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## COMMUNICATION

## Abstraction of $\beta$ -hydrogen *vs.* alkyl groups in reactions of dialkylzinc compounds and bis(oxazolinyl)borane<sup>†</sup>

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An ambiphilic bis(oxazolinyl)borane proligand and zinc dialkyls react *via* alkyl group transfer or  $\beta$ -hydrogen abstraction. The latter process is favored by formation of a bis(oxazolinyl)borane-zinc adduct that positions a  $\beta$ -hydrogen in the proximity of the Lewis acid center.

Reactions of hydrocarbyl metal compounds and Lewis acids such as tris(perfluorophenyl)borane typically proceed by anionic group abstraction to form cationic or zwitterionic metal complexes.<sup>1</sup> These reactions have been studied primarily with β-hydrogen-free groups (H, Me, CH<sub>2</sub>Ph), perhaps because transition-metal alkyls containing β-H often undergo elimination. In contrast, main group organometallics including Et<sub>2</sub>Zn undergo β-elimination only under unusual photolytic or strongly reducing conditions.<sup>2</sup> Therefore, the interaction between a Lewis acid and a main group metal hydrocarbyl could provide insight into the nucleophilic sites of metal alkyls. These reactions could also clarify pathways concealed under catalytic conditions. For example, olefin polymerization systems contain Lewis acids, main group organometallics (e.g., Et<sub>2</sub>Zn), and metal-alkyl chains containing  $\beta$ -hydrogen.<sup>3</sup> While unsaturated polymer end groups are typically associated with β-elimination, β-abstraction also provides olefinic by-products and could be important in polymerization processes.

In fact, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] react with main group organometallic compounds containing  $\beta$ -hydrogen through at least two pathways.<sup>4</sup> Et<sub>2</sub>Zn and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> react to give EtZn( $\mu$ -Et)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, but treatment with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] gives Ph<sub>3</sub>CH, C<sub>2</sub>H<sub>4</sub>, and [EtZn][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].<sup>4a</sup> Sterics may affect  $\beta$ -hydrogen *vs.* alkyl group abstraction; thus ( $\kappa$ <sup>2</sup>-bpzmp)AlEt<sub>2</sub> (bpzmp = bis(pyrazolyl)methane) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> react by ethylgroup abstraction while the isobutyl aluminum compound gives isobutene and  $\kappa$ <sup>2</sup>-(bpzmp)Al(*i*-Bu)HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>4b</sup> The  $\beta$ -abstractions are not limited to alkyls, and a zinc amide and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> react *via*  $\beta$ -hydrogen abstraction.<sup>4d</sup> Furthermore, the proposed mechanisms of Meerwein-Pondorff-Verley reductions and Oppenhauer oxidations involve transfer of a  $\beta$ -hydrogen from a main group alkoxide to the electrophilic carbon of a coordinated carbonyl.  $^{\rm 5}$ 

Interactions of borane-containing ligands with organometallics are interesting in this context, and recent studies of ambiphilic ligands in organometallic chemistry have described M-B bond formations as well as alkyl group abstractions.<sup>6</sup> In the chemistry of oxazolinylboranes, PhB(Ox<sup>Me2</sup>)<sub>2</sub> (Ox<sup>Me2</sup> = bis(4,4-dimethyl-2-oxazolinyl)) and AlMe<sub>3</sub> react to form methide-abstracted { $\kappa^2$ -PhMeB(Ox<sup>Me2</sup>)<sub>2</sub>}AlMe<sub>2</sub>,<sup>7</sup> containing a bis(oxazolinyl)borate ligand.<sup>8</sup> Here we report contrasting reactions of organozine compounds and PhB(Ox<sup>Me2</sup>)<sub>2</sub> that involve alkyl group or  $\beta$ -hydrogen abstraction and strategies to control the relative rates of the two pathways.

