# The Role of Metal Hydroxide Complexes in Late Transition Metal-Mediated Transmetalation Reaction: The Case of Gold

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**Abstract:** In gold chemistry, the hydroxide function on the metal center was observed to act as a potent transmetalation group facilitator when reacted with boronic acids leading to the exceedingly rapid formation of gold-aryl bonds.

**Keywords:** arylboronic acids; gold hydroxide complexes; gold-aryl complexes; N-heterocyclic carbenes; transmetalation

Over the past ten years, the use of gold in homogenous and heterogeneous chemistry has witnessed an explosive growth.<sup>[1]</sup> A key step in catalyst regeneration in these catalytic reactions is the protodeauration of an organogold intermediate. To obtain insight into this mechanism, trapping of such an intermediate has recently been the goal of a number of research groups.<sup>[2]</sup> Common straightforward routes to access these involve the reaction of lithium or Grignard reagents with a [Au(I)(L)(Cl)] (L is 2-electron donor) complexes (Scheme 1).<sup>[3]</sup> However, these procedures suffer from a narrow range of functional group tolerance and poor conversion when sterically hindered substrates are employed.

To address these limitations, recent investigations have focused on using organoboron-based reagents known for their air stability and high tolerance of sensitive functionality. The seminal work of Schmidbaur<sup>[4]</sup> and Fackler<sup>[5]</sup> has highlighted the transfer of a phenyl group from a sodium tetraphenylborate to gold(I) proceeding at room temperature. A significant contri-

L—AuCl + R—X 
$$\rightarrow$$
 R—Au(L)  
X = Mg, Li

**Scheme 1.** Common routes to access organogold(I) complexes.

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bution was made by Gray and co-workers in 2006 when they reported an efficient and selective procedure using a variety of (hetero)arylboronic acids in the presence of Cs<sub>2</sub>CO<sub>3</sub> to access, in good to high yields, phosphane-gold(I) aryls (Scheme 2).<sup>[6]</sup> Further studies demonstrated that this methodology was also successful using a Cl precursor<sup>[7]</sup> and either sterically demanding dialkylbiarylphosphine and N-heterocyclic carbene ligands (NHC) or bulky coupling partners.<sup>[8]</sup> Subsequent investigation led the same group to demonstrate further utilities of boronic acids and esters to provide in good yields diaurated compounds.<sup>[9]</sup> This fundamental reaction is of further interest as the transmetalation reaction represents a key step in the possible role of gold in cross-coupling reactions.

Inspired by those first reports, we envisaged initially to expand the scope of the reaction using (NHC)-gold(I) complexes,<sup>[10]</sup> with the aim of developing a novel, robust methodology of broad synthetic utility and generality for the preparation of substituted (NHC)-gold(I) aryl complexes. As far as we are aware, no mechanistic studies have been performed for such gold reactions until now. Therefore, to probe the inner workings of this fundamental reaction step using gold, experiments and calculations probing the mechanism were next envisioned.

An initial experiment was conducted using [Au-(IPr)Cl] (IPr=1,3-bis(diisopropyl)phenylimidazol-2ylidene) 1 (a Cl not Br bearing precursor) and





**Scheme 2.** Transmetalation of arylboronic acids to phosphane-gold(I) complexes using Gray's conditions.

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Entry	Solvent	Base	Time [h]	Temperature [°C]	Conversion [%] <sup>[a]</sup>	
1	<i>i</i> -PrOH	CsCO <sub>3</sub>	24	70	100	
2	<i>i</i> -PrOH	KOH	24	70	100	
3	THF	KOH	24	70	100	
4	benzene	КОН	24	70	100	
5	toluene	KOH	24	70	100	
6	toluene	KOH	1	50	100	
7	toluene	KOH	1	r.t.	100(>99)	
8 <sup>[b]</sup>	toluene	KOH	1	r.t.	100(>99)	
9	toluene		24	r.t.	0	

Au(IPr)

Table 1. Optimization of the transmetalation of boronic acids to (NHC)-gold(I) complexes.

B(OH)

1, solvent

[a] Determined by <sup>1</sup>H NMR spectroscopy (isolated yields are given in brackets).

