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Carbodiimide and Isocyanate Hydroboration by a Cyclic Carbodiphosphorane Catalyst**

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We report hydroboration of carbodiimide and isocyanate substrates catalyzed by a cyclic carbodiphosphorane catalyst. The cyclic carbodiphosphorane outperformed the other Lewis basic carbon species tested, including other zerovalent carbon compounds, phosphorus ylides, an *N*-heterocyclic carbene, and an *N*-heterocyclic olefin. Hydroborations of seven carbodiimides and nine isocyanates were performed at room temperature to form *N*-boryl formamidine and *N*-boryl formamide products. Intermolecular competition experiments demonstrated the selective hydroboration of alkyl isocyanates over carbodiimide and ketone substrates. DFT calculations support a proposed mechanism involving activation of pinacolborane by the carbodiphosphorane catalyst, followed by hydride transfer and B–N bond formation.

Introduction

Formamidine and formamide products are important units in biologically active compounds with bactericidal, fungicidal, and insecticidal properties.[1–4] The reduction of carbodiimides and isocyanates is an appealing route to these functional groups; however, the presence of multiple polar double bonds in these heterocumulene substrates poses a challenge for selective reduction reactions.

Traditional methods to reduce carbodiimides and isocyanates into formamidines and formamides involve stoichiometric quantities of reducing agents such as $NaBH_4$ or Cp_2ZrHCl.[5–7] Catalytic reduction reactions can decrease the amount of waste generated in the synthesis of these products.

Catalytic carbodiimide hydroboration reactions were first reported in 2016 using magnesium catalysts.[8,9] Since then, catalysts for carbodiimide hydroboration using pinacolborane (HBpin) have been reported from across the periodic table, including transition metal,[10–12] main group,[13–27] and actinide[28] catalysts. Most carbodiimide hydroboration catalysts operate at elevated temperatures (50–80 °C).[8–10,16–24,27,28] Exceptions that operate at room temperature include a carbatrane magnesium hydride complex,[14] the 9-borabicyclo[3.3.1]nonane dimer,[15] manganese(II) bis(hexamethyldisilazide),[11] a boron-functionalized heptaphosphide Zintl cluster,[25] 9,10-dihydro-9,10-diboraanthracene dianions,[26] and an *N*-heterocyclic carbene-supported copper alkoxide complex.[12]

Initial studies of catalytic isocyanate hydroboration reactions in 2016 and 2017 reported magnesium catalysts for the dihydroboration of isocyanates to form *N*,*O*-bis(boryl) hemiaminal products or hydrodeoxygenation reactions to generate *N*-methyl amines.[9,29] Subsequent work has revealed a range of catalysts for the selective hydrodeoxygenation of isocyanates at 50–100 °C.[24,30–38] The monohydroboration of isocyanates has also been observed at long reaction times under catalyst-free conditions[35] or using transition metal,[12,33,35,39] main group,[23,24,30,32,34,38,40] and actinide[37] catalysts. However, notably, none of the existing catalysts for carbodiimide or isocyanate hydroboration are neutral, Lewis basic organocatalysts.

In the present work, we have studied zerovalent carbon compounds (Scheme 1) as catalysts for carbodiimide and isocyanate hydroboration. Low-valent carbon species have attracted significant attention in organic and organometallic chemistry.[41–44] Divalent carbon compounds such as *N*-heterocyclic carbenes have been most extensively studied, and have enabled innovations in materials chemistry,[45,46] transition metal catalysis,[47–49] and organocatalysis.[50–54] Carbones, CL_2, are zerovalent carbon compounds that feature a carbon center with two lone pairs flanked by two donors, such as phosphines or *N*-heterocyclic carbenes (Scheme 1, top).[55,56] While carbones have achieved prominence as strongly donating ligands to support transition metal and main group complexes,[57–61] there are limited reports of their use as metal-free catalysts.[62–66]

This work compares the catalytic activities of a series of zerovalent carbon compounds (**1**–**5**; Scheme 1, bottom) for isocyanate and carbodiimide reduction using pinacolborane. These catalysts were selected to survey a range of carbone species and include both acyclic[67–71] and cyclic[72,65] carbodiphosphoranes (**1**–**3**), a carbophosphinocarbene (**4**),[73] and a

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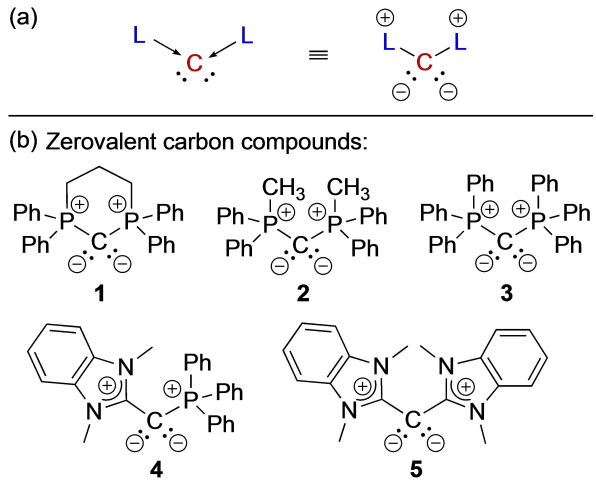


Scheme 1. Two bonding representations of zerovalent carbon (top) and the carbone compounds investigated as hydroboration catalysts in this work (bottom).

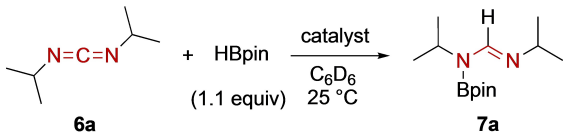
carbodicarbene (**5**)[74] compound. A combination of catalytic studies and DFT calculations provide insight into the fundamental reactivity of carbodiphosphoranes.

