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Frustrated Lewis Pairs beyond the Main Group: Cationic Zirconocene−Phosphinoaryloxide Complexes and Their Application in Catalytic Dehydrogenation of Amine Boranes

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Supporting Information

ABSTRACT: The cationic zirconocene−phosphinoaryloxide complexes $[Cp_2ZrOC_6H_4P(t\text{-Bu})_2][B(C_6F_5)_4]$ (**3**) and $[Cp^*{}_2ZrOC_6H_4P(t\text{-Bu})_2][B(C_6F_5)_4]$ (**4**) were synthesized by the reaction of Cp_2ZrMe_2 or $Cp^*{}_2ZrMe_2$ with 2-(diphenylphosphino)phenol followed by protonation with [2,6-di-*tert*-butylpyridinium]$[B(C_6F_5)_4]$. Compound **3** exhibits a Zr−P bond, whereas the bulkier Cp* derivative **4** was isolated as a chlorobenzene adduct without this Zr−P interaction. These compounds can be described as transition-metal-containing versions of linked frustrated Lewis pairs (FLPs), and treatment of **4** with H_2 under mild conditions cleaved H_2 in a fashion analogous to that for main-group FLPs. Their reactivity in amine borane dehydrogenation also mimics that of main-group FLPs, and they dehydrogenate a range of amine borane adducts. However, in contrast to main-group FLPs, **3** and **4** achieve this transformation in a catalytic rather than stoichiometric sense, with rates superior to those for previous high-valent catalysts.

Solution-phase combinations of sterically hindered (“frustrated”) Lewis acid−Lewis base pairs have been the subject of recent interest, not least because of the high latent reactivity of such species in the activation of small molecules, the reversible heterolytic cleavage of H_2 being the archetypal example.[1−3] The promise of such species lies in the possibility of metal-free catalysis, and catalytic hydrogenations of bulky imines, enamines,[4] and other specific substrates[5] have been reported. Numerous other interesting reactivity patterns[6] have been observed, including heterolytic cleavage of disulfides, reversible CO_2 binding[7] and reduction to methanol,[8,9] ring opening of cyclic ethers,[10] and amine borane dehydrogenation.[11] However, none of these transformations has been achieved in a catalytic sense, usually because the resulting products are too stable. We reasoned that replacing the Lewis acid component of such frustrated Lewis pairs (FLPs), usually a polyfluorinated aryl borane, with an electrophilic transition-metal center such as Zr(IV) might offer a solution to this drawback. Clearly, the implicit notional novelty of metal-free catalysis could not be claimed for such a zirconium−phosphine pair; however, combining the ability of transition-metal complexes in catalysis with the capability of FLPs to activate substrate molecules via ditopic activation offers exciting possibilities for exploiting new activation pathways and reactivity patterns in catalytic processes. Our approach[12] is mirrored in the activation of small molecules using a combination of a low-valent transition-metal center with a pendant Lewis acid function.[13] We report here the synthesis and structural characterization of cationic zirconocene−phosphinoaryloxide complexes that activate H_2. As a model catalytic reaction, we show that these complexes mediate dehydrogenation (dehydrocoupling) of amine borane adducts in a manner analogous to that for metal-free FLPs[11] and that in contrast to purely main-group FLPs, they achieve this transformation in a catalytic rather than stoichiometric sense.

We initially targeted a zirconocene species[14] with a 2-(di-*tert*-butylphosphino)phenoxide ligand, reasoning that this would incorporate favorable design features such as a strong Zr−O bond and an intramolecular phosphine donor that could serve as a potent but sterically encumbered Lewis base. We recently described related phosphino−borinate ester Lewis pairs.[15] The neutral complex $[Cp_2Zr(Me)OC_6H_4P(t\text{-Bu})_2]$ was prepared by reaction of the previously reported[16] $HOC_6H_2P(t\text{-Bu})_2$ with Cp_2ZrMe_2 (Scheme 1) in hexanes under ambient conditions. The novel compound **1** was isolated as an analytically pure, air- and moisture-sensitive crystalline solid in high yield (89%). The phosphine showed no sign of coordination to the zirconium center, as evidenced by NMR spectroscopy [see the Supporting Information (SI)].[17,18] In an entirely analogous fashion, the bulkier pentamethylcyclopentadienyl (Cp*) derivative **2** was obtained in 90% yield.

