CHEMISTRY & SUSTAINABILITY

CHEMSUSCHEM

ENERGY & MATERIALS

Accepted Article

Title: Mild and Efficient Synthesis of Diverse Organo-Au(I)-L Complexes in Green Solvents

Authors: Fredric J. L. Ingner, Ann-Cathrin Schmitt, Andreas Orthaber, Paul J. Gates, and Lukasz T Pilarski

To be cited as: *ChemSusChem* 10.1002/cssc.201903415

Link to VoR: http://dx.doi.org/10.1002/cssc.201903415

A Journal of ChemPubSoc Europe

WILEY-VCH www.chemsuschem.org

WILEY-VCH

FULL PAPER

Mild and Efficient Synthesis of Diverse Organo-Au(I)-L Complexes in Green Solvents

Fredric J. L. Ingner,[a] Ann-Cathrin Schmitt,[a] Andreas Orthaber,[b] Paul J. Gates,[c] Lukasz T. Pilarski*[a]

[a] F. J. L. Ingner, A.-C. Schmitt, Dr. L. T. Pilarski
Department of Chemistry - BMC
Uppsala University
BOX 576, 75-123, Uppsala (Sweden)
E-mail: lukasz.pilarski@kemi.uu.se
[b] Dr. A. Orthaber
Department of Chemistry - Ångström
Uppsala University
BOX 523, 75-120, Uppsala (Sweden)
[c] Dr. P. J. Gates
School of Chemistry
University of Bristol
Cantock's Close, Clifton, Bristol, BS8 1TS (UK)

Supporting information for this article is given via a link at the end of the document.

Abstract: An exceptionally mild and efficient method is presented for the preparation of (hetero)aryl-Au^{I}-L complexes using ethanol or water as the reaction medium at room temperature and R-B(triol)K boronates as the transmetalation partner. The reaction returns up to quantitative yields, needs no exogeneous base or other additives and a simple filtration is the only required purification method, which obviates considerable waste associated with alternative workup methods. A broad reaction scope is demonstrated with respect to both the L and (hetero)aryl ligands on product Au complexes. Despite the polar reaction medium, large polycyclic aromatic hydrocarbon units can be incorporated on the product Au complexes in very good to excellent yields. We demonstrate the use of our approach for the chemoselective manipulation of orthogonally protected aryl boronates to afford a novel new class of NHC-Au-aryl complexes. A mechanistic rationale is proposed.

Introduction

Synthetic chemistry is under ever greater pressure to provide environmentally benign routes to functional molecules. Reducing reliance on hazardous and/or toxic reagents and solvents has acquired increasing urgency. Several legislative measures across the world are set to restrict the future use of various toxic, carcinogenic and/or environmentally damaging solvents.[1] Their replacement with greener alternatives is a growing concern in various areas of synthesis,[2] including in organometallics and homogeneous catalysis[3] and across the pharmaceutical sector.[4] As part of a wide-ranging project in our group aimed at investigating new methods to manipulate aryl-transition metal systems, we sought to develop a reliable and exceptionally mild approach to the synthesis of diverse complexes of the type L-Au^{I}-(hetero)aryl. In recent years, organo-Au^{I} complexes have attracted considerable interest for various forms of biological activity[5] and for their promise in materials applications.[6]

For example, complexes **1a**[7] (Figure 1) and **1b**,[8] respectively, exhibit anti-malarial and anti-cancer properties. L-Au^{I}-(hetero)aryl complexes are also of great interest as intermediates in homogeneous catalysis,[9] as exemplified by **1c**.[10] Herein, we report a uniquely mild, versatile and efficient approach to L-Au^{I}-(hetero)aryl complexes using green solvents and without any need for extraction, recrystalisation or chromatography to obtain analytically pure products.

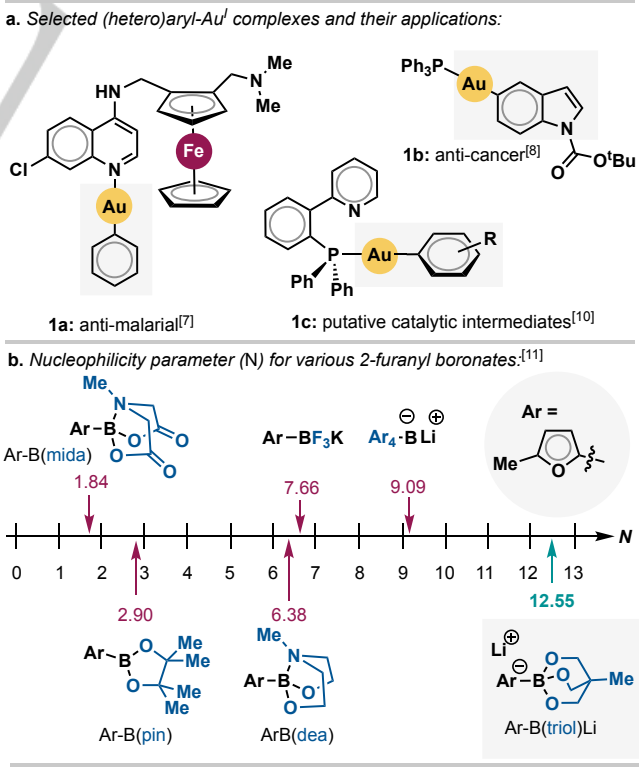
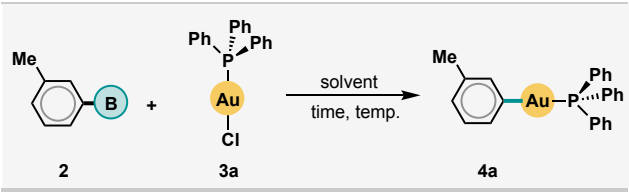
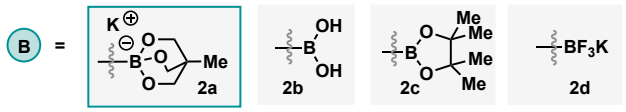


Figure 1. a) Example organo-Au^{I} complexes and their properties; b) Relative nucleophilicities of selected arylboronates reported by Mayr and co-workers.[11]

Table 1. Selected results from the comparison of different boronates in the transmetalation to **3a**. Ph_3PAuCl (0.05 mmol), boronate (1 equiv.), solvent (0.5 mL). Yields determined by ^{31}P NMR spectroscopy.





