

Lewis Acid-Promoted Oxidative Addition at a $[\text{Ni}^0(\text{diphosphine})_2]$ Complex: The Critical Role of a Secondary Coordination Sphere

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Abstract: Oxidative addition represents a critical elementary step in myriad catalytic transformations. Here, the importance of thoughtful ligand design cannot be overstated. In this work, we report the intermolecular activation of iodobenzene (PhI) at a coordinatively saturated 18-electron $[\text{Ni}^0(\text{diphosphine})_2]$ complex bearing a Lewis acidic secondary coordination sphere. Whereas alkyl-substituted diphosphine complexes of Group 10 are known to be unreactive in such reactions, we show that $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ ($\text{P}_2\text{B}^{\text{Cy}}_4 = 1,2\text{-bis}(\text{di}(3\text{-dicyclohexylboranyl})\text{-propylphosphino})\text{ethane}$) is competent for room-temperature PhI cleavage to give $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(\text{Ph})(\text{I})]$. This difference in oxidative addition reactivity has been scrutinized computationally – an outcome that is borne out in ring-opening to provide the reactive precursor – for $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$, a “boron-trapped” 16-electron \square^1 -diphosphine Ni(0) complex. Moreover, formation of $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(\text{Ph})(\text{I})]$ is inherent to the $\text{P}_2\text{B}^{\text{Cy}}_4$ secondary coordination sphere: treatment of the Lewis adduct, $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_3]$ with PhI provides $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_3(\text{I})]$ via iodine-atom abstraction and *not* a $[\text{Ni}^{\text{II}}(\text{Ph})(\text{I})(\text{diphosphine})]$ compound – an unusual secondary sphere effect. Last, the reactivity of $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ with 4-iodopyridine was surveyed, which resulted in a pyridyl-borane linked oligomer. The implications of these outcomes are discussed in the context of designing strongly donating, and yet labile diphosphine ligands for use in a critical bond activation step relevant to catalysis.

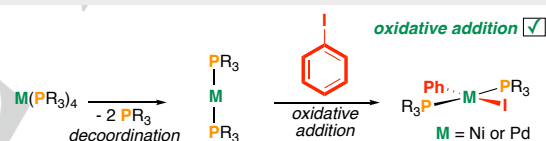
Introduction

As an elementary step, oxidative addition represents a key component of many catalytic cycles mediated by organometallic species.¹ At the core of this transformation are coordinatively-unsaturated electron-rich metal centres (M^n) that engage with X–Y units to generate $\text{M}^{n+2}(\text{X})(\text{Y})$ – species that can be intercepted by transmetalating agents in cross-coupling, for example. Key to this notion are the design of ligands that allow for rapid dissociation and thus, access to reactive low-valent metal centres – such is the case for monophosphine-ligated complexes of Group 10: $[\text{M}^0(\text{PR}_3)_4]$ ($\text{M} = \text{Ni}$ or Pd), which upon dissociation of PR_3 , provide reactive linear “ $[\text{M}^0(\text{PR}_3)_2]$ ” fragments that undergo addition of aryl halides and triflates, to name but a few (**Chart 1A**).² Notably, these reactions occur more rapidly in instances where the PR_3 ligand is bulky, favouring dissociation and revealing orbitals appropriate for X–Y bond cleavage.

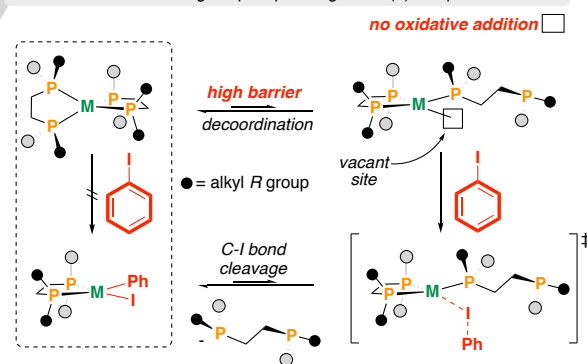
In addition to monodentate phosphines, chelating diphosphine ligands have also been studied *e.g.*, $[\text{M}^0(\text{diphosphine})_2]$, wherein ligand dissociation results in bent “ $[\text{M}^0(\square^1\text{-diphosphine})]$ ” or trigonal planar “ $[\text{M}^0(\square^1\text{-diphosphine})(\square^2\text{-diphosphine})]$ ” complexes that are more reactive than their linear

