

COMMUNICATION

Competitive Gold/Nickel Transmetalation

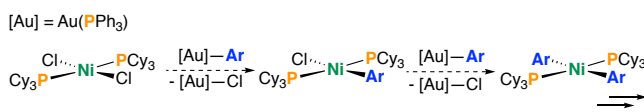
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Transmetalation is a key method for the construction of element-element bonds. Here, we disclose the reactivity of $[\text{Ni}^{\text{II}}(\text{Ar})(\text{l})\text{(diphosphine)}]$ compounds with arylgold(I) transmetalating agents, which is directly 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.

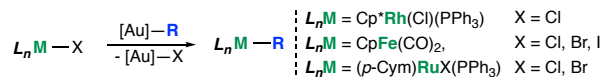
The forging of metal-element bonds *via* transmetalation stands as a pivotal elementary step in catalytic cross-coupling for access to a variety of functionalized molecules, to the extent that cross-coupling reactions are defined and categorised by their transmetalation event.¹ Frequently, this reaction 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–BR₂), Negishi, (R–ZnX), Stille (R–SnR₃), and Hiyama (R–SiR₃), to name a few.^{1,2} As a germane study, in 2009, Hashmi *et al.* contributed to this growing list, introducing organogold(I) compounds ($[\text{R–Au}(L_n)]$; L_n = ligand) as competent partners for catalytic cross-coupling using palladium(0).³

Blum and co-workers subsequently reported the room temperature $[\text{NiCl}_2(\text{PCy}_3)_2]$ -catalysed cross-coupling of $[\text{R–Au}(\text{PPh}_3)]$ complexes with aryl bromides.⁴ This reaction is proposed to proceed *via* an open-shell Ni complex wherein $[\text{Ni}^{\text{II}}(\text{Cl})_2(\text{PCy}_3)_2]$ first undergoes transmetalation with 2 equivalents of $[\text{Ar–Au}(\text{PPh}_3)]$ to give $[\text{Ni}^{\text{II}}(\text{Ar})_2(\text{PCy}_3)_2]$ and 2 equivalents of $[\text{Cl–Au}(\text{PPh}_3)]$, presumably *via* $[\text{Ni}^{\text{II}}(\text{Ar})(\text{Cl})(\text{PCy}_3)_2]$;

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

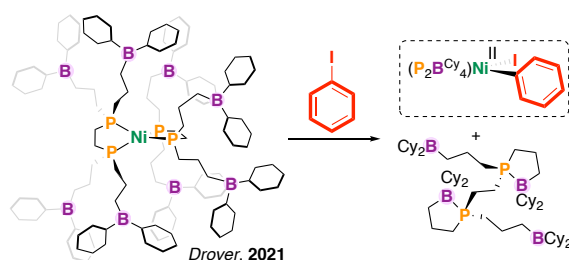
- Observation: reaction of $[\text{Ni}(\text{Cl})_2(\text{PCy}_3)_2]$ and 10 equivs. $[(4-(\text{CH}_3\text{O})\text{C}_6\text{H}_4)\text{-Au-PPh}_3]$ gives Ar–Ar and a paramagnetic Ni complex

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



- reaction driven (in part) by formation of soft-soft $[\text{Au}]\text{-X}$ by-product

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



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

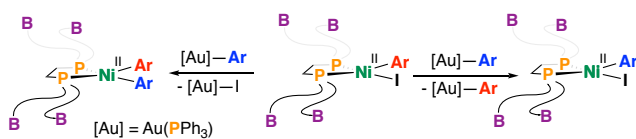


Chart 1. Literature precedent and accessing a $[\text{Ni}(\text{diphosphine})(\text{Ar})(\text{X})]$ precursor and its reactivity with organogold(I) transmetalating reagents.