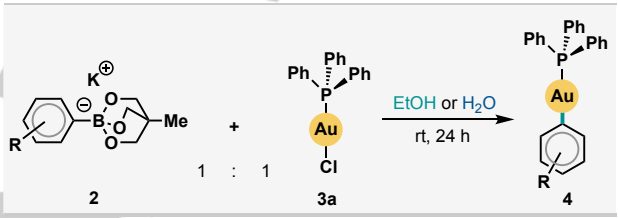
Entry	Boronate	Solvent	Temp (°C)	Time (h)	Yield (%)
1	**2a**	toluene	23	24	43
2	**2a**	CH_2Cl_2	23	24	60
3	**2a**	THF	23	24	46
4	**2a**	EtOAc	23	24	39
5	**2a**	MeCN	23	24	45
6	**2a**	^{n}PrOH	23	24	88
7	**2a**	EtOH	23	24	**97**
8	**2a**	H_2O	23	24	**85**
9	**2b**	H_2O	50	5	0
10	**2c**	H_2O	50	5	0
11	**2d**	H_2O	50	5	0
12	**2a**	H_2O	50	5	87

We specifically set out to develop a protocol to prepare L-Au^I-Ar complexes that tolerated a wide functional group and ligand variety, required only environmentally benign/non-toxic solvent media and, importantly, worked efficiently without any other exogeneous additives or heating using well-defined reagents. Whilst organoboronic acids[12] and their pinacol esters[9m, 12c, 13] have been conventionally used to generate organo-Au^I complexes, the former are not well defined, as they can contain varying amounts of boroxine species, and are often used in excess. Additionally, previously reported methods have often relied on unsustainable/hazardous solvents, with exogeneous additives and at elevated temperatures. With our ambition in mind, we considered boronates of the type [ArB(triol)]M (Figure 1b), which have never been used in this context, as candidate sources of the aryl group.[14] Originally developed by Yamamoto and co-workers as effective reagents in various coupling reactions,[15] such boronates have also been shown by Mayr and co-workers[11] to be significantly more nucleophilic than several of their more commonly used congeners (selected variants are shown in Figure 1b).

The triol itself, 2-(hydroxymethyl)-2-methylpropane-1,3-diol, has low toxicity and a significantly lower price compared to pinacol[16] and is produced on a multi-ton scale annually.[17] We anticipated that the transmetalation of (hetero)aryl groups from such boronates to an Au^I center should be particularly efficient on account of their significantly enhanced nucleophilicity[11, 18] and because they have been shown to benefit transmetalation to other transition metals.[15f, 15g, 19] For example, Chan-Lam aminations using [PhB(triol)]K proceed at three times the rate of the equivalent reactions using $PhB(OH)_2$ or $PhBF_3K$ as the arylating reagent.[20] We envisaged the prospect of an alternative intra-molecular transmetalation pathway *via* intermediate alkoxide adducts (*vide infra*).

Results and Discussion

In initial experiments, we compared a range of 3-tolyl boronates (**2a-d**) in the transmetalation to the Au^I centre of Ph_3PAuCl (**3a**) in various solvents (Table 1, entries 1-8). Triolboronate **2a** proved substantially more efficient in EtOH (entry 7) and even H_2O (entry 8) than in toluene[12a, 12c, 21] or MeCN,[9s, 22] both of which have served as solvents of choice in many previously reported protocols. Moreover, unlike in many previous methods, the transmetalation occurred efficiently without any exogeneous heating. Boronate **2a** was the only one amongst several (**2a-d**) to afford the desired products in H_2O, even if elevated temperatures were used (entries 9-12).



ortho substituents:

meta substituents:

4b: EtOH: **88%**
H_2O: 54%

4c: R = Me, EtOH: **62%**
4d: R = OMe, EtOH: **78%**
H_2O: 56%

4e: R = I,
EtOH: **85%**, **97%**[a,b]
H_2O: 56%

4a: R = Me,
EtOH: **97%**, **90%**[a]
H_2O: **85%**

para substituents:

4f: R = OMe
EtOH: **88%**
H_2O: 65%

4g: R = I
EtOH: **93%**, **91%**[a,b]
H_2O: 55%

4h: R = Br
EtOH: **82%**,
H_2O: 60%

4i: R = Cl
EtOH: 75%, **89%**[a,b]
H_2O: 52%

4j: R = CH=CH_2, EtOH: **83%**
4k: R = CF_3, EtOH: 41%
4l: R = NO_2, EtOH or H_2O: 0%

4m: EtOH: 47%,
96%[a,b]
H_2O: 45%

4n: EtOH: **87%**,
96%[a,b]
H_2O: **84%**

X-ray crystal structure of **4n**

4o: EtOH: 60%

4p: EtOH: 53%, **88%**[a,c]

Scheme 1. Boronate scope in EtOH and H2O solvents. Ph_3PAuCl (0.1 mmol) boronate (1.0 equiv.). Unless otherwise stated, yield determined by ^{31}P NMR spectroscopy. [a] Isolated yield; [b] 3.0 equiv. of boronate used. [c] 1.2 equiv. of boronate used.

