP propagation catalyzed by the metal amide moiety (Scheme 3). Subsequent quenching with water leads to dihydroxyl-terminated PLA.

The activated monomer mechanism to describe Lewis acid catalysts combined with external protic co-initiators leading to very controlled polymerisation was pioneered by Kubisa,[30] and further studied by Carpentier,[28, 31] Mountford[32] and Miller.[33] Arnold and co-workers suggested that functionalized NHC ligands will initiate ring opening of LA with the carbene when the M-C$_{carbene}$ bond is sufficiently weak.[13]

Plots of $1/[LA]_t$ in function of time were linear over all concentrations of **4** with k_{app} values of 0.839(25), 1.478(32), 5.720(354) and 7.848(501) $M^{-1}h^{-1}$ for initial ratios of $[LA]_0/[M]_0$ of 200, 150, 100 and 20 respectively (Figure 4). Strong solvent effects were observed; polymerisations conducted in thf-d_8 were completed before meaningful kinetic data could be recorded. However, the experimental molecular weights were much lower than the calculated ones highlighting the strong presence of chain transfer in polar solvent. Mountford and co-workers reported an apparent second order rate constant of 40 $M^{-1}h^{-1}$ under ambient conditions in thf using a ratio of 200 using an amine co-initiator.[34]

In conclusion, we have described the synthesis and characterisation of the first examples of electropositive metal cyclic (alkyl)(amino)carbene complexes. Preliminary polymerisation data of lactide demonstrated systems that were active under ambient conditions leading to the formation of dihydroxyl-terminated polylactide. The isolation of these complexes now opens the door to a wide range of exciting reactivity and catalysis.

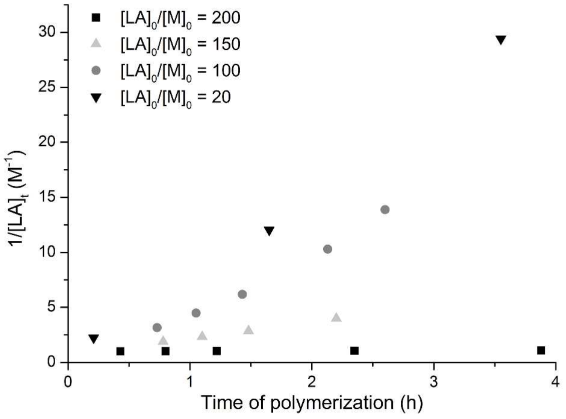


Figure 4. Second-order rate plot of the polymerisation of L-lactide using complex 4.

Notes and references

‡ We thank SCG Chemicals for financial support. Z.R.T also thanks Trinity College for a Junior Research Fellowship. Prof. P. Mountford is gratefully acknowledged for use of the GPC and Chemical Crystallography for use of X-ray diffractometers.

1 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485.
2 M. Soleilhavoup and G. Bertrand, *Acc. Chem. Res.*, 2015, **48**, 256.
3 C. A. Dyker and G. Bertrand, *Science*, 2008, **321**, 1050.
4 R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking and G. Bertrand, *Science*, 2011, **333**, 610.
5 K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter and D. Stalke, *Angew. Chem., Int. Ed.*, 2013, **52**, 1801.
6 D. S. Weinberger, M. Melaimi, C. E. Moore, A. L. Rheingold, G. Frenking, P. Jerabek and G. Bertrand, *Angew. Chem., Int. Ed.*, 2013, **52**, 8964.
7 G. Ung, J. Rittle, M. Soleilhavoup, G. Bertrand and J. C. Peters, *Angew. Chem., Int. Ed.*, 2014, **53**, 8427.
8 V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Angew. Chem., Int. Ed.*, 2006, **45**, 3488.
9 G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Science*, 2007, **316**, 439.
10 D. R. Anderson, V. Lavallo, D. J. O'Leary, G. Bertrand and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2007, **46**, 7262.
11 G. Ung and J. C. Peters, *Angew. Chem., Int. Ed.*, 2015, **54**, 532.
12 S. Bellemin-Laponnaz and S. Dagorne, *Chem. Rev.*, 2014, **114**, 8747.
13 P. L. Arnold and I. J. Casely, *Chem. Rev.*, 2009, **109**, 3599.
14 X. Hu, M. Soleilhavoup, M. Melaimi, J. Chu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2015, DOI: 10.1002/anie.201500224.
15 S. Harder and Editor, *Alkaline-Earth Metal Compounds: Oddities and Applications. [In: Top. Organomet. Chem., 2013; 45]*, Springer GmbH, 2013.
16 Y. Sarazin, D. Roşca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron and J.-F. Carpentier, *Organometallics*, 2010, **29**, 6569.
17 M. P. Coles, *Coord. Chem. Rev.*, DOI: http://dx.doi.org/10.1016/j.ccr.2015.01.018.
18 P. L. Arnold, I. S. Edworthy, C. D. Carmichael, A. J. Blake and C. Wilson, *Dalton Trans.*, 2008, DOI: 10.1039/B803253J, 3739.
19 A. R. Kennedy, J. Klett, R. E. Mulvey and S. D. Robertson, *Eur. J. Inorg. Chem.*, 2011, **2011**, 4675.
20 A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall and M. Tamm, *Organometallics*, 1998, **17**, 3375.
21 H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert and J. Demtschuk, *J. Organomet. Chem.*, 2001, **617–618**, 588.
22 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon and P. A. Procopiou, *Organometallics*, 2008, **27**, 3939.
23 V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2005, **44**, 5705.
24 D. Tapu, D. A. Dixon and C. Roe, *Chem. Rev.*, 2009, **109**, 3385.
25 H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687.
26 M. Brendel, J. Wenz, I. V. Shishkov, F. Rominger and P. Hofmann, *Organometallics*, 2015, **34**, 669.
27 M. S. Hill, G. Kociok-Köhn and D. J. MacDougall, *Inorg. Chem.*, 2011, **50**, 5234.
28 Y. Sarazin, B. Liu, T. Roisnel, L. Maron and J.-F. Carpentier, *J. Am. Chem. Soc.*, 2011, **133**, 9069.
29 K. Stridsberg, M. Ryner and A.-C. Albertsson, *Macromolecules*, 2000, **33**, 2862.
30 M. Baśko and P. Kubisa, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 7071.
31 N. Ajellal, J.-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Helou, V. Poirier, Y. Sarazin and A. Trifonov, *Dalton Trans.*, 2010, **39**, 8363.
32 L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateau and P. Mountford, *Chem. Commun.*, 2010, **46**, 273.

33 H.-Y. Chen, L. Mialon, K. A. Abboud and S. A. Miller, *Organometallics*, 2012, **31**, 5252.
34 L. Clark, G. B. Deacon, C. M. Forsyth, P. C. Junk, P. Mountford, J. P. Townley and J. Wang, *Dalton Trans.*, 2013, **42**, 9294.