Results and Discussion

Carbodiimide hydroboration catalysis

We initially compared the catalytic abilities of a range of Lewis basic carbon species to promote *N*,*N*′-diisopropyl carbodiimide (**6a**) hydroboration reactivity (Table 1). Reactions were performed using 1.1 equiv of pinacolborane and 5 mol % catalyst loading in benzene-d_6 solvent. Reaction yields of the monohydroboration product **7a** relative to a 1,3,5-tris(trifluoromethyl)benzene internal standard were determined after 1 h at 25 °C. The *N*-heterocyclic carbene IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), N-heterocyclic olefin $IPrCH_2$, phosphorus ylides Ph_3PCH_2 and $Ph_3PC(CH_3)_2$, and zerovalent carbon compounds **3**–**5** were catalytically inactive (Table 1, entries 1–4 and 7–9). The highest activity for *N*,*N*′-diisopropyl carbodiimide hydroboration was observed with carbodiphosphoranes **1** and **2** (98% and 82% yield, respectively; Table 1, entries 5 and 6).

Table 1. Catalyst comparison for *N*,*N*′-diisopropyl carbodiimide hydroboration.[a]

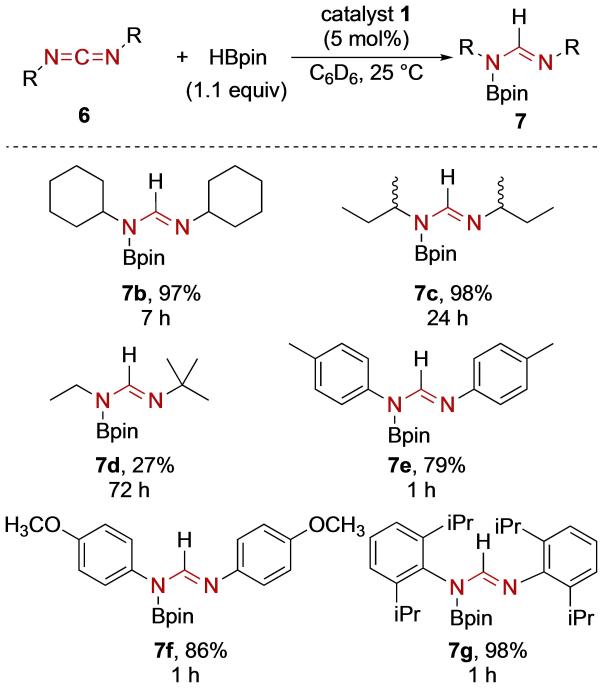


6a **7a**

Entry	Catalyst	Catalyst loading [mol %]	Time [h]	Yield [%][b]
1	IPr	5	1	0%
2	$IPrCH_2$	5	1	0%
3	Ph_3PCH_2	5	1	0%
4	$Ph_3PC(CH_3)_2$	5	1	0%
5	**1**	5	1	98%
6	**2**	5	1	82%
7	**3**	5	1	0%
8	**4**	5	1	0%
9	**5**	5	1	0%

[a] Reaction conditions: *N*,*N*′-diisopropyl carbodiimide (0.24 mmol), pinacolborane (0.27 mmol), and catalyst (0.012 mmol) in benzene-d_6 (0.50 mL) at 25 °C. [b] Yields were determined by ^{1}H NMR integration relative to a 1,3,5-tris(trifluoromethyl)benzene internal standard.

The conversion of a range of carbodiimides (**6b**–**6g**) to their monohydroborated derivatives (**7b**–**7g**) was investigated in the presence of 5 mol % of cyclic carbodiphosphorane catalyst **1** (Scheme 2). Reaction times varied significantly based on the carbodiimide substituents. Symmetrical carbodiimides with cyclohexyl (**6b**) and *sec*-butyl (**6c**) substituents underwent hydroboration in high yields (97% and 98%, respectively); however, reaction times increased going from isopropyl (**6a**, 1 h) to cyclohexyl (**6b**, 7 h) and *sec*-butyl (**6c**, 24 h) substituents. Attempts to reduce *N*,*N*′-di-*tert*-butyl carbodiimide or *N*,*N*′-bis(trimethylsilyl) carbodiimide were unsuccessful. Although hydroboration of 1-*tert*-butyl-3-ethyl carbodiimide (**7d**) was highly regioselective, a low yield (27%) was observed for this substrate after 72 h. Aromatic carbodiimides **6e**–**6g** were reduced in 79–98% yield within 1 h. For all substrate tested,



Scheme 2. Carbodiimide scope for hydroboration reactions. Reaction conditions: carbodiimide (0.24 mmol), pinacolborane (0.27 mmol), and catalyst **1** (0.012 mmol) in benzene-d_6 (0.50 mL) at 25 °C. Yields were determined by ^{1}H NMR integration relative to a 1,3,5-tris(trifluoromethyl)benzene internal standard.

further reduction beyond the monohydroboration product was not observed, even in the presence of 3 equiv of pinacolborane.

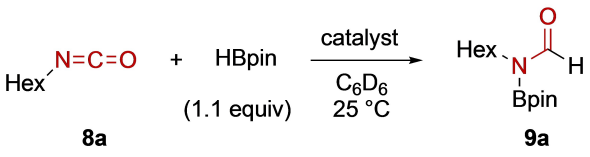
Isocyanate hydroboration catalysis

We next compared carbon Lewis bases (1 or 5 mol %) as potential catalysts towards the reduction of hexyl isocyanate (**8a**) to *N*-boryl formamide product **9a** using 1.1 equiv of HBpin in benzene-d_6 at 25 °C (Table 2). The *N*-heterocyclic carbene IPr and carbodicarbene **5** were catalytically inactive under the conditions tested (Table 2, entries 1 and 14). However, a broader range of catalysts exhibited hydroboration activity towards isocyanate **8a** than carbodiimide **6a**. Moderate yields of hydroboration product **9a** were observed using 5 mol % of the *N*-heterocyclic olefin $IPrCH_2$ or the phosphorus ylide Ph_3PCH_2 (69% and 50% yield after 1 h, respectively; Table 2, entries 2 and 3). Quantitative (99%) yield of **9a** was observed using 5 mol % of carbodiphosphorane **3** or carbophosphinocarbene **4** (entries 10 and 12); however, diminished yields were observed when using 1 mol % catalyst loading (77% after 1 h with **3** and 95% after 15 min with **4**; Table 2, entries 11 and 13). Carbodiphosphoranes **1** and **2** exhibited the highest catalytic activity for hexyl isocyanate hydroboration, furnishing 99% yield of **9a** within 15 min using 1 or 5 mol % catalyst loading of either catalyst (Table 2, entries 6–9). Attempts to observe hexyl isocyanate deoxygenation products were unsuccessful, and monohydroboration of **8a** was exclusively observed using 5 equiv of HBpin with either catalyst **1** or **2**.