Subsequently, we undertook an extensive exploration of the scope with respect to both five- and six-membered (hetero)aryl boronates using **3a** as the gold precursor (Scheme 1).

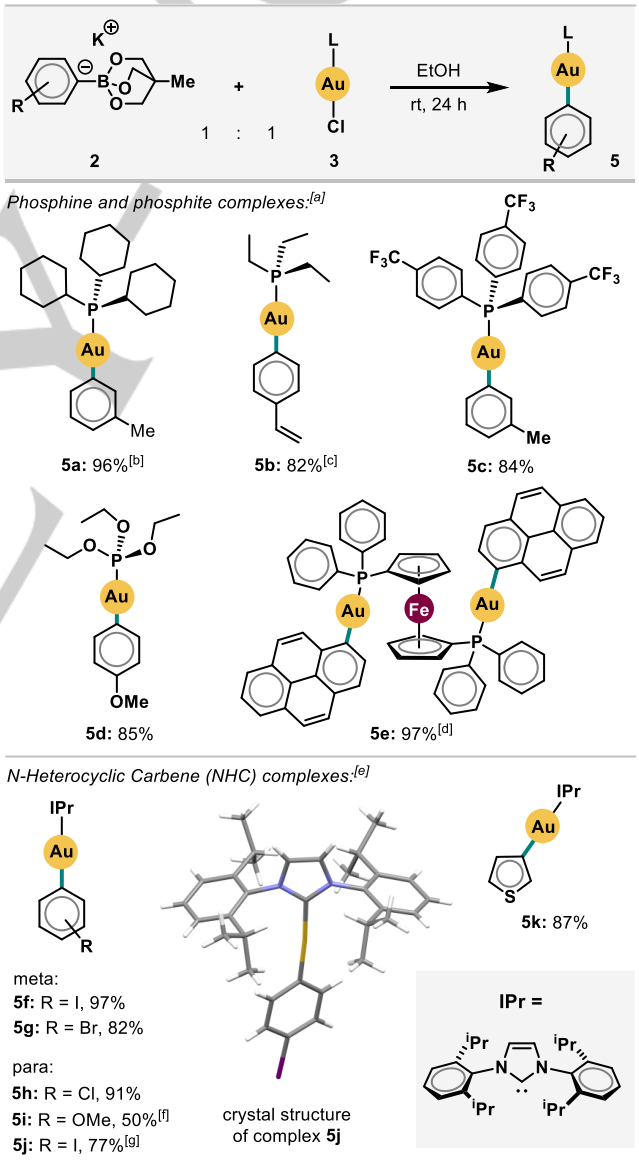
The reactions proved very clean: only starting materials and products could be observed when monitoring reaction progress using ^{31}P NMR spectroscopy. Very good to excellent conversions were obtained with almost all substrates in EtOH at room temperature using only a 1:1 ratio between **2** and **3a**. Boronic acids bearing methyl- (**4a**,**c**), methoxy- (**4d**,**f**), iodo- (**4e**,**g**), bromo- (**4h**), chloro- (**4i**), vinyl- (**4j**) and trifluoromethyl- (**4k**) groups performed well. Gratifyingly, using 1.2–3.0 boronate equivalents invariably returned >99% conversion and very good to near-quantitative yields. For example, the vinyl-Au^I complex **4m** formed in up to 96% yield, whilst 2-furanyl (**4o**) and ferrocenyl (**4p**) units returned 96% and 88% yield, respectively. The identity of product complex **4n** was confirmed using X-ray crystallography (see SI for more details); we also observed no difficulties arising from the previously suggested S···Au coordination in thiophene substrates.[12c] Generally, electron-rich substrates performed slightly better and only the very strongly electron-withdrawing nitro group (**4l**) prevented product formation. Steric hindrance from substituents *ortho*- to the C-Au bond imposed only a modest reduction in yield (*e.g.* **4d** vs **4f**).

Moreover, no recrystallization or chromatographic separation were required: although each reaction mixture remained heterogeneous throughout, analytically pure products could be obtained in simply *via* a sole filtration at the end of the reaction time. This is a marked advantage over previously reported procedures for the preparation of L-Au^I-(hetero)aryl complexes, which have often relied on the use of halogenated solvents during the work-up procedure. Even water proved to be a viable, albeit slightly less effective solvent (Scheme 1, yields from reactions performed in water shown in blue).[2b, 3]

We next sought to test the scope of the reaction with respect a variety of L-type ligands on the Au^I center. Trialkylphosphine ligands with both large (**5a**) and small (**5b**) cone angles[23] performed well. Weaker σ-donor ligands, e.g. tris(4-trifluoromethylphenyl)phosphine (**5c**) and triethylphosphite (**5d**) also gave very good yields.

Our reaction conditions returned the trimetallic ferrocene-based complex **5e** in 97% isolated yield. The efficiency of this reaction is particularly notable, given the presence of multiple planar π-extended and apolar groups. Dinuclear Au^I complexes have attracted attention in various contexts, including as potential anti-cancer therapies[24] and in catalysis.[25] Additionally, NHC-Au-aryl complexes bearing a variety of functional groups formed efficiently (**5f-k**). The only exception was the 4-methoxyphenyl variant (**5i**) presumably due to protodeauration, which is accelerated by polar protic solvents for NHC-Au^I complexes with electron-rich arene ligands[26] (cf. **4f**, Scheme 1). We also noted that the reaction scaled well: Compound **5g** was prepared on a 0.4 mmol scale, which is 40 times the scale used in our initial optimisation.

