**Simple Synthetic Routes to N-Heterocyclic Carbene Gold(I)-Aryl Complexes: Expanded Scope and Reactivity**

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***Abstract:*** *The discovery of sustainable and scalable synthetic protocols leading to gold-aryl compounds bearing N-heterocyclic carbene (NHC) ligands sparked an investigation of their reactivity and potential utility as organometallic synthons. The use of a mild base and green solvents provide access to these compounds, starting from widely available boronic acids and various [Au(NHC)Cl] complexes, with reactions taking place under air, at room temperature and leading to high yields with unprecedented ease. One compound, (N,N’-bis[2,6-(di-isopropyl)phenyl]imidazol-2-ylidene)(4-methoxyphenyl)gold, ([Au(IPr)(4-MeOC6H4)]), was synthesized on a multigram scale and used to gauge the reactivity of this class of compounds towards C-H/N-H bonds and with various acids, revealing simple pathways to gold-based species that possess attractive properties as materials, reagents and/or catalysts.*

Introduction

Metal-carbon bond-bearing complexes are the foundation of organometallic chemistry and the importance of such species is paramount, as their ubiquitous involvement in catalysis attests.[1] We have had a longstanding interest in gold catalysis and the unique stabilizing role *N*-heterocyclic carbenes (NHCs) as supporting ligands.[2] In this context, we have considered the gold-carbon bond (whether involved in bonding as part of the NHC or as part of an additional hydrocarbyl moiety) central to the reactivity of gold complexes.[3,4] More specifically, gold-aryl complexes are frequently invoked as intermediates in gold-mediated reactions.[4] Certain members of this family of organometallic complexes also exhibit interesting photophysical and biological properties, and therefore are extremely valuable materials.[5,6] These compounds have also been used as substrates in cross-coupling reactions,[7] and have recently been shown as efficient pre-catalysts in the acid- and silver-free hydrophenoxylation of alkynes.[8] Despite recent advances,[3-8,9] their reactivity remains largely unexplored, presumably because of the methods used for their preparation, which can be viewed as operationally complex.

Early synthetic approaches proved lacking in efficiency and involved the use of aryl-magnesium and aryl-lithium reagents with all associated drawbacks, such as a limited functional group tolerance and the need for inert conditions and low temperatures,[7d,10] however they are still used to this day.[11] Groundbreaking advances have been achieved by Gray and later by Stockland, Gray and co-workers, who developed synthetic approaches making use of Cs2CO3 and boronic acids to obtain phosphine- as well as *N*-heterocyclic carbene (NHC)-stabilized Au(I)-aryl complexes.[12,13] We have also contributed to this area, by making use of our “golden synthon”, [Au(IPr)OH] (IPr = *N,N’*-bis[2,6-(di-isopropyl)phenyl]imidazol-2-ylidene), in the transmetallation of organosilanes and organoboranes to gold,[14] and also, along with Larrosa, by using a decarboxylative approach to [Au(NHC)(Ar)] complexes.[15] However, all of these approaches involve the use of either harsh reaction conditions, reagents that require special handling, toxic solvents or at least two synthetic steps, and to the best of our knowledge, none of these have been evaluated on large scale, most likely because of a simple lack of practicality (Scheme 1). Herein, we disclose sustainable, operationally simple and scalable synthetic methods for the preparation of these multipurpose organogold complexes. Importantly, we showcase for the first time, that *N*-alkyl substituted NHCs can participate in these processes as we begin to uncover the synthetic potential of [Au(NHC)Ar] (Ar = aryl) complexes.



