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Synthesis of *Bis*(2-pyridylthio)methyl Zinc Hydride and Catalytic Hydrosilylation and Hydroboration of CO₂

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The reactions of *bis*(2-pyridylthio)methane with Me₂Zn and Zn[N(SiMe₃)₂]₂ afford [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂, thereby providing access to a variety of other [Bptm]ZnX derivatives, including the zinc hydride complex [Bptm]ZnH, which serves as a catalyst for the reduction of CO₂ and other carbonyl compounds *via* hydrosilylation and hydroboration.

Although the ubiquity of carbon dioxide prompts its use as a renewable C₁ source for the synthesis of value-added organic chemicals, the utility of CO₂ is hampered by its thermodynamic stability and kinetic resistance to undergo transformations. As such, there is considerable interest in developing catalytic processes for converting CO₂ into more useful compounds, especially systems in which the catalysts feature nonprecious metals. Therefore, we describe here the synthesis of a zinc hydride compound and its ability to serve as a catalyst for both the hydrosilylation and hydroboration of CO₂. Such studies complement systems that are devoid of a Zn–H bond.¹

We previously described the use of the tripodal tris(pyrazolyl)hydroborato ligand system to enable the isolation of the first monomeric terminal hydride complex of zinc, namely [Tp^{Bu^t}]ZnH, and a variety of other [Tp^{R,R'}]ZnX and related derivatives.² Subsequently, we demonstrated that the *tris*(2-pyridylthio)methyl ligand, [Tptm], could also afford a terminal zinc hydride complex and other [Tptm]ZnX derivatives but, in contrast to the [Tp^{R,R'}]ZnX system, the [Tptm] ligand may coordinate *via* either two or three nitrogen donors, depending upon the identity of X.³ For example, while the hydride complex, [Tptm]ZnH, exhibits coordination *via* only two pyridyl donors, the formate derivative, [Tptm]ZnO₂CH, exhibits coordination *via* three pyridyl groups (Fig. 1). Since this variability in coordination mode of the [Tptm] ligand could influence reactivity, we considered it pertinent to investigate a related system that possesses only two pyridyl donors. Therefore, we sought to utilize *bis*(2-pyridylthio)methane

([Bptm]H) to afford a zinc hydride complex, [Bptm]ZnH, and examine its reactivity and catalytic applications.

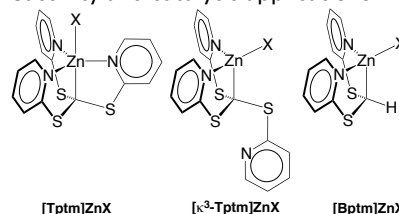
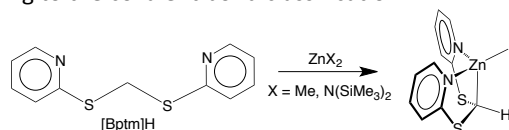


Fig. 1 Coordination of [Tptm] and [Bptm] ligands.

Access to [Bptm]ZnX complexes is provided *via* the reactions of [Bptm]H⁴ with Me₂Zn and Zn[N(SiMe₃)₂]₂ to yield [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂, respectively (Scheme 1). The molecular structures of [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂ (Fig. 2) have been determined by X-ray diffraction, which demonstrate that the [Bptm] ligand coordinates with a κ³-mode and serves as a L₂X ligand according to the covalent bond classification.⁵