subsequent halide transfer and oxidation by Au(I) gives $[\text{Ni}^{\text{III}}(\text{Ar})_2(\text{Cl})(\text{PCy}_3)_2]$ and Au(0). This Ni^{III} species would thus reductively eliminate Ar–Ar to provide $[\text{Ni}^{\text{I}}(\text{Cl})(\text{PCy}_3)_2]$ 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 $[\text{NiCl}_2(\text{PCy}_3)_2]$ with 10 equivalents of $[(4-(\text{MeO})\text{C}_6\text{H}_4)\text{-Au}(\text{PPh}_3)]$ resulted in the homocoupled biaryl product, and a paramagnetic nickel complex that was characterised by EPR spectroscopy (Chart 1A).⁴

Organogold(I) compounds have proven to be competent for transmetalation to other transition metals such as $[\text{CpFe}(\text{CO})_2\text{X}]$

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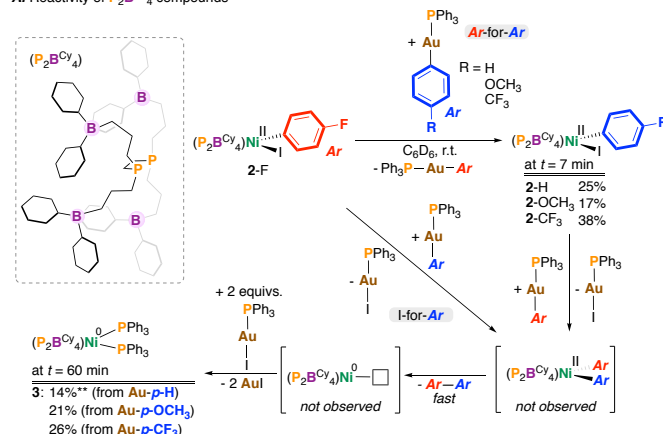
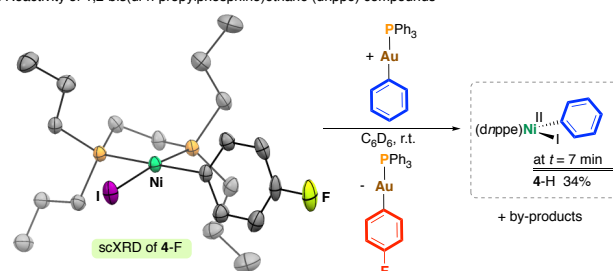
¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹¹B NMR spectra for all complexes. XYZ coordinates for DFT calculations. CCDC 2109283–2109284 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Computational chemistry data underpinning this study can be accessed via the ioChem-BD data repository at [http://\[TBA\]](http://[TBA]).

(Cp = C₅H₅⁻, X = Cl, Br, I),⁵ [(*p*-Cym)Ru(X)₂(PPh₃)] (*p*-Cym = *p*-cymene, X = Br, I),⁵ and [Cp*Rh(Cl)₂(PPh₃)] (Cp* = C₅Me₅⁻) (**Chart 1B**).⁶ For the reaction of [CpFe(CO)₂(X)] with [(4-(NO₂)C₆H₄)—Au(PPh₃)], 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(PPh₃)] by-product.⁵ We refer interested readers 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, [Ni⁰(P₂B^{Cy}₄)₂] (P₂B^{Cy}₄ = 1,2-*bis*(di(3-dicyclohexylboraneyl)propylphosphino)ethane) that undergoes room temperature iodoarene activation to afford [Ni^{II}(P₂B^{Cy}₄)(Ar)(I)] and P₂B^{Cy}₄ (**Chart 1C**).⁸ This reaction is noteworthy as, generally-speaking, treatment of alkyl/aryl-substituted diphosphine complexes of the form [Ni⁰(diphosphine)₂] with haloarenes does not result in C-X bond activation, owing to the significant endergonicity associated with formation of the requisite [Ni⁰(□¹-diphosphine)(□²-diphosphine)] complex required for substrate activation;⁹ [Ni⁰(*dnppe*)₂] (*dnppe* = 1,2-*bis*(*di-n*-propylphosphino)ethane) does not undergo oxidative addition under similar conditions.