The conversion of various isocyanates (**8b**–**8i**) to their corresponding *N*-boryl formamidine products (**9b**–**9i**) was studied at 25 °C in the presence of 1 mol % of cyclic carbodiphosphorane catalyst **1** (Scheme 3). Hydroboration of cyclopentyl- and cyclohexyl-substituted isocyanates (**8b** and **8c**) was observed in >95% yield within 15 min. Reduction of 1-adamantyl isocyanate (**8d**) was inefficient, achieving 23% yield after 20 h. Hydroboration of isocyanates with phenethyl (**8e**), allyl (**8f**), and benzyl substituents required 30 min at 25 °C, while the electron-rich 4-methoxybenzyl derivative (**8h**) required 60 min to reach near-completion. Furthermore, quantitative reduction of both isocyanate groups of hexamethylene diisocyanate (**8i**) was observed within 15 min using 2.2 equiv of HBpin. The attempted hydroboration of phenyl isocyanate with 1.1 equiv of HBpin was unselective, producing both monohydroboration and dihydroboration products. Hydroboration attempts involving cyclohexyl isothiocyanate or *p*-toluenesulfonyl isocyanate were unsuccessful. Overall, isocyanate substrates featuring primary and secondary aliphatic groups, allylic, and benzylic substituents underwent rapid and selective monohydroboration in the presence of cyclic carbodiphosphorane **1** at 25 °C.

In the absence of pinacolborane, cyclic carbodiphosphorane **1** catalyzed cyclotrimerization of alkyl or aryl isocyanates to form isocyanurate products in >95% yield (see Supporting Information for details). Lewis basic catalysts for isocyanate

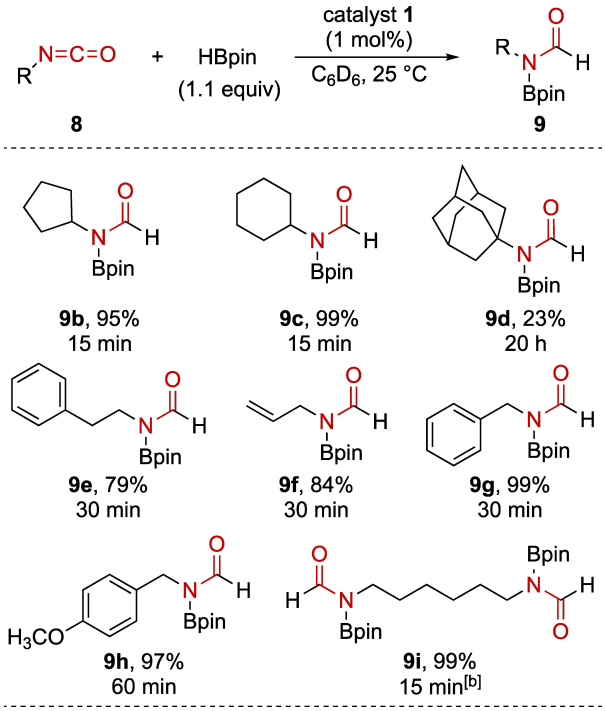
Table 2. Catalyst comparison for hexyl isocyanate hydroboration.[a]



8a **9a**

Entry	Catalyst	Catalyst loading [mol %]	Time [min]	Yield [%][b]
1	IPr	5	60	0%
2	$IPrCH_2$	5	60	69%
3	Ph_3PCH_2	5	60	50%
4	$Ph_3PC(CH_3)_2$	5	15	99%
5	$Ph_3PC(CH_3)_2$	1	15	95%
6	**1**	5	15	99%
7	**1**	1	15	99%
8	**2**	5	15	99%
9	**2**	1	15	99%
10	**3**	5	15	99%
11	**3**	1	60	77%
12	**4**	5	15	99%
13	**4**	1	15	95%
14	**5**	5	60	0%

[a] Reaction conditions: hexyl isocyanate (0.24 mmol), pinacolborane (0.27 mmol), and catalyst (0.012 or 0.0024 mmol) in benzene-d_6 (0.50 mL) at 25 °C. [b] Yields were determined by ^{1}H NMR integration relative to a 1,3,5-tris(trifluoromethyl)benzene internal standard.

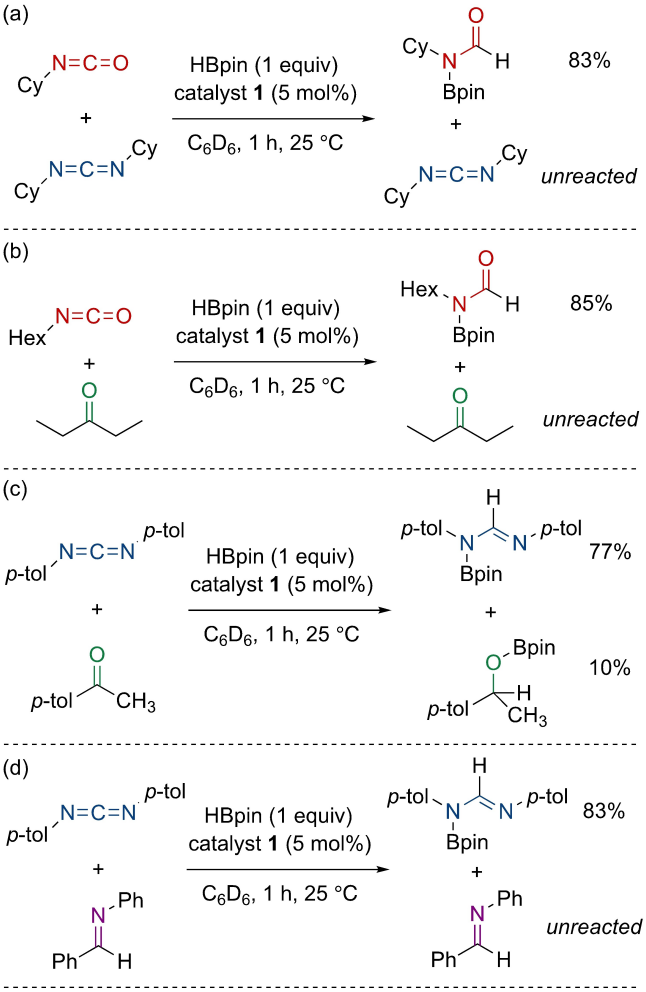


Scheme 3. Isocyanate scope for hydroboration reactions. Reaction conditions: isocyanate (0.24 mmol), pinacolborane (0.27 mmol), and catalyst **1** (0.0024 mmol) in benzene-d_6 (0.50 mL) at 25 °C. Yields were determined by ^{1}H NMR integration relative to a 1,3,5-tris(trifluoromethyl)benzene internal standard. [b] 2.2 equiv of pinacolborane.