Scheme 1 Access to [Bptm]ZnX compounds

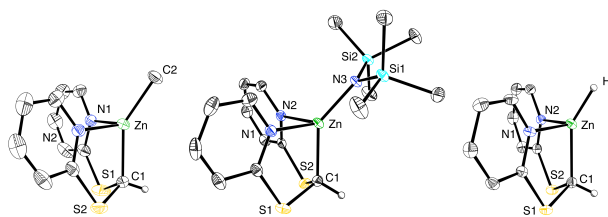


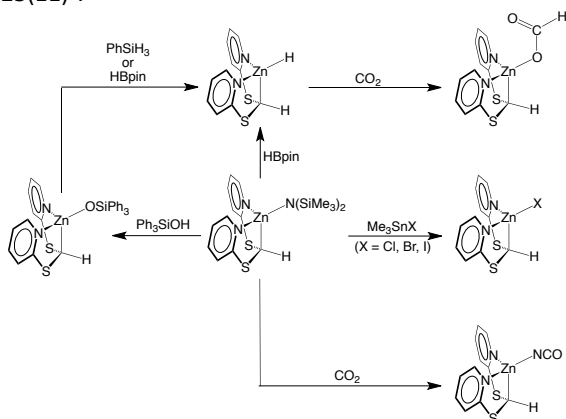
Fig. 2 Molecular structures of [Bptm]ZnX (X = Me, N(SiMe₃)₂, H)

As anticipated, the coordination geometries of [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂ closely resemble those of [κ³-Tptm]ZnX derivatives.^{3a} For example, the Zn–C [2.057(4) Å] and Zn–N [2.119(3) Å and 2.120(3) Å] bond lengths associated with the [Bptm] ligand of [Bptm]ZnMe are comparable to the respective values for [κ³-Tptm]ZnMe [2.098(2) Å, 2.077(2) Å and 2.101(2) Å, respectively].

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The most interesting aspect of the structures of [Bptm]ZnX, however, is the presence of the Zn–C bonds. Specifically, although [Bptm]H has been employed to synthesize a variety of complexes, the products obtained are almost exclusively of the type $\{\kappa^2\text{-[Bptm]H}\}\text{MX}_2$, in which the ligand serves as an L_2 donor such that the compounds are devoid of an M–C bond.^{6,7} Thus, while the Zn–N bond lengths of [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂ are similar to those in $\{\kappa^2\text{-[Bptm]H}\}\text{ZnX}_2$ complexes, the Zn–C distances are very different; for example, the Zn–C_[Bptm] bond length of [Bptm]ZnMe [2.057(4) Å] is much shorter than the nonbonded Zn•••C distance within $\{\kappa^2\text{-[Bptm]H}\}\text{ZnX}_2$ [3.79 Å – 3.87 Å].^{6c,d} Accompanying this variation in Zn•••C distances, the [Bptm] and $\{\text{[Bptm]H}\}$ ligands adopt different conformations of the pyridyl groups such that the N–Zn–N bond angles for [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂ are significantly smaller than those for $\{\kappa^2\text{-[Bptm]H}\}\text{ZnX}_2$. As an illustration, the N–Zn–N bond angle for [Bptm]ZnMe is 99.51(10)° whereas the corresponding values for $\{\kappa^2\text{-[Bptm]H}\}\text{ZnX}_2$ derivatives are in the range 122.87(16)° – 125.23(11)°.^{6c,d}



Scheme 2. Synthesis and reactivity of [Bptm]ZnH

[Bptm]ZnN(SiMe₃)₂ provides access to a variety of other [Bptm]ZnX derivatives (Scheme 2). For example, [Bptm]ZnN(SiMe₃)₂ undergoes metathesis with Ph₃SiOH to afford the siloxide, [Bptm]ZnOSiPh₃, and with Me₃SnX (X = Cl, Br, I) and Me₃SiX (X = Cl, Br, I) to afford the corresponding halide derivatives, [Bptm]ZnX. The molecular structures of [Bptm]ZnX (X = Cl, Br, I, NCO, OSiPh₃) have been determined by X-ray diffraction and the structure of [Bptm]ZnOSiPh₃ is not only of interest because there are few structurally characterized zinc compounds with a terminal triphenylsiloxide ligand, but also because the Zn–O–SiPh₃ bond angle [135.09(9)°] is the smallest reported,⁸ with some examples possessing an almost linear motif.⁹ Moreover, terminal trimethylsiloxide zinc complexes are also typically linear,¹⁰ with an average Zn–O–Si bond angle of 171.75° for structurally characterized compounds listed in the Cambridge Structural Database (CSD).¹¹

