ACS Catalysis

Letter

pubs.acs.org/acscatalysis

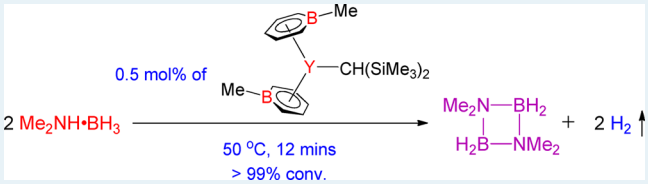
# 1-Methyl Boratabenzene Yttrium Alkyl: A Highly Active Catalyst for Dehydrocoupling of $Me_2NH{\cdot}BH_3$

Erli Lu, Yuanyuan Yuan, Yaofeng Chen,* and Wei Xia

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Supporting Information

**ABSTRACT:** Catalytic activity of rare-earth metal complexes for dehydrocoupling of $Me_2NH{\cdot}BH_3$ is deeply ligand- and metal ion-dependent, and 1-methyl boratabenzene yttrium alkyl shows very high activity for the reaction (TOF > 1000 $h^{-1}$). The transformation of $Me_2NH{\cdot}BH_3$ into $[Me_2N{-}BH_2]_2$ proceeds through an intermediate $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$.




**KEYWORDS:** *N,N-dimethylamine borane, dehydrocoupling, boratabenzene, rare-earth metal*

## INTRODUCTION

The catalyzed dehydrocoupling of amine boranes has attracted great interest recently because of the potential usage of amine boranes as $H_2$ storage materials in future clean energy applications.[1] An increasing number of transition metal and main group metal-based complexes have been investigated as catalysts for dehydrocoupling of amine boranes.[1,2] On the other hand, rare-earth metal complexes have been widely utilized as catalysts for organic synthesis and polymer synthesis in the last two decades;[3] however, their application in dehydrocoupling of amine boranes has been far less explored. Only two rare-earth metal amides, $Sc[N(SiHMe_2)_2]_3(thf)_2$ and $Y[N(SiMe_3)_2]_3$, have been used for dehydrocoupling of dimethylamine borane ($Me_2NH{\cdot}BH_3$). TOFs for the Sc and Y complexes are 33.3 and 2.8 $h^{-1}$, respectively.[4]

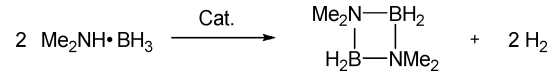
Boratabenzene is a heterocyclic, 6$\pi$-electron aromatic anion that has been introduced into organometallic chemistry as an isoelectronic analogue of the well-known cyclopentadienide anion ($Cp^-$).[5] One distinguishing feature of boratabenzene metal complexes is the existence of an electron-deficient boron atom on the aromatic ligand, and the electron deficiency of the boron atom can be tuned by its substituent (Chart 1).[6] Recently, we synthesized a variety of boratabenzene rare-earth metal complexes.[7] We present here our initial study on the dehydrocoupling of $Me_2NH{\cdot}BH_3$ (Scheme 1) catalyzed by rare-earth metal alkyls with 1-methyl boratabenzene and 1-diethylamino boratabenzene ligands. In the former, the boron atom on boratabenzene is significantly electron-deficient, whereas the latter has a less electron-deficient boron atom as a result of a B–N $\pi$ interaction.[7e] The study shows that the substituent on boron has great influence on the catalytic activity of complexes, and (1-methyl boratabenzene) yttrium alkyl is a highly active catalyst for the dehydrocoupling of $Me_2NH{\cdot}BH_3$. The dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by some other rare-earth metal complexes has also been investigated.

**Chart 1. Boratabenzene Metal Complexes**


(a) (b)

