

# A remarkable inversion of structure–activity dependence on imido N-substituents with varying co-ligand topology and the synthesis of a new borate-free zwitterionic polymerisation catalyst†

Helen R. Bigmore,<sup>a</sup> Stuart R. Dubberley,<sup>a</sup> Mirko Kranenburg,<sup>b</sup> Sally C. Lawrence,<sup>a</sup> Andrew J. Sealey,<sup>a</sup> Jonathan D. Selby,<sup>a</sup> Martin A. Zuideveld,<sup>c</sup> Andrew R. Cowley<sup>a</sup> and Philip Mountford<sup>\*a</sup>

Received (in Cambridge, UK) 12th October 2005, Accepted 3rd November 2005

First published as an Advance Article on the web 5th December 2005

DOI: 10.1039/b514467a

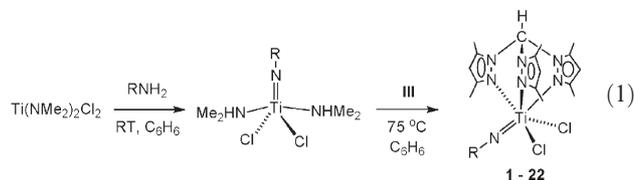
Ethylene polymerisation productivities of tris(pyrazolyl)methane-supported catalysts  $[\text{Ti}(\text{NR})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  show a dramatically different dependence on the imido R-group compared to those of their TACN analogues, attributed to differences in *fac*-N<sub>3</sub> donor topology; when treated with  $\text{Al}^i\text{Bu}_3$ , the zwitterionic tris(pyrazolyl)methide compound  $[\text{Ti}(\text{N}-2\text{-C}_6\text{H}_4^i\text{Bu})\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{THF})]$  also acts as a highly active, single site catalyst (TACN = 1,4,7-trimethyltriazacyclononane).

There continues to be considerable interest in “post-metallocene” olefin polymerisation catalysis.<sup>1</sup> However, efficient terminal imido-supported Ziegler type polymerisation catalysts have been noticeably lacking from Group 4, despite being well-established for Groups 5 and 6.<sup>2</sup> We recently reported the very highly active titanium imido polymerisation catalysts  $[\text{Ti}(\text{NR})(\text{TACN})\text{Cl}_2]$  (**I**, Chart 1). High throughput parallel screening of *ca.* 50 such catalysts under commercially-relevant conditions (T = 100 °C, MAO activation) found that bulky alkyl imido R-substituents (<sup>*i*</sup>Bu, adamantyl and  $\text{CMe}_2\text{CH}_2^i\text{Bu}$ ) provided the highest activities (>200 000 kg(PE) mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> for R = <sup>*i*</sup>Bu) (PE = polyethylene).<sup>3</sup> None of the catalysts of type **I** with bulky aryl R-groups 2,6-C<sub>6</sub>H<sub>3</sub><sup>*i*</sup>Pr<sub>2</sub>, 2-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> or 2-C<sub>6</sub>H<sub>4</sub><sup>*i*</sup>Bu showed any significant activity (<100 kg(PE) mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>). Type **I** compounds with bulky alkyl R-groups are by far the most active of all the imido-supported Ziegler polymerisation catalysts reported to date; this study being the first comprehensive survey of imido substituent–polymerisation activity relationships for any

metal. Well defined monoalkyl cations have also been established for these systems.<sup>4</sup>

Michiue and Jordan have recently shown how tris(pyrazolyl)borate Group 4 complexes  $[\text{M}\{\text{HB}(\text{R}^3\text{R}^5\text{pz})_3\}\text{Cl}_3]$  (**II**, Chart 1; M = Ti or Zr; R<sup>3</sup>R<sup>5</sup>pz = substituted pyrazolyl) generate highly active ethylene polymerisation catalysts with interesting properties on activation with MAO.<sup>5</sup> Versatile as they are, however, pyrazolylborate ligands<sup>6</sup> are not without potential problems, notably facile cleavage of the B–N bonds, as found recently in Lee and Jordan’s cationic zirconium benzyl derivative  $[\text{Zr}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{CH}_2\text{Ph})_2]^+$ .<sup>7</sup>

