Requirements for Late-Stage Hydroboration of Pyridine N-Heterocyclic Carbene Iron(0) Complexes: The Role of Ancillary Ligands

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ABSTRACT: A series of zero-valent iron complexes were synthesized that contain allylic substituents attached to a 2,6-bis(imidazol-2-ylidene)pyridine pincer ligand. These species varied in the identity of their ancillary ligands and were used to study the requirements and limitations of late-stage hydroboration. While late-stage ligand functionalization can facilitate the incorporation of Lewis acidic boranes into a ligand scaffold, thereby alleviating Lewis acid/base incompatibilities of the free ligand, we identify and discuss complicating factors that arise from complexes containing labile M-L bonds.

INTRODUCTION

Interactions of Lewis acids with metal coordinated substrates can facilitate charge transfer, and this principle has been demonstrated to facilitate the reduction of small molecules.[1-12] Although exogenous Lewis acids can improve such reaction activity and also influence subsequent functionalization selectivity, these results necessarily come at the cost of a high entropic penalty – a major liability for any reaction. Intramolecular systems minimize this penalty, potentially allowing the use of significantly weaker Lewis acids.[13-22] From a synthetic perspective, the preparation of ligands containing appended (intramolecular) Lewis acids pose a set of synthetic challenges. Three commonly encountered hurdles for their incorporation include (Figure 1, middle): 1) intra/intermolecular Lewis pair quenching, 2) ligand abstraction when adding the Lewis acid, and 3) metal-centered reactivity (e.g. oxidative addition).[22-23] To overcome these compatibility challenges, one of two routes is most often employed: 1) use of very weak Lewis acids or, 2) late-stage installation/deprotection.

Boron Lewis acids provide high steric and electronic tunability and can be incorporated into a metal-ligand construct through a variety of methods. While the addition of hydro- or haloboranes to metallocycles[24-27] and diol/boronic acid condensation[17] have been used to install boron groups post-metalation, hydroboration strategies offer the greatest ease, versatility, and generality (Figure 1, top).[28-29] The majority of reports using late stage hydroboration strategies overcome the compatibility hurdles by either using metals that form robust M-L bonds (limiting intramolecular Lewis pair formation),[30-34] ancillary ligands that have low affinity for boron Lewis acids (limiting ligand abstraction),[31] or metals do not readily react with HBR_2 reagents (limiting metal-centered reactivity).[35-36] Examples that lack the above properties are rare.

Previously, we described the successful late-stage hydroboration of $(^{\text{allyl}}\text{CNC})\text{Fe}(\text{CO})_2$ (**1**) ($^{\text{allyl}}\text{H}_2\text{CNC}$ = 2,6-bis(3-allyl-1*H*-imidazolium)pyridine)—a zero valent iron complex with substitutionally inert ancillary carbonyl ligands.[31] The hydroborated products marked rare examples of low-valent iron complexes with acids appended in the secondary coordination sphere. Within this framework, we became interested in extending the system to other common ancillary ligands to ultimately probe questions related to metal-ligand cooperativity in reduced systems. Herein, we describe our efforts to better understand the requirements, capabilities, and limitations of late-stage hydroboration in a series of Fe(0) complexes.