M = metal ion, R = alkyl group

**Scheme 1. Dehydrocoupling of Dimethylamine Borane**



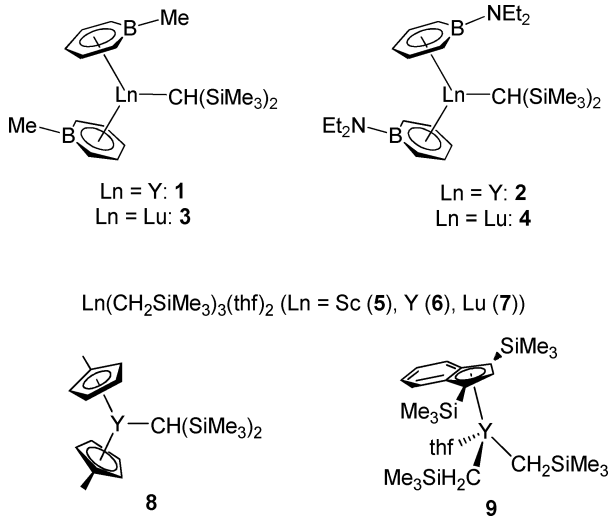

## RESULTS AND DISCUSSION

Boratabenzene yttrium alkyls $(C_5H_5BMe)_2YCH(SiMe_3)_2$ (**1**) and $(C_5H_5BNEt_2)_2YCH(SiMe_3)_2$ (**2**) (Chart 2) were synthesized as we previously reported.[7e] The dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by **1** and **2** was carried out in $C_6D_6$ at 50 °C, and the reactions were monitored by $^{11}B\{^1H\}$ NMR spectroscopy. The complex **1** shows very high activity for the selective dehydrocoupling of $Me_2NH{\cdot}BH_3$ into cyclic dimer $[Me_2N{-}BH_2]_2$ (**A**). Even with a very small amount of **1** (0.5 mol % catalyst loading), >99% conversion of $Me_2NH{\cdot}BH_3$ was achieved within 12 min (Figure 1 and Table 1). About 98% of the product was $[Me_2N{-}BH_2]_2$ (**A**); the remainder was $Me_2N{=}BH_2$ (**C**). Complex **1** has a TOF up to 1000 $h^{-1}$, and to the best of our knowledge, it is the most active early transition metal catalyst for the dehydrocoupling of $Me_2NH{\cdot}BH_3$. The 1-amino-substituted boratabenzene complex

Received: January 9, 2013
Revised: February 14, 2013
Published: February 14, 2013

**Chart 2. Rare-Earth Metal complexes 1−9**



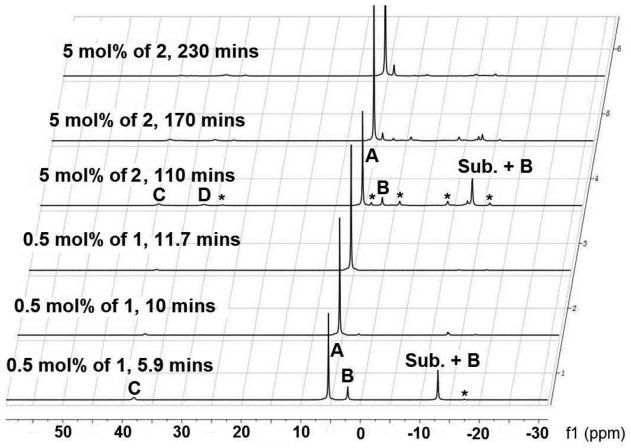




**Figure 1.** $^{11}B\{^1H\}$ NMR spectra showing the dehydrocoupling of $Me_2NH{\cdot}BH_3$ (sub.) catalyzed by **1** and **2**. Conditions: $[sub.]_0$ = 0.68 mol/L, $C_6D_6$ as the solvent, 50 °C. **A**, $[Me_2N{-}BH_2]_2$; **B**, $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$; **C**, $Me_2N{=}BH_2$; **D**, $(Me_2N)_2BH$; *, other boron-containing species.

**Table 1. The Dehydrocoupling of $Me_2NH{\cdot}BH_3$ Catalyzed by the Rare-Earth Metal Complexes 1−9**[a]

| complex | cat. (mol %) | time (min) | conv. of sub. (%) | A[b] (%) | TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| **1** | 0.5 | 11.7 | >99 | 98 | 1015 |
| **2** | 5 | 110 | 86 | 55 | 9.4 |
| **3** | 1 | 28.5 | >99 | 98 | 208 |
| **4** | 5 | 100 | 91 | 72 | 11 |
| **5** | 5 | 150 | 96 | 84 | 7.7 |
| **6** | 5 | 255 | 38 | 24 | 1.8 |
| **7** | 5 | 240 | 73 | 60 | 3.7 |
| **8** | 1 | 80 | >99 | 98 | 74 |
| **9** | 5 | 240 | 46 | 31 | 2.3 |

[a]Conditions: $[sub.]_0$ = 0.68 mol/L, $C_6D_6$ as the solvent, 50 °C. [b]**A**: $[Me_2N{-}BH_2]_2$; the values are the percentages of boron-containing **A**'s in the total product's boron content by $^{11}B\{^1H\}$ NMR spectra; the remaining products are the linear dimer $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (**B**), $Me_2N{=}BH_2$ (**C**), $(Me_2N)_2BH$ (**D**), and some other unidentified species.

