Competitive Gold/Nickel Transmetalation

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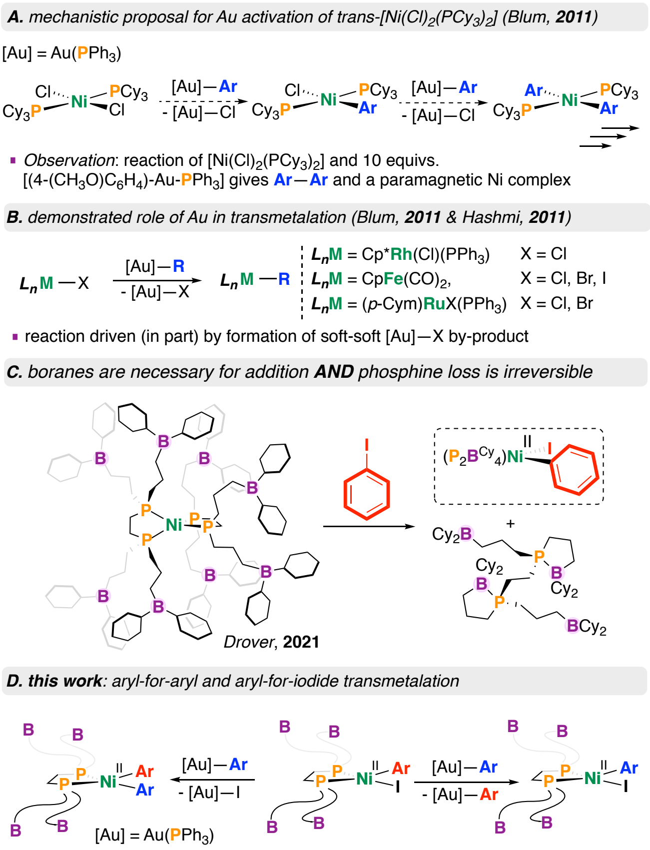
Transmetalation is a key method for the construction of element-element bonds. Here, we disclose the reactivity of [Ni^{II}(Ar)(I)(diphosphine)] compounds with arylgold(I) transmetalating agents, which is directly relevant to cross-coupling catalysis. Both aryl-for-iodide and unexpected aryl-for-aryl transmetalation are witnessed. Despite the strong driving force expected for Au-I bond formation, aryl scrambling can occur during transmetalation and may complicate the outcomes of attempted catalytic cross-coupling reactions.

The forging of metal-element bonds *via* transmetalation stands as a pivotal elementary step in catalytic cross-coupling for access to a variety of functionalized molecules, to the extent that cross-coupling reactions are defined and categorised by their transmetalation event.[1] Frequently, this reaction follows substrate oxidative addition and precedes product reductive elimination.[1] Many such coupling reactions have emerged, relying on electropositive metals for functional group (R) delivery *viz.* Kumada (R—MgBr), Suzuki (R—BR$_2$), Negishi, (R—ZnX), Stille (R—SnR$_3$), and Hiyama (R—SiR$_3$), to name a few.[1,2] As a germane study, in 2009, Hashmi *et al.* contributed to this growing list, introducing organogold(I) compounds ([R—Au(L_n)]; L_n = ligand) as competent partners for catalytic cross-coupling using palladium(0).[3]

Blum and co-workers subsequently reported the room temperature [NiCl$_2$(PCy$_3$)$_2$]-catalysed cross-coupling of [R—Au(PPh$_3$)] complexes with aryl bromides.[4] This reaction is proposed to proceed *via* an open-shell Ni complex wherein [Ni^{II}(Cl)$_2$(PCy$_3$)$_2$] first undergoes transmetalation with 2 equivalents of [Ar—Au(PPh$_3$)] to give [Ni^{II}(Ar)$_2$(PCy$_3$)$_2$] and 2 equivalents of [Cl—Au(PPh$_3$)], presumably *via* [Ni^{II}(Ar)(Cl)(PCy$_3$)$_2$]; subsequent halide transfer and oxidation by Au(I) gives [Ni^{III}(Ar)$_2$(Cl)(PCy$_3$)$_2$] and Au(0). This Ni^{III} species would thus reductively eliminate Ar—Ar to provide [Ni^{I}(Cl)(PCy$_3$)$_2$] and enter the catalytic cycle, undergoing transmetalation, oxidative addition, and reductive elimination, giving a *C—C* coupled product. To buttress this proposal, the stoichiometric reaction of [NiCl$_2$(PCy$_3$)$_2$] with 10 equivalents of [(4-(MeO)C$_6$H$_4$)—Au(PPh$_3$)] resulted in the homocoupled biaryl product, and a paramagnetic nickel complex that was characterised by EPR spectroscopy (**Chart 1A**).[4]