We next sought to access the base-free cationic complexes **3** and **4** by protonolysis of the remaining methyl ligand. Reaction of equimolar quantities of **1** and $[DTBP][B(C_6F_5)_4]$ (DTBP = 2,6-di-*tert*-butylpyridinium) in fluorobenzene (Scheme 1) instantaneously resulted in a bright-yellow solution. ^{31}P NMR spectroscopy revealed that protonation of the pendant phosphine preceded protonation of the methyl ligand, as evidenced by a characteristic doublet at 23.8 ppm with $J = 478$ Hz. Large orange crystals of **3** grown from a layered fluorobenzene/hexane solution at room temperature were used for structure determination (Figure 1).

Complex **3** displays the expected pseudotetrahedral geometry at Zr and a distorted five-membered ring. Noteworthy is the presence of a Zr−P bond, although at 2.8826(5) Å it is long for a Zr(IV)−alkylphosphine bond {e.g., 2.693(4) Å for $[Cp_2Zr(\eta^2\text{-py})PMe_3][BPh_4]$}[19] From the large downfield shift in the ^{31}P NMR spectrum relative to **1** and the lack of observable evidence for coordinated fluorobenzene in the ^{19}F NMR spectrum, it appears that the Zr−P interaction persists in solution, even at temperatures up to 80 °C. We note that there are other examples of main-group FLPs that exhibit the characteristic reactivity but for which structural characterization

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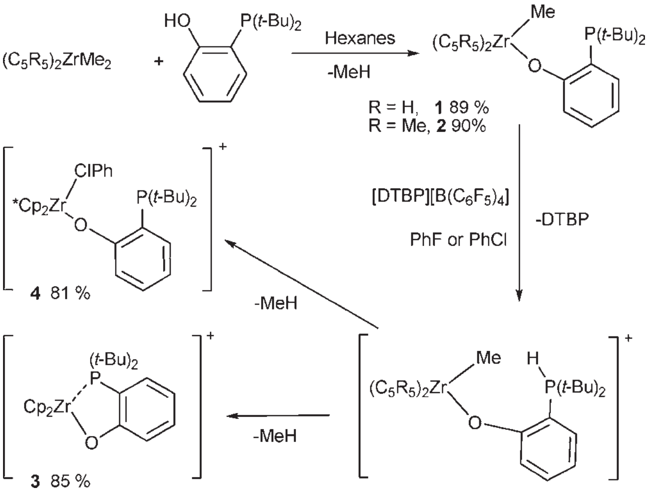
Scheme 1. Synthesis of Compounds 3 and 4



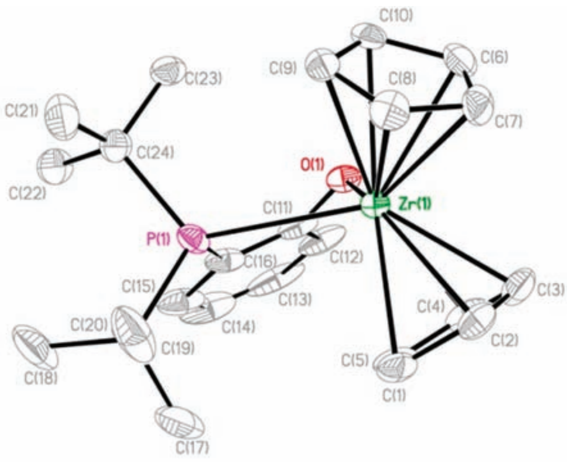
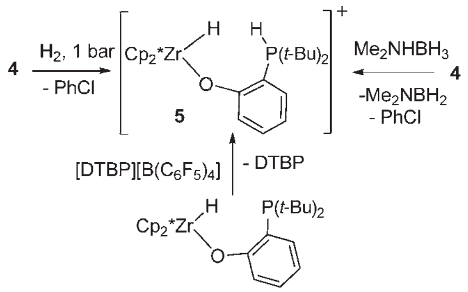


Figure 1. ORTEP representation of the molecular structure of **3**. All H atoms and the borate anion have been omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1−O1, 1.9972(13); Zr1−P1, 2.8826(5); C16−P1, 1.816(2); O1−C11, 1.360(3); O1−Zr1−C11, 124.51(11); O1−Zr1−P1, 70.18(4).

revealed a persistent Lewis acid−base bond.[20,21] With a similar protocol, protonolysis of **2** with $[DTBP][B(C_6F_5)_4]$ in chlorobenzene afforded an orange solution. In this case, a ^{31}P NMR resonance at 7.0 ppm suggested the absence of a Zr−P interaction, and other spectroscopic and elemental analysis data indicated a chlorobenzene adduct. This is a result of the substantially bulkier Cp* ligands, which we presume make the related Zr−P species too sterically congested.

