Journal of Organometallic Chemistry 706-707 (2012) 144-145

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

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

Dehydrocoupling of catecholborane catalyzed by group 4 compounds

Holger Braunschweig*, Christina Claes, Frank Guethlein

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074, Würzburg, Germany

ARTICLE INFO

ABSTRACT

Article history: Received 20 December 2011 Received in revised form 27 January 2012 Accepted 1 February 2012

Keywords: Catalysis Dehydrocoupling Catecholborane Zirconium Hafnium

A D J I KACI

The early transition metal compounds $[Cp_2TiCl_2]$, $[Cp_2ZrCl_2]$ and $[Cp_2HfCl_2]$ were employed as precatalysts for the dehydrocoupling of catecholborane. The product of this reaction, bis(catecholato) diborane (B₂Cat₂), was generated with turnover numbers of up to 90. Heterogeneous catalysis yielded lower turnover numbers, but the metal powders used in these reactions turned out to also display the general ability to promote the dehydrocoupling reaction.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The formation of C–B bonds in organoboranes can be achieved by several synthetic methods, e.g. by classical hydroboration, a protocol which was established by Brown and coworkers over half a century ago. [1–3]. Discovery of the transition metal catalyzed hydroboration reaction yielded products with alternative chemoand regioselectivity [4–6]. Additionally, catalytic diboration of unsaturated compounds [7–9] as well as the borylation of arenes [10,11] and alkanes [12–14] gave access to a much broader variety of organoboranes. The starting material for the latter reactions are diboranes(4) of the general formula (RO)₂B–B(OR)₂, the two most commonly used of which are bis(catecholato)diborane (B₂Cat₂) (**1**) and bis(pinacolato)diborane (B₂Pin₂) (**2**).

The current industrial synthesis of diboranes(4) was established by Brotherton et al. in 1960 and modified several times thereafter [15–21], which employs reductive coupling of bromobis(dimethylamino)borane with sodium as a key step to yield $B_2(NMe_2)_4$. Diboranes **1** and **2** can be obtained by the reaction of this compound with the corresponding diols with loss of dimethylamine [19,21–23]. However, this multistep protocol requires harsh reaction conditions and is rather time-consuming. Additionally, large amounts of waste material are generated, which makes the commercially available diboranes(4) rather expensive. An alternative pathway for the formation of B-B bonds *via* a dehydrocoupling reaction was reported by Sneddon and Corcoran, jr. in the reaction of boranes and carboranes with PtBr₂ [24–26].

Consequently, we investigated the possibility of a catalytic dehydrocoupling reaction to yield **1** and **2** starting from the hydroboranes catecholborane (HBCat) and pinacolborane (HBPin). Using late transition metal catalysts under homogeneous and heterogeneous conditions, we were able to establish an alternative protocol for the synthesis of **1** and **2** [27,28].

Herein we report studies on extending this reactivity to group 4 pre-catalysts. The practice of using derivatives of group 4 metallocenes for dehydrogenative formation of element-element bonds has been previously reported. Harrod et al. employed [Cp₂MMe₂] (M = Ti, Zr, Hf) for the polymerization of primary silanes [29–31]. A catalytically active species in these reactions is the metallocene [Cp₂M], which is formed by decomposition of [Cp₂MMe₂]. Alternatively, this reactive intermediate can be generated by an in situ reduction of the metallocene dichloride with *n*-butyllithium [32] or with an aluminum hydride [33]. Later, similar systems were used not only for the formation of Si–Si bonds [34], but also for dehydrocoupling reactions yielding P-P [35], P-Si [36] and other element-element bonds [37]. The groups of Manners [38,39] and Chirik [40] reported dehydrocoupling reactions of amine-borane adducts catalyzed by group 4 metallocenes. The reactivity of titanocenes towards catecholboranes was investigated by Hartwig et al., whereas several σ -borane complexes were obtained [41–44].



Note



^{*} Corresponding author. Tel.: +49 931 31 85260; fax: +49 931 31 84623. *E-mail address:* h.braunschweig@mail.uni-wuerzburg.de (H. Braunschweig).

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2012.02.004

2. Results and discussion

As mentioned above, the common procedure for generating the reactive [Cp₂M] species involves an in situ reduction with nbutyllithium. Although diluted solutions of HBCat do not react with the pre-catalysts $[Cp_2MCl_2]$ (M = Ti, Zr, Hf) under stoichiometric conditions, the reductive nature of the neat borane is sufficient to generate a catalytically active species without additional activation of the group 4 complexes. In a typical reaction, the pre-catalyst (0.05 mol%) and neat HBCat were heated to 110 °C. Upon heating, the solution turned black and a distinct evolution of gas could be observed (Scheme 1). After 20 h, the turnover numbers (TON) of the reactions were determined by GC. In the case of [Cp₂TiCl₂], the formation of B₂Cat₂ was observed, albeit with a very low TON of 3. However, the two heavier homologs of titanium, that is zirconium and hafnium, turned out to be more efficient pre-catalysts for the dehydrocoupling, with [Cp₂ZrCl₂] affording a TON of 40. With [Cp₂HfCl₂] the TON could be further raised to 90, a value identical to the results achieved with [(dppm)PtCl₂], which turned out to be the most efficient homogeneous late transition metal catalyst under these reaction conditions [27,28]. In the reaction of HBCat with [Cp₂HfCl₂], B₂Cat₂ could be isolated by removing excess borane in vacuo and sublimation of the resulting crude product at 100 °C and 4·10⁻² mbar. After washing the crude product with acetonitrile and hexane, pure 1 was yielded with a TON of 46.

