Journal of Organometallic Chemistry 696 (2012) 4179–4183

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Cationic organoaluminum compounds as intramolecular hydroamination catalysts

Manish Khandelwal, Rudolf J. Wehmschulte*

Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, FL 32901, USA

ARTICLE INFO

Article history:
Received 1 August 2011
Received in revised form
13 September 2011
Accepted 15 September 2011

Keywords:
Hydroamination
Cationic
Alkyl aluminum
Aryl aluminum
Catalysis
Cyclization

ABSTRACT

Cationic dialkylaluminum and *m*-terphenylalkylaluminum compounds catalyze the intramolecular hydroamination of primary and secondary aminopentenes. The reaction rates are strongly dependent on the substrate and the catalyst substituents. The bulky species [Dipp*AlEt][$CHB_{11}H_5I_6$] (Dipp* = 2,6-$Dipp_2C_6H_3$–, Dipp = 2,6-*i*$Pr_2C_6H_3$–), **4**, was the most active catalyst. Although the neutral species $DcpAlEt_2$ (Dcp = 2,6-(2,6-$Cl_2C_6H_3$)$_2C_6H_3$–), **7**, and Dipp*$AlEt_2$, **8**, showed some catalytic activity, they were more than 25 times less reactive than their cationic counterparts [DcpAlEt][$CHB_{11}H_5Cl_6$], **3**, and **4**. The cyclization of secondary benzylaminopentenes with [Et_2Al][$CHB_{11}H_5I_6$], **1**, was strongly dependent on the substitution of the C-2 olefinic carbon.

1. Introduction

The intramolecular hydroamination of olefins allows the construction of nitrogen containing cyclic structures in an atom economical way leading to valuable precursors of biologically active molecules and natural products [1–3]. Base-catalyzed systems have been known for a long time [4], but the application of metal-based catalysts began with Marks' report on lanthanide compounds [5]. Since then, numerous metals have been investigated including lanthanides [6–8], early [9–11] and late transition metals [12–14] and more recently alkaline earth metals [15]. Neutral complexes of the latter metals are isoelectronic with cationic group 13 species. As we have been working with cationic organoaluminum compounds [16,17], we were interested in their potential as hydroamination catalysts. Furthermore, there were only two reports regarding aluminum based hydroamination catalysts: one featured a four-coordinate aluminum amide featuring a bidentate phenylene-diamine ligand [18], the other a five-coordinate aluminum complex with a tridentate OCO-pincer ligand [19]. While these compounds showed some reactivity, we hypothesized that cationic low-coordinate organoaluminum compounds would be more reactive due to their electronic similarity to neutral magnesium and calcium based catalysts. Here, we report the activity of four cationic organoaluminum compounds as catalysts for intramolecular hydroamination of aminopentenes, a comparison with closely related neutral species and two examples of a secondary aminopentene substrate.

2. Experimental

2.1. General methods

All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres dry box unless otherwise noted. Dry, oxygen-free solvents were used unless otherwise indicated. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^{1}H NMR chemical shift values were determined relative to the residual protons in C_6D_6 as internal reference (δ = 7.16 ppm), and ^{13}C NMR spectra were referenced to the solvent signal (δ = 128.39 ppm). Initial samples of the aminopentenes 2,2-diphenyl-4-methylpent-4-en-1-amine, **A**, 2,2-diphenylpent-4-en-1-amine, **B**, (1-allylcyclohexyl)-methanamine, **C**, and 2,2-diphenyl-5,5-dimethylpent-4-en-1-amine, **D**, were provided by Dr. J. Koller and Prof. R. Bergman at the University of California, Berkeley. Larger amounts of **A** [20] and **B** [20] as well as the secondary amines N-benzyl-2,2-diphenylpent-4-en-1-amine, **E** [21], were prepared following the literature. The catalysts [Et_2Al][$CHB_{11}H_5I_6$], **1** [22], [Et_2Al][$CHB_{11}H_5Cl_6$], **2** [22],