In many ways, the "standard" reaction of main-group FLPs is the heterolytic cleavage of H_2, and we were keen to evaluate the behavior of **3** and **4** in this regard. While compound **3** did not react with 1 bar H_2 at 25 °C, **4** rapidly cleaved H_2 in a heterolytic fashion[1] across the Zr and P centers to give Zr−H phosphonium complex **5** in high (93% isolated) yield (Scheme 2). This reactivity is related to that of certain hydrogenation catalysts,[22] where in particular H_2 addition across Ru−N bonds (i.e., with N acting as an internal base) is well-established.

Scheme 2. Dihydrogen Activation by 4



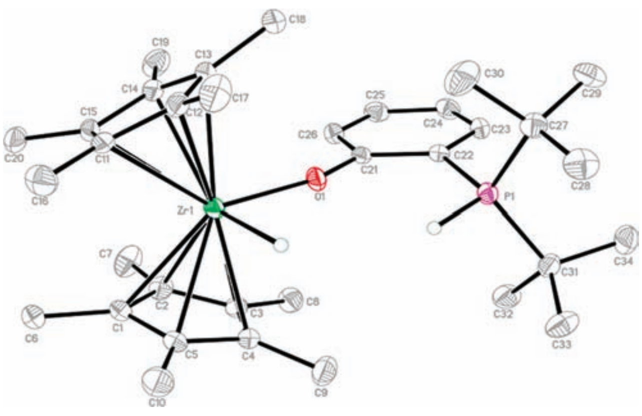


Figure 2. ORTEP representation of the molecular structure of **5**. The borate anion and H atoms except for Zr−H and P−H have been omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1−H1, 2.23(1); Zr1−O1, 2.038(2); C21−O1, 1.324(4); H1−Zr1−O1, 87.8(4); Zr1−O1−C21, 158.8(2).

Compound **5** was also obtained when the neutral complex $[Cp^*_2Zr(H)OC_6H_4P(t\text{-}Bu)_2]$ (Scheme 2; also see the SI) was treated with 1 equiv of $[DTBP][B(C_6F_5)_4]$. Crystals of **5** suitable for X-ray diffraction were grown from a chlorobenzene solution layered with hexane, and the obtained structure is shown in Figure 2. Although the hydride was not unambiguously located by X-ray crystallography, its presence was supported by NMR analysis,[23] the results of the independent synthesis (Scheme 2), and deuterium-labeling experiments (see the SI for detailed discussion). Despite the apparent chemical similarity between **5** and the intermediate $[Cp^*_2Zr(Me)OC_6H_4PH(t\text{-}Bu)_2]$ (Scheme 1), **5** was resistant to the reverse reaction (i.e., intramolecular protonolysis) even at elevated temperatures (1 week, 120 °C) but immediately liberated H_2 upon addition of THF or CH_2Cl_2.

With these promising initial results, we investigated utilizing **3** and **4** for the dehydrogenation (dehydrocoupling) of a series of amine borane adducts **A**−**C** (Figure 3). This reaction has attracted significant attention because of the potential for use of amine borane as a hydrogen storage material and as a controlled route to new inorganic polymers.[24] It is also an ideal test reaction in that it is known only in a stoichiometric sense for main-group FLPs[11] and, despite numerous other transition-metal-based catalysts,[25−33] is at best extremely sluggish (reaction over the course of weeks) for high-valent Zr(IV) systems.[34] When a fluorobenzene solution of complex **3** was treated with 10 equiv of dimethylamine borane (**A**), the evolution of H_2 was observed, and the expected dehydrocoupling reaction proceeded smoothly

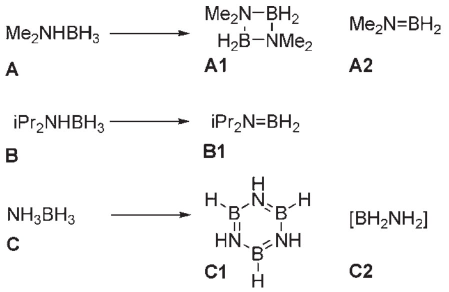


Figure 3. Amine borane dehydrogenation.