**2** is far less active for the reaction than **1**. For example, to obtain 86% conversion of the substrate, a larger catalyst loading (5 mol % of **2**) and longer reaction time (110 min) were needed (Figure 1 and Table 1).

To examine if other boratabenzene rare-earth metal complexes have the same substituent effect, boratabenzene lutetium alkyls $(C_5H_5BMe)_2LuCH(SiMe_3)_2$ (**3**) and $(C_5H_5BNEt_2)_2LuCH(SiMe_3)_2$ (**4**)[7e] were prepared and used for the dehydrocoupling of $Me_2NH{\cdot}BH_3$. As for the yttrium ones, it was observed that 1-methyl-substituted lutetium complex **3** is much more active than its 1-amino-substituted congener **4**. For the reaction catalyzed by **3**, >99% conversion of the substrate was achieved within 29 min with 1 mol % catalyst loading, and 98% of the products is $[Me_2N{-}BH_2]_2$ (**A**). The complexes with 1-methyl-substituted boratabenzene ligand (**1** and **3**) show higher activity than their 1-amino-substituted congeners (**2** and **4**). This is possibly due to the more electron-deficient rare-earth metal centers in **1** and **3**, as 1-methyl boratabenzene is a poorer electronic donor in comparison with 1-diethylamino boratabenzene. Another possible factor is the H···B interaction. The hydric Hs on boron in $Me_2NH{\cdot}BH_3$ or the reaction intermediates may interact with electron-deficient boron atom in 1-methyl boratabenzene to accelerate the reaction.

The $^{11}B\{^1H\}$ NMR spectroscopy monitoring of the dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by **1** and **3** indicated some significant differences from those catalyzed by the magnesium complexes ($Mg^nBu_2$ and $Mg\{CH(SiMe_3)_2\}_2(thf)_2$).[8] In the reactions catalyzed by **1** and **3**, metal species containing $[Me_2N{-}BH_2{-}NMe_2{-}BH_3]^-$ anion were not observed, and the amount of $HB(NMe_2)_2$ are traces (<0.5 mol %). On the other hand, a significant amount of linear dimer $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (**B**) was detected. For example, in the reaction catalyzed by 1 mol % of **3**, ∼34 mol % of the boron-containing species is $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ at 4.4 min after the reaction is initiated (see Figure S1 in the Supporting Information). With the progress of the reaction, $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ was gradually converted into the final product $[Me_2N{-}BH_2]_2$.

To have a better understanding on the dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by rare-earth metal complexes, some other rare-earth metal complexes, (e.g. rare-earth metal trialkyls $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Sc (**5**), Y (**6**), Lu (**7**)),[9] bis(cyclopentadienyl) yttrium alkyl $(C_5H_4Me)_2YCH(SiMe_3)_2$ (**8**),[10] and mono(indenyl)yttrium dialkyl (1,3-$(SiMe_3)_2C_9H_5$)-$Y(CH_2SiMe_3)_2(thf)$ (**9**)[11]) were synthesized and tested for the dehydrocoupling of $Me_2NH{\cdot}BH_3$. The results are summarized in Table 1. These complexes are all capable of catalyzing the dehydrocoupling of $Me_2NH{\cdot}BH_3$, and the TOFs ranged from 1.8 to 74 $h^{-1}$. The catalytic activity is greatly influenced by the ligand and metal ion, and complex **8** shows the highest activity. It is noteworthy that $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (**B**) acts as an intermediate in the reaction catalyzed by **8** (Figure 2).

The presence of $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (**B**) in the dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by **1**, **3**, and **8** indicates a catalytic pathway different from that proposed for the reactions catalyzed by the magnesium complexes ($Mg^nBu_2$ and $Mg\{CH(SiMe_3)_2\}_2(thf)_2$), in which **B** is not involved.[8] The formation of a large amount of the reaction intermediate $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ suggests that the reaction proceeds through two steps as those catalyzed by some Ti,[12,2e] Ru, and Rh catalysts;[13] that is, $Me_2NH{\cdot}BH_3$ is converted into $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ first, and then $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$