To extend the reactivity of such P₂B^{Cy}₄-ligated complexes, we elected to study the behaviour of [Ni^{II}(P₂B^{Cy}₄)(Ar)(I)] with a transmetalating reagent, as a means to explore the second elementary step in a viable cross-coupling sequence using [Ni⁰(P₂B₄)₂]. 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 P₂B^{Cy}₄ ligand scaffold.⁸ Furthermore, these agents are bench-stable and provide [X—Au(PPh₃)] as a by-product, whose formation can be conveniently monitored by ³¹P NMR spectroscopy.¹⁰ In addition to probing the stepwise reactivity of “[Ni^{0/II}(P₂B^{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(PCy₃)₂], above.⁴

[Ni^{II}(P₂B^{Cy}₄)(4-FC₆H₄)(I)] (**2-F**), generated from oxidative addition of 4-fluoriodobenzene at [Ni(P₂B^{Cy}₄)₂] (**1**), was selected as the transmetalation partner, enabling reaction monitoring by ¹⁹F 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-X-C₆H₄)—Au(PPh₃)] (X = H, OCH₃, CF₃) (**Scheme 1**). As a starting point, compound **2-F** was combined with 1 equivalent of [(C₆H₅)—Au(PPh₃)], 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(PPh₃)]. However, monitoring the reaction by ³¹P NMR spectroscopy evidenced formation of [Ni(P₂B^{Cy}₄)(C₆H₅)(I)] (**2-H**) in 25% yield after 7 mins, resulting from ‘aryl-to-aryl’ transmetalation. The fate of the exchanged “4-FC₆H₄” unit was deduced by ¹⁹F NMR spectroscopy, matching data reported for [(4-FC₆H₄)—Au(PPh₃)].¹⁰ In addition to signals for **2-H**, a signal at δ_p = 43 ppm was also noted for [(4-FC₆H₄)—Au(PPh₃)] in the ³¹P NMR spectrum. The formation of 4-fluorobiphenyl, from reductive elimination *via* [Ni(P₂B^{Cy}₄)(4-FC₆H₄)(C₆H₅)], was observed by ¹⁹F 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-X-C₆H₄)—Au(PPh₃)] (X = OCH₃, CF₃) proceeded similarly to give [Ni(P₂B^{Cy}₄)(4-X-C₆H₄)(I)] (**2-X**; X = OCH₃ (17%), CF₃ (38%)) after 7 minutes.

A. Reactivity of P₂B^{Cy}₄ compoundsB. Reactivity of 1,2-*bis*(*di-n*-propylphosphino)ethane (*dnppe*) compounds

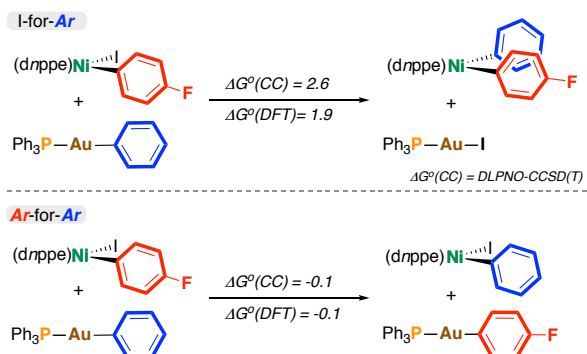
Scheme 1. Transmetalation of **2-F** and **4-F** using [Ar—Au(PPh₃)] reagents. Yields taken after 7 min. Inset of **B** shows the scXRD structure of **4-F** (50% occupancy, hydrogens omitted for clarity). ** The maximum theoretical yield of **3** is 50%. *dnppe* = 1,2-*bis*(*di-n*-propylphosphino)ethane.