14-electron “ $[\text{M}^0(\text{PR}_3)_2]$ ” counterparts (**Chart 1B**).³ Notwithstanding, access to such unsaturated complexes is often obstructed by an inability of such ligands to dissociate, owing (in part) to the chelate effect. As a point of comparison, as early as 1971, it was shown that the 18-electron fragment, $[\text{Pd}^0(\text{dppe})_2]$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) did not react with aryl halides;⁴ this contrasts with $[\text{Pd}^0(\text{PPh}_3)_4]$, which is a textbook precursor for concerted oxidative addition.¹ In 2000, Amatore *et al.* showed that several other $[\text{Pd}(\text{diphosphine})_2]$ complexes

A. oxidative addition using a monophosphine ligated $\text{M}(0)$ complex



B. oxidative addition using a diphosphine ligated $\text{M}(0)$ complex



C. this work: oxidative addition using a modified coordination sphere

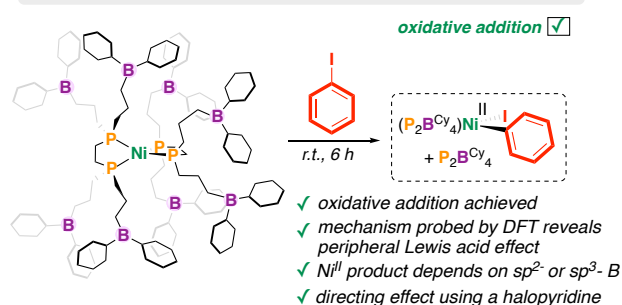


Chart 1. A) Oxidative addition using $[\text{M}(\text{PR}_3)_4]$; B) oxidative addition using $[\text{M}(\text{diphosphine})_2]$; C) this work, exploiting a $\text{P}_2\text{B}^{\text{Cy}}_4$ diphosphine ligand for activation of iodoarenes; $\text{M} = \text{Ni}$ or Pd .

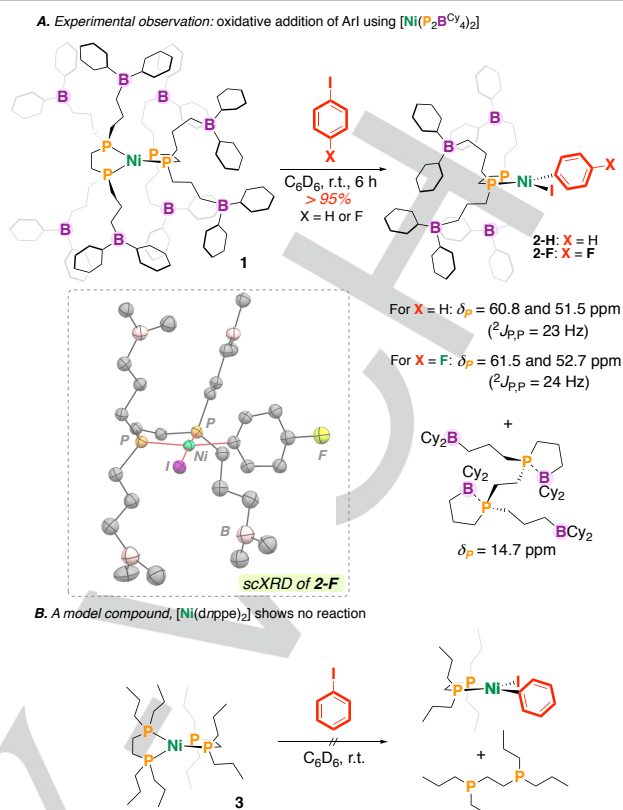
behave similarly, all of which were unreactive toward iodobenzene (PhI).⁵ This reactivity trend can also be extended to nickel(0), where $[\text{Ni}^0(\text{PR}_3)_4]$ ($\text{R} = \text{Ph}^{2a}$ or Et^{2b}) complexes have been reported to activate PhI to give *trans*- $[\text{Ni}^{\text{II}}(\text{PR}_3)_2(\text{Ph})(\text{I})]$, but $[\text{Ni}^0(\text{dppe})_2]$ has proven inert towards Ar-X ($\text{X} = \text{halide}$) oxidative addition.⁶ This lack of performance has been attributed to the endergonicity associated with dppe decoordination.⁷

We thus began to ask, how might one develop *irreversible* routes toward such unsaturated “[M⁰(diphosphine)]” units wherein a displaced diphosphine from “[M⁰(diphosphine)₂]” is unable to return to the primary coordination sphere? In theory, this would permit “[M⁰(diphosphine)]” to remain on cycle, obviating potential [M(diphosphine)(L–L)] resting states where expelled diphosphine or diolefin ligand (L–L) have been shown to encumber turnover.^{6b,8}