*A. mechanistic proposal for Au activation of trans-[Ni(Cl)$_2$(PCy$_3$)$_2$] (Blum, **2011**)*



- *Observation*: reaction of [Ni(Cl)$_2$(PCy$_3$)$_2$] and 10 equivs. [(4-(CH$_3$O)C$_6$H$_4$)-Au-PPh$_3$] gives Ar—Ar and a paramagnetic Ni complex

*B. demonstrated role of Au in transmetalation (Blum, **2011** & Hashmi, **2011**)*

- reaction driven (in part) by formation of soft-soft [Au]—X by-product

*C. boranes are necessary for addition **AND** phosphine loss is irreversible*

***D. this work**: aryl-for-aryl and aryl-for-iodide transmetalation*

Chart 1. Literature precedent and accessing a [Ni(diphosphine)(Ar)(X)] precursor and its reactivity with organogold(I) transmetalating reagents.

Organogold(I) compounds have proven to be competent for transmetalation to other transition metals such as [CpFe(CO)$_2$(X)] (Cp = C$_5$H$_5^-$, X = Cl, Br, I),[5] [(*p*-Cym)Ru(X)$_2$(PPh$_3$)] (*p*-Cym = *p*-cymene, X = Br, I),[5] and [Cp*Rh(Cl)$_2$(PPh$_3$)] (Cp* = C$_5$Me$_5^-$) (**Chart 1B**).[6] For the reaction of [CpFe(CO)$_2$(X)] with [(4-(NO$_2$)C$_6$H$_4$)—Au(PPh$_3$)], the rate of reaction followed the order I > Br > Cl, consistent with the high affinity of gold(I) for soft halides in the [X—Au(PPh$_3$)] by-product.[5] We refer the interested reader to several reviews pertaining to [Au]—based transmetalations.[7]

As an entry-point into this research area, we recently reported the fundamental reactivity of a *bis*(diphosphine) Ni(0) complex, [Ni^0(P$_2$B^{Cy}$_4$)$_2$] (P$_2$B^{Cy}$_4$ = 1,2-*bis*(di(3-dicyclohexylboraneyl)propylphosphino)ethane) that undergoes room temperature iodoarene activation to afford [Ni^{II}(P$_2$B^{Cy}$_4$)(Ar)(I)] and P$_2$B^{Cy}$_4$ (**Chart 1C**).[8] This reaction is noteworthy as, generally-speaking, treatment of alkyl/aryl-substituted diphosphine complexes of the form [Ni^0(diphosphine)$_2$] with haloarenes does not result in C-X bond activation, owing to the significant endergonicity associated with formation of the requisite [Ni^0(κ^1-diphosphine)(κ^2-diphosphine)] complex required for substrate activation;[9] [Ni^0(d*n*ppe)$_2$] (d*n*ppe =

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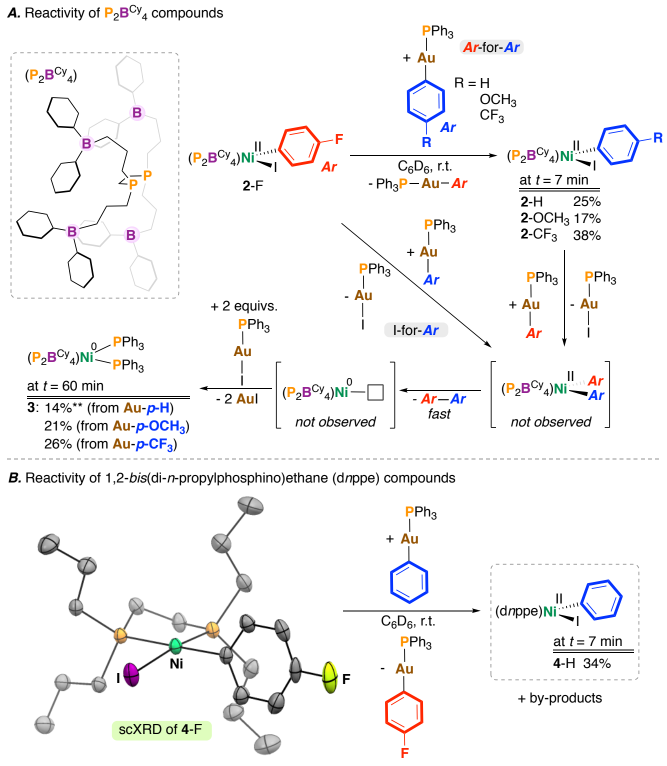
^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B NMR spectra for all complexes. XYZ coordinates for DFT calculations. CCDC **2109283-2109284** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* 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].

1,2-*bis*(di-*n*-propylphosphino)ethane) does not undergo oxidative addition under similar conditions.

To extend the reactivity of such $P_2B^{Cy}{}_4$-ligated complexes, we elected to study the behaviour of $[Ni^{II}(P_2B^{Cy}{}_4)(Ar)(I)]$ with a transmetalating reagent, as a means to explore the second elementary step in a viable cross-coupling sequence using $[Ni^{0}(P_2B^{Cy}{}_4)_2]$. Our interests turned to [Au]—based reagents owing to several alluring characteristics: these reagents are accurately weighed in small quantities, soluble in hydrocarbon solvent, readily tailored, and are unlikely to undergo transfer to the sp^2-hybridized boranes present on the $P_2B^{Cy}{}_4$ ligand scaffold.[8] Furthermore, these agents are bench-stable and provide $[X—Au(PPh_3)]$ as a by-product, whose formation can be conveniently monitored by ^{31}P NMR spectroscopy.[10] In addition to probing the stepwise reactivity of "$[Ni^{0/II}(P_2B^{Cy}{}_4)]$"-type compounds, we were equally interested in contributing to the growing area of gold-to-metal transmetalations starting from a *bona-fide* $[Ni^{II}$(diphosphine)(Ar)(X)] complex, informing studies such as that noted for $[Ni^{II}(Cl)_2(PCy_3)_2]$, above.[4]

$[Ni^{II}(P_2B^{Cy}{}_4)(4\text{-}FC_6H_4)(I)]$ (**2**-F), generated from oxidative addition of 4-fluoroiodobenzene at $[Ni(P_2B^{Cy}{}_4)_2]$ (**1**), was selected as the transmetalation partner, enabling reaction monitoring by ^{19}F NMR spectroscopy.[8] Transmetalation was examined using a number of gold(I) aryl compounds with an electron-donating or –withdrawing group at the *para*-position, $[(4\text{-}X\text{-}C_6H_4)—Au(PPh_3)]$ (X = H, OCH_3, CF_3) (**Scheme 1**). As a starting point, compound **2**-F was combined with 1 equivalent of $[(C_6H_5)—Au(PPh_3)]$, and the reaction was analysed by NMR spectroscopy. Given the literature precedent noted above, we hypothesized that this would represent an ideal pairing, owing to favourable generation of $[I—Au(PPh_3)]$. However, monitoring the reaction by ^{31}P NMR spectroscopy evidenced formation of $[Ni(P_2B^{Cy}{}_4)(C_6H_5)(I)]^{8}$ (**2**-H) in 25% yield after 7 mins, resulting from 'aryl-to-aryl' transmetalation. The fate of the exchanged "$4\text{-}FC_6H_4$" unit was deduced by ^{19}F NMR spectroscopy, matching data reported for $[(4\text{-}FC_6H_4)—Au(PPh_3)]$.[10] In addition to signals for **2**-H, a signal at δ_P = 43 ppm was also noted for $[(4\text{-}FC_6H_4)—Au(PPh_3)]$ in the ^{31}P NMR spectrum. The formation of 4-fluorobiphenyl, from reductive elimination *via* $[Ni(P_2B^{Cy}{}_4)(4\text{-}FC_6H_4)(C_6H_5)]$, was observed by ^{19}F NMR spectroscopy, indicating that both Ar-for-Ar and Ar-for-I transmetalation processes are operative. The treatment of **2**-F with 1 equivalent of $[(4\text{-}X\text{-}C_6H_4)—Au(PPh_3)]$ (X = OCH_3, CF_3) proceeded similarly to give $[Ni(P_2B^{Cy}{}_4)(4\text{-}X\text{-}C_6H_4)(I)]$ (**2**-X; X = OCH_3 (17%), CF_3 (38%)) after 7 minutes of reaction time.



Scheme 1. Transmetalation of **2-F** and **4-F** using $[Ar—Au(PPh_3)]$ reagents. Yields taken after 7 min. Inset of **B** shows the scXRD structure of **4-F** (50% occupancy, hydrogens omitted for clarity). ** The maximum theoretical yield of **3** is 50%. d*n*ppe = 1,2-*bis*(di-*n*-propylphosphino)ethane.

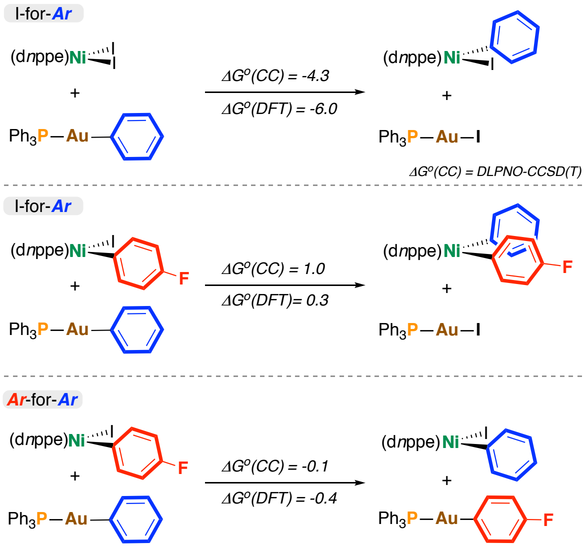
Compounds **2**-X were found to be highly reactive under the conditions studied. The ultimate fate of [at maximum 50%] Ni (after *ca.* 60 mins) in these elementary reactions is accounted for in the formation of $[Ni^{0}(P_2B^{Cy}{}_4)(PPh_3)_2]$ (**3**) δ_P = 34.8 (t, $^{2}J_{P,P}$ = 27 Hz; PPh_3), 19.7 (t, $^{2}J_{P,P}$ = 27 Hz; $P_2B^{Cy}{}_4$), which forms *via* PPh_3 transfer from Au following C(Ar)—C(Ar) reductive elimination in yields ranging from 14 - 26%, based on Ni (**Scheme 1**). The observation of some *S* = 0 Ni(0) product is suggestive of a Ni(0)/Ni(II) elimination pathway. The identity of compound **3** was confirmed by its independent preparation from the reaction of $[Ni^{0}(P_2B^{Cy}{}_4)_2]$ with 2 equivalents of PPh_3. This reaction illustrates the lability of the $P_2B^{Cy}{}_4$ ligand scaffold; the related species $[Ni^{0}$(d*n*ppe)$_2]$, which is devoid of pendant boranes, does not undergo ring-opening and PPh_3 coordination.

To demonstrate the generality of our observations regarding transmetalation between gold and nickel, and to show that this is not a boron effect, [Ni(d*n*ppe)($4\text{-}FC_6H_4$)(I)] (**4**-F) (see SI) was prepared, characterized, and exposed to 1 equiv. of $[(C_6H_5)—Au(PPh_3)]$. Analysis of the reaction mixture after 7 min by NMR spectroscopy showed formation of [Ni(d*n*ppe)(C_6H_5)(I)] (**4**-H) in 34% yield, consistent with previous results for $P_2B^{Cy}{}_4$.

The relevance of such compounds *viz.* $[Ni(P_2B^{Cy}{}_4)_2]$ (**1**) in cross-coupling was also confirmed with 10 mol% **1** enabling the cross-coupling of 4-fluoroiodobenzene and $[(4—FC_6H_4)—Au(PPh_3)]$, delivering the corresponding biaryl in 86% conversion by ^{19}F NMR spectroscopy.

To probe the thermodynamics associated with transmetalation, density functional theory (DFT)[11] and DLPNO-CCSD(T) calculations[12] were carried out on a model reaction between $[Ni^{II}$(d*n*ppe)($4\text{-}FC_6H_4$)(I)] and $[(C_6H_5)—Au(PPh_3)]$ (**Scheme 2**). In all cases, there was excellent agreement between DFT and high-level DLPNO-CCSD(T) calculations. The data from DLPNO-CCSD(T) calculations is discussed in the text, but DFT-derived energies are reported in **Scheme 2** and in the ESI. The transmetalation reaction between $[Ni(I)_2$(d*n*ppe)] and $[(C_6H_5)—Au(PPh_3)]$ is thermodynamically favourable, with $\Delta G°$ = -4.3 kcal mol^{-1}. However, the outcomes from I-for-Aryl and Ar-for-Ar transmetalation at **4**-F were less favourable. Somewhat surprisingly, the exchange of iodine for phenyl is endergonic ($\Delta G°$ = 1.0 kcal mol^{-1}). The exchange of *para*-fluorophenyl for phenyl (i.e. formation of **4**-H from **4**-F) is energetically neutral ($\Delta G°$ = -0.1 kcal mol^{-1}). In the context of catalysis, the product of I-for-Ar transmetalation can undergo reductive elimination, thereby driving catalysis forward if the overall reaction is exergonic; however, these experimental and computational results indicate the potential for aryl scrambling during cross-coupling reactions, eroding reaction selectivity and forming undesired homocoupling products.

Previously, we showed that $[Ni(P_2B^{Cy}{}_4)_2]$ (**1**) coordinates Lewis bases, binding up to eight equivalents of 4-*N*,*N*-dimethylaminopyridine (DMAP).[13] We wondered whether an appropriate gold(I)-pyridyl fragment (i.e. $[Au]—(4\text{-}NC_5H_4)$) might instead be used for coordination. In this regard, the $P_2B^{Cy}{}_4$ ligand