cyclotrimerization have been previously reported, including *N*-heterocyclic carbenes,[75] *N*-heterocyclic olefins,[76] phosphines,[77] and carbodicarbene and carbophosphinocarbene compounds in the presence of benzyl alcohol.[64]

Competition experiments

To assess the selectivity of hydroboration reactions catalyzed by cyclic carbodiphosphorane **1**, competition experiments were performed (Scheme 4). In an experiment with 1 equiv of cyclohexyl isocyanate, 1 equiv of *N*,*N*′-dicyclohexyl carbodiimide, 1 equiv of pinacolborane, and 5 mol % of catalyst **1**, exclusive hydroboration of cyclohexyl isocyanate was observed (Scheme 4a). Preferential reduction of hexyl isocyanate was also observed in the presence of 3-pentanone (Scheme 4b). In an experiment with equimolar *N*,*N*′-di-*p*-tolyl carbodiimide and 4-methylacetophenone, an 8:1 ratio of carbodiimide and ketone hydroboration products was observed (Scheme 4c). In contrast, the exclusive hydroboration of *N*,*N*′-di-*p*-tolyl carbodiimide was observed in the presence of *N*-benzylideneaniline (Scheme 4d).



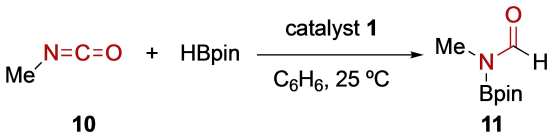
Scheme 4. Intermolecular competition reactions demonstrating hydroboration preferences. Reaction conditions: substrates (0.24 mmol each), pinacolborane (0.24 mmol), and catalyst **1** (0.012 mmol) in benzene-d_6 (0.50 mL) at 25 °C for 1 h. Yields were determined by ^{1}H NMR integration relative to a 1,3,5-tris(trifluoromethyl)benzene internal standard.

Computational studies

Experimental results revealed that carbodiphosphoranes are effective catalysts for carbodiimide and isocyanate hydroboration. However, questions remained about the catalyst geometry and electronics, the nature of the catalyst-substrate interactions, and the likely catalytic hydroboration mechanism. To address these questions, we used DFT to compute plausible reaction paths for carbodiphosphorane-catalyzed isocyanate hydroboration using the model system in Scheme 5. Methyl isocyanate **10** was used as the model substrate to represent the experimental scope of alkyl isocyanates in this study, pinacolborane as the reductant, and cyclic carbodiphosphorane **1** as the catalyst.

Conformational isomers at each stationary point along the reaction coordinates were generated using molecular mechanics based OPLS force field[78] as implemented in *Schrödinger*.[79] All isomers were subject to geometry optimization and vibrational frequency analysis at the ωB97XD[80,81]/6-31G(d,p)[82–85] level. Minimum and transition state stationary points were verified by vibrational analysis. Intrinsic reaction coordinate (IRC) analysis[86,87] of the highest energy transition states confirmed connecting minima along the reaction coordinates (see Supporting Information for details). Subsequent electronic energy single point calculations were computed at the ωB97XD/def2-TZVPP[88–90] level, including the polarized continuum model (PCM)[91,92] for benzene, the solvent used in the experimental study. All quantum mechanical calculations were carried out in *Gaussian 16, Revision B.01*.[93]

We first analyzed the geometry and electronics of cyclic carbodiphosphorane **1** (Figure 1). The computed bond length between the carbone center and each phosphorus atom is 1.65 Å, and the computed P–C–P angle is 117°. These values are consistent with previously reported X-ray crystallographic data for cyclic carbodiphosphorane **1** (P–C bond lengths for **1** = 1.64 and 1.65 Å and P–C–P angle for **1** = 116.8°).[72] Natural atomic and bond orbital calculations reveal that catalyst **1** features significant electronic charge localization at the zerovalent carbon center (natural charge = −1.52). Moreover, the two highest lying occupied orbitals (HOMO-1 and HOMO) are occupied by sigma and pi type lone pairs at the zerovalent carbon, consistent with computational reports for acyclic carbodiphosphorane **3**.[55,94]



10 **11**

Scheme 5. Computational model for investigating plausible hydroboration mechanisms. Geometries and thermochemistry values (at 298 K) computed at the ωB97XD/6-31G(d,p) level. Electronic energies on optimized geometries computed at ωB97XD/def2-TZVPP/PCM(C_6H_6) level.

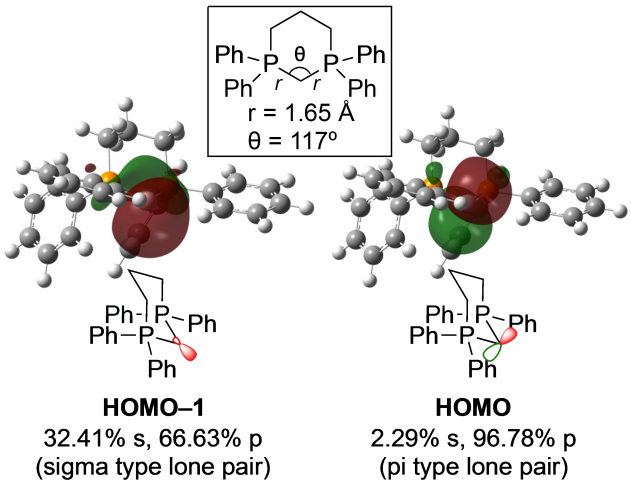


Figure 1. Natural frontier orbitals of catalyst **1** occupied by the lone pairs on the carbone center, computed at the ωB97XD/def2-TZVPP/PCM(C_6H_6) level.