In the realm of ligand discovery, our group⁹ and others¹⁰ have become interested in designing ligands containing peripheral Lewis acids. In the context of our work on diphosphine ligands, these units maintain conventional phosphine donor basicity as compared to their alkyl relatives; however, they bind Lewis bases in their secondary coordination sphere,⁹ and show reactivity that is differential, owing to facile decoordination (**Chart 1C**).^{9c} In the latter case, ligand loss is favoured due to formation of two intramolecular Lewis-acid base adducts.^{9c} As a continuance on our studies of such borane-substituted $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}})_2]$ ^{9a} ($\text{P}_2\text{B}^{\text{Cy}} = 1,2\text{-bis}(\text{di}(3\text{-dicyclohexylboranyl})\text{propylphosphino})\text{ethane}$) complexes, we postulated that such low-valent $[\text{Ni}(\text{diphosphine})_2]$ species might be suitable candidates for the activation of polar C–halide bonds due to the possibility of engagement in intramolecular Lewis acid/base reactions, enabling access to coordinatively-unsaturated, and by extension, reactive (phosphine)Ni(0) species – an area of burgeoning interest.¹¹

Results and Discussion

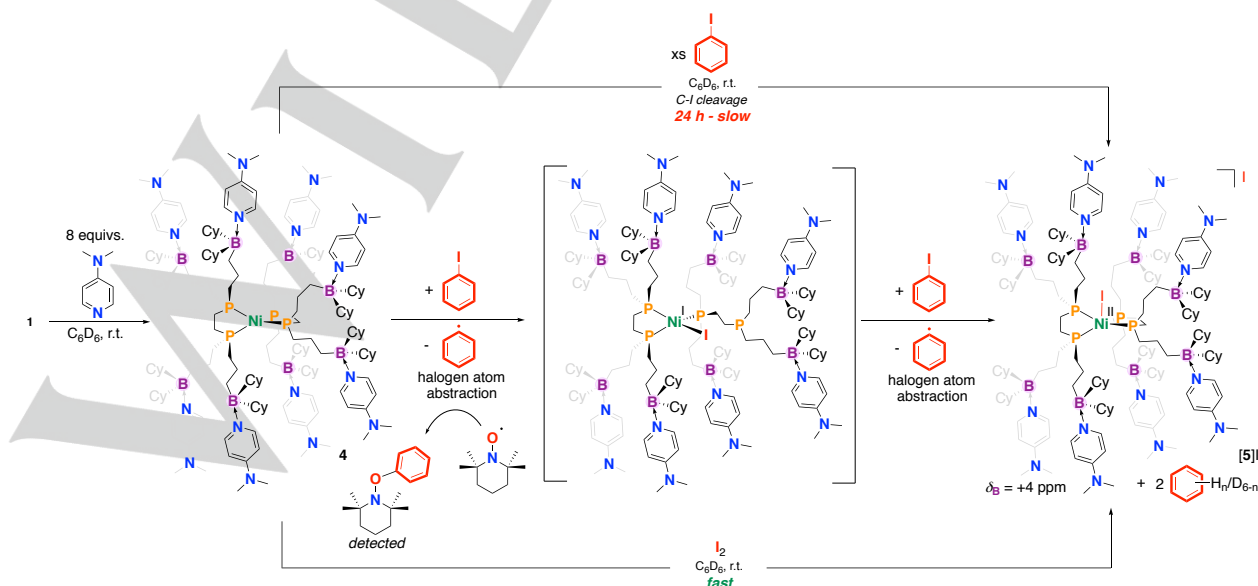
Reactivity with iodoarenes. As a starting point, we treated a C_6D_6 solution of $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}})_2]$ (**1**) with 1 equiv. PhI, which resulted in immediate room-temperature reactivity to reveal the oxidative addition product, $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}})(\text{C}_6\text{H}_5)(\text{I})]$ (**2-H**) ($\delta_{\text{P}} = 60.8$ and 51.5 ppm, $^2J_{\text{P,P}} = 23$ Hz) and free $\text{P}_2\text{B}^{\text{Cy}}$ ligand ($\delta_{\text{P}} = 14.8$ ppm) – a reaction that is complete within 6 h (>95% conversion). By ¹H NMR spectroscopy, three new signals centered at $\delta_{\text{H}} = 7.85$, 7.23 , and 6.92 ppm were observed for the $[\text{Ni}]-\text{C}_6\text{H}_5$ group. Similar results were obtained when **1** underwent reaction with 4-fluoriodobenzene, providing $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}})(4\text{-F-C}_6\text{H}_4)(\text{I})]$ (**2-F**), for which an X-ray crystal structure was obtained (**Scheme 1**). **2-F** features a square planar diphosphine-coordinated $[\text{Ni}^{\text{II}}(4\text{-F-C}_6\text{H}_4)(\text{I})]$ core having four sp^2 -hybridized boranes projecting



Scheme 1. Treatment of **1** or **3** with iodoarenes. Inset shows scXRD structure of **2-F** (hydrogens omitted for clarity, 50% ellipsoids, Cy rings are truncated).

vertically from the horizontal coordination plane. The relative stability of **2-H/F** warrants note as related 1,1'-*bis*(diphenylphosphino)ferrocenyl (dppf) complexes of Ni e.g., $[\text{Ni}^{\text{II}}(\text{dppf})(\text{Ph})\text{I}]$ are known to be promiscuous and are especially unstable in the presence of nickel(0).^{6a,8} Highlighting the relevance of **2-F** in a cross-coupling sequence, reaction with PhMgBr in THF provides the cross-coupled product, 4-fluorobiphenyl in >99% by ¹⁹F NMR spectroscopy. Catalysis is also achieved using 6 mol% **1** in the presence of 4-fluoriodobenzene and PhMgBr, giving a turnover number of ~3 (Yield ~ 20%) over 24 h in THF at room temperature (see ESI).

By contrast, reaction of the control, $[\text{Ni}^0(\text{dnppe})_2]$ ^{9a} (*dnppe* = 1,2-*bis*(di-*n*-propylphosphino)ethane) with PhI did not provide $[\text{Ni}^{\text{II}}(\text{dnppe})(\text{C}_6\text{H}_5)(\text{I})]$ (**Scheme 1**). In addition, treatment of



Scheme 2. Oxidative addition reactivity of pyridine derivative **4**.

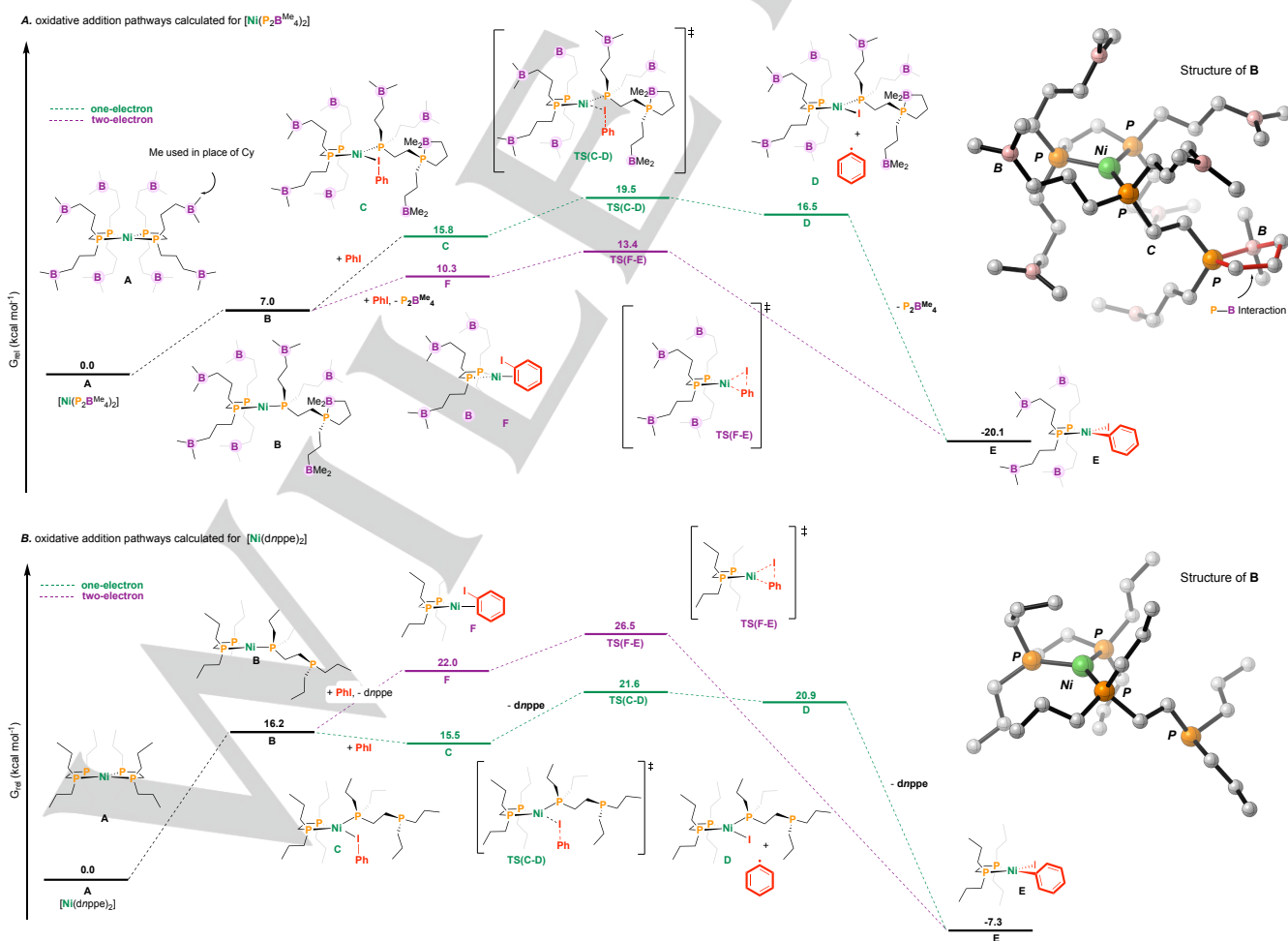
$[\text{Ni}^0(\text{dnppe})_2]$ with two equivalents of a trialkyl borane, $\text{BCy}_2^{\text{Oct}}$ (Oct = octyl) and PhI also did not result in reactivity, indicating that the boranes must be present in the ligand scaffold to decrease the entropic penalty of ring-opening by Lewis adduct formation.

Strikingly, the product of PhI oxidative addition depends on the presence of free Lewis acids in the secondary coordination sphere. In this way, the reaction of $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4\text{-DMAP}_4)_2]$ (**4**) (DMAP = 4-*N,N*-dimethylaminopyridine) with PhI cleanly provides the five-coordinate complex, $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_5(\text{I})]$ (**[5]I**) over 24 h and not $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(\text{DMAP})_4(\text{C}_6\text{H}_5)(\text{I})]$ (**Scheme 2**). Compound **[5]I** displays a singlet in its ^{31}P NMR spectrum at $\delta_{\text{P}} = 48.4$ ppm – the same signal is observed from independent reaction of **4** with I_2 in C_6D_6 . In addition to **[5]I**, the fate of the “Ph” fragment is accounted for in the formation of several $\text{C}_6\text{H}_n\text{D}_{6-n}$ isotopologues that result from H/D exchange with C_6D_6 (see ESI). Performing this reaction in the presence of a radical scavenger, 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)¹² provides the corresponding phenyloxy adduct by ^1H NMR spectroscopy (**Scheme 2**). We contend that **[5]I** results from double iodine atom abstraction from PhI, though decomposition of a nickel(II) oxidative-addition product, in the presence of excess DMAP, cannot be conclusively ruled out – it should be noted, however, that **2-F** is stable in the presence of excess DMAP, generating a [(diphosphine)Ni(4-F-C₆H₄)(I)] compound with N—B linkages (see ESI). This result showcases the ability to not only react with PhI, but also to change the Ni(II) product that results from activation simply on the basis of borane adduct formation – an unusual donor-based secondary sphere effect.

Computational Studies. Given the marked difference in reactivity witnessed by $[\text{Ni}^0(\text{diphosphine})_2]$ complexes **1** and **3**, the mechanism of C-I bond oxidative addition was studied using density functional theory (DFT). This analysis considered two pathways invoking one- and two-electron mechanisms (**Scheme**

3 and ESI).¹³ Conformational searching was conducted using xTB and CREST and the GFN-FF force field.¹⁴ DFT calculations were carried out using Gaussian16 Rev. C.01.¹⁵ The level of theory used for DFT calculations (M06/6-311+G(d,p) with LANL2DZ(d,p) in benzene solvent (SMD) for single points; B3LYP-D3/6-31G(d)+LANL2DZ(d,p)+LANL2TZ(f) for geometries)¹⁶ gives energies for **A-dnppe** and **B-dnppe** that are comparable to DLPNO-CCSD(T)/cc-pVTZ energies for the same geometries using ORCA 5.0.0 (see ESI).¹⁷

For both pathways, transient dissociation of a phosphine ligand arm from an 18-electron complex: $[\text{Ni}^0(\text{P}^2\text{-diphosphine})_2]$ (**A**) was calculated to provide a 16-electron $[\text{Ni}^0(\text{P}^2\text{-diphosphine})(\text{P}^1\text{-diphosphine})]$ (**B**) species – in the case of $\text{P}_2\text{B}^{\text{Me}}_4$, this process is rendered lower in energy than *dnppe* due to intramolecular “trapping” by a pendant borane. The energies associated with ring-opening: 7.0 kcal mol⁻¹ (**B-P₂B^{Me}₄**) and 16.2 kcal mol⁻¹ (**B-dnppe**), are consistent with stabilization of the $\text{P}^1\text{-P}_2\text{B}^{\text{Me}}_4$ framework via an intramolecular P—B interaction, resulting in a difference of 9.2 kcal mol⁻¹ (the optimized geometries of all ring-opened species (**B**) are depicted at the top right-hand side within their respective potential energy surface). The alternative trigonal planar complex in which there is no P-B interaction has a relative free energy of 18.3 kcal mol⁻¹, which is comparable to **B-dnppe**. Next, PhI coordination gives $[\text{Ni}^0(\text{P}^1\text{-Ph})(\text{P}^2\text{-diphosphine})(\text{P}^1\text{-diphosphine})]$ (**C**). For the one-electron mechanism (green), **C** was connected to a halide abstraction transition state (**TS(C-D)**) associated with C-I bond cleavage and Ni-I bond formation to afford $[\text{Ni}^{\text{I}}(\text{I})(\text{P}^2\text{-diphosphine})(\text{P}^1\text{-diphosphine})]$ (**D**) and a phenyl radical. This transition state, **TS(C-D)** was found to be +19.5 kcal mol⁻¹ (**TS(C-D)-P₂B^{Me}₄**) and +21.6 kcal mol⁻¹ (**TS(C-D)-dnppe**). Taken together, these energies suggest that for the *dnppe* ligand system, reaction via a one-electron mechanism is less favorable. Ligand decoordination and radical recombination with Ph• gives the



Scheme 3. Proposed mechanism for oxidative addition using complexes **1** and **3**. BCy_2 has been modeled as BMe_2 . Free energy change (kcal mol⁻¹). All geometry optimizations and frequency calculations were performed using M06/6-311+G(d,p)+LANL2DZ(d,p) (ECP on I only).¹³

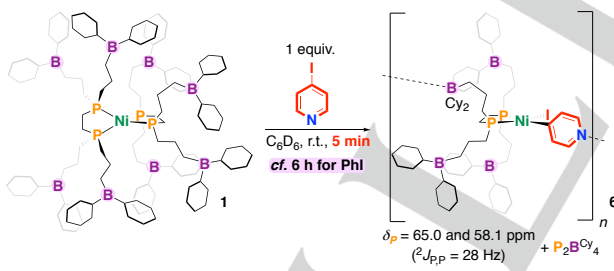
product, $[\text{Ni}^{\text{II}}(\text{Ph})(\text{I})(\text{P}^2\text{-diphosphine})]$ (**E**), which across both ligand platforms represents a global minimum: $-20.1 \text{ kcal mol}^{-1}$ (**E-P₂B^{Me}₄**) and $-7.3 \text{ kcal mol}^{-1}$ (**E-dnppe**). Notably, activation barriers for both compounds are accessible at 298 K,¹⁸ though oxidative addition for the *dnppe* system is less favorable.

The two-electron mechanism (purple) as seen in **Scheme 3** involves a concerted three-membered transition state involving Ni and the C(aryl)-I bond. For this pathway, diphosphine ligand loss provides $[\text{Ni}^0(\eta^2\text{-C,C-PhI})(\text{P}^2\text{-diphosphine})]$ (**F**): $+10.3 \text{ kcal mol}^{-1}$ (**F-P₂B^{Me}₄**) and $22.0 \text{ kcal mol}^{-1}$ (**F-dnppe**) uphill, respectively compared to **A**. This intermediate was found to undergo carbon-iodine bond cleavage *via* a three-membered transition state, **TS(F-E)**, which was found to be $13.4 \text{ kcal mol}^{-1}$ (**TS(F-E)-P₂B^{Me}₄**) and $26.5 \text{ kcal mol}^{-1}$ (**TS(F-E)-dnppe**), respectively compared to **A**. Following bond cleavage, the product $[\text{Ni}^{\text{II}}(\text{Ph})(\text{I})(\text{P}^2\text{-diphosphine})]$ (**E**) results. For the *dnppe* system, high barriers suggest that oxidative addition *via* a two-electron mechanism is not favorable at 298 K.¹⁸ However, the significant additional stability afforded to free *versus* bound ligand in the **P₂B^{Me}₄** system as a result of two intramolecular Lewis acid/Lewis base interactions renders the complete dissociation of a bisphosphine ligand highly favorable and the subsequent two-electron oxidative addition step feasible and irreversible at 298 K.

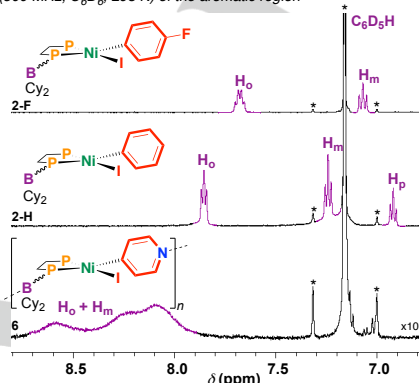
In summary, dissociation of **P₂B^{Me}₄** (unlike *dnppe* and related alkyl-substituted diphosphines) is advantageous, encouraging PhI coordination and subsequent activation to give $[\text{Ni}^{\text{II}}(\text{Ph})(\text{I})(\text{P}_2\text{B}^{\text{Cy}}_4)]$ (**2-H**), likely *via* a two-electron pathway.

Reactivity with 4-iodopyridine. Having surveyed the intermolecular reactivity of PhI in the presence and absence of a substituted pyridine (DMAP), we wondered how **1** might behave toward a substituted pyridine bearing a carbon-iodine bond. More precisely, we wished to test whether a boron effect would alter reactivity, owing to the potential for boron-directed C-I bond cleavage – a unique approach in the context of haloheterocycle activation/functionalization.¹⁹ The reactivity of **1** with 1 equiv. 4-iodopyridine²⁰ was thus examined, rapidly providing $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(4\text{-Pyr})(\text{I})]_n$ (**6**) ($\delta_{\text{P}} = 65.0$ and 58.1 ppm , $^2J_{\text{P,P}} = 28 \text{ Hz}$) and free **P₂B^{Cy}₄** ligand (**Scheme 4**) in $< 5 \text{ min}$. This timeframe is considerably shorter than that noted for PhI above (6 h), possibly suggesting a directing effect owing to the

A. Acceleration of oxidative addition using a Lewis acidic ligand

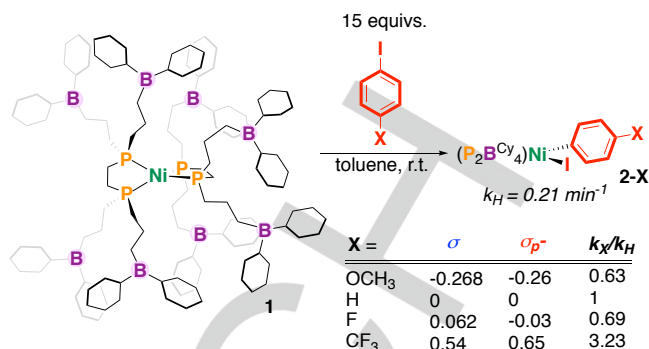


B. ¹H NMR (500 MHz, C₆D₆, 298 K) of the aromatic region

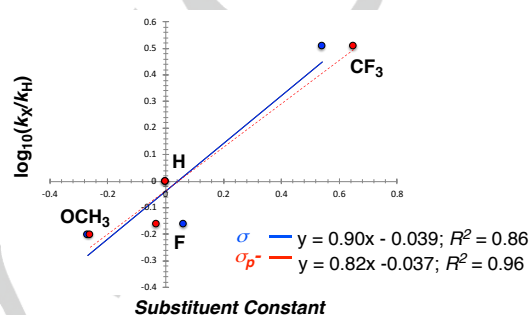


Scheme 4. Lewis-acid accelerated addition of 4-iodopyridine. Inset shows ¹H NMR (500 MHz, C₆D₆, 298 K) showing the aromatic region of **2-H/F**, and **6** (o = ortho, m = meta, p = para), * = C₆D₅H.

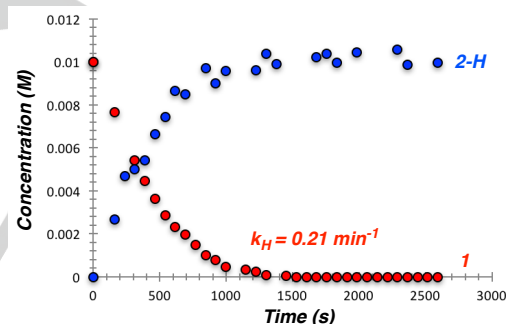
A. Oxidative addition of *p*-X-iodoarenes



B. Hammett plot analysis for oxidative addition



C. Concentration vs. time for formation of **2-H** from **1** and PhI



Scheme 5. **A.** Oxidative addition of *p*-X-iodoarenes. **B.** Hammett Plot. **C.** Concentration versus time plot for reaction of **1** with PhI, generating **2-H**.

formation of N—B linkages; it is noteworthy, however, to highlight the difference in electronics between phenyl- and pyridyl-based haloarenes,²¹ an effect that cannot be excluded, despite both having similar C—I bond dissociation energies.²⁰ Consistent with a fluxional oligomer, the ¹H NMR spectrum of **6** provides a broad feature at $8.80 \geq \delta_{\text{H}} \geq 7.90 \text{ ppm}$ for the aromatic pyridyl ortho and meta hydrogens (**Scheme 4**), while the ¹¹B NMR spectrum was featureless. Variable temperature ¹H NMR spectroscopy showed decoalescence of this broad feature at low temperature to aryl signals attributed to isomers of complex **6** (see *ES*). Markedly, no reaction is observed between **3** and 4-iodopyridine, again underscoring the utility of the **P₂B^{Cy}₄** diphosphine ligand. Thus, the **P₂B^{Cy}₄** framework not only provides opportunities in promoting oxidative addition reactions (by contrast to related alkyl diphosphine ligands), but also enables the activation of a haloheterocycle, resulting in a Ni/pyridyl-based oligomer.