**Scheme 1.** State-of-the-art methods for the synthesis of gold(I)-aryl complexes.

**Results and Discussion**

Our initial approach questioned whether the transmetallation reaction between [Au(IPr)Cl] (**1**) and an equimolar amount of phenylboronic acid was feasible in technical grade acetone in the presence of K2CO3 (entry 1, Table 1). This initial hypothesis is based on our recent work using a weak inorganic base to form M-C bonds.[16] Even though the desired aryl-gold complex **2a** was obtained, traces of **1** were still present in the reaction crude, thus suggesting that a small excess of the boron reagent was required to reach full conversion. A reaction carried out in isopropanol at lower temperatures led to a 94% yield of **2a**, highlighting that very high temperatures were unnecessary as were anhydrous solvents and anaerobic conditions (entry 2, Table 1).[12,13] This prompted us to examine ethanol as a more sustainable and lower boiling solvent. [17] The reaction at room temperature led to a 96% yield of **2a** (entry 3, Table 1). An attempt was made to synthesize **2a** in a telescoping fashion, starting directly from the precursors of **1** and phenylboronic acid, and led to a 64% yield yet produced significant decomposition (entry 4, Table 1). The two-step approach appears optimum. Interestingly, the synthesis of **2a** can be carried out in an ethyl acetate/water mixture leading to a high yield of the product without the need for a filtration step (*vide infra*), and allows for visual monitoring, since the initial biphasic suspension turns into a biphasic clear solution after complete conversion of **1** (entries 5 and 6, Table 1). The use of K3PO4, another mild and sustainable base, led to an 85% yield of **2a**, this time in an ethanol/water mixture. When the reaction was carried out in water, full conversion was not observed even after 2 days (entries 7-10, Table 1). Of note, using phenylboronic acid pinacol ester as the boron reagent led to a similar reaction outcome (entry 11, Table 1).

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| **Table 1.** Optimization of the synthetic protocol. | | | | |
| **Entry**[a] | **Solvent** | **Base** | **Temp (oC)** | **Isolated yield (%)** |
| 1[b] | Me2CO | K2CO3 | 60 | 81[c] |
| 2 | iPrOH | K2CO3 | 50 | 94 |
| **3** | **EtOH** | **K2CO3** | **RT**[d] | **96** |
| 4 | EtOH | K2CO3 | RT | 64[e] |
| 5 | 40% EtOH/H2O | K2CO3 | RT | 92 |
| 6 | 50% EtOAc/H2O | K2CO3 | RT | 94 |
| 7 | EtOH | K3PO4 | RT | -[c] |
| 8 | 50% EtOAc/H2O | K3PO4 | RT | -[c] |
| 9 | 40% EtOH/H2O | K3PO4 | RT | 85 |
| 10 | H2O | K2CO3 | RT | -[c] |
| 11 | EtOH | K2CO3 | RT | 95[f] |
| [a] Conditions unless otherwise noted: [Au(IPr)Cl] (50 mg, 0.08 mmol), Phenylboronic acid (1.1 equiv.), Base (3.0 equiv.), 0.5 mL of solvent, 16 hours. [b] Phenylboronic acid (1.0 equiv.). [c] Incomplete conversion. [d] Room temperature (RT) under operating condition can range from 25 to 35**o**C. [e] [Au(DMS)Cl] (0.10 mmol), IPr•HCl (1 equiv.), Phenylboronic acid (1.1 equiv,), K2CO3 (5.0 equiv.). [f] Phenylboronic acid pinacol ester (1.1 equiv.). | | | | |