* Corresponding author. Tel.: +1 321 674 7659; fax: +1 321 674 8951.
E-mail address: rwehmsch@fit.edu (R.J. Wehmschulte).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.09.010

[DcpAlEt][$CHB_{11}H_5Cl_6$] (Dcp = 2,6-(2,6-$Cl_2C_6H_3$)$_2C_6H_3$–), **3** [17], [Dipp*AlEt][$CHB_{11}H_5I_6$] (Dipp* = 2,6-Dipp$_2C_6H_3$–, Dipp = 2,6-*i*Pr$_2C_6H_3$–), **4** [17], DcpAlEt$_2$, **7** [17], and Dipp*AlEt$_2$, **8** [17], were synthesized according to the literature procedures.

2.2. *N*-benzyl-4-methyl-2,2-diphenylpent-4-en-1-amine, *F*

This compound was prepared in analogy to **E** [21] using **A** as a precursor and obtained as a colorless, viscous oil. Yield: 0.58 g, 85%. ^{1}H NMR (400.13 MHz, C_6D_6): 0.78 (br s, 1H, N*H*), 1.14 (s, 3H, Me), 3.08 (s, 2H, CH_2), 3.32 (s, 2H, CH_2), 3.54 (s, 2H, CH_2), 4.82 (s, 1H, =CH_2), 4.90 (s, 1H, =CH_2), 6.98–7.19 (m, 15H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6): 25.1 (Me), 44.9(CH_2), 50.8 (*C*Ph$_2$), 54.8(*C*H_2Ph), 55.5(CH_2), 115.9(=*C*H_2), 126.6, 127.4, 128.5, 128.8, 141.5, 143.3, 147.9.

2.3. Hydroamination experiments

For a typical NMR scale experiment, 100 μmol of aminoalkene, 10 μmol of catalyst, 2 mg of 2,6-di-*tert*-butylpyridine (10 μmol) and a known amount of hexamethylbenzene (2–4 mg, 12–25 μmol) as internal standard were dissolved in C_6D_6 (0.8 mL). The solution was transferred into a J. Young valve fitted NMR tube. The sealed NMR tube was then heated in a temperature controlled silicone-oil bath at 135(±2) °C for the specified amount of time (see Tables 1 and 2), and the reaction progress was monitored via ^{1}H NMR spectroscopy. All product signals were in good agreement with previously published data of identical products [18,20,21,23].

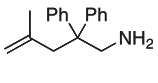
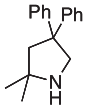
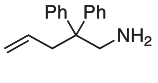
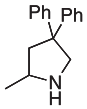
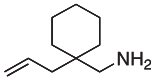
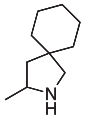
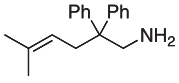
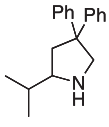
2.4. Hydroamination with in situ generated *1* (entry B9, Table 2)

A mixture of AlEt$_3$ (6 mg, 52 μmol), [Ph_3C][$CHB_{11}H_5I_6$] (62 mg, 54 μmol), was heated at 80 °C inside a J. Young type NMR tube until the AlEt$_3$ was consumed (2 d) (The reaction time for this reaction was rather long due to the use of just an equimolar amount of AlEt$_3$ and crystalline instead of microcrystalline or amorphous trityl salt.). A small portion of the solution (110 mg, ca. 8 μmol of catalyst) was taken into a separate J. Young type NMR tube, and hexamethylbenzene (3 mg, 18 μmol) and 2,2-diphenyl-pent-4-en-1-amine (19 mg, 78 μmol) were added. The resulting mixture was heated at 135 °C for 70 h while the progress of the reaction was monitored by ^{1}H NMR spectroscopy. Conversion 98% Yield 82% with respect to the internal reference. For conversion and yield after 30 h see Table 2, entry B9.