In addition to simple metathesis reactions, the Zn–N bond is also subject to insertion of CO₂ to generate the isocyanate derivative [Bptm]ZnNCO (Scheme 2) via a sequence that is proposed to occur *via* the initial insertion of CO₂ into the Zn–N(SiMe₃)₂ bond.¹² The most significant reactivity of [Bptm]ZnN(SiMe₃)₂, however, is that it enables the synthesis of

the zinc hydride complex, [Bptm]ZnH, upon treatment with pinacolborane (HBpin) at room temperature. The formation of [Bptm]ZnH by the use of HBpin is of note because Zn–N(SiMe₃)₂ bonds are not typically cleaved by hydrosilanes at room temperature to afford terminal hydride compounds; for example, elevated temperatures are employed to achieve the reaction of Zn[N(SiMe₃)₂]₂ with PhSiH₃ in the presence of IPr.¹³ Thus, the metathesis of Zn–N(SiMe₃)₂ bonds with HBpin provides a new approach for the synthesis of terminal zinc hydride compounds that complements the methods currently employed.¹⁴ In addition to metathesis of [Bptm]ZnN(SiMe₃)₂ with HBpin, [Bptm]ZnH can also be obtained *via* the reactions of [Bptm]ZnOSiPh₃ with either PhSiH₃ or HBpin.

The hydride complex [Bptm]ZnH has been characterized structurally by X-ray diffraction (Fig. 2) in two different crystallographic forms and the average Zn–H bond length (1.55 Å) is comparable to the mean value of structurally characterized compounds listed in the CSD.¹¹ Spectroscopically, [Bptm]ZnH is identified by a signal at δ 5.48 in the ¹H NMR spectrum and an absorption at 1742 cm⁻¹ in the IR spectrum.

As expected, the Zn–H bond of [Bptm]ZnH is reactive and undergoes metathesis reactions with Me₃SiX (X = NCO, Cl, Br, I) and Me₃SnX (X = Cl, Br, I) to afford [Bptm]ZnX (X = NCO, Cl, Br, I). In addition, [Bptm]ZnH undergoes insertion of CO₂ to afford the formate complex, [Bptm]ZnO₂CH.¹⁵ The formate ligand is known to coordinate to zinc *via* both bridging and terminal modes,¹⁶ and X-ray diffraction (Fig. 3) clearly demonstrates that [Bptm]ZnO₂CH adopts the latter motif. Furthermore, consideration of the Zn–O distances indicates that the formate ligand coordinates in a monodentate rather than bidentate mode. Specifically, the Zn–O distances of 1.941 Å and 2.846 Å differ by 0.905 Å, which is much greater than the minimum threshold of 0.60 Å for assigning monodentate coordination.^{17–19}

In this regard, the formate ligand of the [Tptm]ZnO₂CH counterpart, with a difference of 0.634 Å exhibits a greater degree of bidentate character, despite the fact that the [Tptm] ligand coordinates *via* three pyridyl groups.

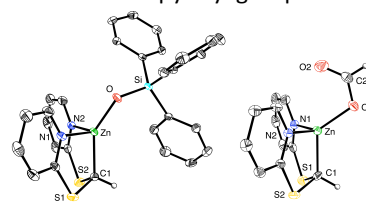
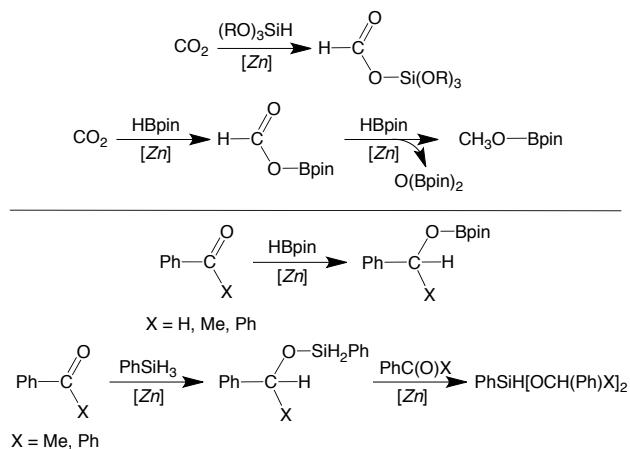