[b] Using 1 equiv. of phenylboronic acid.

2 equivalents of phenylboronic acid 2 as substrate under the conditions previously described by Gray.<sup>[6]</sup> After 24 h, the reaction reached completion. The reaction conditions were next optimized and results of this optimization are summarized in Table 1. We were pleased to see that the reaction proceeded smoothly when replacing Cs<sub>2</sub>CO<sub>3</sub> with less expensive KOH base (Table 1, entry 2). Further optimization showed that a complete conversion could be obtained at ambient temperature (Table 1, entry 7). Also, the reaction time could be shortened from 24 h to 1 h. Gratifyingly, one equivalent of boronic acid was sufficient to lead the reaction to completion (Table 1, entry 8).

Further optimizations were carried out in toluene as reaction solvent as its use made the reaction completion easy to monitor with all organometallic species becoming soluble at the endpoint. As expected, no reaction occurred in the absence of base.

With this new protocol in hand, the substrate scope and limitations of the reaction were explored. The results are summarized in Table 2. Phenylboronic acids with both electron-donating and electron-withdrawing substituents afforded the corresponding organogold complexes in good to excellent yields within 10 h. In most reactions, one equivalent of boronic acid was sufficient for the reaction to reach completion in the

		ArB(OH) <sub>2</sub> + <b>1</b> + KOH (1 equiv.) (2.5 equiv.) <sup>r.t.</sup>	—► [Au(IPr)(Ar)] 3–19	
Entry	Boronic acid	Time [h]	Product	Yield [%] <sup>[a]</sup>
1	B(OH)2	1	Au(IPr)	> 99
2 <sup>[b]</sup>		2	Au(IPr)	> 99
3	B(OH) <sub>2</sub>	6		84
4	B(OH)2	7	Au(IPr)	97

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toluono

Table 2. Transmetalation of arylboronic acids to [Au(IPr)Cl] (1).

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Entry	Boronic acid	Time [h]	Product	Yield [%] <sup>[a]</sup>
5	CI-B(OH)2	1	CI-Au(IPr)	> 99
6	Br B(OH) <sub>2</sub>	2	Br Au(IPr) 7	66
7	CI CI B(OH) <sub>2</sub>	0.3		> 99
8 <sup>[b,c]</sup>	O <sub>2</sub> N-C-B(OH) <sub>2</sub>	1.5	O <sub>2</sub> N-Au(IPr)	77
9	MeO-	10	MeO-Au(IPr)	> 99
10 <sup>[c]</sup>	Me <sub>2</sub> N-B(OH) <sub>2</sub>	2	Me <sub>2</sub> N-Au(IPr)	78
11	FB(OH)2	4	F-Au(IPr)	90
12	<i>t</i> -Bu(Me) <sub>2</sub> SiO——B(OH) <sub>2</sub>	0.25	t-Bu(Me)₂SiO ─∕ Au(IPr) 13	91
13	B(OH)2	1	Au(IPr)	86
14	B(OH)2	2	Au(IPr)	92
15 <sup>[c]</sup>	B(OH) <sub>2</sub>	3	Au(IPr)	88
16 <sup>[c]</sup>	B(OH)2	10	Au(IPr)	88
17 <sup>[c]</sup>	Fe	5	Fe 18	62
18	B(OH) <sub>2</sub>	24	Au(IPr) 19	0

T-LL 2	(C + 1)
Table 2.	Continued)

<sup>[a]</sup> Isolated yields.

<sup>[b]</sup> 50°C.

<sup>[c]</sup> Using 2.5 equiv. of boronic acid

reported time. We were pleased to see that the process was not sensitive at all to halogenated substrates while these substrates would have suffered from competing side-reaction using organolithium or Grignard reagents (Table 2, entries 5, 6, 7 and 11). The reaction proceeded smoothly with *o*-biphenyl substituent affording the corresponding 2-biphenylgold(I) in 97% yield (Table 2, entry 4). For direct comparison, under heating using bulky (dicyclohexyl)(2-biphenyl)phosphine ligand the reaction required 30 h to reach completion and the corresponding biphenylgold was obtained in 90% yield.<sup>[8c]</sup> Rapid reactivity (<30 min)

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was encountered in the case of 3,4-dichlorobenzeneboronic acid (Table 2, entry 7) and 4-[(*tert*-butyldimethylsilyl)oxy]phenylboronic acid (Table 2, entry 12). These led to quantitative yields of the expected products.