2.5. [$AlEt_2${$NH_2CH_2C(Ph)_2CH_2CHCH_2$}$_2$][$CHB_{11}H_5Cl_6$], *5*

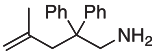
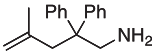
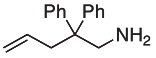
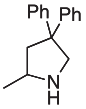
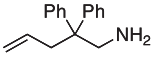
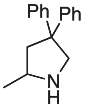
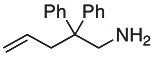
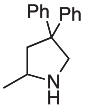
A J. Young valve fitted NMR tube was charged with [Ph_3C][$CHB_{11}H_5Cl_6$] (200 mg, 0.34 mmol) and AlEt$_3$ (66 mg, 0.58 mmol) in benzene (0.8 mL). The suspension was stirred at room temperature until the red solid turned into a pale white solid. The solid was washed with hexanes (3 × 1 mL) and dried (yield: 130 mg, 0.29 mmol, 85%). Benzene (0.8 mL) and $NH_2CH_2C(Ph)_2CH_2CHCH_2$, **B**, (138 mg, 0.58 mmol) were added to the dry solid. The mixture was gently heated (80 °C) to obtain a clear solution. The product precipitated out of the solution upon cooling to room temperature. Yield 126 mg (0.14 mmol, 50.5%). Mp 155–157 °C. ^{1}H NMR (400.13 MHz, C_6D_6): −0.20 (q, *J* = 8.2 Hz, 4H, AlCH_2CH$_3$), 0.70 (t, *J* = 8.1 Hz, 6H, AlCH$_2$CH_3), 1.58 (s, 1H, C*H-carborane*), 2.92 (d, *J* = 6.7 Hz, 4H, C*H*), 3.04 (s, 4H,NH_2), 3.2 (s, 4H, CH_2) 4.93 (d, *J* = 10.2 Hz, 2H, C*H*'), 5.21 (m, 2H, C*H*), 5.39 (d, *J* = 17.0 Hz, 2H, C*H*), 6.95–6.99 (m, 12H, Ph), 7.07–7.11 (m, 8H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6): −2.7 (AlCH_2CH$_3$), 8.7 (AlCH_2CH$_3$), 40.7 (CH_2), 48.5 (CH_2NH$_2$), 50.9 (*C*(Ph$_2$)), 120.6(=CH_2), 128.9 (Ph), 129.7 (Ph), 130.2 (Ph), 133.1(*C*H), 143.4 (Ph). ^{11}B NMR (128.38 MHz, C_6D_6): −23.1 (d broad, 5B, BH), −5.3 (s, 5B, *m*-BCl), 1.1 (s, broad, 1B, *p*-BCl).

Table 1
Catalytic hydroamination of aminoalkenes (**A**–**D**) by cationic aluminum species (**1**–**4**).

Entry[a]	Substrate	Product	Catalyst	Time (h)	% Conversion[b]	% Yield[b]
A1			**1**	5	>99	78
A2			**2**	5	86	74
A3			**3**	34	>99	85
A4			**4**	1.5	>99	60
B1			**1**	28	88	70 + 15[c]
B2			**2**	39	95	70 + 10[c]
B3			**3**	3	>99	83
B4			**4**	0.25	>99	90
C1			**1**	110	89	84
C3			**3**	103	90	85
C4			**4**	1[d]	98	88
D1			**1**	70	0	0

1 = [$AlEt_2$][$CHB_{11}H_5I_6$]; **2** = [$AlEt_2$][$CHB_{11}H_5Cl_6$]; **3** = [DcpAlEt][$CHB_{11}H_5Cl_6$]; **4** = [Dipp*AlEt][$CHB_{11}H_5I_6$].
[a] All reactions were carried out in C_6D_6 at 135 °C and 10 mol% catalyst loading.
[b] Determined by integration of ^{1}H NMR signals of reactant and product versus an internal standard.
[c] Isomerized product.
[d] 17.5 mol % catalyst loading in C_6D_6 at 135 °C.