Fig. 3 Molecular structures of [Bptm]ZnOSiPh₃ and [Bptm]ZnO₂CH

Monomeric terminal zinc hydride compounds^{2,14} are an interesting class of molecules that have relevance for providing catalytic systems that are distinct from the multifarious roles played by zinc centers in biological systems in which the zinc centers typically serve as Lewis acids. Therefore, we have investigated the catalytic applications of [Bptm]ZnH with respect to reduction reactions. In this regard, the reduction of CO₂ is an important objective, not only because it facilitates its use as a renewable C₁ source for the synthesis of value-added organic chemicals, but also because it contributes to abating the increasing levels of carbon dioxide in the atmosphere.^{20,21}

However, since the reduction of CO₂ to formic acid by addition of the H–H bond is thermodynamically unfavorable, we have investigated hydrosilylation for which the addition of the Si–H bond is favorable.²²



Scheme 3. Hydrosilylation and hydroboration of CO₂ and carbonyl compounds catalyzed by [Bptm]ZnH

Significantly, [Bptm]ZnH serves as a catalyst for the hydrosilylation of CO₂ by (RO)₃SiH (R = Me, Et) to afford the silyl formate, HCO₂Si(OR)₃ (Scheme 3). However, since the transformation requires elevated temperatures, we investigated another approach to reduce CO₂ and have discovered that [Bptm]ZnH catalyzes the room temperature hydroboration of CO₂ by HBpin to afford HCO₂Bpin (TOF = 0.43 h⁻¹). This transformation is noteworthy because, in contrast to hydrosilylation,²³ the use of zinc hydride complexes as catalysts for the hydroboration of CO₂ has received very little attention,^{24,25} with there being only two reports of the use of zinc catalysts for the selective formation of HCO₂Bpin.^{24a,b,26} Furthermore, the observation emphasizes that hydroboration of CO₂ is more facile than hydrosilylation, which is significant because there are few such direct comparisons of hydroboration and hydrosilylation of CO₂.^{27,28} Undoubtedly, the availability of a 2p orbital on the three-coordinate boron of HBpin provides means to coordinate to a formate oxygen atom,²⁹ and thereby facilitate Zn–O/B–H bond metathesis.

In addition to reducing CO₂ to the formic acid level, it is also possible to reduce it to the methanol level. Specifically, upon removing the CO₂ atmosphere, the formate compound HCO₂Bpin reacts further with HBpin to form the methoxy derivative MeOBpin, accompanied by formation of O(Bpin)₂ (Scheme 3). In this regard, the zinc formate complex [Bptm]ZnO₂CH also reacts with HBpin at room temperature to form the methoxy derivative, MeOBpin. The formation of MeOBpin is postulated to occur *via* a sequence that involves the reaction of [Bptm]ZnO₂CH with HBpin to form a borylacetate derivative, [Bptm]ZnOCH₂O(Bpin), which, in the presence of excess HBpin, transforms to MeOBpin and the zinc borate ester, [Bptm]ZnOBpin; subsequent metathesis of [Bptm]ZnOBpin with HBpin would regenerate [Bptm]ZnH and release O(Bpin)₂.^{30,31}