Reaction of  $\beta$ -hydrogen-free ZnMe<sub>2</sub> and PhB(Ox<sup>Me2</sup>)<sub>2</sub> gives { $\kappa^2$ -PhMeB(Ox<sup>Me2</sup>)<sub>2</sub>}ZnMe [1; eqn (1)]. The <sup>1</sup>H NMR spectrum of  $C_s$ -symmetric 1 contained a ZnMe singlet at -0.18 ppm and a broad BMe signal at 0.94 ppm. The latter resonance was unambiguously assigned by a crosspeak in a <sup>1</sup>H-<sup>11</sup>B HMBC experiment that correlated with a <sup>11</sup>B NMR resonance at -16.7 ppm. The  $C_{2v}$ -symmetric structural isomer Me<sub>2</sub>B(Ox<sup>Me2</sup>)<sub>2</sub>ZnPh is not observed nor is ZnMe/BMe exchange detected in an EXSY experiment, suggesting that B-Me bond formation is irreversible. The spectroscopic data is consistent with 1 as a monomeric species containing a three-coordinate zinc center because dimeric [{PhMeB(Ox<sup>Me2</sup>)<sub>2</sub>}Zn(\mu-Me)]<sub>2</sub> would likely be a mixture of diastereomers.



This assignment is further supported by DOSY experiments.<sup>9</sup> Similar diffusion coefficients of **1** (8.27 ×  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, 296 K) and crystallographically characterized monomeric To<sup>M</sup>ZnMe<sup>10</sup> (7.45 ×  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, 296 K) suggest similar hydrodynamic radii for the two compounds and that **1** is monomeric.

Reactions of PhB(Ox<sup>Me2</sup>)<sub>2</sub> and Ph<sub>2</sub>Zn or Bn<sub>2</sub>Zn (Bn = CH<sub>2</sub>Ph) in benzene provide the expected products **2** and **3** [eqn (1)]. However, the reaction of PhB(Ox<sup>Me2</sup>)<sub>2</sub> and Et<sub>2</sub>Zn in benzene- $d_6$  gives a mixture of ethylborate and hydridoborate compounds after 1 day (Fig. 1). The <sup>11</sup>B NMR spectrum of the reaction mixture contained a singlet at -15.1 ppm and a doublet at -19.1 ppm (<sup>1</sup>J<sub>BH</sub> = 88 Hz).

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<sup>&</sup>lt;sup> $\dagger$ </sup> Electronic supplementary information (ESI) available: Synthesis and characterization of oxazolinylboratozinc compounds 1–3, 5, 7, 9, 10, and Et<sub>2</sub>Zn(DPE) and details for DOSY experiments. See DOI: 10.1039/c1cc16113j



Fig. 1 Effects of benzene *versus* THF as solvent in reactions of  $\beta$ -hydrogen-containing dialkylzinc compounds and PhB(Ox<sup>Me2</sup>)<sub>2</sub>.

Ethylene (5.25 ppm) and two sets of zinc ethyl resonances were detected in the <sup>1</sup>H NMR spectrum, and these data suggested ethyl-abstracted {PhEtB( $Ox^{Me2}$ )<sub>2</sub>}ZnEt (4) and hydridoborate {PhHB( $Ox^{Me2}$ )<sub>2</sub>}ZnEt (5) as the products. The former product is suggested by the pathway described by eqn (1), while the latter species is independently synthesized (see below) and apparently forms by transfer of a  $\beta$ -hydrogen from the ethyl ligand to boron. Mixtures of hydridoboratozinc and alkylborato organozinc compounds are also formed upon treatment of PhB( $Ox^{Me2}$ )<sub>2</sub> with *n*-Pr<sub>2</sub>Zn or *i*-Bu<sub>2</sub>Zn (Fig. 1).

In contrast, these reactions are selective for hydridoborate formation in THF. For example, PhB(Ox<sup>Me2</sup>)<sub>2</sub> and Et<sub>2</sub>Zn give 5 in THF or THF- $d_8$  as the only product detected over 1 day or isolated (Fig. 1). The <sup>1</sup>H NMR spectrum of isolated 5, recorded in benzene- $d_6$ , contained only one set of ethyl resonances at 0.62 (2 H) and 1.51 ppm (3 H). In a  ${}^{1}\text{H}-{}^{11}\text{B}$ HMQC experiment, the borohydride resonance at 3.53 ppm correlated with the <sup>11</sup>B NMR doublet at  $-19.1 (^{1}J_{BH} = 88 \text{ Hz})$ . These spectra confirm that 5 is one of the two species generated in benzene. Similar results are obtained upon treatment of PhB(Ox<sup>Me2</sup>)<sub>2</sub> with *n*-Pr<sub>2</sub>Zn and *i*-Bu<sub>2</sub>Zn in THF to form  $\{\kappa^2$ -PhHB(Ox<sup>Me2</sup>)<sub>2</sub> $\}$ Zn(*n*-Pr) (7) and  ${\kappa^2-PhHB(Ox^{Me2})_2}Zn(i-Bu)$  (9). Thus, zinc dialkyls containing β-CH groups react with PhB(Ox<sup>Me2</sup>)<sub>2</sub> in THF via β-hydrogen abstraction rather than alkyl group abstraction, whereas both alkyl group abstraction and  $\beta$ -hydrogen abstraction are observed in benzene.