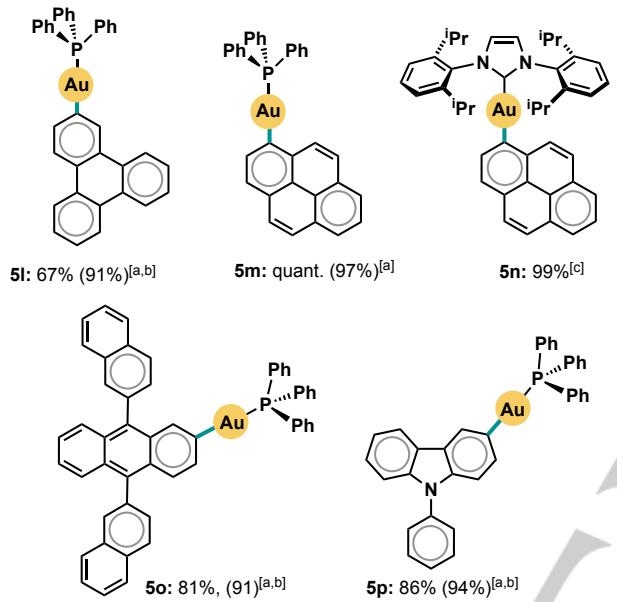
Various organometallic complexes incorporating polycyclic aromatic hydrocarbons (PAHs), including those of Au^I, have attracted attention for their interesting photophysical properties and potential applications in molecular recognition.[13b, 27] Encouraged by the excellent yield of **5e**, we turned our attention to the synthesis of complexes based on several PAH units (Scheme 3). Products **5l-p** were isolated in very good to quantitative yield: up to 97% yield (**5m**) using only one equivalent of the appropriate [aryl-B(triol)]K reagent and in up to 99% yield (**5n**) using only 1.2 equivalents. This is a significant improvement over several previous reports concerning the synthesis of PAH-containing Au^I complexes, for which poor to moderate yields have been common until now.[13b, 22c, 28] For all our examples, analytically pure products could be obtained via a simple filtration, obviating the need for additional extraction, recrystalisation or chromatography. This is especially pleasing, as purification has relied in some previous reports on the use of chlorinated solvents, which are increasingly the subject of evermore stringent legislative regulation.[1]



Scheme 2. Scope with respect to the L ligand. Isolated yields unless otherwise specified. 0.1 mmol scale of LAuCl [a] 1.0 equiv. of boronate used.; [b] 1.5 equiv. boronate; [c] Yield determined by ^{31}P NMR spectroscopy; [d] Ratio of reagents used: [(dppf)$(AuCl)_2$] 1:2 boronate; [e] 1.2 equiv boronate [f] Yield determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as standard. [g] Reaction performed on 0.4 mmol scale.

N-Aryl carbazole units feature in a range of organic electronic applications as easily tunable charge transporters.[29] The auration under our conditions of N-Phenyl carbazole (product **5p**) occurred with 86% conversion using only 1 equivalent of the corresponding triol boronate and in 94% isolated yield using 3 equivalents.

In a more general context, the manipulation of PAHs can often suffer from their poor solubility in many solvents. In contrast to their -B(pin) and -BF_3K congeners, each of the starting material [aryl-B(triol)]K substrates dissolved easily in EtOH at room temperature (Figure 2). This should open new opportunities for the manipulation of PAHs.[30]



Scheme 3. Synthesis of PAH-containing complexes. General conditions as in Scheme 2. PPh_3AuCl complex (0.1 mmol), boronate (1 equiv.). Yields determined by ^{31}P NMR spectroscopy unless otherwise stated; [a] Isolated yield. [b] 3.0 equiv. boronate used. [c] 1.2 equiv. boronate used.

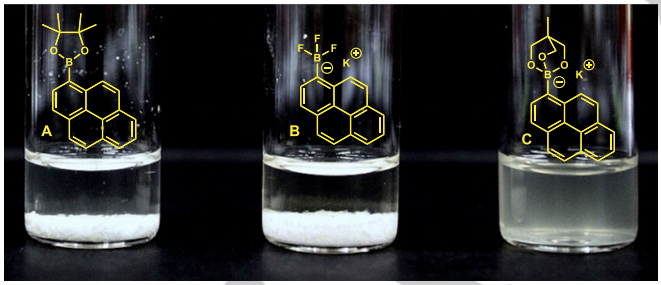
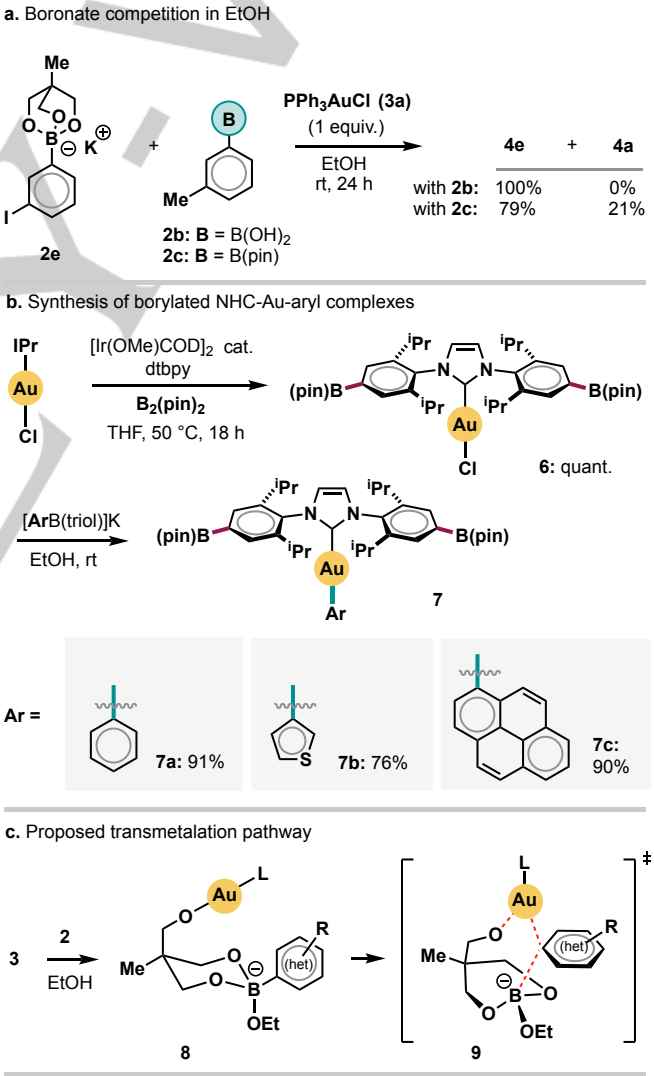