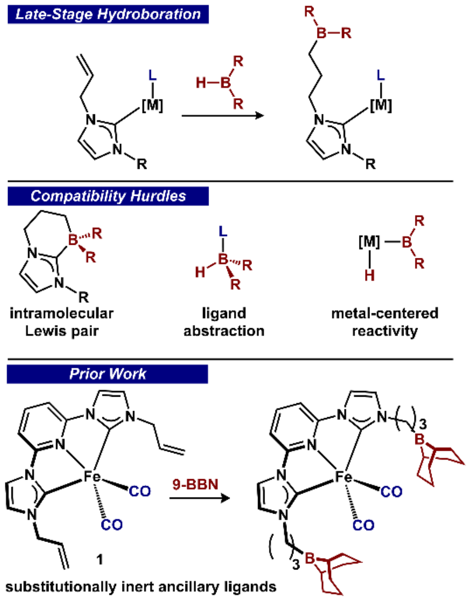
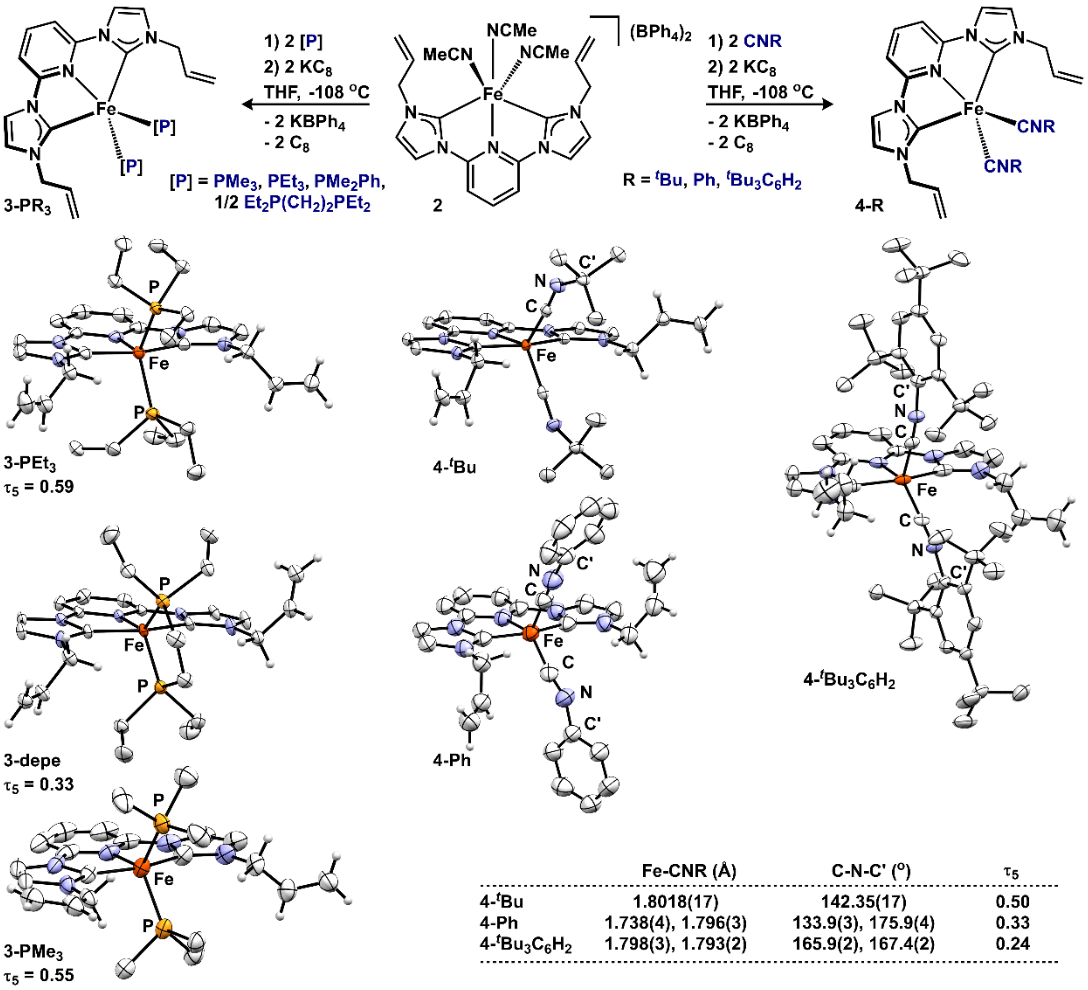


Figure 1. Top: late-stage hydroboration of a N-heterocyclic carbene ligated metal complex. Middle: compatibility issues associated with late-stage hydroboration. Bottom: prior work with compound **1**.



	Fe-CNR (Å)	C-N-C' (°)	τ_5
4-^{t}Bu	1.8018(17)	142.35(17)	0.50
4-Ph	1.738(4), 1.796(3)	133.9(3), 175.9(4)	0.33
4-^{t}Bu$_3$C$_6$H$_2$	1.798(3), 1.793(2)	165.9(2), 167.4(2)	0.24

Figure 2. Synthesis of compounds **3-PR$_3$** and **4-R** and corresponding molecular structures. All structures are displayed with 50% probability ellipsoids. All H-atoms are omitted for clarity except those attached to allylic moieties.

RESULTS AND DISCUSSION

Synthesis of Fe-phosphine and Fe-isocyanide complexes

We initiated our studies by targeting reduced iron complexes of the type (^{allyl}CNC)Fe(L)$_2$ that contain appended allylic moieties to study late-stage hydroboration. Phosphine and isocyanide co-ligands were assessed due to steric and electronic tunability of these co-ligand classes. Stirring a THF slurry of the ferrous dication, [(^{allyl}CNC)Fe(MeCN)$_3$][BPh$_4$]$_2$ (**2**),[31] with two equivalents of a phosphine followed by reduction with potassium graphite at low temperature (-108 °C) afforded (^{allyl}CNC)Fe(PR$_3$)$_2$ (**3-PR$_3$**; PR$_3$ = PMe$_3$, PEt$_3$, PMe$_2$Ph, ½ Et$_2$P(CH$_2$)$_2$PEt$_2$) as dark brown solids (Figure 2).[37] Each complex is diamagnetic and displays a diagnostic Fe-$C_{carbene}$ resonance in the ^{13}C NMR spectrum near 211-214 ppm (C$_6$D$_6$, Figures S2, S6, S10, S13). This resonance does not follow a perceptible trend based on PR$_3$ donor properties (Tolman steric and electronic parameters[38]) and is likely complicated due to multiple σ-donor/π-acceptor ligands present.[39] Single crystal X-ray diffraction studies were performed on **3-PMe$_3$**, **3-PEt$_3$**, and **3-depe**. Each five-coordinate complex displays an intermediate geometry between trigonal bipyramidal and square pyramidal. These contrast the more square pyramidal geometries observed for related iron(0) complexes that contain sterically demanding groups attached to each N-heterocyclic carbene.[40] The bidentate phosphine in **3-depe** displays the shortest Fe-P contacts (2.1524(14), 2.1640(15) Å) of the series and these contacts are considerably shorter than those observed in the related bis(imino)pyridine complex.[41] Importantly, each allylic moiety is not interacting with the metal center, suggesting **3-PR$_3$** should be suitable subjects to investigate late-stage hydroboration.