Altogether, geometric and electronic data for **1** led to our mechanistic hypothesis that the primary role of the carbodiphosphorane catalyst is to provide Lewis base activation of the substrate(s) via σ-donation from the carbone center in the hydroboration reaction. We envisioned two plausible catalytic cycles based on whether the carbodiphosphorane (CDP) coordinates to pinacolborane first (CDP-borane adduct cycle) or to the isocyanate substrate first (CDP-isocyanate adduct cycle); for each, we computed the minimum energy pathway on the reaction coordinate (Figure 2).

Carbodiphosphorane-borane adduct cycle (favored)

Facile coordination of carbodiphosphorane **1** to pinacolborane yields adduct **12** (ΔG = −4.8 kcal/mol). We have reported ^{11}B NMR data consistent with the formation of this adduct in earlier studies of ketone hydroboration catalysis using carbodiphosphorane **1**.[65] Hydride transfer from **12** to methyl isocyanate is the irreversible step in the CDP-borane adduct cycle and results in an ion pair **13** consisting of a cationic carbodiphosphorane-Bpin adduct and amide anion (ΔG = −20.1 kcal/mol). Coupling of the ion pair through B–N bond formation yields stabilized carbodiphosphorane-*N*-boryl formamide adduct **14** (ΔG = −31.2 kcal/mol). The product release and catalyst regeneration elementary step is endergonic by 4.8 kcal/mol. However, upon product release, the reverse carbodiphosphorane-product adduct formation (i.e., from **11** to **14** through $\mathbf{TS}_{(14-11)}$, $\Delta G^{\ddagger}$ = 9.3 kcal/mol) is less energetically likely than coordination of carbodiphosphorane to another pinacolborane (i.e., from **1** to **12** through $\mathbf{TS}_{(1-12)}$, $\Delta G^{\ddagger}$ = 6.6 kcal/mol) or the irreversible hydride transfer step (from **12** to **13** through $\mathbf{TS}_{(12-13)}$, $\Delta G^{\ddagger}$ = 8.4 kcal/mol) in the forward reaction. The computed reaction coordinate thus supports the efficient turnover of carbodiphosphorane **1** as observed in experiments.

Carbodiphosphorane-isocyanate adduct cycle (disfavored)

On the other hand, coordination of carbodiphosphorane **1** to methyl isocyanate is expected to be slower than coordination to pinacolborane ($\Delta\triangle G^{\ddagger}$ $\mathbf{TS}_{(1-15)}$–$\mathbf{TS}_{(1-12)}$ = 9.9 kcal/mol), although the former results in a more stable adduct **15** compared to the latter adduct **12** (ΔΔG **15**–**12** = −8.2 kcal/mol). Ramirez and co-workers have previously described the synthesis of adducts between hexaphenylcarbodiphosphorane (**3**) and aryl isocyanates and carbodiimides.[95] Adduct **15** features an interaction between the isocyanate N and the P site of the carbodiphosphorane (P–N distance = 2.0 Å, see Figure 2), thus indicating that in addition to the σ-donating ability at the carbone center of carbodiphosphoranes, the phosphorus site could also serve as a π-acceptor. Such interactions have been observed in a previously reported solid state structure and DFT calculations of carbodicarbene-isocyanate adducts.[64] Subsequent coordination of **15** to pinacolborane via B–N bond formation yields **16**. Intramolecular hydride transfer via a strained 4-membered ring is the highest energy transition state in this cycle ($\mathbf{TS}_{(16-17)}$, $\Delta G^{\ddagger}$ = 21.7 kcal/mol) and leads to the carbodiphosphorane-product adduct **17**. Here again, the phosphorus site on the carbodiphosphorane serves as a π-acceptor, attenuating the charge buildup at the oxygen. A related 1,2-oxaphosphetane generated by the treatment of hexaphenylcarbodiphosphorane (**3**) with hexafluoroacetone has been characterized by X-ray crystallography and NMR spectroscopy.[96,97] In this cycle, product release and catalyst regeneration from **17** is exergonic by 4.2 kcal/mol.

The computed reaction is highly exergonic, with an overall reaction Gibbs free energy (ΔG_{rxn}) of −26.4 kcal/mol. The carbodiphosphorane-*borane* adduct cycle, which is kinetically favored, has a Gibbs free energy span[98] of 14.1 kcal/mol (i.e., $\Delta G^{\ddagger}$ at $\mathbf{TS}_{(14-11)}$–ΔG at **14**). This is consistent with an experimentally observed >95% yield of *N*-boryl formamide products at room temperature within 30 min. In contrast, the carbodiphosphorane-*isocyanate* adduct cycle, which is kinetically disfavored, has a Gibbs free energy span of 39.8 kcal/mol (i.e., $\Delta G^{\ddagger}$ at $\mathbf{TS}_{(16-17)}$–ΔG at **16**); this computed free energy span is inconsistent with experimental observations. Therefore, we conclude that the likely catalytic hydroboration pathway involves the activation of pinacolborane by the carbodiphosphorane catalyst, followed by hydride transfer to the isocyanate and B–N bond formation to form the *N*-borylated products.

Conclusions

In summary, we report the efficient hydroboration of carbodiimides and isocyanates by cyclic carbodiphosphorane catalyst **1** at 25 °C. Highly selective monohydroboration of carbodiimides and alkyl isocyanates produce *N*-boryl formamidine and *N*-boryl formamide products, respectively. For both carbodiimide and isocyanate substrates, the cyclic carbodiphosphorane **1** outperformed the other zerovalent carbon compounds (**2**–**5**) and phosphorus ylides that were tested. To our knowledge, these results represent the first report of carbodiimide or isocyanate