In addition to hydroboration of CO₂, [Bptm]ZnH also catalyzes the hydroboration of carbonyl compounds,^{25b} namely PhCHO, Ph₂CO, and PhC(O)Me.³² While not common, there is

precedent for the use of zinc compounds as catalysts for such transformations.³³

Significantly, these hydroboration reactions catalyzed by [Bptm]ZnH are also more facile than corresponding hydrosilylation reactions.^{33a} For example, addition of Ph₂CO to a mixture of HBpin and PhSiH₃ in the presence of [Bptm]ZnH results in the initial formation of Ph₂CH(OBpin), followed by slower formation of PhSiH₂(OCHPh₂) and PhSiH(OCHPh₂)₂.³⁴

In summary, the reactions of *bis*(2-pyridylthio)methane with Me₂Zn and Zn[N(SiMe₃)₂]₂ afford [Bptm]ZnMe and [Bptm]ZnN(SiMe₃)₂, which thereby provide access to a variety of other [Bptm]ZnX derivatives. Of particular relevance, the reaction of [Bptm]ZnN(SiMe₃)₂ with HBpin produces [Bptm]ZnH, which is a new approach for synthesizing zinc hydride compounds. The Zn–H bond of [Bptm]ZnH is reactive towards a variety of substrates, which thereby provides a means for it to serve as a catalyst for the reduction of CO₂ and other carbonyl compounds *via* hydrosilylation and hydroboration, with the latter being more facile.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

- (1) (a) Revunova, K.; Nikonov, G. I. *Dalton Trans.*, **2015**, *44*, 840. (b) Kostera, K.; Peruzzini, M.; Gons, L. *Catalysts* **2021**, *11*, 58.
- (2) (a) Han, R.; Gorrell, I. B.; Looney, A. G.; Parkin, G. *J. Chem. Soc. Chem. Commun.* **1991**, 717. (b) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274. (c) Rauch, M.; Rong, Y.; Sattler, W.; Parkin, G. *Polyhedron* **2016**, *103*, 135. (d) Kreider-Mueller, A.; Quinlivan, P. J.; Rauch, M.; Owen, J. S.; Parkin, G. *Chem. Commun.* **2016**, *52*, 2358.
- (3) (a) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2011**, *133*, 9708. (b) Sattler, W.; Parkin, G. *Chem. Sci.* **2012**, *3*, 2015. (c) Sattler, W.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2013**, *135*, 18714.
- (4) de Castro, V. D.; de Lima, G. M.; Filgueiras, C. A. L.; Gambardella, M. T. P. *J. Mol. Struct.* **2002**, *609*, 199.
- (5) Green, M. L. H.; Parkin, G. *J. Chem. Educ.* **2014**, *91*, 807.
- (6) (a) Lago, A. B.; Amoedo, A.; Carballo, R.; García-Martínez, E.; Vázquez-López, E. M. *Dalton Trans.* **2010**, *39*, 10076. (b) Amoedo-Portela, A.; Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Sanchez-Gonzalez, A.; Sordo, J.; Vazquez-Lopez, E. M. *Polyhedron* **2003**, *22*, 1077. (c) Amoedo-Portela, A.; Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Sanchez-Gonzalez, A.; Sordo, J.; Vazquez-Lopez, E. M. *Main Group Met. Chem.* **2002**, *25*, 311. (d) Amoedo-Portela, A.; Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Gomez-Alonso, C.; Sanchez-Gonzalez, A.; Sordo, J.; Vazquez-Lopez, E. M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 939.