Mechanistic Studies. To probe the mechanism of oxidative addition experimentally, a Hammett plot was constructed using the relative rates of oxidative addition between compound **1** and 4-substituted iodoarenes. Such studies have been proven useful in differentiating amongst concerted and single electron transfer mechanisms.^{2,22} Thus, monitoring of the reaction between **1** and 15 equivalents of substituted iodoarene under pseudo-first order

conditions was performed by ^{31}P NMR spectroscopy using $\text{Ph}_3\text{P}=\text{O}$ as an internal standard. The data are summarized in **Scheme 5**; compound **1** obeys pseudo-first order kinetics with a rate constant of $k_H = 0.21 \text{ min}^{-1}$. Other substrates were also tested providing k_{rel} values of 0.63 ($p\text{-OCH}_3$), 0.69 ($p\text{-F}$), and 3.2 ($p\text{-CF}_3$). Plots of $\log_{10}(k_{\text{rel}})$ ($k_{\text{rel}} = k_X/k_H$) against the Hammett parameters, σ/σ_p^- were linearly fit giving a slope of $\rho = 0.90$ ($R^2 = 0.86$; \square) or $\rho = 0.82$ ($R^2 = 0.96$; \square_p^-). These values suggest build-up of negative charge in the transition state,²³ and are in keeping with those observed for related nickel systems wherein a two-electron mechanism proceeding via a three-centered transition-state is invoked.^{2,21} Moreover, reaction monitoring revealed a consistent mass balance of $[\text{Ni}]$ throughout the reaction, suggesting the absence of $S > 0$ Ni species (**Scheme 5C**).

Conclusion

In sum, we have determined that a borane-appended $[\text{Ni}^0(\text{diphosphine})_2]$ complex readily promotes the carbon-iodine bond cleavage of iodoarenes at room temperature. This reactivity is sourced from favorable $\text{P}_2\text{B}^{\text{Cy}}_4$ ligand loss, exposing a coordinatively unsaturated and hence reactive $\text{Ni}(0)$ center. This work contrasts with previous reports on saturated alkyl-substituted $[\text{Ni}^0(\text{diphosphine})_2]$ complexes, which are inactive for this transformation, bringing forth a new ligand design concept that might well show promise for catalyst development. As an extension, we have also shown that the mechanism of carbon-iodine bond rupture is inherent to the nature of the boron-rich secondary coordination sphere with free boranes resulting in formation of **2-H/F** and borane-pyridine adducts providing $[\text{5}]^+$. The ability to controllably discriminate between these two pathways using the same diphosphine ligand provides a lucrative platform for the development of organometallic complexes that possess a boron-based "switch" that permits shuttling between reaction outcomes. Finally, we demonstrate the utility of the $\text{P}_2\text{B}^{\text{Cy}}_4$ ligand scaffold for the activation of halopyridines, an attractive development in the area of carbon-halogen bond oxidative addition.

Supporting Information

^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra for **2-H/F**, **[5]**, and **6** as well as .xyz coordinate files for all DFT-calculated molecules. CCDC 2057049 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Computational chemistry data underpinning this study can be accessed via the ioChem-BD data repository at [http://\[TBA\]](http://[TBA]).²⁴

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Keywords: boron • nickel • cross-coupling • diphosphine ligands • metal-ligand cooperativity

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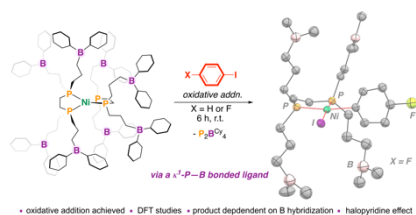
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The elementary steps of metal-mediated catalysis *e.g.*, oxidative addition, transmetalation, and reductive elimination are pertinent to the design of superior routes into specialty chemicals, pharmaceuticals, and agrochemicals. For over 50 years, pioneering work has shown that 18-electron alkyl/aryl-substituted diphosphine complexes of Group 10 $[M(\text{diphosphine})_2]$ *do not* oxidatively add haloarenes. Herein, we report a compound that is contrary to this 'rule', advancing our understanding of oxidative addition at coordinatively saturated organometallic complexes and providing new opportunities for bond activation.

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