Given these results and  $\beta$ -H abstraction in an aluminum isobutyl,<sup>4a</sup> the interactions of PhB(Ox<sup>Me2</sup>)<sub>2</sub> and aluminum alkyls were revisited. However, AlEt<sub>3</sub> and PhB(Ox<sup>Me2</sup>)<sub>2</sub> in benzene or THF provide only the alkyl-abstracted product { $\kappa^2$ -PhEtB(Ox<sup>Me2</sup>)<sub>2</sub>}AlEt<sub>2</sub> [10, eqn (2)].



Next, these reactions were more closely investigated to identify the factors that influence the pathway to favor alkyl

 Table 1
 Reactant concentration and alkyl: hydridoborate product ratio<sup>a</sup>

Reactant concentration (mM)	[ <b>4</b> ]:[ <b>5</b> ] <sup>b</sup>	
10.1	4.2:1	
5.3	3.3:1	
2.7	2.9:1	
1.8	2.1:1	

<sup>*a*</sup> Effect of concentration on the ratio of  $[Ph(Et)B(Ox^{Me2})_2ZnEt]$ (4):  $[Ph(H)B(Ox^{Me2})_2ZnEt]$  (5) formed in the reaction of  $PhB(Ox^{Me2})_2$ and  $Et_2Zn$  in benzene- $d_6$ . <sup>*b*</sup> The ratio was measured by integration of the <sup>1</sup>H NMR spectrum of the reaction mixture.

group abstraction or β-hydrogen abstraction. First, we verified that alkyl or hydride group abstraction is irreversible. Dissolution of a solid mixture of **4** and **5** (formed in benzene- $d_6$ ) in THF- $d_8$ gives the same mixture in the same ratio as obtained in benzene. Heating this THF- $d_8$  solution to 80 °C does not change the ratio of hydridoborate to ethylborate zinc. Additionally, **5** is unchanged in benzene- $d_6$  at 80 °C for at least 2 days. Although we do not know which product is thermodynamically favored, the irreversibility of the reactions suggest that the products form under kinetic control.

The reactants' concentrations affect the ratio of alkylborate to hydridoborate products. Table 1 shows that as the concentration of the reactants increases, the relative amount of alkyl group transfer increases from 2:1 to 4:1. Qualitative kinetics experiments show that the rate of reaction also increases as concentration increases. The change in product ratio indicates that the alkyl group abstraction rate increases at the expense of  $\beta$ -hydrogen abstraction. We suggest, then, that alkyl group abstraction may involve a bi-molecular interaction of PhB(Ox<sup>Me2</sup>)<sub>2</sub> and Et<sub>2</sub>Zn whereas hydride abstraction occurs primarily through an intramolecular rate-determining step that is less affected by concentration.

Selective hydride abstraction in THF can be rationalized in the context of this competition between intramolecular and intermolecular reaction pathways that favors the former. Coordination of THF to PhB( $Ox^{Me2}$ )<sub>2</sub> to give (THF)BPh( $Ox^{Me2}$ )<sub>2</sub> inhibits alkyl group transfer during bi-molecular collisions by coordinating to the Lewis acid site.<sup>11</sup> However, coordination of (THF)BPh( $Ox^{Me2}$ )<sub>2</sub> to Et<sub>2</sub>Zn is not blocked by formation of Et<sub>2</sub>Zn(THF)<sub>2</sub> but instead gives the intermediate (THF)BPh( $Ox^{Me2}$ )<sub>2</sub>ZnEt<sub>2</sub> [bis(oxazolines are better ligands for Zn(II) than THF]. Upon dissociation of THF to form BPh( $Ox^{Me2}$ )<sub>2</sub>ZnEt<sub>2</sub>, intramolecular  $\beta$ -hydrogen abstraction provides **5** (Fig. 2).