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 [Ni⁰(P₂B^{Cy}₄)(PPh₃)₂] (**3**) δ_p = 34.8 (t, ²J_{p,p} = 27 Hz; PPh₃), 19.7 (t, ²J_{p,p} = 27 Hz; P₂B^{Cy}₄), which forms *via* PPh₃ 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 [Ni⁰(P₂B^{Cy}₄)₂] with 2 equivalents of PPh₃. This reaction illustrates the lability of the P₂B^{Cy}₄ ligand scaffold; the related species [Ni⁰(*dnppe*)₂], which is devoid of pendant boranes, does not undergo ring-opening and PPh₃ 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(*dnppe*)(4-FC₆H₄)(I)] (**4-F**) (see SI) was prepared, characterized, and exposed to 1 equiv. of [(C₆H₅)—Au(PPh₃)]. Analysis of the reaction mixture after 7 min by NMR spectroscopy showed formation of [Ni(*dnppe*)(C₆H₅)(I)] (**4-H**) in 34% yield, consistent with previous results for P₂B^{Cy}₄.

The relevance of such compounds *viz.* [Ni(P₂B^{Cy}₄)₂] (**1**) in cross-coupling was also confirmed with 10 mol% **1** enabling the cross-coupling of 4-fluoriodobenzene and [(4-FC₆H₄)—Au(PPh₃)], delivering the corresponding biaryl in 86% conversion by ¹⁹F NMR spectroscopy.

To probe the thermodynamics associated with transmetalation, density functional theory (DFT)¹¹ and DLPNO-CCSD(T) calculations¹² were carried out on model reactions (**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 are



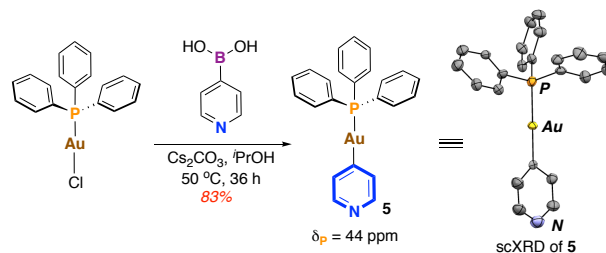
Scheme 2. Thermodynamics of transmetalation (kcal mol^{-1}). $\Delta G^\circ(\text{CC})$ was calculated using DLPNO-CCSD(T), and $\Delta G^\circ(\text{DFT})$ using DFT.^{11,12}

discussed in the text, but DFT-derived energies are reported in **Scheme 2** and in the ESI. The outcomes from I-for-Aryl and Ar-for-Ar transmetalation at 4-F are endergonic and energetically neutral, respectively. Somewhat surprisingly, the exchange of iodine for phenyl is endergonic ($\Delta G^\circ = +2.6 \text{ kcal mol}^{-1}$). The exchange of *para*-fluorophenyl for phenyl (i.e. formation of 4-H from 4-F) is essentially energetically neutral ($\Delta G^\circ = -0.1 \text{ kcal mol}^{-1}$) (similar trends are observed with gold reagents having *p*-F₃CC₆H₄, *p*-H₃COC₆H₄, and 4-pyridyl substituents (*vide infra*) – see ESI). 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.