Similar reaction conditions were employed for the synthesis of the isocyanide analogues. Treating THF solutions of **1** with two equivalents of an isocyanide followed by reduction with potassium graphite at low temperature (-108 °C) afforded **4-R** (CNR = CN^{t}Bu, CNPh, CN(2,4,6-^{t}Bu$_3$Ph)). Compared to **3-PR$_3$**, the individual isocyanide complexes **3-R** show greater discrepancies between their spectroscopic and metrical parameters. The molecular structures of **4-R** were determined by single crystal X-ray diffraction studies and are displayed in Figure 2. The steric encumbrance required by the bulky aryl substituent in **4-^{t}Bu$_3$C$_6$H$_2$** results in a geometry closest to square pyramidal (τ_5 = 0.24) while **4-^{t}Bu** is the furthest from square pyramidal (τ_5 = 0.50). The relatively small allylic moieties that flank the metal center enable more geometric flexibility as compared to the sterically encumbering diisopropylphenyl (DIPP) group in (^{DIPP}CNC)Fe(CNAr)$_2$ (Ar = 2,6-Me$_2$C$_6$H$_3$; τ_5 = 0.01).[42] The most intriguing difference between compounds **4** are the stark variations in isocyanide C-N-C angle—previously described as an indicator of back donation from an electron rich metal.[43-44] Both isocyanides in **4-^{t}Bu$_3$C$_6$H$_2$** are nearly linear (165.9(2) and 167.4(2)°), likely a consequence of the *ortho*-*tert*-butyl substituents. While relieving steric pressure in **4-^{t}Bu** allows the C-N-C angle to decrease to 142.35(17)°, the Fe-C$_{\text{isocyanide}}$ distances are identical (1.8018(17) for **3-^{t}Bu**; 1.796(3)$_{\text{ave}}$ for **4-^{t}Bu$_3$C$_6$H$_2$**). **4-Ph** displays both extremes of the C-N-C angle: one phenylisocyanide ligand is nearly linear (175.9(4)°) with a long Fe-C$_{\text{isocyanide}}$ contact (1.796(3) Å) while the other phenylisocyanide ligand is bent (133.9(3)°) with a short Fe-C$_{\text{isocyanide}}$ contact (1.738(4) Å).

The IR spectrum (KBr) of **4-^{t}Bu$_3$C$_6$H$_2$** resembles that of related dicarbonyl complexes—two well-defined absorptions at 1992 and 1896 cm^{-1} assigned to C≡N stretching modes (Figure S65).[45-47] The IR absorption profiles of **4-Ph** and **4-^{t}Bu** (KBr) are more challenging to interpret (Figure S66-S67). Each displays a combination of weak and strong, ill-defined absorptions in the energy range of 2090-1680 cm^{-1} and the lower energy vibrations indicate increased activation of the isocyanide ligands in **4-Ph** and **4-^{t}Bu**. These IR data are consistent with the solid-state depiction and may suggest more reactive isocyanide moieties in **4-Ph** and **4-^{t}Bu**.

Late-Stage Hydroboration

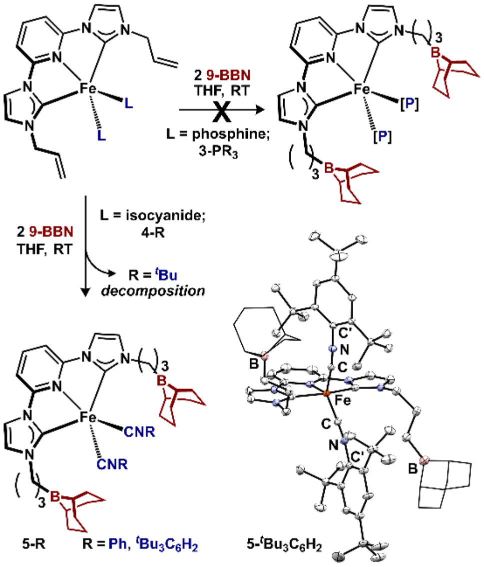


Figure 3. Attempted late-stage hydroboration of complexes **3-PR$_3$** and **4-R** with 9-BBN. Molecular structure of **5-^{t}Bu$_3$C$_6$H$_2$** displayed with 50% probability ellipsoids. The H-atoms are omitted and the 9-BBN substituents are displayed in wireframe for clarity.