Table 2
Catalytic hydroamination of aminoalkenes (**A** and **B**) by neutral aluminum compounds.

Entry[a]	Substrate	Product	Catalyst	Time (h)	% Conversion[b]	% Yield[b]
A6		No reaction	**6**	6	0	0
A7		No reaction	**7**	70	0	0
B7			**7**	70	73	50
B8			**8**	70	53	30 + 10[c]
B9			$AlEt_3$ + $[Ph_3C][CHB_{11}H_5I_6]$	30	83	69 + 18[c]

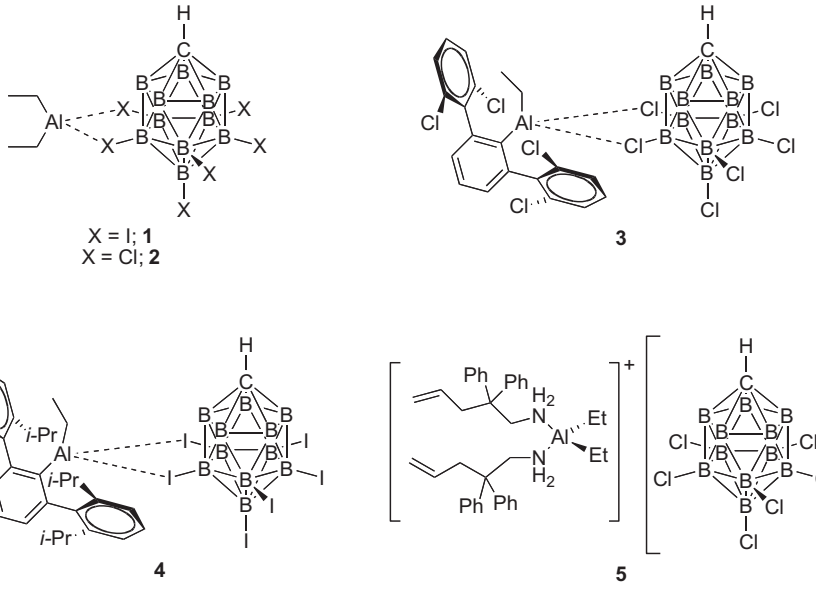
6 = $AlEt_3$, **7** = $DcpAlEt_2$, **8** = Dipp*$AlEt_2$.
[a] All reactions were carried out in C_6D_6 at 135 °C and 10 mol% catalyst loading.
[b] Determined by integration of ^1H NMR signals of reactant and product versus an internal standard.
[c] Isomerized product.

3. Results and discussion

3.1. Hydroamination of primary amines

The activity of four cationic organoaluminum compounds as intramolecular hydroamination catalysts was determined using four aminopentene substrates (Table 1). The complexes $[Et_2Al][CHB_{11}H_5I_6]$, **1** [22], and $[Et_2Al][CHB_{11}H_5Cl_6]$, **2** [22], differ only in the anion, whereas $[DcpAlEt][CHB_{11}H_5Cl_6]$, **3** [17], and [Dipp*AlEt] $[CHB_{11}H_5I_6]$, **4** [17], carry large *m*-terphenyl substituents. All four compounds are tight ion-pairs with four-coordinate aluminum centers in the solid state and most likely also in aromatic solutions. They readily coordinate amine ligands to afford solvent separated ion-pairs such as $[Et_2Al(NC_5H_5)_2][CHB_{11}H_5Br_6]$ [22] and [DcpAlEt$(NH_2$-*t*Bu$)_2][CHB_{11}H_5I_6]$ [17]. The aminopentenes differ in the substitution pattern of the double bond as well as the central quaternary carbon (Scheme 1).