- (7) Indeed, there is only one report of a κ^3 -derivative, namely [Bptm]PdOAc(HOAc). See: Halder, P.; SantaLucia, D. J.; Park, S. V.; Berry, J. F. *Inorg. Chem.* **2019**, *58*, 2270.
- (8) For another compound with a small Zn–O–SiPh₃ bond angle, see: Feng, G.; Du, C.; Xiang, L.; del Rosal, I.; Li, G.; Leng, X.; Chen, E. Y. X.; Maron, L.; Chen, Y. *ACS Catal.* **2018**, *8*, 4710.
- (9) For example, Zn–O–Si = 172.35(9)°. See Ballmann, G.; Martin, J.; Langer, J.; Farber, C.; Harder, S. *Z. Anorg. Allg. Chem.* **2020**, *646*, 593.
- (10) Ruccolo, S.; Sattler, W.; Rong, Y.; Parkin, G. *J. Am. Chem. Soc.* **2016**, *138*, 14542.
- (11) Cambridge Structural Database (CSD version 5.42). Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Cryst.* **2016**, *B72*, 171.
- (12) For other examples of the formation of isocyanate compounds derived from the insertion of CO₂ into the M–N(SiMe₃)₂ bond of main group compounds, see reference 3a and (a) Hammond, M.; Rauch, M.; Parkin, G. *J. Am. Chem. Soc.* **2021**, *143*, 10553. (b) Rong, Y.; Parkin, G. *Aust. J. Chem.* **2013**, *66*, 1306 (c) Chakrabarti, N.; Ruccolo, S.; Parkin, G. *Inorg. Chem.* **2016**, *55*, 12105.
- (13) Roberts, A. J.; Clegg, W.; Kennedy, A. R.; Probert, M. R.; Robertson, S. D.; Hevia, E. *Dalton Trans.* **2015**, *44*, 8169.
- (14) (a) Sadow, A. D. *Comp. Coord. Chem. III*, Chapter 3.06; Constable, E. C.; Parkin, G.; Que, L., Jr. (Eds.) Elsevier, 2021. (b) Wiegand, A. K.; Rit, A.; Okuda, J. *Coord. Chem. Rev.* **2016**, *314*, 71. (c) Roy, M. M. D.; Omana, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021**, *121*, 12784–12965.
- (15) For other examples of insertion of CO₂ into a Zn–H bond, see reference 14.
- (16) Sattler, W.; Shlian, D. G.; Sambade, D.; Parkin, G. *Polyhedron* **2020**, *187*, 114542.
- (17) Neary, M. C.; Parkin, G. *Polyhedron* **2016**, *116*, 189.
- (18) Kreider-Mueller, A.; Quinlivan, P. J.; Owen, J. S.; Parkin, G. *Inorg. Chem.* **2015**, *54*, 3835.
- (19) The monodentate coordination mode is also supported by IR spectroscopic studies since the $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ vibrational frequencies associated with the formate ligand (1614 cm⁻¹ and 1312 cm⁻¹) differ by 302 cm⁻¹. See: Deacon, G. B.; Huber, F.; Phillips, R. J. *Inorg. Chim. Acta* **1985**, *104*, 41.
- (20) Dabral, S.; Schaub, T. *Adv. Synth. Catal.* **2019**, *361*, 223.
- (21) (a) Song, Q.-W.; Zhou, Z.-H.; He, L.-N. *Green Chem.* **2017**, *19*, 3707. (b) Chauvier, C.; Cantat, T. *ACS Catal.* **2017**, *7*, 2107. (c) Bao, J.; Yang, G.; Yoneyama, Y.; Tsubaki, N. *ACS Catal.* **2019**, *9*, 3026.
- (22) (a) Fernandez-Alvarez, F. J.; Oro, L. A. *ChemCatChem* **2018**, *10*, 4783. (b) Chen, J. W.; McGraw, M.; Chen, E. Y. X. *ChemSusChem* **2019**, *12*, 4543.
- (23) For other examples of zinc-catalyzed hydrosilylation of CO₂, see references 8, 9, 14, 22 and (a) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2012**, *134*, 17462. (b) Rauch, M.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 18162.