Slightly longer reaction times were required for 4methoxyphenyl substituent (Table 2, entry 9). No clear influence of the electronic environment could be observed but as previously reported the use of bulkier substrates such as mesitylene or xylene required an increase to 2.5 equivalents of the starting material (Table 2, entries 15 and 16). Still the arylgolds were obtained in good yields (88% yield). Direct comparison with phosphane systems developed by Gray only allowed, for example, isolation of the corresponding phosphane mesitylgold(I) in 87% yield after 60 h.<sup>[8c]</sup> Similar to Gray's work, an increase to 2.5 equivalents for the 4-nitrophenyl- and ferrocenylboronic acids was needed to drive the reaction to completion (Table 2, entries 8 and 17).<sup>[6]</sup> The tendency of sulfur to form strong bonds to gold could explain the lack of reactivity for 2-thiopheneboronic acid. Overall, various functionalities are tolerated by this methodology including methoxy, amino, bromide, chloride, nitro and fluoride, which can permit further synthetic derivatization or functionalization. This NHC system shows closely related reactivity as the phosphanebased system developed by Gray. Representative crystal structures of two organogold compounds, obtained by slow diffusion of pentane into a saturated dichloromethane solution containing the complex, are shown in Figure 1.<sup>[11]</sup>

Complexes 5 and 17 exist as two-coordinated, gold(I) complexes, as expected. In 17, a nearly linear environment for the  $C_{carbene}$ -Au- $C_{aryl}$  bond angle is present, very close to 180°, as expected for NHC-gold(I) complexes while in 5 the  $C_{carbene}$ -Au- $C_{aryl}$  bond angle is slightly distorted. Moreover, both Au-

 $C_{carbene}$  bond distances are identical within experimental error in **5** and **17** and are similar to those previously encountered for gold-NHC complexes (ranging from 1.942 to 2.018 Å).<sup>[6,8c,12]</sup> The Au– $C_{aryl}$  bond lengths are also equal in both complexes and comparable to previously reported Au–C bonds in NHC complexes.<sup>[6,8c,12]</sup> The aryl group bound to the gold center in the two crystal structures is almost perpendicular to the imidazole core in order to minimize any steric hindrance between the *ortho*-substituent groups and the isopropyl groups of the NHC ligands.

Although known since the first report of carboncarbon coupling by Suzuki and extensively studied, the mechanism of transmetalation has long remained obscure. The role of the base was especially unclear. Plausible hypotheses involve it in either the formation of an "ate" complex at the boron or to coordinate the metal to form a metal hydroxo complex.<sup>[13]</sup> Very recently, Hartwig<sup>[14]</sup> and Amatore and Jutand<sup>[15]</sup> have reported kinetic studies of stoichiometric reactions exploring the two possible pathways. Their results support a hypothesis where the transmetalation reaction involves a palladium hydroxide reacting with the boronic acid. Thus we hypothesized two plausible pathways for our gold transmetalation reaction (Scheme 3).<sup>[16]</sup> Path A involves the initial coordination of the hydroxide to the boron to form phenylborate species 20 (Scheme 3, Path A).

This would enhance the nucleophilicity of the organic group on boron and thus facilitate its transfer to the more electropositive gold center. The second pathway (Scheme 3, **Path B**) would first involve the *in situ* formation of [Au(IPr)(OH)] (**21**)<sup>[17]</sup> that would react with the organoboron species to afford the final arylgold. Experiments were carried out to determine which of the two possible pathways was involved in this reaction manifold. To probe the viability of both pathways, "intermediates" **20** and **21**<sup>[17]</sup> were respectively reacted with **1** and **2**. The progress of the reactions was monitored by NMR spectroscopy [Eq. (1) and Eq. (2)].