The reactions were conducted with 10% catalyst loading in C_6D_6 solution at 135 °C. The activity pattern for catalysts **1** and **2**, i. e. the $[Et_2Al]^+$ species, closely follows that observed for C_6H_4-*o*-(3,5-*t*$Bu_2C_6H_3NH)_2AlNMe_2(NHMe_2)$ [18]. The nature of the anion, $[CHB_{11}H_5I_6]^-$ or $[CHB_{11}H_5Cl_6]^-$, does not significantly effect the outcome. The higher conversion rate for substrate **B** over **C** may be explained by the Thorpe–Ingold effect [24], and the failure of any



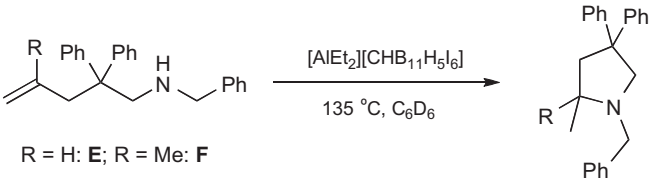
Scheme 1. Structures of compounds **1**–**5**.

conversion for **D** by unfavorable sterics in 1,2-disubstituted or 1,1,2-trisubstituted olefins [6]. Overall, the activity of the simple $[Et_2Al]^+$ catalysts **1** and **2** is about twice as high as C_6H_4-*o*-(3,5-$tBu_2C_6H_3$–NH)$_2AlNMe_2(NHMe_2)$ at a slightly lower temperature (135 versus 150 °C). A significant increase in activity was found for the sterically more encumbered $[Dipp^*AlEt]^+$ cation, **4**. The biggest increase was observed for substrates **B** and **C** by factors of approximately 100 with respect to catalyst **1**. The results for the cation $[DcpAlEt]^+$, **3**, were mixed: there was also a significant increase for substrate **B**, no difference for substrate **C** and a seven-fold decrease for substrate **A**.

Attempts to gain insight into the mechanism were inconclusive. Addition of two equivalents of **B** to a solution of **2** led to the formation of the 1:2 adduct $[AlEt_2\{NH_2CH_2C(Ph)_2CH_2CHCH_2\}_2][CHB_{11}H_5Cl_6]$, **5**. Heating of this compound at 135 °C for 6 h led to the evolution of some ethane, but extensive line broadening in the ^1H NMR spectrum prevented the analysis of the product. Similarly, heating of a 1:4 mixture of **2** and **B** at 135 °C for 6 h resulted in an NMR spectrum featuring mainly broad signals and some ethane. The ^1H NMR spectra of the catalytic reactions (Table 1) also showed the loss of the AlEt signals and the appearance of ethane, but the gaseous nature of ethane and its incomplete dissolution in C_6D_6 prevented quantitative analysis. The generally accepted mechanism for lanthanide, calcium and lithium catalyzed hydroamination involves the formation of a metal amide complex. Subsequently, the amide nitrogen attacks the olefin, which may have been activated by coordination to the metal center. The observed ethane evolution is in agreement with this mechanism (Scheme 2).

Whereas trialkylalanes readily react with primary and secondary amines under ethane elimination to give dialkylaluminum amides [25], the analogous reaction is more difficult for cationic organoaluminum compounds [17]. We suggest that under the reaction conditions only one of the ethyl groups is displaced and that species such as $[EtAlN(H)R\{NH_2R\}_n]^+$ may be present in the reaction mixture. This is further supported by the observation, that the aminolysis of **1** with 2–3 equivalents of *t*-$BuNH_2$ at 135 °C is incomplete even after 6 h and the observed strong influence of the substituents on the aluminum catalysts. The latter strongly indicates that the Al–C(Terphenyl) bond is not cleaved during the reaction.

For comparison, the effectiveness of the neutral organoaluminum compounds Et_3Al, **6**, $DcpAlEt_2$, **7**, and $Dipp^*AlEt_2$, **8**, was tested with substrates **A** and **B** under the same conditions as the cationic species (Table 2). No reaction was observed for substrate **A**, but a rather slow conversion took place for substrate **B** and the catalysts **7** and **8** (70 h for 50 + % conversion vs. 3 and 0.25 h for **3** and **4**, respectively). Apparently, the cationic nature of the catalysts is necessary for conversion in a reasonable time period. *In situ* generation of the cationic catalyst (entry B9, Table 2) gives a result similar to that of the preformed catalyst (entry B1, Table 1).