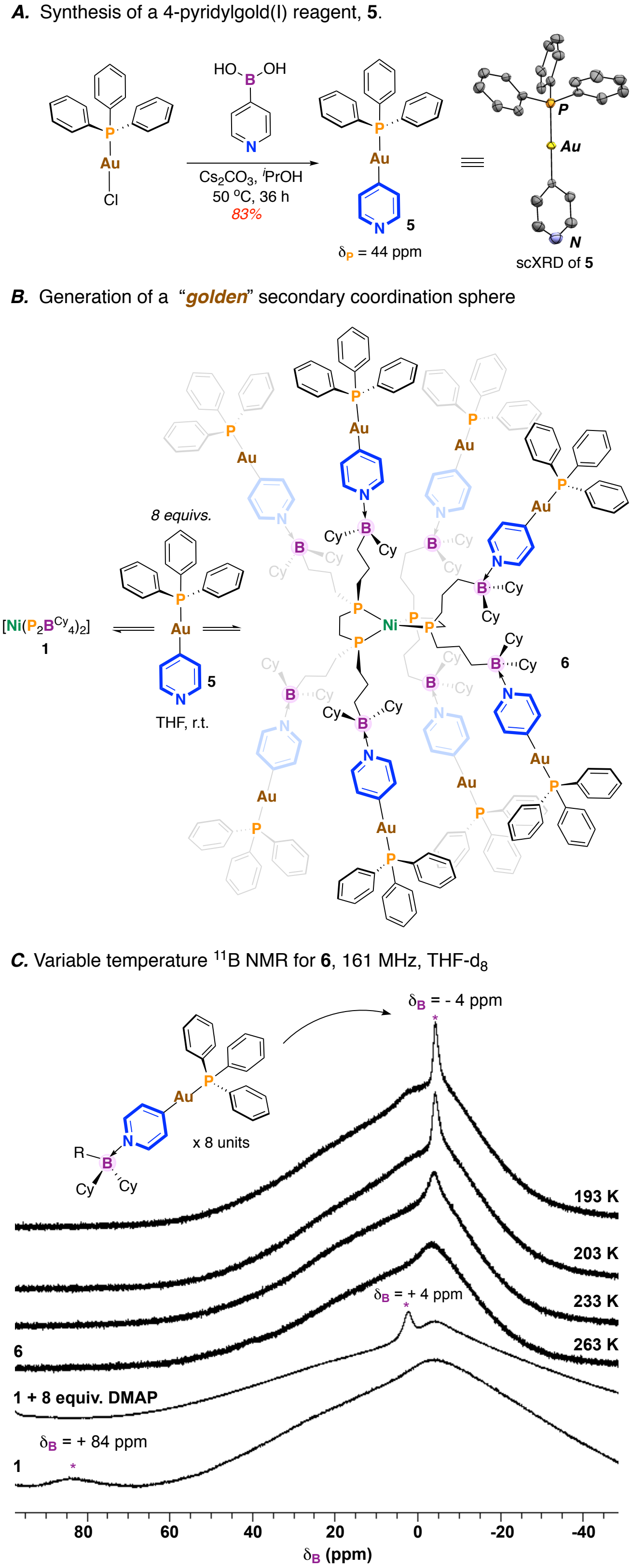


Scheme 2. Thermodynamics of transmetalation (kcal mol^{-1}). ΔG^o(CC) was calculated using DLPNO-CCSD(T), ΔG^o(DFT) was calculated using DFT.[11,12]

would serve in a directing capacity, luring transmetalating agents into close proximity with a Ni(II) fragment that can undergo transmetalation. With this proposal in mind, the new compound, [(4-NC_5H_4)—Au(PPh_3)] (**5**) was prepared *via* the reaction of [Br—Au(PPh_3)] with 4-pyridylboronic acid and was isolated as a white crystalline solid in 75% yield (**Scheme 3A**).[14] Formation of **5** is substantiated by NMR spectroscopy (δ_P = 43 ppm) and single crystal X-ray diffraction, which evidences formation of a linear gold(I) unit (<P—Au—C = 180°) (**Scheme 3A**). Importantly, compound **5** boasts an accessible Lewis basic pyridine, allowing for possible interaction with the pendant boraneyl groups of [Ni($P_2B^{Cy}{}_4$)$_2$] (**1**).

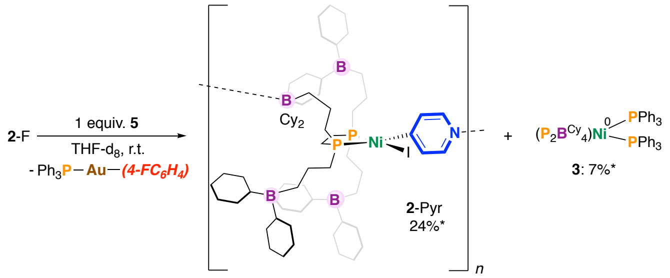
The reaction of **1** with 8 equivalents of **5** in THF[15] provided an immediate colour change from light yellow to dark brown to give [Ni^0($P_2B^{Cy}{}_4$)$_2${(4—NC_5H_4)—Au^I(PPh_3)}$_8$] (**6**) (**Scheme 3B**). Analysis by ^{31}P NMR spectroscopy (THF-d_8) provided two broad signals at δ_P = 42 and 36 ppm that are shifted upfield compared to uncoordinated **5** ($\Delta\delta_P$ = -1 ppm) and **1** ($\Delta\delta_P$ = -3 ppm) (see ESI).[13] Consistent with an array of interacting borane-pyridine groups, the ^{31}P NMR signature for the equivalent [Ni]—P fragments is similar to [Ni^0($P_2B^{Cy}{}_4$)$_2$(DMAP)$_8$] (δ_P = 35 ppm).[13] No signal is detected by ^{11}B NMR spectroscopy at 298 K *cf.* δ_B = 84 ppm for free [Ni^0($P_2B^{Cy}{}_4$)$_2$] and δ_B = +4 ppm for [Ni^0($P_2B^{Cy}{}_4$)$_2$(DMAP)$_8$].[13] To probe the possibility of fluxional solution behaviour, a variable temperature (VT) NMR study was undertaken. On decreasing the temperature to 193 K, the ^{31}P NMR spectrum changes markedly; the broad signal associated with [Au]—P groups decoalesces, while the signal for the [Ni]—P groups moves upfield and the baseline broadens (see ESI). Fluxional behaviour is also witnessed by VT ^{11}B NMR spectroscopy, which at 263 K shows an averaged signal for the sp^3-hybridized boraneyl groups at δ_B = —4 ppm; this signal sharpens considerably at 193 K (**Scheme 3C**). These data demonstrate the proclivity of the pendant boranes of the [Ni^0($P_2B^{Cy}{}_4$)$_2$] framework to support a metal-rich secondary coordination sphere, an attractive approach towards accessing multimetallic complexes that are "docked" *via* Lewis acid/base interactions.

Previously, we showed that reaction of [Ni^0($P_2B^{Cy}{}_4$)$_2$(DMAP)$_8$] with PhI resulted in the formation of [Ni^{II}($P_2B^{Cy}{}_4$)$_2$(DMAP)$_8$(I)]I *via* iodine atom abstraction.[8] We thus wished to probe the reactivity of **6** with 4-fluoroiodobenzene; however, productive reactivity was not witnessed due to protection of the Ni(0) site by a "golden"



Scheme 3. **A**. Synthesis of a 4-pyridylgold(I) reagent **5**. Inset shows the scXRD structure of **5** (50% occupancy, hydrogens omitted for clarity). **B**. Synthesis of octaaurated compound **6**. **C**. ^{11}B NMR spectroscopy (THF-d_8, 161 MHz).

secondary coordination sphere, preventing oxidative addition. Nonetheless, switching the order of addition and first allowing **1** to fully react with 4-fluoroiodobenzene to give $[Ni^{II}(P_2B^{Cy}{}_4)(4\text{-}FC_6H_4)(I)]$ (**2**-F), followed by addition of **5**, provided the pyridyl-linked oligomer, $[Ni^{II}(P_2B^{Cy}{}_4)(4\text{-}NC_5H_4)(I)]_n$[8] in 24% yield after 7 mins by ^{31}P NMR spectroscopy, which results from aryl-to-pyridyl transmetalation (**Scheme 4**). Under these reaction conditions **2-Pyr** was noted to be more robust *c.f.* **2-X**, producing less of **3**; 4-(4-fluorophenyl)pyridine was not detected by ^{19}F NMR spectroscopy. Interestingly, reaction between $[Ni^{II}(dnppe)(4\text{-}FC_6H_4)(I)]$ (**3**-F) and **5** in THF provides a cloudy reaction mixture and $[Ni^{II}(dnppe)(4\text{-}Pyr)(I)]$ is not observed.



Scheme 4. Transmetalation using a Au-based 4-pyridyl reagent. * = Yield after 60 min (the maximum theoretical yield of **3** is 50%).

In sum, we have confirmed that isolated $[Ni^{II}(diphosphine)(Ar)(X)]$ compounds undergo aryl-for-aryl in addition to aryl-for-iodide transmetalation in the presence of arylgold(I) reagents. Furthermore, we have exploited the boron-rich secondary coordination sphere of $[Ni(P_2B^{Cy}{}_4)_2]$ to host a metal (gold)-rich secondary coordination sphere *via* pyridine-borane dative interactions, a starting point toward achieving metal-metal cooperativity using such boron-rich ligand scaffolds in an elementary cross-coupling transformation. This study expands our knowledge of Au-to-metal transmetalation and provides insights into the initial steps associated with metal-to-metal functional group transfer relevant to carbon-carbon cross-coupling.

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Conflicts of interest

There are no conflicts to declare.

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