- (24) (a) Mukherjee, D.; Wiegand, A.-K.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2017**, *46*, 6183. (b) Wang, X.; Chang, K.; Xu, X. *Dalton Trans.* **2020**, *49*, 7324. (c) Chambenahalli, R.; Bhargav, R. M.; McCabe, K. N.; Andrews, A. P.; Ritter, F.; Okuda, J.; Maron, L.; Venugopal, A. *Chem. Eur. J.* **2021**, *27*, 7391. (d) Janes, T.; Osten, K.M.; Pantaleo, A.; Yan, E.; Yang, Y.; Song, D. *Chem. Commun.* **2016**, *52*, 4148.
- (25) For hydroboration of CO₂ by other metals and nonmetals, see, for example: (a) Bontemps, S. *Coord. Chem. Rev.* **2016**, *308*, 117. (b) Shegavi, M. L.; Bose, S. K. *Catal. Sci. Technol.* **2019**, *9*, 3307. (c) Eberhardt, N. A.; Guan, H. R. in *Pincer Compounds: Chemistry and Applications*. Elsevier Science Bv: Amsterdam, 2018; p 67–99. (d) Espinosa, M. R.; Charboneau, D. J.; Garcia de Oliveira, A.; Hazari, N. *ACS Catalysis* **2019**, *9*, 301.
- (26) While CO₂ does not react with HBpin under the conditions employed here, certain boron hydrides, such as anionic derivatives, are known to react with CO₂, without the need of a catalyst. See, for example: (a) Knopf, I.; Cummins, C. C. *Organometallics* **2015**, *34*, 1601. (b) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52*, 13155. (d) Lombardo, L.; Ko, Y.; Zhao, K.; Yang, H. N.; Züttel, A. *Angew. Chem. Int. Edit.* **2021**, *60*, 9580. (e) Lombardo, L.; Yang, H.; Zhao, K.; Dyson, P. J.; Züttel, A. *ChemSusChem* **2020**, *13*, 2025.
- (27) For other examples of more facile hydroboration than hydrosilylation of CO₂, see reference 24c and Lu, Z.; Hausmann, H.; Becker, S.; Wegner, H. A. *J. Am. Chem. Soc.* **2015**, *137*, 16, 5332.
- (28) It is also pertinent to note that transfer of hydride from a B–H bond is generally more thermodynamically favorable than for a Si–H bond. See, for example: Heiden, Z. M.; Lathem, A. P. *Organometallics* **2015**, *34*, 1818.
- (29) Ma, N.; Xu, Q.; Zhang, G. *Phys. Chem. Chem. Phys.* **2021**, *23*, 19111.
- (30) Sahoo, R. K.; Sarkar, N.; Nembenna, S. *Angew. Chem. Int. Edit.* **2021**, *60*, 11991.
- (31) (a) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catal.* **2017**, *7*, 1853. (b) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2018**, *24*, 13624.
- (32) Some reactions that employ HBpin have been proposed to occur *via* the intermediacy of BH₃. However, evidence that such pathways do not operate here is provided by the observation that the catalysis is not quenched by the presence of TMEDA which serves as a trap for BH₃. See: Bage, A. D.; Hunt, T. A.; Thomas, S. P. *Org. Lett.* **2020**, *22*, 4107.
- (33) (a) Sahoo, R. K.; Mahato, M.; Jana, A.; Nembenna, S. *J. Org. Chem.* **2020**, *85*, 11200. (b) Lummis, P. A.; Momeni, M. R.; Lui, M. W.; McDonald, R.; Ferguson, M. J.; Miskolzie, M.; Brown, A.; Rivard, E. *Angew. Chem., Int. Ed.* **2014**, *53*, 9347. (c) Dawkins, M. J. C.; Middleton, E.; Kefalidis, C. E.; Dange, D.; Juckel, M. M.; Maron, L.; Jones, C. *Chem. Commun.* **2016**, *52*, 10490. (d) Kumar, G. S.; Harinath, A.; Narvariya, R.; Panda, T. K. *Eur. J. Inorg. Chem.* **2020**, 467. (e) 24a.
- (34) For examples of hydrosilylation of carbonyl compounds catalyzed by zinc compounds, see: (a) Sattler, W.; Ruccolo, S.; Chaijan, M. R.; Allah, T. N.; Parkin, G. *Organometallics* **2015**, *34*, 4717. (b) Alshakova, I. D.; Nikonov, G. I. *Synthesis* **2019**, *51*, 3305.