Figure 2. Photograph of pyrenyl boronates (2 mmol) in EtOH (2 mL).

To address a related environmental aspect, and to mitigate concerns that the overall method is reliant on unrenewable solvents, we synthesized a representative range of the parent ArB(triol)K reagents in 2-methyltetrahydrofuran, a solvent obtained from renewable resources.[31] These syntheses returned comparable or higher yields than the more commonly used THF or toluene solvents (see SI for further details).

Species bearing multiple, differentiated boronate groups can impart various unique advantages in synthesis.[32] As part of a wider program of studies into Au^I complexes, we sought to exploit the differentiated reactivity of **2a**, **2b** and/or **2c** to generate a new class of decorated NHC-Au^I-aryl complexes that retained versatile boronate functionality for further manipulation. In a competition experiment, boronate **2e** gave significantly faster transmetalation to PPh_3AuCl (**3a**) than did **2b** or **2c** in EtOH (Scheme 4a). As shown in Scheme 4b, we found that Ir-catalyzed borylation[33] of IPr-Au-Cl gave diborylated complex **6** in quantitative yield. To the best of our knowledge, this marks the first reported use of C-H functionalization methodology to derivatize coordinated NHC ligands.[34]

Subsequently, several aryl groups could be introduced in good to excellent yields (products **7a-c**) to the Au^I center using [ArB(triol)]K boronates under our mild conditions without any evidence of C-B bond cleavage on the boryl NHC moiety in **6**. By contrast, attempts to generate complexes **7** from the corresponding (hetero)arylboronic acids invariably led to intractable mixtures.



Scheme 4. a. Competition study: Ph_3PAuCl (0.1 mmol) and boronates (1 equiv. each) were used. **b.** Use of differentiated boronate reactivity to generate novel organogold complexes. **c.** Tentative intramolecular transmetalation pathway based on preliminary mechanistic data (see SI for further information).

We propose that, in addition to their significant nucleophilicity, boronates **2** benefit from the lability of an alkoxide residue, leading to the formation of complexes **8.** Thereafter, fast intramolecular transmetalation (transition states **9**, Scheme 4c) presumably occurs; hydroxide and alkoxide organo-Au^{I} complexes are known to participate in transmetalation processes.[12c, 35]. Experiments in support of this proposed pathway are presented in the Supporting Information.

Conclusion

In summary, we have described that triol-based boronates afford a mild, convenient, high-yielding and versatile pathway to L-Au^{I}-(hetero)aryl complexes. Our method works efficiently in green solvents at room temperature, often without an excess of the boronate reagent. No extraction, recrystallisation or chromatography methods are required: product isolation relies solely on filtration. Uniquely, our scope includes phosphine, phosphite and NHC L-type ligands, as well as diversely substituted (hetero)aryl and PAH-based aryl groups transferred to the Au^{I} center. The significantly greater efficiency of transmetalation from triol-based boronates compared to their congeners permits the diversification of C-H borylated NHC-Au complexes. We envisage that this can be leveraged to construct new Au^{I} complexes with valuable bioactivity profiles and properties useful in organic electronics applications. Work on this continues in our laboratory.

Experimental Section

Representative procedure: To a 12 mL microwave vial equipped with a magnetic stirrer bar were added Ph_3PAuCl (0.1 mmol, 1 equiv.) and the desired triol-based aryl boronate (0.3 mmol, 3 equiv.). EtOH (1.0 mL) was added and the resulting heterogeneous mixture was stirred at room temperature for the indicated time. After stirring, the precipitate was washed with EtOH (2 x 4 mL) and dried under reduced pressure to afford the analytically pure corresponding aryl Au(I) complex.

Acknowledgements

We thank the Swedish Research Council (Vetenskapsrådet) for funding, as well as Dr Johanna Larsson, and Dr Christine Dyrager for proof-reading the manuscript.