The dehydrocoupling of pinacolborane was far less straightforward in comparison to catecholborane. In the direct reaction of the borane with the metallocene dichlorides no B₂Pin₂ was formed. After addition of *n*-butyllithium to the pre-catalyst [Cp₂HfCl₂], trace amounts of **2** were detected by GC, which suggests that HBPin is not strong enough as a reducing agent for an *in situ* activation of the precatalyst. However, even after the activation of the pre-catalyst, accumulation of this product could not be achieved, indicating further differences in the reactivity of HBCat and HBPin towards the group 4 complexes, which could not be elucidated from the available data.

The observation of an increase in catalytic activity of hafnocene dichloride in comparison to its lighter homologs is generally in agreement with our findings for late transition metal catalysts. It is noteworthy, however, that the groups of Manners and Chirik observed the opposite reactivity pattern in the dehydrogenation of aminoboranes, with titanocenes being more effective than zirconium- or hafnium-based compounds [38–40].

As in the case of late transition metals, we sought to employ heterogeneous catalytic conditions for the dehydrocoupling. However, in contrast to palladium and platinum, the scope of available heterogeneous catalysts of early transition metals is very limited. Therefore we investigated the reactivity of HBCat towards titanium, zirconium and hafnium metal powders. However, titanium afforded a TON of only 5, while the TONs for Zirconium (10) and Hafnium (13) are significantly lower than those observed under homogeneous conditions (Table 1). Nevertheless, we have shown that these systems are generally able to catalyze the dehydrocoupling reaction, a reactivity which, to the best of our knowledge, has not been reported before for these metals in their elemental form.

In conclusion, we have successfully employed group 4 systems as catalysts for the dehydrocoupling of catecholborane. The product bis(catecholato)diborane was generated with turnover numbers of up to 90, with [Cp₂HfCl₂] turning out to be the most efficient pre-catalyst.



Scheme 1. Catalytic dehydrocoupling of HBCat.

Table 1

Catalytic dehydrocoupling of HBC	at.
----------------------------------	-----

Pre-catalyst (loading [mol%]) ^a	Turnover number (GC) ^b
[Cp ₂ TiCl ₂] (0.05%)	3
[Cp ₂ ZrCl ₂] (0.05%)	40
[Cp ₂ HfCl ₂] (0.05%)	90
Ti Powder (0.4%)	5
Zr Powder (0.1%)	10
Hf Powder (0.1%)	13

 $^{\rm a}\,$ Reaction conditions: neat borane was heated with the pre-catalyst to 110 $^\circ {\rm C}$ for 20 h.

^b Turnover numbers were determined by GC with docosane as internal standard. The numbers given are the average of two or more runs.

Furthermore we observed that group 4 metal powders can also catalyze this dehydrocoupling, albeit with lower turnover numbers.