Hydroboration of terminal alkenes is typically facile.[29] Although the pendent allyl groups in **3-PR$_3$** and **4-R** are uncoordinated, initial hydroboration reactivity studies were not successful, and showed varied reactivity profiles across the series. To assess the requirements, capabilities, and limitations of late-stage hydroboration, we conducted a systematic hydroboration study. Initial efforts focused on the phosphine ligated variants, **3-PR$_3$** (Figure 3)

Treating **3-PMe$_3$** with two equiv. 9-borabicyclo[3.3.1]nonane (9-BBN) in THF resulted in a complex mixture, as assessed by ^{1}H and ^{31}P NMR spectroscopy. While some resonances in the spectrum could be attributed to a successful hydroboration, the majority of the allylic moieties remained unreacted.[48] The largest resonances in the ^{31}P NMR spectrum are attributed to the Lewis acid/base adduct of PMe$_3$ and 9-BBN (vide infra). These data suggest that multiple reaction pathways were operative. In an attempt to limit the possible reaction sites, we evaluated reactions with phosphines of sequentially increasing steric profile (PMe$_3$ < PMe$_2$Ph < PEt$_3$).[38] Treating **3-PMe$_2$Ph** or **3-PEt$_3$** with two equiv. 9-BBN under analogous reaction conditions did not provide evidence of a successful late-stage hydroboration, similar to **3-PMe$_3$**. These results were surprising and suggested the phosphine ligands in **3-PR$_3$** may be more labile than anticipated. We hypothesized that the chelate effect in **3-depe** would overcome ligand lability while still providing a generous steric profile to enable successful late-stage hydroboration. Unfortunately, attempts to perform a late-stage hydroboration of **3-depe** were unsuccessful without consumption of the allylic moieties.

A series of experiments were undertaken with the isocyanide analogues, **4-R**, to determine if late-stage hydroboration of these species could be tolerated (Figure 3). Treating **4-^{t}Bu** with two equiv. 9-BBN resulted in decomposition of the starting material without evidence of hydroboration. While discouraging, we note that the spectroscopic signatures and solid-state structures of **4-R** suggested that the series of molecules exhibits varied electronic and steric environments. Successful hydroboration was achieved with **4-Ph**: treating a THF solution of **4-Ph** with two equiv 9-BBN resulted in clean, anti-Markovnikov hydroboration of the allylic groups to afford ($^{\text{BBN}}$CNC)Fe(CNPh)$_2$ (**5-Ph**). The formation of **5-Ph** was assessed by ^{1}H and ^{13}C NMR spectroscopy (Figure S23-S24). In C$_6$D$_6$ solution, however, **5-Ph** gradually decomposed over 16 hr to unidentified precipitated species, accompanied by a color change from deep purple/red to green-brown.

The degradation process observed in **5-Ph** was not encountered with the product of late-stage hydroboration of **4-^{t}Bu$_3$C$_6$H$_2$**, ($^{\text{BBN}}$CNC)Fe(CN^{t}Bu$_3$C$_6$H$_2$)$_2$ (**5-^{t}Bu$_3$C$_6$H$_2$**). The ^{1}H NMR spectrum (C$_6$D$_6$, Figure S26) of **5-^{t}Bu$_3$C$_6$H$_2$** is consistent with a C$_{2v}$ symmetric species formed by anti-Markovnikov hydroboration. The solution stability of **5-^{t}Bu$_3$C$_6$H$_2$** enabled the identification of its molecular structure by single crystal X-ray diffraction studies (Figure 3). Refinement of the data revealed a primary coordination environment about **5-^{t}Bu$_3$C$_6$H$_2$** that is unperturbed with respect to **4-^{t}Bu$_3$C$_6$H$_2$** (Table S14). Within the secondary coordination sphere, the appended trialkylboranes do not display any Lewis acid/base interactions (ΣBα = 359.82(11) and 360.00(13)°).

Insight into Hydroboration Requirements

The differing reactivity for late-stage hydroboration by the set of complexes, **1**, **3-PR$_3$**, and **4-R**, inform on to the requirements for this process, and provide a reasonable outline for making reaction predictions. Previously, our work with **1** demonstrated that, in the zero-valent state, both the N-heterocyclic carbenes and the carbonyl ligands were substitutionally inert.[31] In contrast, divalent **2** was incompatible with hydroboration conditions, consistent with increased lability of the N-heterocyclic carbene or acetonitrile ligands. We hypothesized that the overriding factor that determined late-stage hydroboration success was ancillary ligand lability. Ligand lability would dictate whether deleterious adducts form between the ancillary ligand (PR$_3$, CNR) and the Lewis acid (9-BBN, R-BBN).[49-52] To probe this supposition, we undertook a set of NMR experiments to define the steric and acidity requirements for an undesirable Lewis acid/base adduct formation (Figure 4).