In an attempt to gather information about the events that transpire prior to transmetallation, general procedure A was followed in the absence of the boronic acid (See Experimental Section). An aliquot was taken from the reaction mixture *via* pipette and was dried under high vacuum for 30 minutes. To that was added deuterated chloroform, which had been neutralized by filtration through (dried) basic alumina and the sample was transferred to an NMR tube. Comparison of the obtained spectra with those of [Au(IPr)Cl] and [Au(IPr)OH] (prepared the same way) revealed that [Au(IPr)Cl] was no longer present in the reaction mixture, as it had been converted to a mixture of [Au(IPr)OH] as determined by the presence of a singlet at 7.11 ppm and [Au(IPr)OEt], as determined by the presence of a broad singlet at 7.13 ppm (NHC backbone: NC*H*, Figure 1). It should be noted that [Au(IPr)OH] could be generated in the reaction mixture because of the existence of water in the reaction.[14c] It is also possible however, that its presence in the obtained spectra is attributed to the reaction of [Au(IPr)OEt] with water present in the NMR solvent. Repeating this experiment several times led to varying ratios of the two complexes, suggesting that the water content variations affect this measurement. This however, does not invalidate the possibility that [Au(IPr)OH] is actually an intermediate in this transformation, as [Au(IPr)OEt] is not a stable complex and would react with moisture as well as with the boronic acid.[14a,14c,18,19] Importantly, following general procedures B and C in the absence of the boronic acid lead to 0% conversion of [Au(IPr)Cl]. This suggests that the solvent effect is paramount for the observation of this phenomenon and also raises a question as to whether these reactions involve the same intermediates or follow different pathways. Furthermore, signals attributed to the presence of ethanol in the obtained NMR spectra, suggest that ethanol might have a stabilizing interaction with the generated [Au(IPr)OEt] (Figure 1). Repeated attempts to isolate both intermediates from the reaction mixture were not successful. However, this phenomenon is observed for the first time in such systems and sheds light on possible intermediates, the involvement of which has only been postulated thus far.[14c] Interestingly, no other solvent/base combination described here lead to such observable intermediates.



**Figure 1.** Stacked 1H-NMR spectra of [Au(IPr)Cl] (1), [Au(IPr)OH] (2) and an aliquot (3, taken from the reaction and dried under high vacuum) in CDCl3 .

The reaction conditions shown in entry 3 (Table 1) were chosen in order to explore the scope of boronic acids (Scheme 2). An electron-donating 4-methoxy group led to **2b** in excellent yield. A more sterically demanding boronic acid also led to high yield of the corresponding gold complex under these conditions (**2c**). Compound **2d**, which was shown to possess interesting physical properties, was obtained in an excellent yield.[12e] Boronic acids bearing electron-withdrawing groups at various positions also led to the desired gold-aryl complexes in high yields (**2e**, **2f** and **2g**). A boronic acid pinacol ester bearing an alkyne group was successfully aurated (**2h**), demonstrating the high functional group tolerance of this method and its potential as a tool for gold installation on complex organic scaffolds. A heteroaryl-boronic acid was also compatible to these reaction conditions, leading to compound **2i** in quantitative yield. Of note, the synthesis of **2i** was the only case described here where a considerable excess of the boron reagent had to be used (1.4 equiv.) to reach full conversion to the aurated-heteroaryl product.



**Scheme 2.** Scope of boron reagents. [a] Conditions unless otherwise noted: [Au(IPr)Cl] (100 mg, 0.161 mmol), boron reagent (1.1 equiv.), K2CO3 (3.0 equiv.), EtOH (0.8 mL), 16 hours. [b]. From the corresponding boronic acid pinacol ester. [c] 2-furanylboronic acid (1.4 equiv.).

In order to assess the scalability of this approach the synthesis of **2b** was successfully carried out on a gram scale, leading to a nearly quantitative yield of the product (Scheme 3). A greater than 6-gram-scale synthesis of **2b** was successfully performed, using the convenient biphasic system which obviates reaction monitoring and allowed the separation/removal of by-products by decantation of the aqueous phase in a simple separatory funnel.



**Scheme 3.** Synthesis of **2b** on larger scale. Conditions A: [Au(IPr)Cl] (1.00 g, 1.61 mmol), 4-methoxy-phenylboronic acid (0.257 g, 1.69 mmol, 1.05 equiv.), EtOH (8 mL), 4 hours. Conditions B: [Au(IPr)Cl] (6.00 g, 9.66 mmol), 4-methoxy-phenylboronic acid (1.50 g, 9.85 mmol,1.02 equiv.), EtOAc (30 mL)/H2O (30 mL), 16 hours.