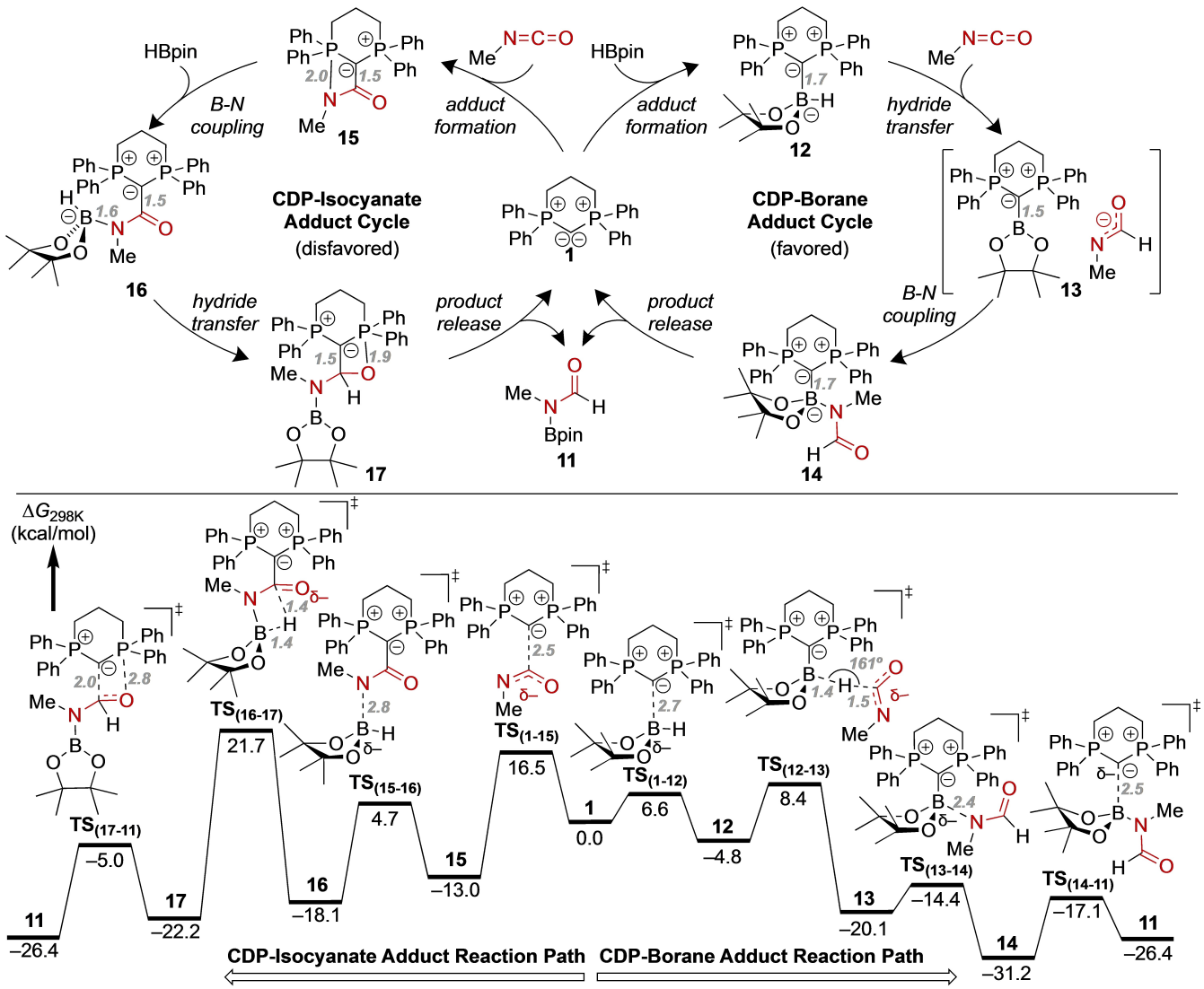


Figure 2. Computed catalytic cycles for carbodiphosphorane-catalyzed hydroboration of methyl isocyanate with pinacolborane. Geometries and thermochemistry values (at 298 K) were computed at the ωB97XD/6-31G(d,p) level. Electronic energies on the optimized geometries were computed at the ωB97XD/def2-TZVPP/PCM(C_6H_6) level. Distances are reported in Ångströms (Å).

reduction catalyzed by a neutral, Lewis basic organocatalysts. Furthermore, the DFT studies are a rare example of a computed reaction mechanism for a zerovalent carbon catalyst.[62,64] The present work suggests that the operative mechanism for isocyanate hydroboration catalysis involves coordination of cyclic carbodiphosphorane **1** to pinacolborane and subsequent hydride transfer and B–N bond formation. However, our results do not yet explain the differences in catalytic activity observed between carbone catalysts **1**–**5**. In future work, we hope to demonstrate further catalytic applications of carbodiphosphoranes and elucidate why zerovalent carbon compound structure substantially impacts catalytic activity.

Experimental Section

Experimental procedures, characterization data, and details regarding DFT calculations are described in the Supporting Information.

Supporting Information

The authors have cited additional references within the Supporting Information.[99–105]

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: carbodiphosphorane · hydroboration · Lewis bases · organocatalysis · zerovalent carbon