Ancillary ligand abstraction (L) from the iron center could occur prior to hydroboration (L-B(H)R$_2$) or after hydroboration

(L-BR_3). To mimic the hydroboration sequence in the presence of a labile "L" type donor, we treated a C_6D_6 solution of 9-BBN with a phosphine (PMe_3, PEt_3, PMe_2Ph, ½ $Et_2P(CH_2)_2PEt_2$) or isocyanide (CN^tBu, CNPh, $CN(2,4,6\text{-}^tBu_3Ph)$). In the case of the phosphines, simple Lewis acid/base adduct formation (R_3P-$B(H)R_2$) is observed in all instances.[53] Importantly, the adducts generated by this method were also observed in the unsuccessful hydroborations of complexes **3-PR₃**. The spectroscopic analysis of reactions between isocyanides and 9-BBN are more complex: both 1,1-hydroboration[54-55] and acid/base adduct formation (RNC-$B(H)R_2$) are apparent for all of the isocyanides employed.[56] These collective experiments suggest that a labile "L" type ligand can introduce multiple undesirable reaction pathways that ultimately prevent allylic hydroboration.

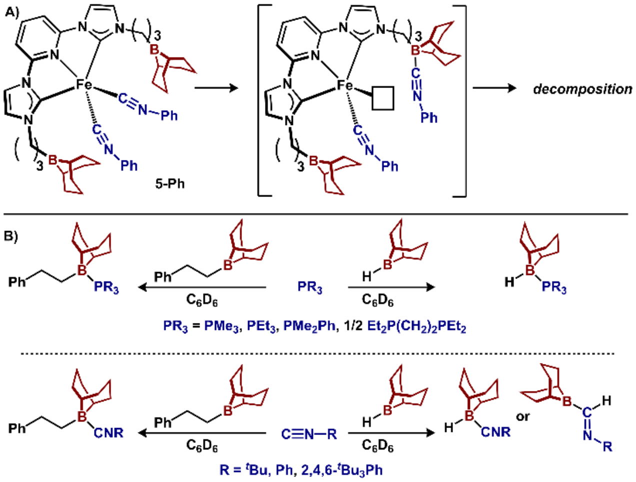


Figure 4. A) hypothesized decomposition pathway for **5-Ph**. B) model systems to probe Lewis acid/base adduct formation.

Given that hydroboration was prevented by either ligand lability (**3-PR₃**), or decomposition (**5-Ph**), we sought to evaluate more general compatibility guidelines. Lewis acid/base adduct formation (in the form of "L" abstraction from the metal) after hydroboration may be an operative pathway that results in decomposition of the metal complex. The trialkylboranes in **5-Ph** (R-$(CH_2)_3$-BBN) have a distinct steric profile compared to 9-BBN. We employed a surrogate, $Ph(CH_2)_2BBN$, with a similar acidity and steric profile to probe whether acid/base adduct formation was a plausible explanation for the decomposition of **5-Ph**. Treating stoichiometric quantities of $Ph(CH_2)_2BBN$ with PR_3 (PMe_3, PEt_3, PMe_2Ph, ½ $Et_2P(CH_2)_2PEt_2$) or CNR (CN^tBu, CNPh, $CN(2,4,6\text{-}^tBu_3Ph)$) resulted in Lewis acid/base adduct formation as assessed by ^1H NMR spectroscopy (C_6D_6, Figure 4B). These data confirm that, in all instances, the steric and acidity requirements for binding a Lewis acid are satisfied if the auxiliary ligand dissociates from the metal, i.e. formation of a Lewis acid/base adduct is feasible.