in the presence of 1 mol % **3** to give 100% conversion of **A** after only 10 min at room temperature. ^{11}B NMR analysis of the reaction mixture revealed nearly quantitative conversion to the cyclic dimer **A1** along with small quantities (8−10% yield)[35] of **A2**, which slowly converted into **A1**. In contrast to the Cp_2TiCl_2/*n*-BuLi system reported by Manners and co-workers,[36] none of the linear dimer was observed at any point during the reaction. The activity of our catalyst [in this case, a turnover frequency (TOF) of 600 h^{-1}] was exceptional in comparison with all known group 4 systems.[37] Compound **4** facilitated the same catalytic reaction, although the reaction was more sluggish in this case, affording 99% yield after 8.5 h with a catalyst loading of 5 mol %. The isostructural Hf analogue of **3** (for full details, see the SI) was also active (99% yield after 1 h at 1% catalyst loading). Encouraged by these results, we repeated the experiment with diisopropylamine borane and 5 mol % **3**. ^{11}B NMR analysis of the reaction mixture after 3 h showed 100% conversion to the previously reported dehydrocoupled aminoborane **B1**.[37] Repeating the reaction with 1 mol % **3** gave **B1** in 100% yield after 19 h. To complete the series, we investigated the utility of **3** and **4** in the catalytic dehydrocoupling of ammonia borane (**C**). Treatment of **C** with 5 mol % **3** or **4** gave traces (~5%) of borazene (**C1**) and products consistent with polymers **C2** of the type $(BH_2NH_2)_n$.[25] When the same reaction was carried out in the presence of a 10-fold excess of cyclohexene relative to **C**, 50% conversion to the trapped hydroboration product Cy_2BNH_2 was observed, suggesting the intermediacy of monomeric H_2BNH_2.[38] It is noteworthy that the existing group 4 catalyst Cp_2TiCl_2/*n*-BuLi is completely inactive toward **C**.

In an effort to probe the catalytic cycle, we carried out the stoichiometric reaction of **3** with the fully deuterated isotopomer of **A** ($\mathbf{A_D}$).[39] $^{11}B\{^1H\}$, $^{31}P\{^1H\}$, and ^{2}H NMR analysis of the reaction mixture immediately after mixing (~5 min) revealed only **3**, $\mathbf{A1_D}$, $\mathbf{A2_D}$, and D_2. Adding a further 10 equiv gave after 10 min >99% conversion to $\mathbf{A1_D}$ and $\mathbf{A2_D}$, **3**, and traces of a species with a singlet resonance at 8.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum, which we attributed to the σ-complex intermediate $[Cp_2Zr(D_3BNDMe_2)OC_6H_4P(t\text{-}Bu)_2]^+$. Carrying out an analogous set of experiments with **4** and $\mathbf{A_D}$ gave only $\mathbf{5_D}$,[40] $\mathbf{A1_D}$, and $\mathbf{A2_D}$. Approximately 1 h after treatment with a further 10 equiv of $\mathbf{A_D}$, the ^{31}P NMR spectrum showed only a singlet resonance at 8.0 ppm, while the ^{11}B NMR spectrum showed ~75% conversion to $\mathbf{A1_D}$ and a broad resonance at −14.0 ppm,[41] which we again attributed to the intermediate $[Cp^*_2Zr(D_3BNDMe_2)OC_6H_4P(t\text{-}Bu)_2]^+$. After 16 h, $\mathbf{5_D}$ and $\mathbf{A1_D}$ were the only species observable by NMR analysis. Because of the inherent reactivity of complexes **3** and **4** with **A**, only tentative spectroscopic evidence for the σ-complex adducts could be obtained. We reasoned that the use of Me_3NBH_3, which cannot undergo dehydrogenation, would allow isolation of compounds structurally similar to the proposed intermediates, as demonstrated by Weller and co-workers.[32] Although **3** showed no reaction with Me_3NBH_3 at room temperature,[42] **4** reacted immediately, and the desired complex $[Cp^*_2Zr(H_3BNMe_3)OC_6H_4P(t\text{-}Bu)_2][B(C_6F_5)_4]$ (**6**) was isolated in nearly quantitative yield. The structure of **6** is shown in Figure 4. The intermediacy of both **5** and **6** in the catalytic cycle is supported by the fact that each acts as a catalyst for the transformation of **A** to **A1**.