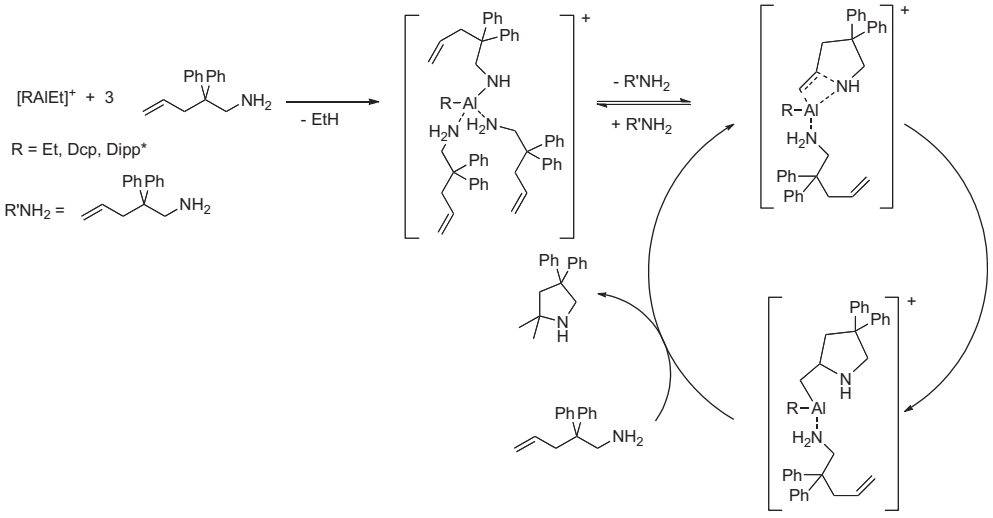
R	T (h)	% conv.
H	0.5	>99
Me	11	64

Scheme 3. Hydroamination of secondary aminopentenes.

3.2. Hydroamination of secondary amines

Inspired by these results, we decided to test the reactivity of secondary aminopentenes **E** and **F** (Scheme 3) with catalyst **1**. Hydroamination catalysts often display different activities toward primary and secondary aminoolefins [26,27].

Interestingly, the conversion of both aminopentenes is reversed with respect to their primary analogs **A** and **B**. Whereas substrate **A** bearing a substituted olefinic group was converted within 5 h, its benzylated derivative **F** could not be converted completely within 11 h. On the other hand, aminopentene **B**, which is unsubstituted at the olefinic functionality required 28 h for 88% conversion, whereas its benzylated counterpart **E** was converted within one half hour. This together with the fact that only a minor amount of ethane was generated indicates that a different mechanism might have been at work. Possibly, the alkene was activated by coordination to the Lewis acidic aluminum center and subsequently attacked by the nucleophilic amine nitrogen. A similar but significantly faster



Scheme 2. Possible catalytic cycle.

conversion preference for secondary aminopentenes was reported for the $Et_2Zn/[PhNHMe_2][B(C_6F_5)_4]$ catalytic system [28].

4. Conclusions

Cationic organometallic aluminum compounds catalyze the intramolecular hydroamination of aminopentenes. The reaction rates are strongly dependent on the substrate and the catalyst. Bulky substituents on the catalyst generally increase the reactivity. Control experiments with closely related neutral organoaluminum catalysts showed that the positive charge on the aluminum center is required for reasonable conversion rates.

Acknowledgments

Financial support for this work from the National Science Foundation (CHE 0718446) is gratefully acknowledged. We further thank the National Science Foundation (CHE 03422510) for the purchase of the Bruker Avance 400 NMR spectrometer. We are also grateful to Dr. Jürgen Koller and Professor Robert G. Bergman at the University of California in Berkeley who provided us with initial samples of the four primary aminopentenes.

Appendix A. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.09.010.

References

[1] T.E. Müller, K.C. Hultzsch, M. Yus, F. Foubelo, M. Tada, Chem. Rev. 108 (2008) 3795–3892.
[2] S. Doye, Sci. Synth. 40a (2009) 241–304.
[3] R. Severin, S. Doye, Chem. Soc. Rev. 36 (2007) 1407–1420.
[4] J. Seayad, A. Tillack, C.G. Hartung, M. Beller, Adv. Synth. Catal. 344 (2002) 795–813.
[5] M.R. Gagne, T.J. Marks, J. Am. Chem. Soc. 111 (1989) 4108–4109.
[6] S. Hong, T.J. Marks, Acc. Chem. Res. 37 (2004) 673–686.
[7] J. Hannedouche, J. Collin, A. Trifonov, E. Schulz, J. Organomet. Chem. 696 (2011) 255–262.
[8] G. Zi, Dalton Trans. (2009) 9101–9109.
[9] G. Zi, J. Organomet. Chem. 696 (2011) 68–75.
[10] M.A. Antunes, R.F. Munhá, L.G. Alves, L.L. Schafer, A.M. Martins, J. Organomet. Chem. 696 (2011) 2–6.
[11] R.O. Ayinla, T. Gibson, L.L. Schafer, J. Organomet. Chem. 696 (2011) 50–60.
[12] K.D. Hesp, M. Stradiotto, ChemCatChem 2 (2010) 1192–1207.
[13] E.M. Beccalli, G. Broggini, A. Fasana, M. Rigamonti, J. Organomet. Chem. 696 (2011) 277–295.
[14] R.A. Widenhoefer, Chem.-Eur. J. 14 (2008) 5382–5391.
[15] A.G.M. Barrett, M.R. Crimmin, M.S. Hill, P.A. Procopiou, Proc. R. Soc. A 466 (2010) 927–963.
[16] J.D. Young, M.A. Khan, R.J. Wehmschulte, Organometallics 23 (2004) 1965–1967.
[17] T. Klis, D.R. Powell, L. Wojtas, R.J. Wehmschulte, Organometallics 30 (2011) 2563–2570.
[18] J. Koller, R.G. Bergman, Chem. Commun. 46 (2010) 4577–4579.
[19] J. Koller, R.G. Bergman, Organometallics 29 (2010) 3350–3356.
[20] M.R. Crimmin, M. Arrowsmith, A.G.M. Barrett, I.J. Casely, M.S. Hill, P.A. Procopiou, J. Am. Chem. Soc. 131 (2009) 9670–9685.
[21] C.F. Bender, R.A. Widenhoefer, J. Am. Chem. Soc. 127 (2005) 1070–1071.
[22] K.-C. Kim, C.A. Reed, G.S. Long, A. Sen, J. Am. Chem. Soc. 124 (2002) 7662–7663.
[23] M. Dochnahl, J.-W. Pissarek, S. Blechert, K. Loehnwitz, P.W. Roesky, Chem. Commun. (2006) 3405–3407.
[24] M.E. Jung, G. Piizzi, Chem. Rev. 105 (2005) 1735–1766.
[25] M. Lappert, P. Power, A. Protchenko, A. Seeber, Metal Amide Chemistry. John Wiley & Sons, Chichester, UK, 2009.
[26] H. Ohmiya, T. Moriya, M. Sawamura, Org. Lett. 11 (2009) 2145–2147.
[27] A. Mukherjee, S. Nembenna, T.K. Sen, S.P. Sarish, P.K. Ghorai, H. Ott, D. Stalke, S.K. Mandal, H.W. Roesky, Angew. Chem. Int. Ed. 50 (2011) 3968–3972.
[28] J.-W. Pissarek, D. Schlesiger, P.W. Roesky, S. Blechert, Adv. Synth. Catal. 351 (2009) 2081–2085.