[1] R. M. Hollingworth, *Environ. Health Perspect.* **1976**, 13.
[2] P. D. Evans, J. D. Gee, *Nature* **1980**, *287*, 60–62.
[3] J. Pouessel, O. Jacquet, T. Cantat, *ChemCatChem* **2013**, *5*, 3552–3556.
[4] T. M. E. Dine, D. Evans, J. Rouden, J. Blanchet, *Chem. Eur. J.* **2016**, *22*, 5894–5898.
[5] K. Kaji, H. Matsubara, H. Nagashima, Y. Kikugawa, S. Yamada, *Chem. Pharm. Bull.* **1978**, *26*, 2246–2249.
[6] T. Peddarao, A. Baishya, M. K. Barman, A. Kumar, S. Nembenna, *New J. Chem.* **2016**, *40*, 7627–7636.
[7] V. Pace, K. de la Vega-Hernández, E. Urban, T. Langer, *Org. Lett.* **2016**, *18*, 2750–2753.
[8] C. Weetman, M. S. Hill, M. F. Mahon, *Chem. Eur. J.* **2016**, *22*, 7158–7162.
[9] D. Mukherjee, S. Shirase, T. P. Spaniol, K. Mashima, J. Okuda, *Chem. Commun.* **2016**, *52*, 13155–13158.
[10] M. Khononov, N. Fridman, M. Tamm, M. S. Eisen, *Eur. J. Org. Chem.* **2020**, *2020*, 3153–3160.
[11] P. Ghosh, A. Jacobi Von Wangelin, *Angew. Chem. Int. Ed.* **2021**, *60*, 16035–16043.
[12] L. E. English, T. M. Horsley Downie, C. L. Lyall, M. F. Mahon, C. L. McMullin, S. E. Neale, C. M. Saunders, D. J. Liptrot, *Chem. Commun.* **2023**, *59*, 1074–1077.
[13] M. D. Anker, M. Arrowsmith, R. L. Arrowsmith, M. S. Hill, M. F. Mahon, *Inorg. Chem.* **2017**, *56*, 5976–5983.
[14] M. Rauch, S. Ruccolo, G. Parkin, *J. Am. Chem. Soc.* **2017**, *139*, 13264–13267.
[15] A. Ramos, A. Antiñolo, F. Carrillo-Hermosilla, R. Fernández-Galán, D. García-Vivó, *Chem. Commun.* **2019**, *55*, 3073–3076.
[16] Q. Shen, X. Ma, W. Li, W. Liu, Y. Ding, Z. Yang, H. W. Roesky, *Chem. Eur. J.* **2019**, *25*, 11918–11923.
[17] Y. Ding, X. Ma, Y. Liu, W. Liu, Z. Yang, H. W. Roesky, *Organometallics* **2019**, *38*, 3092–3097.
[18] N. Sarkar, S. Bera, S. Nembenna, *J. Org. Chem.* **2020**, *85*, 4999–5009.
[19] T. K. Panda, I. Banerjee, S. Sagar, *Appl. Organomet. Chem.* **2020**, *34*, e5765.
[20] X. He, B. Yan, C. Ni, Y. Zhao, Z. Yang, X. Ma, *Asian J. Org. Chem.* **2021**, *10*, 196–201.
[21] M. K. Bisai, K. Gour, T. Das, K. Vanka, S. S. Sen, *J. Organomet. Chem.* **2021**, *949*, 121924.
[22] B. Yan, X. He, C. Ni, Z. Yang, X. Ma, *ChemCatChem* **2021**, *13*, 851–854.
[23] B. L. L. Réant, B. Van IJzendoorn, G. F. S. Whitehead, M. Mehta, *Dalton Trans.* **2022**, *51*, 18329–18336.
[24] N. Sarkar, R. K. Sahoo, S. Nembenna, *Eur. J. Org. Chem.* **2022**, ejoc.202200941.
[25] B. Van IJzendoorn, S. F. Albawardi, I. J. Vitorica-Yrezabal, G. F. S. Whitehead, J. E. McGrady, M. Mehta, *J. Am. Chem. Soc.* **2022**, *144*, 21213–21223.
[26] S. E. Prey, C. Herok, F. Fantuzzi, M. Bolte, H.-W. Lerner, B. Engels, M. Wagner, *Chem. Sci.* **2023**, *14*, 849–860.
[27] R. K. Sahoo, A. G. Patro, N. Sarkar, S. Nembenna, *Organometallics* **2023**, *42*, 1746–1758.
[28] H. Liu, K. Kulbitski, M. Tamm, M. S. Eisen, *Chem. Eur. J.* **2018**, *24*, 5738–5742.
[29] Y. Yang, M. D. Anker, J. Fang, M. F. Mahon, L. Maron, C. Weetman, M. S. Hill, *Chem. Sci.* **2017**, *8*, 3529–3537.
[30] R. K. Sahoo, N. Sarkar, S. Nembenna, *Angew. Chem. Int. Ed.* **2021**, *60*, 11991–12000.
[31] Q. Xiao, S. Zang, Z. Chen, W. Yao, J. Zheng, M. Ma, *Chin. J. Org. Chem.* **2021**, *41*, 357–363.
[32] Z. Du, B. Behera, A. Kumar, Y. Ding, *J. Organomet. Chem.* **2021**, *950*, 121982.
[33] V. K. Pandey, S. Sahoo, A. Rit, *Chem. Commun.* **2022**, *58*, 5514–5517.
[34] C. Ni, X. Ma, Z. Yang, H. W. Roesky, *ChemistrySelect* **2022**, *7*, e202202878.
[35] K. A. Gudun, S. Tussupbayev, A. Slamova, A. Y. Khalimon, *Org. Biomol. Chem.* **2022**, *20*, 6821–6830.
[36] J. Shi, M. Luo, X. Zhang, T. Yuan, X. Chen, M. Ma, *Org. Biomol. Chem.* **2023**, *21*, 3628–3635.
[37] K. Makarov, I. Ritacco, N. Fridman, L. Caporaso, M. S. Eisen, *ACS Catal.* **2023**, 11798–11814.
[38] Y.-C. Teo, D. Loh, B.-X. Leong, Z.-F. Zhang, M.-D. Su, C.-W. So, *Inorg. Chem.* **2023**, acs.inorgchem.3c02424.
[39] S. Ostrowska, P. Arnaut, D. J. Liptrot, C. S. J. Cazin, S. P. Nolan, *Chem. Commun.* **2023**, *59*, 9126–9129.
[40] R. Kumar, V. Sharma, S. Banerjee, K. Vanka, S. S. Sen, *Chem. Commun.* **2023**, *59*, 2255–2258.
[41] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92.
[42] P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862–892.
[43] P. Bellotti, M. Koy, M. N. Hopkinson, F. Glorius, *Nat. Chem. Rev.* **2021**, *5*, 711–725.
[44] S. Kumar Kushvaha, A. Mishra, H. W. Roesky, K. Chandra Mondal, *Chem. Asian J.* **2022**, *17*, e202101301.
[45] C. A. Smith, M. R. Narouz, P. A. Lummis, I. Singh, A. Nazemi, C.-H. Li, C. M. Crudden, *Chem. Rev.* **2019**, *119*, 4986–5056.
[46] H. Shen, G. Tian, Z. Xu, L. Wang, Q. Wu, Y. Zhang, B. K. Teo, N. Zheng, *Coord. Chem. Rev.* **2022**, *458*, 214425.
[47] C. S. J. Cazin, *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, Springer, Dordrecht; New York, **2011**.
[48] S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676.
[49] C. Chen, F. Liu, M. Szostak, *Chem. Eur. J.* **2021**, *27*, 4478–4499.
[50] A. T. Biju, *N-Heterocyclic Carbenes in Organocatalysis*, Wiley-VCH, Weinheim, **2019**.
[51] D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606–5655.
[52] S. J. Ryan, L. Candish, D. W. Lupton, *Chem. Soc. Rev.* **2013**, *42*, 4906–4917.
[53] S. Dwivedi, S. Gupta, S. Das, *COCAT* **2014**, *1*, 13–39.
[54] D. M. Flanigan, F. Romanov-Michailidis, N. A. White, T. Rovis, *Chem. Rev.* **2015**, *115*, 9307–9387.
[55] G. Frenking, R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597–614.
[56] M. Fustier-Boutignon, N. Nebra, N. Mézailles, *Chem. Rev.* **2019**, *119*, 8555–8700.
[57] W. Petz, G. Frenking, in *Transition Metal Complexes of Neutral Eta1-Carbon Ligands* (Eds.: R. Chauvin, Y. Canac), Springer Berlin Heidelberg, Berlin, Heidelberg, **2010**, pp. 49–92.
[58] M. Alcarazo, in *Modern Ylide Chemistry* (Ed.: V. H. Gessner), Springer International Publishing, Cham, **2017**, pp. 25–50.
[59] T.-H. Wang, W.-C. Chen, T.-G. Ong, *J. Chin. Chem. Soc.* **2017**, *64*, 124–132.
[60] S. Liu, W.-C. Shih, W.-C. Chen, T.-G. Ong, *ChemCatChem* **2018**, *10*, 1483–1498.
[61] L. Zhao, C. Chai, W. Petz, G. Frenking, *Molecules* **2020**, *25*, 4943.
[62] R. Dobrovetsky, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 2516–2519.
[63] W.-C. Chen, J.-S. Shen, T. Jurca, C.-J. Peng, Y.-H. Lin, Y.-P. Wang, W.-C. Shih, G. P. A. Yap, T.-G. Ong, *Angew. Chem. Int. Ed.* **2015**, *54*, 15207–15212.
[64] Y. Chan, Y. Bai, W. Chen, H. Chen, C. Li, Y. Wu, M. Tseng, G. P. A. Yap, L. Zhao, H. Chen, T. Ong, *Angew. Chem. Int. Ed.* **2021**, *60*, 19949–19956.
[65] C. R. Aversa-Fleener, D. K. Chang, A. L. Liberman-Martin, *Organometallics* **2021**, *40*, 4050–4054.
[66] A. L. Liberman-Martin, *Cell Reports Physical Science* **2023**, 101519.
[67] F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539–3540.
[68] C. Zybill, G. Mueller, *Organometallics* **1987**, *6*, 2489–2494.