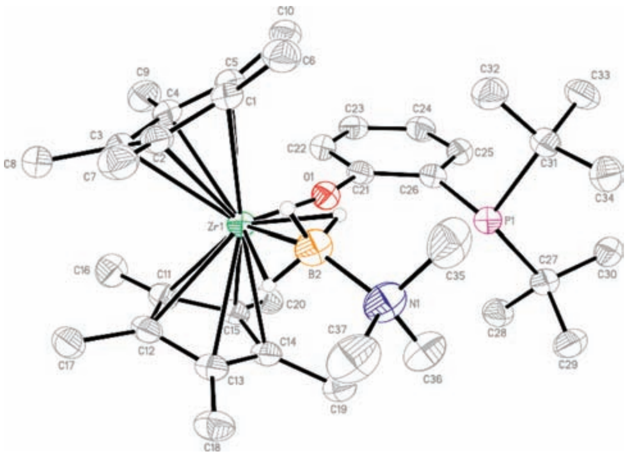
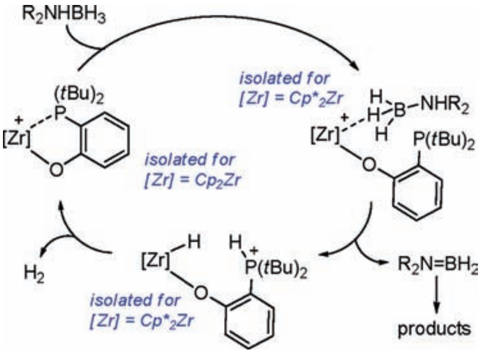


Figure 4. ORTEP representation of the molecular structure of **6**. The borate anion and H atoms except B−H have been omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1−H38A, 2.23(2); Zr1−H38B, 2.31(2); Zr1−H38C, 3.32(3); Zr1−B2, 2.728(3); Zr1−O1, 1.983(2); B2−N1, 1.588(3). C21−O1−Zr1, 160.1(1); O1−Zr1−H38A, 116.0(6); O1−Zr1−H38B, 78.1(6); O1−Zr1−H38C, 110.0(5).

Scheme 3. Proposed Catalytic Cycle



On the basis of these experiments, we propose that the catalysis proceeds as depicted in Scheme 3. Despite the superficial similarity of previous group 4 metallocene catalysts for amine borane dehydrogenation, our catalysts are fundamentally different. Catalysts based on titanocene fragments have been shown in detailed mechanistic studies[36] to be based on Ti(II) species formed either in situ from Cp_2TiCl_2/*n*-BuLi or as well-defined $Cp_2Ti(PMe_3)_2$ complexes. Catalysis then proceeds via a metal-centered oxidative addition (to yield Cp_2TiH_2)/reductive elimination manifold. In contrast to these highly active titanium systems, the analogous zirconium species exhibited at best only very low activity, requiring high catalyst loadings and extended reaction times to achieve even modest conversion (e.g., 65% conversion of **A** after 20 h with

10 mol % catalyst), while the Hf system was found to be totally inactive.[36] In our systems, only high-valent zirconium is present, and our observations point to a mechanism similar to that of the stoichiometric dehydrogenation with the metal-free Lewis pair $P(t\text{-}Bu_3)/B(C_6F_5)_3$,[11,43] with the crucial difference that H_2 elimination is facile under these conditions, regenerating the active catalyst and leading to catalytic turnover (Scheme 3). All of the illustrated intermediates were observed and structurally characterized. Critically, the essential nature of the phosphine fragment was highlighted when we attempted the dehydrogenation of **A** using the known complex $[Cp_2ZrOR][B(C_6F_5)_4]$ (R = *t*-Bu).[44] Even with loadings of this species as high as 50 mol %, no detectable quantities of **A1** or **A2** were observed by ^{11}B NMR analysis.

In conclusion, we have synthesized cationic zirconocene—phosphinoaryloxide complexes that under various conditions activate H_2 and dehydrogenate amine boranes. We suggest that drawing an analogy between our systems and frustrated Lewis pairs is useful. Although much of the previous literature highlights the metal-free nature of FLPs, we see value in extending this concept to frustrated combinations of electrophilic transition-metal species and Lewis bases. Certainly, all of the reactivity we have observed is well-described as FLP chemistry, with the crucial addition that our systems achieve amine borane dehydrogenation in a catalytic sense.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, selected NMR spectra, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.

(2) Stephan, D. W.; Ullrich, M. *J. Am. Chem. Soc.* **2009**, *131*, 52.

(3) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskel, M.; Repo, T.; Pyykk, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117.

(4) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Froehlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543.

(5) Kirill, V.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2009**, *28*, 5148.

(6) For a comprehensive review of FLP reactivity, see: Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46.