Ancillary ligand (PR_3 or CNR) abstraction *after* successful hydroboration may be a plausible explanation for the degradation of **5-Ph** (Figure 4A). We designed a series of complexes that contain weakly acidic boron Lewis acids within the secondary sphere to investigate whether the observed decomposition can be directly attributed to the presence of Lewis acidic boranes in the aforemention examples. Appended -$B(O_2C_2Me_4)$ Lewis acids are established to be compatibile with N-heterocyclic carbene ligands,[20] and, previously, we reported $[(^{BPin}CNC)Fe(MeCN)_3][BPh_4]_2$ as a viable precursor to zero-valent iron complexes ($^{BPin}H_2CNC$ = 2,6-bis(3-$(CH_2)_3$BPin)-1*H*-imidazolium)pyridine; BPin = $B(O_2C_2Me_4)$).[31] Employing similar protocol as described for the allylic variant, we synthesized phosphine- and isocyanide-ligated complexes bearing this ligand, $(^{BPin}CNC)Fe(PMe_3)_2$ (**6-PMe₃**) and $(^{BPin}CNC)Fe(CNPh)_2$ (**6-CNPh**), respectively. The molecular structure of **6-PMe₃** is displayed in Figure 5 and is unremarkable in comparison to **3-PMe₃**. Importantly, the alkyl-BPin fragments are not interacting with any Lewis bases ($\Sigma B\alpha$ = 359.9(3)°) and their presence did not impede the synthesis. A single crystal X-ray diffraction experiment performed on low-quality crystals of **6-CNPh** confirmed molecular connectivity that is analogous to **4-CNPh**; unfortunately, further discussions of metrical data are not possible.[57] The tri-*tert*-butylphenyl variant, $(^{BPin}CNC)Fe(CN^tBu_3C_6H_2)_2$ (**6-CN^{t}Bu₃C₆H₂**), was synthesized as an analogue and provided single crystals suitable for X-ray diffraction (Figure 5). As anticipated, the molecular structures of **6-CN^{t}Bu₃C₆H₂** and **3-^{t}Bu₃C₆H₂** and are analogous to one another, except the trigonal alkyl-BPin moieties in **6-CN^{t}Bu₃C₆H₂**. The synthesis of compounds **6**—species bearing a weak Lewis acid in the secondary coordination sphere—highlights a key principle: the stability of low-valent compounds with appended boron Lewis acids is dependent upon the strength of those Lewis acids.

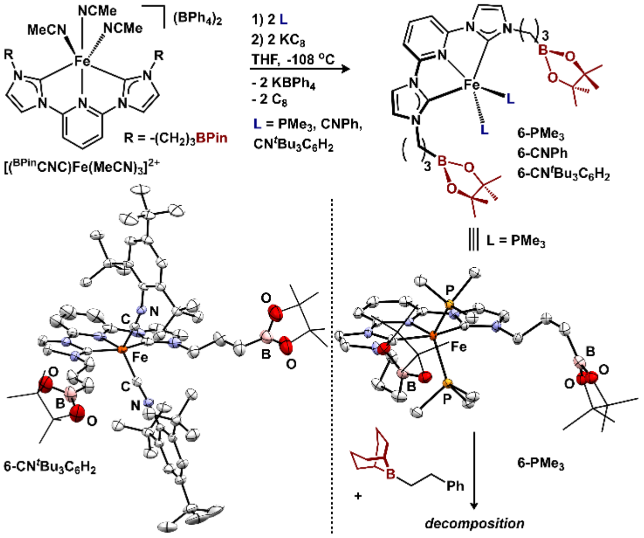


Figure 5. Formation of complexes **6** and decomposition of **6-PMe₃** upon exposure to exogenous trialkylborane. The molecular structures of **6-CN^{t}Bu₃C₆H₂** and **6-PMe₃** are displayed with 50% probability ellipsoids. All H-atoms are omitted and the BPin C-atoms are displayed in wireframe for clarity.

The isolation of compounds **6** enabled a direct assessment of whether their exposure to a trialkylborane of comparable Lewis acidity to the those in **5-^{t}Bu₃C₆H₂** would result in decomposition. Treating **6-PMe₃** with $Ph(CH_2)_2BBN$ in C_6D_6 under 1 atm of N_2 afforded an equilibrium mixture of $(^{BPin}CNC)Fe(PMe_3)(N_2)$ (ν_{N2} = 1975 cm^{-1}; KBr; Figure S76)[58] and **6-PMe₃** as well as the Lewis acid/base adduct, Me_3P-$BBN(CH_2)_2Ph$.[59] These data suggest ancillary ligand abstraction by a Lewis acid may be a reversible process. Repeating the reaction under static vacuum resulted in a mixture of **6-PMe₃** and a proposed hydride-containing species, $[trans\text{-}(^{BPin}CNC)Fe(PMe_3)_2H]^+$, as the only phosphorus-containing species on the basis of NMR spectroscopy (see pgs S36-S47 for further discussion).[60] We hypothesize that [*trans*-

$(^{BPin}CNC)Fe(PMe_3)_2H]^+$ was formed by the reaction of $(^{BPin}CNC)Fe(PMe_3)(N_2)$ (generated by PMe_3 abstraction) and the Lewis pair, $Me_3P\text{-}BBN(CH_2)_2Ph$.[61] These experiments further illuminate potential degradation pathways available to complexes containing labile ancillary ligands in the presence of Lewis acids.