Next, we turned our attention to the nature of the ligands that could be compatible with the synthetic route (Scheme 4). In this regard, **3** bearing a carbene ligand with a saturated backbone was obtained in 74% (a slightly higher yields than that obtained with the more elaborate state-of-the-art method).[8] Complex **4**, possessing electron-withdrawing chloride substituents on the NHC backbone, was efficiently synthesized. Importantly, gold-aryl complexes **5** and **6**, stabilized by electron-rich, *N*-alkyl substituted NHCs, were obtained in high yields. Such compounds are unprecedented in the literature, and the fact that the corresponding [Au(NHC)OH] complexes present a non-trivial synthetic challenge, renders the current approach particularly expedient in these cases.[20] Finally, the methodology was used to synthesize a phosphine ligated gold-aryl complex (**7**), illustrating the versatility of this approach.



**Scheme 4.** Scope of ligands. Conditions: [Au(L)Cl] (1.0 equiv.), boronic acid (1.1 equiv.), K2CO3 (3.0 equiv.), EtOH (0.5-0.8 mL), 16 hours.

Intrigued by the fact that **2b** can be produced sustainably on a multigram scale, we probed its reactivity. When **2b** was dissolved in acetonitrile and HBF4•Et2O was added, the cationic gold **8** was rapidly formed (Scheme 5).[21] This catalytically active complex is also a valuable precursor to the [{Au(IPr)}2(*µ*-OH)][BF4] catalyst.[22] When **2b** was treated with *p*-toluenesulfonic acid in benzene at room temperature, complex **9** was observed along with another species that was identified as a *gem*-diaurated arene.[23] Heating the mixture with an excess of the sulfonic acid led to **9** after workup. Interestingly, treatment of **2b** with methylsulfonic acid led to **10** directly. A similar result was obtained when (+)-camphorsulfonic acid was employed, forming **11**, which is a novel gold complex bearing a chiral counterion. Mesitylsulfonic acid led to a similar outcome as *p*-toluenesulfonic, as heating was required for the *gem*-diaurated species to be eliminated from the mixture (**12**). When **2b** and phenylacetylene were reacted in benzene, **13** was efficiently obtained, a rapid reaction involving the C-H bond is attributed to the methoxy group electronic effect, as recent literature suggests that this reaction does not take place under such mild conditions with **2a**.[10b] Finally, when **2b** and carbazole were reacted in benzene, the gold-amido complex **14** was obtained in high yield, easily activating the N-H bond and significantly improving upon the state-of-the-art method for access to such complexes.[24]



**Scheme 5.** Exploration of the reactivity of **2b**.

All new complexes were fully characterized and their molecular structures were unambiguously determined by single crystal X-ray diffraction analysis, as shown in Figure 2.[25] Based on key structural features outlined in the legend of Scheme 2, no conclusions can be drawn with regards to the effect of the electron-donating character of the NHC on the length of the Au-CAr bond in the solid state, as only slight differences are observed. With regards to the sulfonate counterion-bearing complexes, the length of the Au-O bond is slightly higher in the case of **11**. Interestingly, in the solid state, the distance between the hydrogen atoms of the methyl groups of the camsylate anion and those of the IPr ligand is around 3 Å in some cases, however no related crosspeaks were detected in 2D-NOESY NMR. This suggests that in solution these distances are significantly larger. However, as judged by the 1H-NMR spectrum of **11**, the two *N*-Aryl groups of IPr give distinct signals, suggesting that this anion is in close proximity to gold in solution and has a relatively fixed orientation with respect to IPr.



**Figure 2.** X-ray molecular structures of new complexes are presented, showing thermal displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity. In the case of complex **6**, three distinct structures exist in the unit cell, one of which was arbitrarily chosen for this figure.[25] Selected bond lengths (Å) and angles (o) for each complex: **2h** (CNHC-Au = 2.027(9), Au-CAr = 2.033(9), CNHC-Au-CAr = 175.7(3)), **4** (CNHC-Au = 2.015(2), Au-CAr = 2.028(2), CNHC-Au-CAr = 177.6(1)), **5** (CNHC-Au = 2.047(2), