Transmetalation is a key method for the construction of element-element bonds. Here, we disclose the reactivity of [NiII(Ar)(Cl)(PCy3)] 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-II bond formation, aryI 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. Frequently, this reaction follows substrate oxidative addition and precedes product reductive elimination. Many such coupling reactions have emerged, relying on electrophoretic metals for functional group (R) delivery viz. Kumada (R=MgBr), Suzuki (R=Br2), Negishi (R=ZnBr), Stille (R=SnR3), and Hiyama (R-SiR3), to name a few. As a germane study, in 2009, Hashmi et al. contributed to this growing list, introducing organogold(I) compounds ([R—Au(PCy3)]2) as competent partners for catalytic cross-coupling using palladium(0). Blum and co-workers subsequently reported the room temperature [NiCl2(PCy3)2]-catalysed cross-coupling of [R—Au(PPh3)] complexes with aryl bromides. This reaction is proposed to proceed via an open-shell Ni complex wherein [NiII(Cl)(PCy3)] first undergoes transmetalation with 2 equivalents of [Ar—Au(PPh3)] to give [Ni(II)(Ar)(PCy3)] and 2 equivalents of [Cl—Au(PPh3)], presumably via [Ni(II)(Ar)(Cl)(PCy3)]; subsequent halide transfer and oxidation by Au(I) gives [Ni(II)(Ar)(Cl)(PCy3)] and Au(0). This NiII species would thus reductively eliminate Ar—Ar to provide [Ni(II)(Ar)(Cl)(PCy3)] 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 [NiCl2(PCy3)2] with 10 equivalents of [(4-(MeO)C6H4)2—Au(PPh3)] resulted in the homocoupled biaryl product, and a paramagnetic nickel complex that was characterised by EPR spectroscopy (Chart 1A). Organogold(I) compounds have proven to be competent for transmetalation to other transition metals such as [CpFe(CO)(X)].
As an entry-point into this research area, we recently reported the fundamental reactivity of a bis(diphasphine) Ni(0) complex, \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(\text{Ar})(\text{X})]\) complex, informing studies such as that of Faglia et al., who were equally interested in contributing to the growing area of gold-to-nickel transmetalations.\(^5\) The treatment of \([\text{Ar}(\text{Cl})_2(\text{PCy}_3)_2]\) with 1 equiv. of [\(4-(\text{FC}_6\text{H}_4)\text{Au}(\text{PPh}_3)\)], was confirmed by its independent preparation from the reaction of \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)](\text{Ar})(\text{X})]\) with 2 equiv. of \(\text{PPh}_3\). This reaction is noteworthy as, generally-speaking, treatment of alkyl/aryl-substituted diphasphine complexes of the form \([\text{Ni}^{II}(\text{diphosphine})]\) with haloarenes does not result in C-X bond activation, owing to the significant endergonicity associated with formation of the requisite \([\text{Ni}^{II}(\text{k}^2\text{-diphosphine})(\text{k}^2\text{-diphosphine})]\) complex required for substrate activation.\(^9\) \([\text{Ni}^{II}(\text{dppe})_2]\) (dppe = 1,2-bis(di-n-propylphosphino)ethane) does not undergo oxidative addition under similar conditions.

To extend the reactivity of such \(\text{P}_2\text{B}_{\text{Cy}}\text{X}\)-ligated complexes, we elected to study the behaviour of \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)](\text{Ar})(\text{X})]\) with a transmetalating reagent, as a means to explore the second elementary step in a viable coupling sequence using \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)](\text{Ar})(\text{X})]\). Our interests turned to [Au]-based reagents owing to several alluring characteristics: these reagents are accurately weighed in small quantities, soluble in hydrocarbon solvents, readily tailored, and are unlikely to undergo transfer to the sp\(^2\)-hybridized boranes present on the \(\text{P}_2\text{B}_{\text{Cy}}\text{X}\) ligand scaffold.\(^8\) Furthermore, these agents are bench-stable and provide \([\text{X}\rightarrow\text{Au}(\text{PPh}_3)]\) as a by-product, whose formation can be conveniently monitored by \(^{31}\text{P}\) NMR spectroscopy.\(^10\) In addition to probing the stepwise reactivity of \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(\text{Ar})(\text{X})]\)-type compounds, we were equally interested in contributing to the growing area of gold-to-nickel transmetalations starting from a \(\text{bona-fide} \) \([\text{Ni}^{II}(\text{diphosphine})(\text{Ar})(\text{X})]\) complex, informing studies such as that noted for \([\text{Ni}^{II}(\text{PCy}_3)(\text{PCy}_3)](\text{Ar})(\text{X})]\), above.\(^6\)

\([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(4-\text{FC}_6\text{H}_4\text{H}_2)](\text{I})\) (2-F), generated from oxidative addition of 4-fluoriodobenzene at \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(\text{Ar})(\text{I})]\) (1), was selected as the transmetalation partner, enabling reaction monitoring by \(^{31}\text{F}\) NMR spectroscopy.\(^5\) Transmetalation was examined using a number of gold(I) aryl complexes with an electron-donating or -withdrawing group at the para-position, \((\text{4-X-CH}_2\text{H}_5)\text{Au}(\text{PPh}_3)\) (X = H, \(\text{OCH}_3\), \(\text{CF}_3\)) (Scheme 1). As a starting point, compound 2-F was combined with 1 equiv. of \((\text{CF}_3\text{H})\text{Au}(\text{PPh}_3)\), 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 \([\text{I}\rightarrow\text{Au}(\text{PPh}_3)]\). However, monitoring the reaction by \(^{31}\text{P}\) NMR spectroscopy evidenced formation of \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(\text{CH}_2\text{H}_5)](\text{I})\) (2-H) in 25% yield after 7 mins, resulting from an ‘aryl-to-aryl’ transmetalation. The fate of the exchanged \(\text{4-FC}_6\text{H}_4\text{H}_2\) unit was deduced by \(^{31}\text{F}\) NMR spectroscopy, matching data reported for \((\text{4-FC}_6\text{H}_4\text{H}_2)\text{Au}(\text{PPh}_3)\).\(^10\) In addition to signals for 2-H, a signal at \(\delta = 43\) ppm was also noted for \((4\text{-FC}_6\text{H}_4\text{H}_2)\text{Au}(\text{PPh}_3)\) in the \(^{19}\text{F}\) NMR spectrum. The formation of 4-fluorobiphenyl, from reductive elimination via \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(4\text{-FC}_6\text{H}_4\text{H}_2)(\text{CH}_2\text{H}_5)](\text{I})\), was observed by \(^{19}\text{F}\) NMR spectroscopy, indicating that both Ar-for-Ar and Ar-for-I transmetalation processes are operative. The treatment of 2-F with 1 equiv. of \((\text{4-X-CH}_2\text{H}_5)\text{Au}(\text{PPh}_3)\) (X = \(\text{OCH}_3\), \(\text{CF}_3\)) proceeded similarly to give \([\text{Ni}^{II}(\text{P}_2\text{BCy}_4)(4\text{-X-CH}_2\text{H}_5\text{H}_2)](\text{I})\) (2-X; X = \(\text{OCH}_3\) (17%), \(\text{CF}_3\) (38%)) after 7 minutes.
A study was undertaken. On decreasing the temperature to 193 K, the phenyl is endergonic (ΔG° = +2.6 kcal mol⁻¹). The exchange of phenyl for fluorophenyl for phenyl (i.e. formation of 4-H from 4-F) is essentially energetically neutral (ΔG° = -0.1 kcal mol⁻¹) (similar trends are observed with gold reagents having −H from −F) (see ESI). The exchange of iodine for fluorine under reductive elimination, thereby driving catalysis forward if the overall reaction is exergonic; however, these experimental and computational results indicate the potential for ary1 scrambling during cross-coupling reactions, eroding reaction selectivity and forming undesired homocontacted products.

Previously, we showed that [Ni(P₂B₇Cy₃)] (1) coordinates Lewis bases, binding up to eight equivalents of 4-N,N-dimethylaminopyridine (DMAP). We wondered whether an appropriate gold(I)-pyridyl fragment (i.e. [Au]−(4-NC₅H₄)) might instead be used for coordination. In this regard, the P₂B₇Cy₃ ligand would serve in a directing capacity, luring transmetalating agents into close proximity with a Ni(I) fragment that can undergo transmetallation. With this proposal in mind, the new compound, [4-NC₅H₄]Au(PPh₃) (5) was prepared via the reaction of [Br−Au(PPh₃)] with 4-pyridylboronic acid and was isolated as a white crystalline solid in 75% yield (Scheme 3A). Formation of 5 is substantiated by NMR spectroscopy (δB = 43 ppm) and single crystal X-ray diffraction, which evidences formation of a linear gold(I) unit (δB = +4 ppm) (Scheme 3A). Importantly, compound 5 boasts an accessible Lewis basic pyridine, allowing for possible interaction with the pendant boronyl groups of [Ni(P₂B₇Cy₃)] (1).

The reaction of 1 with 8 equivalents of 5 in THF provided an immediate colour change from light yellow to dark brown to give [Ni(P₂B₇Cy₃)(4-NC₅H₄)Au(PPh₃)] (6) (Scheme 3B). Analysis by ¹³P NMR spectroscopy (THF-d₈) provided two broad signals at δP = 42 and 36 ppm that are shifted upfield compared to uncoordinated 5 (δP = 1 ppm) and 1 (δP = 3 ppm) (see ESI). Consistent with an array of interacting borane-pyridine groups, the ¹³P NMR signature for the equivalent [Ni]−P fragments is similar to [Ni(P₂B₇Cy₃)(DMAP)] (δP = 35 ppm). No signal is detected by ¹¹B NMR spectroscopy at 298 K cf. δB = 84 ppm for free [Ni(P₂B₇Cy₃)] and δB = 44 ppm for [Ni(P₂B₇Cy₃)(DMAP)]. To probe the possibility of fluxional solution behaviour; a variable temperature (VT) NMR study was undertaken. On decreasing the temperature to 193 K, the ¹³P 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

Scheme 2. Thermodynamics of transmetallation (kcal mol⁻¹). ΔG°(CC) was calculated using DLPNO-CCSD(T), and ΔG°(DFT) using DFT. ¹¹B NMR spectroscopy (THF-d₈, 161 MHz).

A. Synthesis of a 4-pyridylgold(I) reagent, 5.

B. Generation of a “golden” secondary coordination sphere

C. Variable temperature ¹¹B NMR for 6, 161 MHz, THF-d₈.
behaviour is also witnessed by VT $^{11}$B NMR spectroscopy, which at 263 K shows an averaged signal for the sp$^2$-hybridized boraneyl groups at $\delta_B = -4$ ppm; this signal sharpens considerably at 193 K (Scheme 3C). These data demonstrate the proclivity of the pendant boranes of the [Ni($^2$P$_2$BCy$_4$)$_2$]$_2$ framework to support a metal-rich secondary coordination sphere, an attractive approach towards accessing multimetallic complexes that are “docked” via Lewis base/acid interactions.

Previously, we showed that reaction of [Ni($^2$P$_2$Cy$_4$)$_2$(DMAP)$_4$] with Phi resulted in the formation of [Ni($^2$P$_2$Cy$_4$)$_2$(DMAP)$_4$]$_2$ via iodine atom abstraction. 8 We thus wished to probe the reactivity of 6 with 4-fluoriodobenzene; however, productive reactivity was not witnessed due to protection of the Ni(0) site by a “golden” secondary coordination sphere, preventing oxidative addition. Nonetheless, switching the order of addition and first allowing 1 to fully react with 4-fluoriodobenzene to give [Ni($^2$P$_2$Cy$_4$)$_2$(4-FC$_2$H$_4$)$_2$] (2-F), followed by addition of 5, provided the pyridyl-linked oligomer, [Ni($^2$P$_2$Cy$_4$)$_2$(4-NC$_2$H$_4$)$_2$]$_n$ in 24% yield after 7 mins by $^{31}$P NMR spectroscopy, which results from aryl-to-pyridyl transmetalation (Scheme 4). 16 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 $^{31}$P NMR spectroscopy. Interestingly, reaction between [Ni(dnpy)$_2$(4-FC$_2$H$_4$)$_2$] (3-F) and 5 in THF provides a cloudy reaction mixture and [Ni($^3$P$_2$Cy$_4$)$_2$(dnpy)](4-Pyr)$_2$] is not observed.

In sum, we have confirmed that isolated [Ni($^3$P$_2$)(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($^2$P$_2$Cy$_4$)$_2$]$_2$ 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.

**Notes and references**

15. This reaction mixture precipitated from benzene or toluene, and required THF as solvent. Notably, both components (1 and 5) are soluble in benzene or toluene, indicating persistent adduct formation.
16. In addition, reaction of [Ni($^2$P$_2$)(4-CH$_3$CO$_2$CH$_3$)$_2$][2-OCH$_3$] with 5 provided the pyridyl-linked oligomer, [Ni($^2$P$_2$)(4-NC$_2$H$_4$)$_2$][4], in 48% yield.

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