Tris(pyrazolyl)methane ligands, as exemplified by  $\text{HC}(\text{Me}_2\text{pz})_3$  (**III**, Chart 1),<sup>8</sup> are the neutral analogues of the tris(pyrazolyl)borates.<sup>6</sup> These readily available ligands have been little used in early transition metal chemistry. Furthermore, only one report of their use in olefin polymerisation catalysis is known, this being a preliminary communication of  $[\text{Sc}\{\text{HC}(\text{Me}_2\text{pz})_3\}(\text{CH}_2\text{SiMe}_3)_3]$ .<sup>9</sup> Two reports of Group 4 tris(pyrazolyl)methane compounds have appeared,<sup>10,11</sup> but no structural authentication accompanied them and neither were in the context of catalytic chemistry. Here we report preliminary studies of a library of tris(pyrazolyl)methane-supported titanium imido compounds, their evaluation under laboratory and commercially-relevant conditions, and steps towards new borate-free zwitterionic catalysts.



Eqn. 1 summarises the one pot synthesis (carried out in parallel using semi-automated procedures) of the primary catalyst library  $[\text{Ti}(\text{NR})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  (**1–22**, 56–78% yield).† The intermediates  $[\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2]$  were not isolated, but a number of them or their homologues have been fully described elsewhere.<sup>12</sup> All of the compounds **1–22** gave satisfactory high resolution (accurate mass) MS and/or <sup>1</sup>H NMR spectra. The compounds showing the most promising polymerisation performance (**3**,<sup>10</sup> **6**, **15**, **16**, **20–22**; see Fig. 1) were fully characterised in the usual way.† Poorly performing catalyst **9** was also scaled up. The catalytic performance of a particular compound did not depend on the method of synthesis.

The primary library **1–22** was screened for homopolymerisation of ethylene at room temperature using MAO co-catalyst ( $\text{Al}/\text{Ti} = 1500$ ), and their productivities are illustrated in Fig. 1.† For

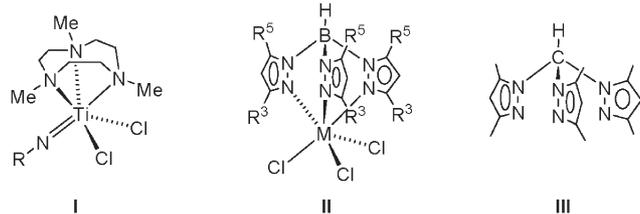


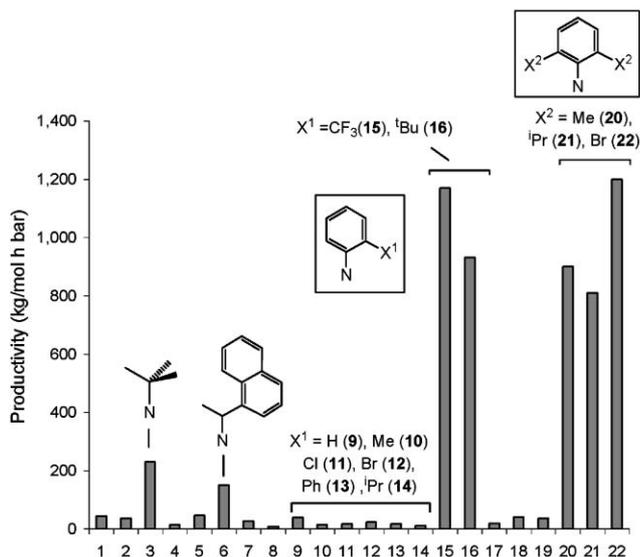
Chart 1

<sup>a</sup>Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, UK OX1 3TA

<sup>b</sup>DSM Elastomers, Global R&D, PO Box 1130, 6160 BC, Geleen, The Netherlands

<sup>c</sup>DSM Research, PO Box 18, 6160 MD, Geleen, The Netherlands

† Electronic Supplementary Information (ESI) available: Characterising data and details of the polymerisation experiments. See DOI: 10.1039/b514467a



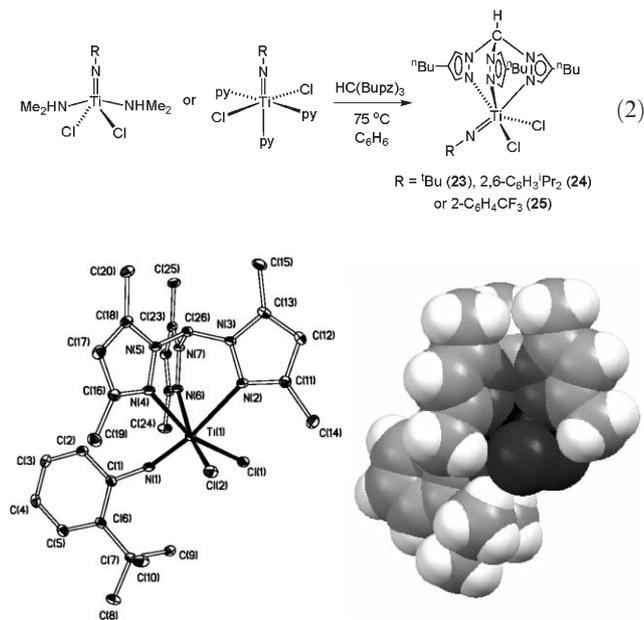
**Fig. 1** Room temperature ethylene polymerisation productivities for MAO-activated  $[\text{Ti}(\text{NR})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  (**1–22**).<sup>†</sup>

the most productive catalysts, the PE molecular weights ( $M_w$ ) were in the range 334 000–1 515 000 with PDIs (polydispersity indices) in the range 3.2–4.8 (except for **15** and **21**, which had values of 5.9 and 7.0, respectively). Only aryl imido compounds with either two *ortho*-substituents or one very bulky *ortho*-substituent were very highly productive; the bulky alkyl imido compounds **3** and **6** had reasonable productivities under these conditions but were extremely poor in comparison to their aryl imido homologues. Evaluation of the more promising leads **3**, **15**, **16** and **20–22**, together with compounds **9**, **10** and **12**, under more industrially-relevant conditions (100 °C, 7 bar  $\text{C}_2\text{H}_4$ , 10 min, MAO,  $\text{Al}/\text{Ti} = 3200$ )<sup>13</sup> gave extremely high productivity values of 133 700  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$  for **15** ( $M_w = 343\,000$ ,  $\text{PDI} = 3.8$ ) and 152 500  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$  for **16** ( $M_w = 404\,500$ ,  $\text{PDI} = 2.4$ ). None of the other compounds showed any significant activity, including the *tert*-butyl imide, **3**. Note, for comparison, the productivities of the TACN analogues of **15** and **16** (**I**,  $\text{R} = 2\text{-C}_6\text{H}_4\text{CF}_3$  or  $2\text{-C}_6\text{H}_4\text{tBu}$ ) under identical conditions were *three* orders of magnitude lower (*ca.* 500  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$ ). The dramatic inversion of the imido substituent–polymerisation activity relationship for the  $\text{HC}(\text{Me}_2\text{pz})_3$ -supported catalysts, compared to the (apparently) closely related TACN series **I**, is very striking. These results show conclusively that simply choosing a “bulky” imido ligand substituent is insufficient for optimal catalyst design.

The “valued added” benefit of the *ortho*-substituted aryl imido substituents in the catalyst family  $[\text{Ti}(\text{NR})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  can be traced to fundamental differences in *fac*- $\text{N}_3$  co-ligand topology. Thus while  $\text{HC}(\text{Me}_2\text{pz})_3$  ligands have clefts between the  $\text{Me}_2\text{pz}$  rings which are able to accommodate the aryl substituent of an imido ligand, TACN has no such feature. This “self-constrained” feature of the  $\text{HC}(\text{Me}_2\text{pz})_3$ -supported catalysts can readily be appreciated by reference to the solid state structure of  $[\text{Ti}(\text{N}-2\text{-C}_6\text{H}_4\text{tBu})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  (**16**) (Fig. 2).<sup>‡</sup> The steric protection of the imido ligand N lone pairs and/or potentially reactive  $\text{Ti}=\text{N}$  multiple bond<sup>14</sup> by the favourably-oriented *ortho-tert*-butyl substituent is self-evident. This orientation of the *tert*-butyl group will

also disfavour cation–anion and/or cation– $\text{AlMe}_3$  association in the catalyst system derived from **16** and MAO.<sup>4,15</sup>

The space filling representation of **16** (Fig. 2, right) suggests that the pyrazolyl ring 3-methyl substituents play a key role in the “self-constrained” geometry of **16** and the other aryl imido complexes in Fig. 1. As a probe, selected homologues of **1–22** were prepared using the ring 3,5-non-substituted ligand  $\text{HC}(\text{Bupz})_3$  ( $\text{Bupz} = 4\text{-}n\text{-butylpyrazolyl}$ ), namely  $[\text{Ti}(\text{NR})\{\text{HC}(\text{Bupz})_3\}\text{Cl}_2]$  ( $\text{R} = \text{tBu}$  (**23**),  $\text{R} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$  (**24**) or  $\text{R} = 2\text{-C}_6\text{H}_4\text{CF}_3$  (**25**)) (eqn. 2). The room temperature productivity of **23** (150  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$ ) was not dissimilar to that of **3**, but those of **24** and **25** were much reduced (300 and 260  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$ , respectively) in comparison with **21** and **15**. At 100 °C, **23** and **24** were, like **3** and **21**, inactive. Compound **25** produced PE ( $M_w = 1\,305\,000$ ;  $\text{PDI} = 2.0$ ) but the productivity was only 1 770  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$  (*cf.* 133 700  $\text{kg}(\text{PE}) \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$  for **15**). Therefore the ring 3-substituents are clearly important in correctly aligning the imido-bound aryl rings. In support of this, the  $^1\text{H}$  NMR spectrum of **24** showed no evidence for restricted rotation about the  $\text{Ar}-\text{NTi}$  bond, even at 233 K (unlike that of **21**, which shows that this process is “frozen out” at room temperature—*e.g.*, inequivalent *iso*-propyl group methine protons at 4.98 and 2.85 ppm).



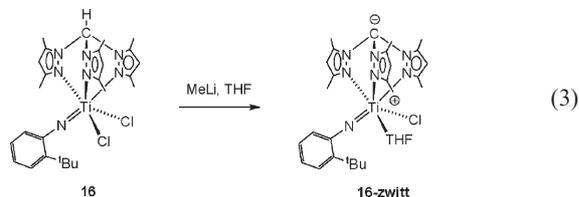
**Fig. 2** Molecular structure of  $[\text{Ti}(\text{N}-2\text{-C}_6\text{H}_4\text{tBu})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  (**16**): Displacement ellipsoid plot (left) and space filling representation (right).

The family of compounds  $[\text{Ti}(\text{NR})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$  also form the basis for the preparation of borate-free, zwitterionic tris(pyrazolyl)methide-supported catalysts. Electron deficient alkyl cations are the accepted active species in Ziegler type olefin polymerisation.<sup>1,15</sup> It is also well known that the use of very weakly coordinating anions is essential for high polymerisation activity, and considerable efforts have been made in developing such species.<sup>15–17</sup> Another approach has been to incorporate the counteranion into the ligand framework in order to prevent close association of the anion with the alkyl cation’s vacant site(s). Borate-based systems are the most studied in this regard,<sup>18–22</sup>

though others have also been reported to a much lesser extent.<sup>23,24</sup> Catalytically-competent, carbanion-based zwitterions have not previously been disclosed.

It has recently been shown that reaction of the free HC(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub> ligand with MeLi in THF gives the zwitterionic lithium salt [C(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub>Li(THF)], containing no direct C⋯Li bond because of the steric protection afforded by the pyrazolyl ring 5-substituents.<sup>25</sup> In an analogous way, **3** was apically deprotonated in THF to give structurally characterized [Ti(N<sup>t</sup>Bu){C(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub>}Cl(THF)] (**3-zwitt**).<sup>10</sup> No catalytic or other reaction chemistry of this compound has been described and no other tris(pyrazolyl)methide chemistry has been established.

Polymerisation of ethylene with **3-zwitt** in the presence of MAO at 100 °C proceeded with relatively poor activity (510 kg(PE) mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>) to afford PE with a broad and featureless molecular weight distribution. Guided by the results in Fig 1, we therefore turned to a zwitterionic derivative of the successful *ortho-tert-butyl phenyl imide*, **16-zwitt**. The THF-stabilised compound [Ti(N-2-C<sub>6</sub>H<sub>4</sub><sup>t</sup>Bu){C(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub>}Cl(THF)] (**16-zwitt**) was synthesised according to eqn. 3 in 64% yield.



Activation of **16-zwitt** with MAO at 100 °C (Al/Ti = 3200) gave a very highly active catalyst with a productivity of 131 000 kg(PE) mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>. In contrast to the PE made with **16** under identical conditions, that produced with **16-zwitt** was bimodal with a low (78 wt%,  $M_w = 62\,570$ , PDI ~ 2.3) and high (22 wt%,  $M_w = 1\,380\,000$ , PDI ~ 1.6) molecular weight fraction, showing that the catalytic species derived from **16-zwitt** is different to that derived from **16**. However, the activation of **16-zwitt** with Al<sup>t</sup>Bu<sub>3</sub> (Al/Ti = 3200, all other parameters remaining unchanged) gave an excellent productivity of 146 700 kg(PE) mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> and PE with a unimodal molecular weight distribution ( $M_w = 409\,000$ , PDI = 2.5). Assuming that the Lewis acidic Al<sup>t</sup>Bu<sub>3</sub> acts both as an alkylating and THF abstracting agent, the catalytically-active species in this system is likely to be a charge-neutral, zwitterionic alkyl cation of the type [Ti(N-2-C<sub>6</sub>H<sub>4</sub><sup>t</sup>Bu){C(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub>}R] (R = growing polymeryl chain).

In conclusion, we have demonstrated that varying the co-ligand topology can dramatically invert structure–activity relationships in imido-supported polymerisation catalysts. These catalysts, some of which are highly productive under industrially relevant conditions, are the first in Group 4 to contain the so far under-exploited HC(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub> ligand. Although a neutral donor (benefiting from no formal ionic contribution to the metal–ligand bonding), its binding to the metal is clearly sufficient to withstand harsh catalytic reaction conditions. The high activity of the robust zwitterionic precatalyst **16-zwitt** suggests that the tris(pyrazolyl)methide ligand

family (analogues of the ubiquitous tris(pyrazolyl)borates) may find applications in a number of other catalytic systems, especially perhaps where the potential lability of the B–N bonds of pyrazolylborates may hinder the development of robust systems.

We thank the EPSRC, DSM Elastomers, DSM Research and Millennium Pharmaceuticals Ltd. for support, Albermarle for samples of MAO, Mr. Bing Wang for the polymerisation experiments with [Ti(N<sup>t</sup>Bu){C(Me<sub>2</sub>p<sub>z</sub>)<sub>3</sub>}Cl(THF)] and Mr. Dan Cowell for assistance with the library synthesis.