Keywords: gold • green solvents • boronates • NHCs • synthesis

[1] J. Sherwood, *Angew. Chem. Int. Ed.* **2018**, *57*, 14286-14290.
[2] a) C. J. Clarke, W.-C. Tu, O. Levers, A. Bröhl, J. P. Hallett, *Chem. Rev.* **2018**, *118*, 747-800; b) T. Kitanosono, K. Masuda, P. Xu, S. Kobayashi, *Chem. Rev.* **2018**, *118*, 679-746.
[3] C. I. Herrerías, X. Yao, Z. Li, C.-J. Li, *Chem. Rev.* **2007**, *107*, 2546-2562.
[4] a) K. L. Wilson, J. Murray, H. F. Sneddon, K. M. P. Wheelhouse, A. J. B. Watson, *Chem* **2017**, *3*, 365-368; b) C. P. Ashcroft, P. J. Dunn, J. D. Hayler, A. S. Wells, *Org. Proc. Res. Dev.* **2015**, *19*, 740-747; c) T. Welton, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science* **2015**, *471*; d) J. D. Hayler, D. K. Leahy, E. M. Simmons, *Organometallics* **2019**, *38*, 36-46.
[5] a) M. Mora, M. C. Gimeno, R. Visbal, *Chem Soc Rev* **2019**, *48*, 447-462; b) B. Đ. Glišić, M. I. Djuran, *Dalton Trans.* **2014**, *43*, 5950-5969; c) H. E. Abdou, A. A. Mohamed, J. P. Fackler, A. Burini, R. Galassi, J. M. López-de-Luzuriaga, M. E. Olmos, *Coord. Chem. Rev.* **2009**, *253*, 1661-1669; d) C.-M. Che, R. W.-Y. Sun, *Chem. Commun.* **2011**, *47*, 9554-9560; e) T. Zou, C. T. Lum, C.-N. Lok, J.-J. Zhang, C.-M. Che, *Chem. Soc. Rev.* **2015**, *44*, 8786-8801.
[6] a) S. N. Islam, A. Sil, S. K. Patra, *Dalton Trans.* **2017**, *46*, 5918-5929; b) A. Moeller, P. Bleckenwegner, U. Monkowius, F. Mohr, *J. Organomet. Chem.* **2016**, *813*, 1-6; c) R. Visbal, M. C. Gimeno, *Chem. Soc. Rev.* **2014**, *43*, 3551-3574.
[7] H. Bjelosevic, I. A. Guzei, L. C. Spencer, T. Persson, F. H. Kriel, R. Hewer, M. J. Nell, J. Gut, C. E. J. van Rensburg, P. J. Rosenthal, J. Coates, J. Darkwa, S. K. C. Elmroth, *J. Organomet. Chem.* **2012**, *720*, 52-59.
[8] S. Craig, L. Gao, I. Lee, T. Gray, A. J. Berdis, *J. Med. Chem.* **2012**, *55*, 2437-2451.
[9] a) R. Ye, J. Zhao, B. B. Wickemeyer, F. D. Toste, G. A. Somorjai, *Nature Cat.* **2018**, *1*, 318-325; b) M. O. Akram, S. Banerjee, S. S. Saswade, V. Bedi, N. T. Patil, *Chem. Commun.* **2018**, *54*, 11069-11083; c) S. A. Shahzad, M. A. Sajid, Z. A. Khan, D. Canseco-Gonzalez, *Synth. Commun.* **2017**, *47*, 735-755; d) D. Pflästerer, A. S. K. Hashmi, *Chem. Soc. Rev.* **2016**, *45*, 1331-1367; e) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180-3211; f) S. Taschinski, R. Döpp, M. Ackermann, F. Rominger, F. de Vries, M. F. S. J. Menger, M. Rudolph, A. S. K. Hashmi, J. E. M. N. Klein, *Angew. Chem. Int. Ed.* **2019**, *58*, 16988-16993; g) Y. Yang, L. Eberle, F. F. Mulks, J. F. Wunsch, M. Zimmer, F. Rominger, M. Rudolph, A. S. K. Hashmi, *J. Am. Chem. Soc.* **2019**, *141*, 17414-17420; h) M. T. Johnson, J. Marthinus Janse van Rensburg, M. Axelsson, M. S. G. Ahlquist, O. F. Wendt, *Chem. Sci.* **2011**, *2*, 2373-2377; i) S. Witzel, K. Sekine, M. Rudolph, A. S. K. Hashmi, *Chem. Commun.* **2018**, *54*, 13802-13804; j) J. Xie, K. Sekine, S. Witzel, P. Krämer, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2018**, *57*, 16648-16653; k) Y. Yang, P. Antoni, M. Zimmer, K. Sekine, F. F. Mulks, L. Hu, L. Zhang, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2019**, *58*, 5129-5133; l) M. P. Robinson, G. C. Lloyd-Jones, *ACS Catal.* **2018**, *8*, 7484-7488; m) M. J. Harper, C. J. Arthur, J. Crosby, E. J. Emmett, R. L. Falconer, A. J. Fensham-Smith, P. J. Gates, T. Leman, J. E. McGrady, J. F. Bower, C. A. Russell, *J. Am. Chem. Soc.* **2018**, *140*, 4440-4445; n) L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Science* **2012**, *337*, 1644-1648; o) L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Chem. Eur. J.* **2012**, *18*, 2931-2937; p) L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *J. Am. Chem. Soc.* **2014**, *136*, 254-264; q) T. J. A. Corrie, L. T. Ball, C. A. Russell, G. C. Lloyd-Jones, *J. Am. Chem. Soc.* **2017**, *139*, 245-254; r) C. García-Morales, X.-L. Pei, J. M. Sarria Toro, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2019**, *58*, 3957-3961; s) M. S. Winston, W. J. Wolf, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 7777-7782; t) A. M. Echavarren, A. S. K. Hashmi, F. D. Toste, *Adv. Synth. Catal.* **2016**, *358*, 1347-1347; u) H. Kawai, W. J. Wolf, A. G. DiPasquale, M. S. Winston, F. D. Toste, *J. Am. Chem. Soc.* **2016**, *138*, 587-593; v) S. Kim, J. Rojas-Martin, F. D. Toste, *Chem. Sci.* **2016**, *7*, 85-88; w) H. F. Jónsson, S. Evjen, A. Fiksdahl, *Org. Lett.* **2017**, *19*, 2202-2205; x) A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Nat. Commun.* **2017**, *8*, 565; y) C.-Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* **2015**, *517*, 449; z) M. Joost, A. Zeineddine, L. Estévez, S. Mallet−Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 14654-14657.
[10] A. Tabey, M. Berlande, P. Hermange, E. Fouquet, *Chem. Commun.* **2018**, *54*, 12867-12870.
[11] G. Berionni, B. Maji, P. Knochel, H. Mayr, *Chem. Sci.* **2012**, *3*, 878-882.
[12] a) D. V. Partyka, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem. Int. Ed.* **2006**, *45*, 8188-8191; b) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592-597; c) S. Dupuy, L. Crawford, M. Bühl, A. M. Z. Slawin, S. P. Nolan, *Adv. Synth. Catal.* **2012**, *354*, 2380-2386.