**Figure 1.** Ball-and-stick representations of  $[Au(IPr)(C_{12}H_9)]$ **5** (*left*) and  $[Au(IPr)(C_9H_{11})]$  **17** (*right*). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **5**: C31–Au1 2.052(17), Au1–C1 2.026(10), C1–Au1–C31 172.5(6). For **17**: Au1–C4 2.050 (5), Au1–C2 2.023(5), C2–Au1–C4 178.1(2). Phenyltrihydroxoborate **20** reacted with **1** in a 1:1 ratio in toluene- $d_8$  at room temperature and afforded **3** in 1 h [Eq. (1)]. Similarly, the gold hydroxide **21** was



**Scheme 3.** Two plausible pathways for the transmetalation reaction involving gold.

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possible transition state

Scheme 4. Possible reaction pathway leading to  $[Au(IPr)(C_6H_5)]$  (3).

reacted with phenylboronic acid 2 in a 1:1 ratio at room temperature [Eq. (2)]. The latter reaction proved *instantaneous*! Such a significant difference in reactivity clearly illustrates that pathway B is more facile and suggests that, as with palladium in the Suzuki–Miyaura reaction, transmetalation of boronic acids to gold may very well proceed through the formation of a metal hydroxide complex (Scheme 4).

These experiments point out that pathway B will be the favored one if the *in situ* [Au(IPr)(OH)] can be formed during the reaction. This would obviously depend of the reaction conditions and on the nature of the base used. Thus under our reaction conditions, the presence of both the trihydroxoborate and gold hydroxo species cannot be excluded and both pathways may be involved. Indeed, the transmetalation of **20** to **21** was experimentally determined to also be possible [Eq. (3)].



This result is not without reminding us of the seminal work of Schmidbaur in which a gold oxide  $[(t-Bu)_3PAuO]BF_4$  was successfully reacted with NaBPh<sub>4</sub>.<sup>[4]</sup> With this first insight of the nature of the active species in the reaction, it could therefore be also envisaged that a similar pathway could occur using Gray's conditions, especially using a protic solvent such as 2-propanol in the presence of cesium carbonate as base (Scheme 5). The formation of a gold isopropoxide intermediate **iiia** may occur and be hypothesized as an active species. Or a hydroxide species **iiib** could be formed if traces of water were present in the medium. The latter would then react with either arylboronic acid or activated arylborate to afford the desired arylgold compound.

The transmetalation reaction was modelled using DFT calculations.<sup>[18]</sup> Calculations were performed on the reaction between phenylboronic acid **2** and **21** and results confirm that no significant activation barrier exist when the reaction proceeds through **Path B** (Figure 2). Several transition states were also located and have similar energies to the starting material. The proposed first transition state contains a "boronate complex" formed *via* coordination of the O atom of **21** and the boron atom of the boronic acid. The second transition state corresponds to the formation of a cationic gold complex facing the phenyl group of the boron species in order to preserve the "hypercoordination" of the boron center.

With our computational protocol the entry into **path B**, that is, formation of **21** from **1**, is more diffi-

L-AuBr 
$$\xrightarrow{Cs_2CO_3}$$
 L-Au-**O**-*i*-**Pr** or L-Au-**OH**  $\xrightarrow{\text{Ar-B}(OH)_2}$  L-AuAr  
*i*-PrOH *iiia iiib* or Ar-B(OH)\_2X

L = PR<sub>3</sub>, NHC

Scheme 5. Plausible pathways using Gray's system

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**Figure 2.** Energy profile for the transmetalation **Path B** (PBE0-D3 level), see Supporting Information, Figure S1 for an enlarged colour version.

cult to model quantitatively, because of the large medium effects on the small ions OH<sup>-</sup> and Cl<sup>-</sup> and the possible need to include counterions as well. From the conditions necessary for this reaction, how-ever,<sup>[7b]</sup> it is clear that substantial activation is needed.