dx.doi.org/10.1021/cs4000206 | ACS Catal. 2013, 3, 521−524

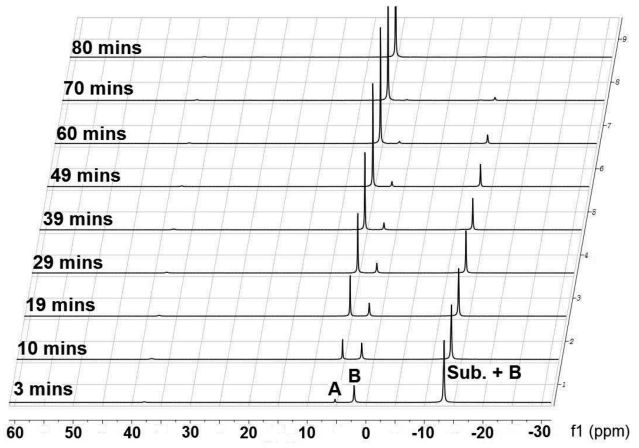



**Figure 2.** $^{11}B\{^1H\}$ NMR spectroscopy monitoring of the dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by 1 mol % of **8** in $C_6D_6$ at 50 °C. Conditions: $[sub.]_0$ = 0.68 mol/L, $C_6D_6$ as the solvent, 50 °C. **A**, $[Me_2N{-}BH_2]_2$; **B**, $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$.

undergoes a catalytic cyclization to give the final product, $[Me_2N{-}BH_2]_2$. However, due to the high reduction potential of Ln(III) to Ln(II) (Ln = Y, Lu), the oxidative addition and reductive elimination in the Ti-catalyzed dehydrocoupling should not occur here in the yttrium and lutetium catalyzed dehydrocoupling.

In summary, a series of rare-earth metal complexes have been investigated as catalysts for dehydrocoupling of $Me_2NH{\cdot}BH_3$. Catalytic activity of complexes is deeply dependent on the ligand and metal ion. The 1-methyl boratabenzene yttrium alkyl shows very high activity for the selective dehydrocoupling of $Me_2NH{\cdot}BH_3$ into cyclic dimer $[Me_2N{-}BH_2]_2$. The formation of a larger amount of the reaction intermediate $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ suggests that the reaction proceeds through two steps. The detailed mechanism is under investigation.

## ■ ASSOCIATED CONTENT

### Supporting Information

General procedure of NMR experiments and $^{11}B\{^1H\}$ NMR spectra showing the dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by **3**-**7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: yaofchen@mail.sioc.ac.cn.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants Nos. 21272256, 21132002, and 21121062), the State Key Basic Research & Development Program (Grant No. 2011CB808705), and the Chinese Academy of Sciences.

## ■ REFERENCES

(1) (a) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613. (b) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279. (c) Umegaki, T.; Yan, J. M.; Zhang, X. B.; Shioyama, H.; Kuriyama, N.; Xu, Q. *Int. J. Hydrogen Energy* **2009**, *34*, 2303. (d) Smythe, N. C.; Gordon, J. C. *Eur. J. Inorg. Chem.* **2010**, 509. (e) Staubitz, A.; Robertson, A. P. M.; Manners, I. *Chem. Rev.* **2010**, *110*, 4079. (f) Less, R. J.; Melen, R. L.; Wright, D. S. *RSC Adv.* **2012**, *2*, 2191.

(2) For representative works in 2012 and 2013, see: (a) Sewell, L. J.; Lloyd-Jones, G. C.; Weller, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 3598. (b) Baker, R. T.; Gordon, J. C.; Hamilton, C. W.; Henson, N. J.; Lin, P.-H.; Maguire, S.; Murugesu, M.; Scott, B. L.; Smythe, N. C. *J. Am. Chem. Soc.* **2012**, *134*, 5598. (c) Schreiber, D. F.; O'Connor, C.; Grave, C.; Ortin, Y.; Müller-Bunz, H.; Phillips, A. D. *ACS Catal.* **2012**, *2*, 2505. (d) Tang, C. Y.; Phillips, N.; Bates, J. I.; Thompson, A. L.; Gutmann, M. J.; Aldridge, S. *Chem. Commun.* **2012**, *48*, 8096. (e) Helten, H.; Dutta, B.; Vance, J. R.; Sloan, M. E.; Haddow, M. F.; Sproules, S.; Collison, D.; Whittell, G. R.; Llyod-Jones, G. C.; Manners, I. *Angew. Chem., Int. Ed.* **2013**, *52*, 437.