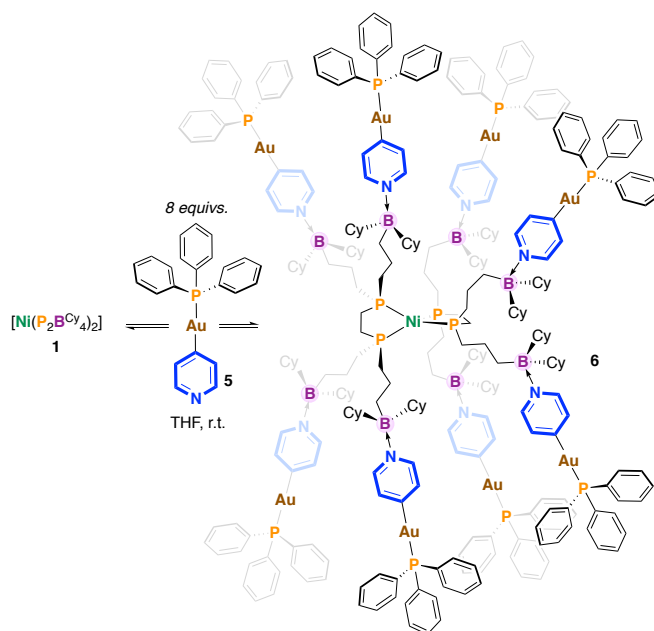
Previously, we showed that $[\text{Ni}(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ (**1**) coordinates Lewis bases, binding up to eight equivalents of 4-*N,N*-dimethylaminopyridine (DMAP).¹³ We wondered whether an appropriate gold(I)-pyridyl fragment (i.e. $[\text{Au}-(4\text{-NC}_5\text{H}_4)]$) might instead be used for coordination. In this regard, the $\text{P}_2\text{B}^{\text{Cy}}_4$ ligand 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, $[(4\text{-NC}_5\text{H}_4)\text{-Au}(\text{PPh}_3)]$ (**5**) was prepared *via* the reaction of $[\text{Br}\text{-Au}(\text{PPh}_3)]$ 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 ($\delta_{\text{P}} = 43 \text{ ppm}$) and single crystal X-ray diffraction, which evidences formation of a linear gold(I) unit ($\angle \text{P}\text{-Au}\text{-C} = 180^\circ$) (**Scheme 3A**). Importantly, compound **5** boasts an accessible Lewis basic pyridine, allowing for possible interaction with the pendant borane groups of $[\text{Ni}(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ (**1**).

The reaction of **1** with 8 equivalents of **5** in THF¹⁵ provided an immediate colour change from light yellow to dark brown to give $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2\{(4\text{-NC}_5\text{H}_4)\text{-Au}(\text{PPh}_3)\}_8]$ (**6**) (**Scheme 3B**). Analysis by ³¹P NMR spectroscopy (THF-*d*₈) provided two broad signals at $\delta_{\text{P}} = 42$ and 36 ppm that are shifted upfield compared to uncoordinated **5** ($\delta_{\text{P}} = -1 \text{ ppm}$) and **1** ($\delta_{\text{P}} = -3 \text{ ppm}$) (see ESI).¹³ Consistent with an array of interacting borane-pyridine groups, the ³¹P NMR signature for the equivalent $[\text{Ni}]\text{-P}$ fragments is similar to $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_8]$ ($\delta_{\text{P}} = 35 \text{ ppm}$).¹³ No signal is detected by ¹¹B NMR spectroscopy at 298 K *cf.* $\delta_{\text{B}} = 84 \text{ ppm}$ for free $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ and $\delta_{\text{B}} = +4 \text{ ppm}$ for $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_8]$.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 ³¹P NMR spectrum changes markedly; the broad signal associated with $[\text{Au}]\text{-P}$ groups decoalesces, while the signal for the $[\text{Ni}]\text{-P}$ groups moves upfield and the baseline broadens (see ESI). Fluxional

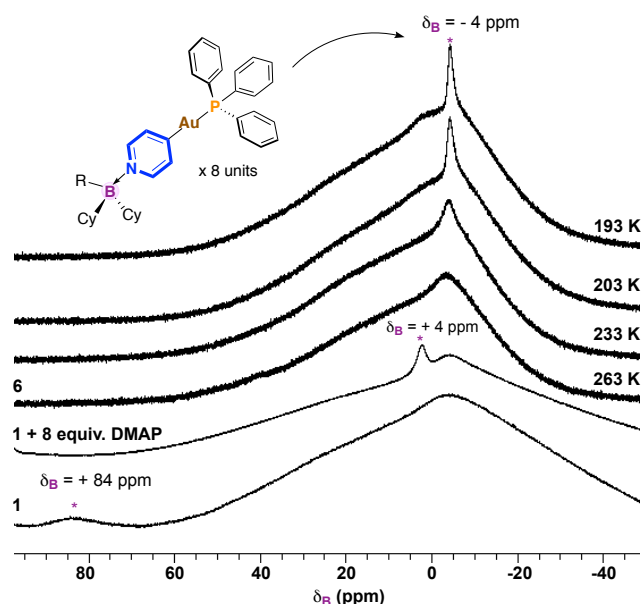
A. Synthesis of a 4-pyridylgold(I) reagent, **5**.