[69] C. Pranckevicius, D. A. Iovan, D. W. Stephan, *Dalton Trans.* **2016**, *45*, 16820–16825.
[70] M. Gruber, W. Bauer, H. Maid, K. Schöll, R. R. Tykwinski, *Inorg. Chim. Acta* **2017**, *468*, 152–158.
[71] M. S. Hussain, H. Schmidbaur, *Z. Naturforsch. B* **1976**, *31*, 721–726.
[72] H. Schmidbaur, T. Costa, B. Milewski-Mahrla, U. Schubert, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 555–556.
[73] S. Liu, W.-C. Chen, G. P. A. Yap, T.-G. Ong, *Organometallics* **2020**, *39*, 4395–4401.
[74] C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 3206–3209.
[75] H. A. Duong, M. J. Cross, J. Louie, *Org. Lett.* **2004**, *6*, 4679–4681.
[76] C. Li, W. Zhao, J. He, Y. Zhang, *Chem. Commun.* **2019**, *55*, 12563–12566.
[77] S. M. Raders, J. G. Verkade, *J. Org. Chem.* **2010**, *75*, 5308–5311.
[78] W. L. Jorgensen, J. Tirado-Rives, *J. Am. Chem. Soc.* **1988**, *110*, 1657–1666.
[79] Schrödinger. *Schrödinger Release 2021–3: Macromodel; Schrödinger*, LLC: New York, NY, **2021**.
[80] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
[81] J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 084106.
[82] J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, *102*, 939–947.
[83] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.* **1982**, *104*, 2797–2803.
[84] V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, L. A. Curtiss, *J. Comput. Chem.* **2001**, *22*, 976–984.
[85] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665.
[86] K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363–368.
[87] H. P. Hratchian, M. J. Frisch, *J. Chem. Phys.* **2011**, *134*, 204103.
[88] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[89] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.
[90] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.
[91] B. Mennucci, J. Tomasi, R. Cammi, J. R. Cheeseman, M. J. Frisch, F. J. Devlin, S. Gabriel, P. J. Stephens, *J. Phys. Chem. A* **2002**, *106*, 6102–6113.
[92] B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158.
[93] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
[94] R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260–3272.
[95] F. Ramirez, J. F. Pilot, N. B. Desai, C. P. Smith, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1967**, *89*, 6273–6276.
[96] G. H. Birum, C. N. Matthews, *Chem. Commun.* **1967**, 137–138.
[97] G. Chioccola, J. J. Daly, *J. Chem. Soc. A* **1968**, 568–577.
[98] S. Kozuch, S. Shaik, *Acc. Chem. Res.* **2011**, *44*, 101–110.
[99] W. J. Transue, J. Yang, M. Nava, I. V. Sergeyev, T. J. Barnum, M. C. McCarthy, C. C. Cummins, *J. Am. Chem. Soc.* **2018**, *140*, 17985–17991.
[100] A. K. Swarnakar, S. M. McDonald, K. C. Deutsch, P. Choi, M. J. Ferguson, R. McDonald, E. Rivard, *Inorg. Chem.* **2014**, *53*, 8662–8671.
[101] L. Hintermann, *Beilstein J. Org. Chem.* **2007**, *3*, DOI 10.1186/1860-5397-3-22.
[102] M. Pompeo, R. D. J. Froese, N. Hadei, M. G. Organ, *Angew. Chem. Int. Ed.* **2012**, *51*, 11354–11357.
[103] K. Powers, C. Hering-Junghans, R. McDonald, M. J. Ferguson, E. Rivard, *Polyhedron* **2016**, *108*, 8–14.
[104] V. Ramirez, E. B. Van Pelt, R. K. Pooni, A. J. Melchor Bañales, M. B. Larsen, *Org. Biomol. Chem.* **2022**, *20*, 5861–5868.
[105] Z. Guo, Y. Xu, X. Wu, X. Wei, C. Xi, *Dalton Trans.* **2019**, *48*, 8116–8121.

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