References

- [1] H.C. Brown, B.C. Rao, J. Org. Chem. 22 (1957) 1136-1137.
- [2] H.C. Brown, B.C. Rao, J. Org. Chem. 22 (1957) 1137–1138.
- [3] H.C. Brown, Hydroboration, Wiley-Interscience, New York, 1962.
- [4] R. Wilczynski, L.G. Sneddon, Inorg. Chem. 20 (1981) 3955–3962.
- [5] T.B. Marder, J.D. Hewes, J.W. Kreimendahl, M.F. Hawthorne, J. Am. Chem. Soc. 106 (1984) 5757–5759.
- [6] D. Männig, H. Nöth, Angew. Chem. 97 (1985) 854–855; Angew. Chem. Int. Ed. 24 (1985) 878–879.
- [7] T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, J. Am. Chem. Soc. 115 (1993) 11018–11019.
- [8] T.B. Marder, N.C. Norman, Top. Catal. 5 (1998) 63-73.
- [9] T. Ishiyama, N. Miyaura, J. Organomet. Chem. 611 (2000) 392-402.
- [10] K.M. Waltz, X. He, C. Muhoro, J.F. Hartwig, J. Am. Chem. Soc. 117 (1995) 11357–11358.
- [11] I.A.I. Mkhalid, J.H. Barnard, T.B. Marder, J.M. Murphy, J.F. Hartwig, Chem. Rev. 110 (2010) 890–931.
- [12] K.M. Waltz, J.F. Hartwig, Science 277 (1997) 211–213.
- [13] H. Chen, S. Schlecht, T.C. Semple, J.F. Hartwig, Science 287 (2000) 1995–1997.
 [14] J.F. Hartwig, Chem. Soc. Rev. 40 (2011) 1992–2002.
- [15] R.J. Brotherton, A.L. McCloskey, L.L. Petterson, H. Steinberg, J. Am. Chem. Soc. 82 (1960) 6242–6245.
- [16] R.J. Brotherton, A.L. McCloskey, J.L. Boone, H.M. Manasevit, J. Am. Chem. Soc. 82 (1960) 6245–6248.
- [17] P. Nguyen, G. Lesley, N.J. Taylor, T.B. Marder, N.L. Pickett, W. Clegg, M.R.J. Elsegood, N.C. Norman, Inorg. Chem. 33 (1994) 4623–4624.
- [18] D. Loderer, H. Nöth, H. Pommerening, W. Rattay, H. Schick, Chem. Ber. 127 (1994) 1605–1611.
- [19] T. Ishiyama, M. Murata, T.A. Ahiko, N. Miyaura, Org. Synth. 77 (2000) 176-185.
- [20] H.A. Ali, I. Goldberg, M. Srebnik, Eur. J. Inorg. Chem. (2002) 73–78.
- [21] M.J.G. Lesley, N.C. Norman, C.R. Rice, D.W. Norman, R.T. Baker, Inorg. Synth. 34 (2004) 1–5.
- [22] C.N. Welch, S.G. Shore, Inorg. Chem. 7 (1968) 225-230.
- [23] H. Nöth, Z. Naturforsch. B. Chem. Sci. 39B (1984) 1463-1466.
- [24] E.W. Corcoran Jr., L.G. Sneddon, Inorg. Chem. 22 (1983) 182.
- [25] E.W. Corcoran Jr., L.G. Sneddon, J. Am. Chem. Soc. 106 (1984) 7793-7800.
- [26] E.W. Corcoran Jr., L.G. Sneddon, J. Am. Chem. Soc. 107 (1985) 7446-7450.
- [27] H. Braunschweig, F. Guethlein, Angew. Chem. 123 (2011) 12821-12824;
- Angew. Chem. Int. Ed. 50 (2011) 12613–12616.
- [28] H. Braunschweig, F. Guethlein, EP 11176448.6, (submitted) for publication.
- [29] C. Aitken, J.F. Harrod, E. Samuel, J. Organomet. Chem. 279 (1985) C11-C13.
- [30] C.T. Aitken, J.F. Harrod, E. Samuel, J. Am. Chem. Soc. 108 (1986) 4059–4066.[31] C. Aitken, J.P. Barry, F. Gauvin, J.F. Harrod, A. Malek, D. Rousseau, Organo-
- metallics 8 (1989) 1732–1736.
- [32] J.Y. Corey, X.H. Zhu, T.C. Bedard, L.D. Lange, Organometallics 10 (1991) 924–930.
 [33] H.G. Woo, S.Y. Kim, M.K. Han, E.J. Cho, I.N. Jung, Organometallics 14 (1995)
- 2415–2421.
- [34] J.Y. Corey, Adv. Organomet. Chem. 51 (2004) 1-52.
- [35] S. Xin, H.G. Woo, J.F. Harrod, E. Samuel, A.M. Lebuis, J. Am. Chem. Soc. 119 (1997) 5307–5313.
- [36] R. Shu, L. Hao, J.F. Harrod, H.G. Woo, E. Samuel, J. Am. Chem. Soc. 120 (1998) 12988–12989.
- [37] F. Gauvin, J.F. Harrod, H.G. Woo, Adv. Organomet. Chem. 42 (1998) 363-405.
- [38] T.J. Clark, C.A. Russell, I. Manners, J. Am. Chem. Soc. 128 (2006) 9582-9583.
- [39] M.E. Sloan, A. Staubitz, T.J. Clark, C.A. Russell, G.C. Lloyd-Jones, I. Manners, I. Am. Chem. Soc. 132 (2010) 3831–3841.
- [40] D. Pun, E. Lobkovsky, P.J. Chirik, Chem. Commun. (2007) 3297–3299.
- [41] J.F. Hartwig, C.N. Muhoro, X. He, O. Eisenstein, R. Bosque, F. Maseras, J. Am. Chem. Soc, 118 (1996) 10936–10937.
- [42] C.N. Muhoro, J.F. Hartwig, Angew. Chem. 109 (1997) 1536–1538; Angew. Chem. Int. Ed. 36 (1997) 1510–1512.
- [43] C.N. Muhoro, X. He, J.F. Hartwig, J. Am. Chem. Soc. 121 (1999) 5033-5046.
- [44] W.H. Lam, Z. Lin, Organometallics 19 (2000) 2625–2628.