(3) (a) The special issue "Recent Advances in the Organometallic Chemistry of Group 3 and Lanthanoid elements. Guest Editors: Lappert, M. F., Evans, W. J. *J. Organomet. Chem.* **2002**, *647*, issues 1−2. (b) The special issue "Frontiers in Lanthanide Chemistry. Guest Editor: Kagan, H. B. *Chem. Rev.* **2002**, *102*, issue 6. (c) The themed issue "New Horizons in Organo-f-element Chemistry. Guest Editor: Cloke, G. *Dalton Trans.* **2010**, *39*, issue 29. (d) The special issue "Organo-f-element Chemistry at Pacifichem 2010. Guest Editor: Edelmann, F. T. *J. Organomet. Chem.* **2010**, *695*, issues 25−26.

(4) Hill, M. S.; Kociok-Köhn, G.; Robinson, T. P. *Chem. Commun.* **2010**, *46*, 7587.

(5) (a) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199. (b) Fu, G. C. *Adv. Organomet. Chem.* **2001**, *47*, 101. (c) Ashe, A. J., III; Al-Ahmad, S.; Fang, X. G. *J. Organomet. Chem.* **1999**, *581*, 92. (d) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (e) Rogers, J. S.; Bu, X. H.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 730. (f) Ashe, A. J., III; Al-Ahmad, S.; Fang, X. D.; Kampf, J. W. *Organometallics* **2001**, *20*, 468. (g) Herberich, G. E.; Basu Baul, T. S.; Englert, U. *Eur. J. Inorg. Chem.* **2002**, 43. (h) Languérand, A.; Barnes, S. S.; Bélanger-Chabot, G.; Maron, L.; Berrouard, P.; Audet, P.; Fontaine, F. G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6695. (i) Bélanger-Chabot, G.; Rioux, P.; Maron, L.; Fontaine, F. G. *Chem. Commun.* **2010**, *46*, 6816. (j) Pammer, F.; Lalancette, R. A.; Jäkle, F. *Chem.—Eur. J.* **2011**, *17*, 11280. (k) Glockner, A.; Cui, P.; Chen, Y. F.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *New J. Chem.* **2012**, *36*, 1392. (l) Macha, B. B.; Boudreau, J.; Maron, L.; Maris, T.; Fontaine, F. G. *Organometallics* **2012**, *31*, 6428.

(6) (a) Herberich, G. E.; Hessner, B. D.; Köffer, D. P. J. *J. Organomet. Chem.* **1989**, *362*, 243. (b) Sperry, C. K.; Cotter, W. D.; Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7791.

(7) (a) Cui, P.; Chen, Y. F.; Zeng, X. H.; Sun, J.; Li, G. Y.; Xia, W. *Organometallics* **2007**, *26*, 6519. (b) Cui, P.; Chen, Y. F.; Wang, G. P.; Li, G. Y.; Xia, W. *Organometallics* **2008**, *27*, 4013. (c) Cui, P.; Chen, Y. F.; Li, G. Y.; Xia, W. *Angew. Chem., Int. Ed.* **2008**, *47*, 9944. (d) Yuan, Y. Y.; Chen, Y. F.; Li, G. Y.; Xia, W. *Organometallics* **2008**, *27*, 6307. (e) Yuan, Y. Y.; Chen, Y. F.; Li, G. Y.; Xia, W. *Organometallics* **2010**, *29*, 3722. (f) Cui, P.; Chen, Y. F.; Zhang, Q.; Li, G. Y.; Xia, W. *J. Organomet. Chem.* **2010**, *695*, 2713. (Special Issue for Organo-f-Element Chemistry at Pacifichem 2010). (g) Cui, P.; Chen, Y. F.; Li, G. Y.; Xia, W. *Organometallics* **2011**, *30*, 2012. (h) Yuan, Y. Y.; Wang, X. F.; Li, Y. X.; Fan, L. Y.; Xu, X.; Chen, Y. F.; Li, G. Y.; Xia, W. *Organometallics* **2011**, *30*, 4330.

(8) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. *Chem.—Eur. J.* **2010**, *16*, 8508.

(9) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126.

(10) Evans, W. J.; Meadows, J. H.; Kostka, A. G.; Closs, G. L. *Organometallics* **1985**, *4*, 324.

(11) Xu, X.; Chen, Y. F.; Feng, J.; Zou, G.; Sun, J. *Organometallics* **2010**, *29*, 549.

(12) Sloan, M. E.; Staubitz, A.; Clark, T. J.; Russell, C. A.; Lloyd-Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 3831.

(13) (a) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424. (b) Käβ, M.; Friedrich, A.; Drees, M.;

Schneider, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 905. (c) Friedrich, A.; Drees, M.; Schneider, S. *Chem.—Eur. J.* **2009**, *15*, 10339. (d) Douglas, T. M.; Chaplin, A. B.; Weller, A. S.; Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2009**, *131*, 15440.