Working under the hypothesis that ancillary ligand lability is a key contributing factor that hinders successful late-stage hydroboration, we sought a quantitative metric to correlate ligand lability and hydroboration success. Qualitatively, we found that ancillary ligand exchange studies with **3-PMe$_3$** and CN*ᵗ*Bu in C_6D_6 follows the trend PR_3 ~ CNR > CO, similar to the results of other reported competition studies.[45, 62-63] We turned our attention to electronic absorption spectroscopy to quantify these observations. All complexes display rich absorption spectra that feature one or two well defined charge transfer (CT) transitions. The **3-PR$_3$** complexes are all dark brown and display an intense (13,500-18,500 $M^{-1}cm^{-1}$) visible absorption between 416-441 nm (THF; Fig. S77) that is minimally solvatochromic.[64] The energy of this charge transfer band follows **3-PMe$_3$** > **3-PMe$_2$Ph** > **3-PEt$_3$** > **3-depe**.[65] In **4-R**, the electronic absorption spectrum of each complex displays a similar profile: one band in the far UV and one color-producing band in the visible region (THF; Fig. S78). Although the visible band does not follow an apparent trend with ligand donor properties, the energy of the far UV absorption inversely tracks with the σ-donor properties[66] of the isocyanide (PhNC = 366 nm; $^tBu_3C_6H_2NC$ = 392 nm; ^tBuNC = 408 nm).[63, 67]

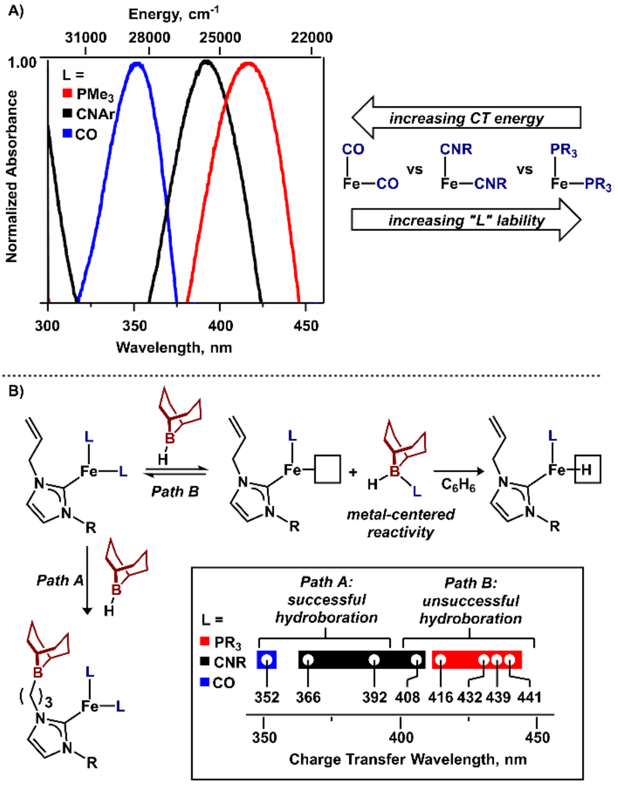


Figure 6. A) Energy comparison of the charge transfer band of $(^{allyl}CNC)Fe(L)_2$ (L = CO, $CN^tBu_3C_6H_2$, PMe_3) and inverse correlation between charge transfer energy and ligand lability. B) Proposed pathways for successful hydroboration and unsuccessful hydroboration.

We employed the energy of the charge transfer (CT) band as an evaluative measure of late-stage hydroboration compatibility. Particularly instructive are comparisons between the energy of this transition across the series of complexes with varied ancillary ligands (i.e. CO vs. CNR vs. PR_3; Figure 6). We found that the CT energy (CO > CNR > PMe_3) inversely correlates with the σ-donor properties.[68-69] Experimentally, we observed that the CT energy dictates whether late-stage hydroboration with 9-BBN is feasible: hydroboration was successful if the energy is ≥ 25510 cm^{-1} (392 nm), but fails when the energy was ≤ 24510 cm^{-1} (408 nm; Figure 6). We assign this transition as a ligand-to-metal charge transfer that populates the $d(x^2\text{-}y^2)$.[62, 70] The energy of this transition correlates with whether we observe decomposition, suggesting a nuanced system that is on the edge of M-L lability. Species with labile ligands are more prone to ancillary ligand abstraction by the Lewis acidic hydroborating agent, 9-BBN, to generate $L\text{-}B(H)R_2$. Importantly, each failed hydroboration of **3-PR$_3$** revealed the product of ancillary ligand abstraction, $R_3P\text{-}B(H)R_2$, regardless of the identity of the phosphine. In contrast, **4-^{t}Bu$_3$C$_6$H$_2$** is stable to a greater than 10-fold excess of 9-BBN.