## Notes and references

‡ Crystal Data for **16-2(CH<sub>2</sub>Cl<sub>2</sub>)**: C<sub>28</sub>H<sub>39</sub>Cl<sub>6</sub>N<sub>7</sub>Ti,  $M_w = 734.28$ , monoclinic,  $P2_1/n$ ,  $a = 10.2075(2)$ ,  $b = 24.0696(3)$ ,  $c = 14.0799(2)$  Å,  $\beta = 90.9514(4)^\circ$ ,  $U = 3458.82(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150$  K,  $\mu = 0.741$  cm<sup>-1</sup>, 5159 reflections  $I > 3\sigma(I)$ ,  $R_{int} = 0.084$ ,  $R = 0.0502$ ,  $R_w = 0.0592$ . CCDC 286735. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514467a

- V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
- P. D. Bolton and P. Mountford, *Adv. Synth. Catal.*, 2005, **347**, 355.
- N. Adams, H. J. Arts, P. D. Bolton, D. Cowell, S. R. Dubberley, N. Friederichs, C. Grant, M. Kranenbrug, A. J. Sealey, B. Wang, P. J. Wilson, A. R. Cowley, P. Mountford and M. Schröder, *Chem. Commun.*, 2004, 434.
- P. D. Bolton, E. Clot, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2005, 3313.
- K. Michiue and R. F. Jordan, *Organometallics*, 2004, **23**, 460.
- S. Trofimenko, *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
- H. Lee and R. F. Jordan, *J. Am. Chem. Soc.*, 2005, **127**, 9384.
- H. R. Bigmore, S. C. Lawrence, P. Mountford and C. S. Tredget, *Dalton Trans.*, 2005, 635.
- S. C. Lawrence, B. D. Ward, S. R. Dubberley, C. M. Kozak and P. Mountford, *Chem. Commun.*, 2003, 2880.
- S. C. Lawrence, M. E. G. Skinner, J. C. Green and P. Mountford, *Chem. Commun.*, 2001, 705.
- A. Sánchez-Méndez, G. F. Silvestri, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez and P. Gómez-Sal, *Eur. J. Inorg. Chem.*, 2004, 3287.
- N. Adams, H. R. Bigmore, T. L. Blundell, C. L. Boyd, S. R. Dubberley, A. J. Sealey, A. R. Cowley, M. E. G. Skinner and P. Mountford, *Inorg. Chem.*, 2005, **44**, 2882.
- 10 minute polymerisation run times were used in order that the intrinsic catalyst productivities would not be masked by mass transport limitation effects.
- N. Hazari and P. Mountford, *Acc. Chem. Res.*, 2005, **38**, 839.
- M. Bochmann, *J. Organomet. Chem.*, 2004, **689**, 3982.
- E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391.
- J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223.
- M. Bochmann, S. J. Lancaster and O. B. Robinson, *J. Chem. Soc., Chem. Commun.*, 1995, 2081.
- Y. Chen, G. Wu and G. C. Bazan, *Angew. Chem., Int. Ed.*, 2005, **44**, 1108.
- G. Erker, *Chem. Commun.*, 2003, 1469.
- C. C. Lu and J. C. Peters, *J. Am. Chem. Soc.*, 2002, **124**, 5272.
- W. E. Piers, *Chem.–Eur. J.*, 1998, **4**, 13.
- H. Y. Kim, H. T. Kim, N. Y. Kim, E. S. Cho, B. Y. Lee, D. M. Shin and Y. K. Chung, *Organometallics*, 2003, **22**, 1503.
- P. J. Bailey, D. Loroño-González and S. Parsons, *Chem. Commun.*, 2003, 1426.
- F. Breher, J. Grunenberg, S. C. Lawrence, P. Mountford and H. Rügger, *Angew. Chem., Int. Ed.*, 2004, **43**, 2521.