[13] a) M. Hofer, A. Genoux, R. Kumar, C. Nevado, *Angew. Chem. Int. Ed.* **2017**, *56*, 1021-1025; b) L. Gao, M. A. Peay, D. V. Partyka, J. B. Updegraff, T. S. Teets, A. J. Esswein, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2009**, *28*, 5669-5681; c) M. D. Levin, F. D. Toste, *Angew. Chem. Int. Ed.* **2014**, *53*, 6211-6215.

[14] A. J. J. Lennox, G. C. Lloyd-Jones, *Chem. Soc. Rev.* **2014**, *43*, 412-443.

[15] a) Y. Yamamoto, M. Takizawa, X.-Q. Yu, N. Miyaura, *Angew. Chem. Int. Ed.* **2008**, *47*, 928-931; b) X.-Q. Yu, Y. Yamamoto, N. Miyaura, *Chem. Asian J.* **2008**, *3*, 1517-1522; c) G.-Q. Li, S. Kiyomura, Y. Yamamoto, N. Miyaura, *Chem. Lett.* **2011**, *40*, 702-704; d) Y. Yamamoto, *Heterocycles* **2012**, *85*, 799-819; e) Y. Yamamoto, M. Takizawa, X.-Q. Yu, N. Miyaura, *Heterocycles* **2009**, *80*, 359-368; f) G.-Q. Li, Y. Yamamoto, N. Miyaura, *Synlett* **2011**, *2011*, 1769-1773; g) G.-Q. Li, Y. Yamamoto, N. Miyaura, *Tetrahedron* **2011**, *67*, 6804-6811.

[16] As the time of writing (2020-01-15), from Sigma-Aldrich 500 g (4160 mmol) of 1,1,1-Tris(hydroxymethyl)ethane can be purchased for USD $30.50 or $0.0073/mmol. For comparison, the price of pinacol from the same supplier is USD $497.00 for 500 g (4231 mmol), or $0.11/mmol. By this measure, pinacol is over 16 times more expensive than 1,1,1-tris(hydroxymethyl)ethane. .

[17] a) P. Werle, M. Morawietz, S. Lundmark, K. Sörensen, E. Karvinen, J. Lehtonen, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, **2008**; b) K. P. Singh, S. Gupta, A. Kumar, D. Mohan, *Chem. Res. Toxicol.* **2014**, *27*, 741-753.

[18] G. Berionni, A. I. Leonov, P. Mayer, A. R. Ofial, H. Mayr, *Angew. Chem. Int. Ed.* **2015**, *54*, 2780-2783.

[19] S. Sakashita, M. Takizawa, J. Sugai, H. Ito, Y. Yamamoto, *Org. Lett.* **2013**, *15*, 4308-4311.

[20] X.-Q. Yu, Y. Yamamoto, N. Miyaura, *Chemistry – An Asian Journal* **2008**, *3*, 1517-1522.

[21] M. M. Hansmann, F. Rominger, M. P. Boone, D. W. Stephan, A. S. K. Hashmi, *Organometallics* **2014**, *33*, 4461-4470.

[22] a) M. O. Akram, P. S. Shinde, C. C. Chintawar, N. T. Patil, *Org. Biomol. Chem.* **2018**, *16*, 2865-2869; b) T. Cornilleau, P. Hermange, E. Fouquet, *Chem. Commun.* **2016**, *52*, 10040-10043; c) W. Zang, Y. Wei, M. Shi, *Chemistry – An Asian Journal* **2018**, *13*, 2791-2795; d) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi, F. Rominger, *Angew. Chem. Int. Ed.* **2009**, *48*, 8243-8246.

[23] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348.

[24] a) T. Zou, C. T. Lum, C.-N. Lok, W.-P. To, K.-H. Low, C.-M. Che, *Angew. Chem. Int. Ed.* **2014**, *53*, 5810-5814; b) C.-H. Chui, R. S.-M. Wong, R. Gambari, G. Y.-M. Cheng, M. C.-W. Yuen, K.-W. Chan, S.-W. Tong, F.-Y. Lau, P. B.-S. Lai, K.-H. Lam, C.-L. Ho, C.-W. Kan, K. S.-Y. Leung, W.-Y. Wong, *Bioorg. Med. Chem.* **2009**, *17*, 7872-7877.