CONCLUSION

The results of this study suggest inherent issues are associated with molecular design strategies that rely on late-stage hydroboration. Subtle variations in the primary coordination sphere about a metal will result in largely divergent late-stage hydroboration compatibility. Within the iron(0) pyridine(dicarbene) platform, all attempts to hydroborate the allylic moieties of **3-PR$_3$** with 9-BBN were futile. In contrast, the isocyanide variants, **4-R**, were dependent upon the identity of the isocyanide. It is probable that these drawbacks and limitations could be alleviated by diminishing the Lewis acidity of the appended Lewis acid or by increasing the steric bulk of the appended borane. Each compromise, however, would have obvious drawbacks when considering reaction design. The hydroboration studies presented herein are distinct from that of the robust carbonyl analogue, $(^{allyl}CNC)Fe(CO)_2$ (**1**), where late-stage hydroboration with 9-BBN, dicyclohexylborane, and di(*sec*-isoamyl)borane was tolerated.[31] Even upon exposure to very potent Lewis acids such as $B(C_6F_5)_3$, the ancillary carbonyl ligands remained intact.[71]

While research into metal-ligand cooperativity continues to provide new avenues to perform challenging chemical transformations, our studies aim to provide a commentary on reaction compatibility that may be needed to pursue those studies. Late-stage ligand modification has the potential to enable rapid diversification of a single target molecule rather than requiring exhaustive ligand preparation. Our study begins to clarify important considerations for performing late-stage hydroborations on traditional coordination/organometallic complexes. While ancillary ligand lability appears to be the overriding factor when determining hydroboration success, steric and electronic tuning of those ligands can be employed to obtain satisfactory results. Our lab is currently translating these results to new frameworks that enable access to alternate geometries and spin states of the metal.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website and contains experimental procedures and spectroscopic characterization of all species (PDF).

Accession Codes

CCDC 2084280-2084291 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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56. These reactions are likely further complicated by Lewis acid/base adduct formation after 1,1-hydroboration occurs.

57. A description of the structure of **6-CNPh** is provided in the supporting information.

58. A related complex, (^{DIPP}CNC)Fe(PMe$_3$)(N$_2$), displays ν_{N_2} = 2023 cm^{-1} (KBr). See Fig. S79.

59. Placing this mixture under static vacuum (0.14 torr) produces [*trans*-(^{BPin}CNC)Fe(PMe$_3$)$_2$H]$^+$ with consumption of Me$_3$P-BBN(CH$_2$)$_2$Ph and (^{BPin}CNC)Fe(PMe$_3$)(N$_2$).

60. We have been unable to isolate this complex, therefore the assignment is tentative. Diagnostic spectroscopic data: ^{1}H NMR (700 MHz, C_6D_6) δ = -12.98 (t, J_{P-H} = 72.1, Fe-H). ^{31}P NMR (283 MHz, C_6D_6) δ = 24.85 (d, J_{P-H} = 72.1, Fe(PMe$_3$)$_2$). The same species is obtained by protonating **6-PMe$_3$** with Brookhart's acid.

61. Similar complexes have been exploited for isotope exchange with arene solvents and likely proceed through hydride intermediates. See: (a) Rummelt, S. M.; Darmon, J. M.; Yu, R. P.; Viereck, P.; Pabst, T. P.; Turner, Z. R.; Margulieux, G. W.; Gu, S.; Chirik, P. J., Synthesis, Structure, and Hydrogenolysis of Pyridine Dicarbene Iron Dialkyl Complexes. *Organometallics* **2019**, *38*, 3159-3168; (b) Pony Yu, R.; Hesk, D.; Rivera, N.; Pelczer, I.; Chirik, P. J., Iron-catalysed tritiation of pharmaceuticals. *Nature* **2016**, *529*, 195-199; (c) Yu, R. P.; Darmon, J. M.; Semproni, S. P.; Turner, Z. R.; Chirik, P. J., Synthesis of Iron Hydride Complexes Relevant to Hydrogen Isotope Exchange in Pharmaceuticals. *Organometallics* **2017**, *36*, 4341-4343; (d) Corpas, J.; Viereck, P.; Chirik, P. J., C(sp^2)–H Activation with Pyridine Dicarbene Iron Dialkyl Complexes: Hydrogen Isotope Exchange of Arenes Using Benzene *d*$_6$ as a Deuterium Source. *ACS Catal.* **2020**, *10*, 8640-8647. A comparable reaction

between $(^{DIPP}CNC)Fe(N_2)_2$ and N-benzylideneaniline afforded an Fe(II)-H species. See ref. 42.

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64. $(^{BPin}CNC)Fe(PMe_3)_2$ (**6-PMe$_3$**) was chosen for the solvatochromic study due to its high solubility, see SI. Solvent, λ_{max}: THF, 430 nm; cyclohexane, 434 nm; benzene, 436 nm. See Fig. S84.

65. We propose that geometric constraints in **3-depe** may account for it containing the lowest energy transition of the series.

66. An alternate description is that the energy tracks with π-acceptor properties of the isocyanide.

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