(7) Moemming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643.

(8) Menard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796.

(9) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839.

(10) Birkmann, B.; Voss, T.; Geier, S. J.; Ullrich, M.; Kehr, G.; Erker, G.; Stephan, D. W. *Organometallics* **2010**, *29*, 5310.

(11) Miller, A. J. M.; Bercaw, J. E. *Chem. Commun.* **2010**, *46*, 1709.

(12) During the preparation of this manuscript, N_2O activation by a nonlinked zirconocene phosphine Lewis pair was reported. See: Neu, R. C.; Otten, E.; Lough, A.; Stephan, D. W. *Chem. Sci.* **2011**, *2*, 170.

(13) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 11874. Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2010**, *132*, 3301.

(14) Complexes of the type $Cp_2Zr(X)CH_2PPh_2$ are known. See: Schore, N. E.; Young, S. J.; Olmstead, M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.

(15) Chapman, A.; Haddow, M. F.; Orton, J. P. H.; Wass, D. F. *Dalton Trans.* **2010**, *39*, 6184.

(16) Bornand, M.; Torker, S.; Chen, P. *Organometallics* **2007**, *26*, 3585.

(17) Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449.

(18) Miguel, L.; Basso-Bert, M.; Choukroun, R.; Madhouni, R.; Eichhorn, B.; Sanchez, M.; Mazières, M.; Jaud, J. *J. Organomet. Chem.* **1995**, *490*, 21.

(19) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546.

(20) Erker, G.; Kehr, G.; Bergander, K.; Frohlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072.

(21) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476.

(22) For example, see: Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201.

(23) Hoskin, A. J.; Stephan, D. W. *Organometallics* **2000**, *19*, 2621.

(24) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279.

(25) Sloan, M. E.; Clark, T. J.; Manners, I. *Inorg. Chem.* **2009**, *48*, 2429.

(26) Templeton, A. C.; Wuelfing, M. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 2.

(27) Jiang, Y.; Berke, H. *Chem. Commun.* **2007**, 3571.

(28) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Organometallics* **2009**, *28*, 5493.

(29) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844.

(30) Friedrich, A.; Drees, M.; Schneider, S. *Chem.—Eur. J.* **2009**, *15*, 10339.

(31) Kawano, Y.; Uruichi, M.; Shimoi, M.; Taki, S.; Kawaguchi, T.; Kakizawa, T.; Ogino, H. *J. Am. Chem. Soc.* **2009**, *131*, 14946.

(32) Douglas, T. M.; Chaplin, A. B.; Weller, A. S.; Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2009**, *131*, 15440.

(33) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776.

(34) Pun, D.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2007**, 3297.

(35) We also detected traces (<1% yield) of $Me_2NB(H)NMe_2$ ($^{11}B\{^1H\}$ NMR: 27.8 ppm) and $[H_2B(\mu\text{-}H)(\mu\text{-}NMe_2)BH_2]$ ($^{11}B\{^1H\}$ NMR: −19.0 ppm). See: Whittell, G. R.; Balmond, E. I.; Robertson, A. P. M.; Patra, S. K.; Haddow, M. F.; Manners, I. *Eur. J. Inorg. Chem.* **2010**, 3967.

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

(37) Staubitz, A.; Robertson, A. P.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, *110*, 4023.

(38) Shrestha, R. P.; Diyabalanage, H. V. K.; Semelsberger, T. A.; Ott, K. C.; Burrell, A. K. *Int. J. Hydrogen Energy* **2009**, *34*, 2616.

(39) The deuterated analogue of **A1** (**A1**$_\mathbf{D}$) reduced the reaction rate and facilitated the unambiguous observation of $[P{-}D]^+$ intermediates.

(40) Unlabeled **5** was also present as a result of incomplete deuteration of **A**$_\mathbf{D}$.

(41) The $^{11}B\{^1H\}$NMR spectrum attributed to $[Cp^*{}_2Zr(D_3BNDMe_2)OC_6H_4P(t\text{-}Bu)_2]$ coincided with the resonance for unreacted **A**$_\mathbf{D}$, but a small shift and accompanying broadened line shape were also observed for the related compound **6** relative to free Me_3NBH_3 (see the SI).

(42) We attribute the lack of reaction to the presence of the Zr—P bond and noticed related trends; for example, while **4** reacted instantly with NEt_3, **3** required extended reaction times and elevated temperatures (80 °C, 1 week).

(43) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880.

(44) Stoebenau, E. J.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 8162.