B. Generation of a “golden” secondary coordination sphere



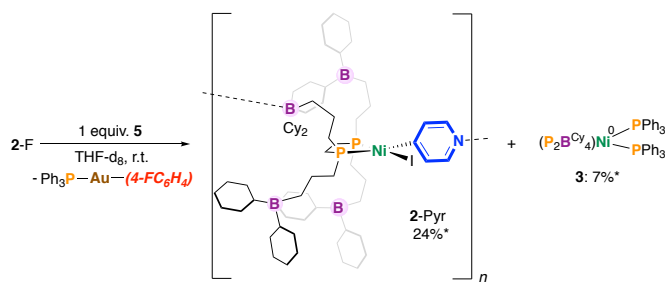
C. Variable temperature ¹¹B NMR for **6**, 161 MHz, THF-*d*₈



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. ¹¹B NMR spectroscopy (THF-*d*₈, 161 MHz).

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 $\delta_{\text{B}} = -4$ ppm; this signal sharpens considerably at 193 K (Scheme 3C). These data demonstrate the proclivity of the pendant boranes of the $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ 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 $[\text{Ni}^0(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_8]$ with PhI resulted in the formation of $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)_2(\text{DMAP})_8(\text{I})]$ 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 $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(4\text{-FC}_6\text{H}_4)(\text{I})]$ (**2-F**), followed by addition of **5**, provided the pyridyl-linked oligomer, $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(4\text{-NC}_5\text{H}_4)(\text{I})]_n$ 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 ^{19}F NMR spectroscopy. Interestingly, reaction between $[\text{Ni}^{\text{II}}(\text{dnpp})_2(4\text{-FC}_6\text{H}_4)(\text{I})]$ (**3-F**) and **5** in THF provides a cloudy reaction mixture and $[\text{Ni}^{\text{II}}(\text{dnpp})_2(4\text{-Pyr})(\text{I})]$ 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 $[\text{Ni}^{\text{II}}(\text{diphosphine})(\text{Ar})(\text{X})]$ 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 $[\text{Ni}(\text{P}_2\text{B}^{\text{Cy}}_4)_2]$ 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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of Strathclyde; we thank Mr. J. Buzzard, Dr. K. Kubiak-Ossowska, and Dr. R. Martin for their assistance with this facility.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- J. F. Hartwig, *Organotransition Metal Chemistry From Bonding to Catalysis*. Chapter 7, University Science Books, Mill Valley, California, 2010.
- a) R. Jana, T. P. Pathak and M. S. Sigman, *Chem. Rev.*, 2011, **111**, 1417-1492; b) N. Hazari, P. R. Melvin and M. M. Beromi, *Nat. Rev. Chem.*, 2017, **1**, 0025; c) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4442-4489.
- a) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthy and F. Rominger, *Angew. Chem., Int. Ed.*, 2009, **48**, 8243-8246; b) M. Hansmann, M. Pernpointner, R. Dopp and A. S. K. Hashmi, *Chem. –Eur. J.*, 2013, **19**, 15290-15303; c) For a related study, see: S. Witzel, M. Hoffmann, M. Rudolph, F. Rominger, A. Dreuw and A. S. K. Hashmi, *Adv. Synth. Catal.*, 2021, DOI: 10.1002/adsc.202101113.
- J. J. Hirner and S. A. Blum, *Organometallics*, 2011, **30**, 1299-1302.