An alternative pathway, in which a  $Et_2ZnL_2$  species undergoes  $\beta$ -hydrogen elimination to give  $Et(H)ZnL_2$  followed by



Fig. 2 Proposed mechanism for hydridoborate formation.

Table 2 Effect of diamine ligands on  $\beta$ -hydrogen vs. alkyl group abstraction<sup>a</sup>

Reactant	Concentration (mM)	[4] : [5] <sup>t</sup>
Et <sub>2</sub> Zn	5.3	3.3:1
$Et_2Zn(TMEDA)$	5.1	4.5:1
$\tilde{E}t_2Zn(DPE)$	5.1	5.7:1
<sup>a</sup> C 1:t:		

<sup>*a*</sup> Conditions: room temperature in benzene- $d_6$ . <sup>*b*</sup> The ratio was measured by integration of the <sup>1</sup>H NMR spectrum of the reaction mixture.

zinc hydride abstraction, is unlikely for several reasons. First, diethylzinc itself does not readily β-H eliminate,<sup>2</sup> and the higher coordinate, 18-electron Et<sub>2</sub>Zn(THF)<sub>2</sub> and PhB(Ox<sup>Me2</sup>)<sub>2</sub>ZnEt<sub>2</sub> species that lack open orbitals are even less likely to undergo β-elimination. Furthermore, the β-elimination intermediate, Et(H)ZnL<sub>2</sub>, would likely transfer both hydride and ethyl groups to boron, whereas only hydrogen abstraction is observed in THF. Comparison of these mechanism also reveals that olefinic (or more generally, unsaturated) by-products do not provide sufficient evidence to distinguish β-hydrogen elimination from abstraction.

The proposed mechanism was further tested by treatment of PhB(Ox<sup>Me2</sup>)<sub>2</sub> with Et<sub>2</sub>Zn(TMEDA) or Et<sub>2</sub>Zn(DPE) (TMEDA = tetramethylethylenediamine; DPE = dipyrrolidine ethane),<sup>12</sup> where the diamine zinc starting materials might inhibit formation of PhB(Ox<sup>Me2</sup>)<sub>2</sub>ZnEt<sub>2</sub>. In fact, increased alkyl group transfer relative to β-H abstraction occurs in the presence of TMEDA and DPE (Table 2) further supporting the notion that alkyl borate formation occurs through a bimolecular rate-determining step. Despite the effect by TMEDA and DPE on the reaction pathway, [Ph(R)B(Ox<sup>Me2</sup>)<sub>2</sub>]<sup>-</sup> (R = H, Et) are superior ligands for zinc, and the final zinc products are **4** and **5**.

Upon addition of two equiv. of TMEDA or DPE (relative to  $Et_2Zn$ ), reaction times exceed 2 days in both benzene and THF. Presumably, the diamines coordinate to PhB(Ox<sup>Me2</sup>)<sub>2</sub> and  $Et_2Zn$ . However, the effect of TMEDA is sufficient to give a trace amount of alkylborate product **4** in THF. Furthermore, with 2 equiv. of TMEDA in benzene, the hydride abstraction pathway is greatly suppressed yielding **4** as the major product.

Finally, selective ethyl group transfer from AlEt<sub>3</sub> by PhB(Ox<sup>Me2</sup>)<sub>2</sub> is consistent with alkyl abstraction following an intermolecular mechanism. Formation of the requisite { $\kappa^2$ -PhB(Ox<sup>Me2</sup>)<sub>2</sub>}AlEt<sub>3</sub> for  $\beta$ -H abstraction is unlikely based on the smaller ionic radius of four-coordiante Al(III) (0.39 Å) *vs.* Zn(II) (0.6 Å)<sup>13</sup> which gives apparent coordinative saturation at four ligands in these systems.<sup>7</sup>

Our results show that the  $\beta$ -hydrogen in zinc alkyls have significant nucleophilicity. These results contrast the lack of alkylzinc-based  $\beta$ -agostic structures and  $\beta$ -hydrogen elimination reactions that are typically associated with activated C-H's. Furthermore, we show that the selectivity between  $\beta$ -hydrogen and alkyl group abstraction is not only governed by sterics, but also by the trajectory by which the electrophilic center encounters the alkyl ligand. Thus,  $\beta$ -hydrogen is readily transferred from an zinc alkyl group to electrophiles when the electrophile and alkyl ligand are appropriately positioned. These observations may provide strategies for controlling hydride and alkyl transfer processes in synthetic applications.