[25] a) V. Vreeken, D. L. J. Broere, A. C. H. Jans, M. Lankelma, J. N. H. Reek, M. A. Siegler, J. I. van der Vlugt, *Angew. Chem. Int. Ed.* **2016**, *55*, 10042-10046; b) R. S. Ramón, S. Gaillard, A. M. Z. Slawin, A. Porta, A. D'Alfonso, G. Zanoni, S. P. Nolan, *Organometallics* **2010**, *29*, 3665-3668; c) M. Lankelma, V. Vreeken, M. A. Siegler, J. I. van der Vlugt, *Inorganics* **2019**, *7*, 28.

[26] K. E. Roth, S. A. Blum, *Organometallics* **2010**, *29*, 1712-1716.

[27] a) D. Nuevo, M. Poyatos, E. Peris, *Organometallics* **2018**, *37*, 3407-3411; b) C. Mejuto, L. Escobar, G. Guisado-Barrios, P. Ballester, D. Gusev, E. Peris, *Chem. Eur. J.* **2017**, *23*, 10644-10651; c) S. Ibáñez, M. Poyatos, E. Peris, *Organometallics* **2017**, *36*, 1447-1451; d) C. Biz, S. Ibáñez, M. Poyatos, D. Gusev, E. Peris, *Chem. Eur. J.* **2017**, *23*, 14439-14444; e) R. M. Edkins, K. Fucke, M. J. G. Peach, A. G. Crawford, T. B. Marder, A. Beeby, *Inorg. Chem.* **2013**, *52*, 9842-9860; f) R. A. Vogt, M. A. Peay, T. G. Gray, C. E. Crespo-Hernandez, *J. Phys. Chem. Lett.* **2010**, *1*, 1205-1211; g) G. Yang, L. Fang, K. Tan, S. Shi, Z. Su, R. Wang, *Organometallics* **2007**, *26*, 2082-2087; h) D. V. Partyka, A. J. Esswein, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2007**, *26*, 3279-3282; i) W. Y. Heng, J. Hu, J. H. K. Yip, *Organometallics* **2007**, *26*, 6760-6768.

[28] S. Pankajakshan, T.-P. Loh, *Chemistry – An Asian Journal* **2011**, *6*, 2291-2295.

[29] G. Sathiyan, E. K. T. Sivakumar, R. Ganesamoorthy, R. Thangamuthu, P. Sakthivel, *Tetrahedron Lett.* **2016**, *57*, 243-252.

[30] Enhanced solubility of some triol-protected boronates has been noted previously: M. R. Akula, M.-L. Yao, G. W. Kabalka, *Tetrahedron Lett.* **2010**, *51*, 1170-1171.

[31] a) V. Pace, P. Hoyos, L. Castoldi, P. Domínguez de María, A. R. Alcántara, *ChemSusChem* **2012**, *5*, 1369-1379; b) V. Pace, P. Hoyos, M. Fernández, J. V. Sinisterra, A. R. Alcántara, *Green Chem.* **2010**, *12*, 1380-1382; c) S. Monticelli, L. Castoldi, I. Murgia, R. Senatore, E. Mazzeo, J. Wackerlig, E. Urban, T. Langer, V. Pace, *Monatshefte für Chemie - Chemical Monthly* **2017**, *148*, 37-48.

[32] a) L. Xu, S. Zhang, P. Li, *Chem. Soc. Rev.* **2015**, *44*, 8848-8858; b) L. Xu, S. Ding, P. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 1822-1826; c) T. Yamamoto, A. Ishibashi, M. Suginome, *Org. Lett.* **2017**, *19*, 886-889; d) E. Demory, K. Devaraj, A. Orthaber, P. J. Gates, L. T. Pilarski, *Angew. Chem. Int. Ed.* **2015**, *54*, 11765-11769.

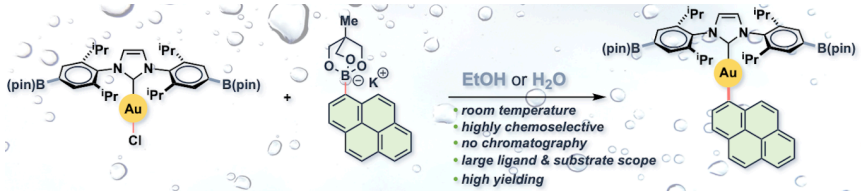
[33] a) M. A. Larsen, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 4287-4299; b) H. Tajuddin, P. Harrisson, B. Bitterlich, J. C. Collings, N. Sim, A. S. Batsanov, M. S. Cheung, S. Kawamorita, A. C. Maxwell, L. Shukla, J. Morris, Z. Lin, T. B. Marder, P. G. Steel, *Chem. Sci.* **2012**, *3*, 3505-3515; c) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992-2002; d) I. A. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890-931.

[34] Recently, Cazin, Nolan and co-workers reported the fascinating reactivity of L-Au(I)-B(pin) species: C. M. Zinser, F. Nahra, L. Falivene, M. Brill, D. B. Cordes, A. M. Z. Slawin, L. Cavallo, C. S. J. Cazin, S. P. Nolan, *Chem. Commun.* **2019**, *55*, 6799-6802.

[35] a) F. Nahra, S. R. Patrick, A. Collado, S. P. Nolan, *Polyhedron* **2014**, *84*, 59-62; b) S. Gaillard, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 2742-2744.

10.1002/cssc.201903415

Entry for the Table of Contents



Triols and triturations: The high-yielding syntheses of diverse aryl-Au(I) complexes is achieved under mild conditions in green solvents (ethanol or water) by harnessing the unique properties of aryl-B(triol)K boronates. The method permits transmetalation from aryl-B(triol)K boronates whilst preserving aryl-B(pin) boronates on the substrate. Pure products are obtained through a simple filtration.