- A. S. K. Hashmi and L. Molinari, *Organometallics*, 2011, **30**, 3457-3460.
- Y. Shi and S. A. Blum, *Organometallics*, 2011, **30**, 1776-1779.
- a) J. J. Hirner, Y. Shi and S. A. Blum, *Acc. Chem. Res.*, 2011, **44**, 603-613; b) L. –P. Piu and G. B. Hammond, *Chem. Soc. Rev.*, 2012, **41**, 3129-3139.
- J. A. Zurakowski, B. J. H. Austen, M. C. Dufour, D. M. Spasyuk, D. J. Nelson and M. W. Drover, *Chem. –Eur. J.*, 2021, DOI: 10.1002/chem.202103121
- a) C. Amatore, G. Broeker, A. Jutand and F. Khalil, *J. Am. Chem. Soc.*, 1997, **119**, 5176-5185; b) P. Fitton and E. A. Rick, *J. Organomet. Chem.*, 1971, **28**, 287-291; c) A. L. Clevenger, R. M. Stolley, N. D. Staudaher, N. Al, A. L. Rheingold, R. T. Vanderlinden and J. Louie, *Organometallics*, 2018, **37**, 3259-3268; d) G. Yin, I. Kalvet, U. Englert and F. Schoenebeck, *J. Am. Chem. Soc.*, 2015, **137**, 4164-4172.
- C. Croix, A. Longeau-Balland, H. Allouchi, M. Giorgi, A. Duchêne and J. Thibonnet, *J. Organomet. Chem.*, 2005, **690**, 4835-4843.
- DFT calculations were carried out using Gaussian16 Rev. C.01 (Gaussian 16, Revision C.01, M. J. Frisch, *et al.*, Gaussian, Inc., Wallingford CT, 2016) at the M06/6-311+G(d,p) + LANL2DZ(d,p) + LANL2DZ(f) + SMD(benzene)//B3LYP-D3/6-31G(d) + LANL2DZ(d,p) + LANL2TZ(f) level of theory. DLPNO-CCD(T) single points were obtained using ORCA 5.0.0 on DFT-optimised geometries using a cc-pVTZ-PP basis set and SK-MCDHF-RSC ECP on Au and I, and a cc-pVTZ basis set on all other atoms. For more details, see the Supporting Information.
- a) C. Riplinger, P. Pinski, U. Becker, E. F. Valeev and F. Neese, *J. Chem. Phys.*, 2016, **144**, 024109; b) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.*, 2013, **139**, 134101.
- M. W. Drover, M. C. Dufour, L. A. Lesperance-Nantau, R. P. Noriega, K. Levin and R. W. Schurko, *Chem. –Eur. J.*, 2020, **26**, 11180-11186.
- For examples of Au-arene synthesis, see: a) N. Ahlsten, G. J. P. Perry, X. C. Cambeiro, T. C. Boorman and I. Larrosa, *Catal. Sci. Tech.*, 2013, **3**, 2892-2897; b) N. V. Tzouras, M. Saab, W. Janssens, T. Cauwenbergh, K. Van Hecke, F. Nahra and S. P. Nolan, *S. P. Chem. –Eur. J.*, 2020, **26**, 5541-5551; c) F. J. L. Ingner, Z. X. Giustra, S. Novosedlik, A. Orthaber, P. J. Gates, C. Dyrager and L. T. Pilarski, L. T., *Green Chem.*, 2020, **22**, 5648-5655; d) D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Inorg. Chem.*, 2012, **51**, 8394-8401.
- 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.
- In addition, reaction of $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(4\text{-CH}_3\text{OC}_6\text{H}_4)(\text{I})]$ (**2-OCH3**) with **5** provided the pyridyl-linked oligomer, $[\text{Ni}^{\text{II}}(\text{P}_2\text{B}^{\text{Cy}}_4)(4\text{-NC}_5\text{H}_4)(\text{I})]_n$ in 48% yield.