Likewise **path** A is difficult to model because one of the putative products,  $B(OH)_3CI^-$ , is inherently unstable in the gas phase. We were able, however, to locate a transition state for substitution of the chloride ligand in 1 with the boronate 20, affording an alternative entry into **path** B (see Figure S2 in the Supporting Information,). A low enthalpic barrier for this "*in-situ*" formation of the hydroxide is computed, *ca.* 7 kcalmol<sup>-1</sup>, but because the interaction between the reactants is weak, the entropic penalty for this associative process imparts some kinetic hindrance. In contrast, complex formation between 2 and 21 (to form INT1 in Figure 2) is quite exothermic, which should be an important factor contributing to the enhanced reactivity of 21 compared to that of 1.<sup>[19]</sup>

With evidence of [Au(IPr)(OH)] **21** being an active species, it was reacted with several boronic acids employing our previously optimized protocol. All reactions involving **21** reached completion within 5 min [Eq. (4)].



When the initial scope of the reaction was explored, the 2- and 4-formylbenzeneboronic acids did not lead to product under our conditions. One hypothesis was simply that a side-reaction such as the Cannizzaro reaction had occurred, although no side-products could be isolated. But when **21** was used as a gold source, both reactions proceeded to completion within 30 min [Eq. (5)] and both products **24** and **25** could be isolated in good yields. As expected, the less activated 2formylbenzeneboronic acid reacted more slowly than its *para*-substituted relative.



In summary, we have described the development of a new methodology for the transmetalation from boronic acids to NHC-gold(I) complexes. Mild conditions were used as compared to previous reports for this reaction and our process is as efficient as other recently reported gold systems, even better for some substrates. This method is a practical alternative to the use of lithium or Grignard reagents for the synthesis of variously functionalized organogold compounds. Moreover, mechanistic studies enabled us to obtain a clearer picture of the active species in this reaction and may be extrapolated to other previously developed gold systems. These studies have shown that the reaction occurs preferentially through the "hydroxide pathway" rather than the expected "borate pathway". Although pathway B is the kinetically favored reaction route, pathway A cannot be excluded under the experimental reaction conditions. The present results provide the first key fundamental insight into the mechanism of transfer of the organic fragment from boron to gold and establishes that the reactivity of gold is similar to that of palladium for this important fundamental reaction step. Furthermore, the fact that gold mimics palladium along this reactivity manifold suggests to us that other late transition metal hydroxides (or more generally LTM alkoxides<sup>[20]</sup>) may behave in this manner. The basic understanding of this transmetalation reaction of boron to gold could also allow for further synthetic functionalization (or to rapidly gain molecular complexity) in one-pot reactions involving diverse electrophiles. The reactivity of these organogold complexes is the subject of ongoing studies in our laboratories.

## **Experimental Section**

#### General Procedure for the Synthesis of Arylgold Complexes

A scintillation vial was charged with [Au(IPr)Cl] (1) (50 mg, 0.08 mmol), KOH (9 mg, 0.16 mmol) and the corresponding arylboronic acid (0.08 mmol) in toluene (0.8 mL). The reaction mixture was stirred at room temperature and monitored



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by <sup>1</sup>H NMR spectroscopy. Upon completion, the solvent was removed under vacuum, the residue extracted into benzene, and filtered through Celite. The filtrate was taken to near dryness and pentane was added to precipitate the product. The resulting white suspension was filtered, and the collected solids were washed with pentane  $(3 \times 3 \text{ mL})$  to afford the title compound as a microcrystalline solid.

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- [10] As far as we are aware, only 2 examples using IPr and SIPr as ligands has been reported in the litterature using Gray's conditions for the synthesis of arylgold compounds (see ref.<sup>[8a]</sup>).
- [11] CCDC 863704 (5) and CCDC 863705 (17) contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.
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- [18] Computations were performed at the PBE0-D3/SDD/ 6-311+G\*\* level, for computational details see the Supporting Information.
- [19] Arguably, the putative σ-bond metathesis on path A will have a higher barrier than the ΔH<sup>+</sup>≈7 kcalmol<sup>-1</sup> required for chloride substitution; thus, intrinsically (i.e., without counterions), the system in Scheme 3 would clearly prefer path B.
- [20] Initial experiments with KO-*t*-Bu instead of KOH under optimum conditions in Table 1 leads to product formation in 30 min. The role of alternative alkoxide bases is presently being further explored.

## COMMUNICATIONS

8 The Role of Metal Hydroxide Complexes in Late Transition Metal-Mediated Transmetalation Reaction: The Case of Gold

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