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## Notes and references

- (a) E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391–1434; (b) X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015–10031.
- R. E. Linney and D. K. Russell, J. Mater. Chem., 1993, 3, 587–590; (b) Y. S. Kim, Y. S. Won, H. Hagelin-Weaver, N. Omenetto and T. Anderson, J. Phys. Chem. A, 2008, 112, 4246–4253; (c) A. Lennartson, M. Håkansson and S. Jagner, Angew. Chem., Int. Ed., 2007, 46, 6678–6680.
- 3 D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman and T. T. Wenzel, *Science*, 2006, **312**, 714–719.
- 4 (a) D. A. Walker, T. J. Woodman, D. L. Hughes and M. Bochmann, Organometallics, 2001, 20, 3772–3776; (b) S. Milione, F. Grisi, R. Centore and A. Tuzi, Organometallics, 2006, 25, 266–274; (c) K. Yan, B. M. Upton, A. Ellern and A. D. Sadow, J. Am. Chem. Soc., 2009, 131, 15110–15111; (d) L. E. Garner, H. Zhu, M. L. Hlavinka, J. R. Hagadorn and E. Y. X. Chen, J. Am. Chem. Soc., 2006, 128, 14822–14823.
- W. N. Moulton, R. E. V. Atta and R. R. Ruch, J. Org. Chem., 1961, 26, 290–292; (b) B.-T. Ko, C.-C. Wu and C.-C. Lin, Organometallics, 2000, 19, 1864–1869; (c) Y.-C. Liu, B.-T. Ko, B.-H. Huang and C.-C. Lin, Organometallics, 2002, 21, 2066–2069; (d) C. R. Graves, H. Zhou, C. L. Stern and S. T. Nguyen, J. Org. Chem., 2007, 72, 9121–9133.
- 6 (a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, Angew. Chem., Int. Ed., 2006, 45, 1611–1614; (b) M.-H. Thibault, J. Boudreau, S. Mathiotte, F. Drouin, O. Sigouin, A. Michaud and F.-G. Fontaine, Organometallics, 2007, 26, 3807–3815; (c) F.-G. Fontaine, J. Boudreau and M.-H. Thibault, Eur. J. Inorg. Chem., 2008, 5439–5454; (d) E. Khaskin, P. Y. Zavalij and A. N. Vedernikov, J. Am. Chem. Soc., 2008, 130, 10088–10089; (e) A. Fischbach, P. R. Bazinet, R. Waterman and T. D. Tilley, Organometallics, 2008, 27, 1135–1139; (f) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, J. Am. Chem. Soc., 2008, 130, 16729–16738; (g) J. Boudreau and F.-G. Fontaine, Organometallics, 2011, 30, 511–519.
- 7 J. F. Dunne, K. Manna, J. W. Wiench, A. Ellern, M. Pruski and A. D. Sadow, *Dalton Trans.*, 2010, **39**, 641–653.
- 8 C. Mazet, V. Kohler and A. Pfaltz, Angew. Chem., Int. Ed., 2005, 44, 4888–4891.
- 9 (a) P. S. Pregosin, E. Martínez-Viviente and P. G. A. Kumar, *Dalton Trans.*, 2003, 4007–4014; (b) M. Valentini, P. S. Pregosin and H. Ruegger, *Organometallics*, 2000, **19**, 2551–2555.
- 10 D. Mukherjee, R. R. Thompson, A. Ellern and A. D. Sadow, *ACS Catal.*, 2011, **1**, 698–702.
- 11 The <sup>11</sup>B NMR spectrum of oligomeric PhB(Ox<sup>Me2</sup>)<sub>2</sub> in toluene is featureless at room temperature (see ref. 7), but in THF a signal is observed at -8.77 ppm for a monomeric THF-borane adduct.
- (a) J. G. Noltes and J. Boersma, J. Organomet. Chem., 1967, 9, 1–4;
   (b) F. F. Blicke and E.-P. Tsao, J. Am. Chem. Soc., 1953, 75, 3999–4002.
- 13 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, 32, 751.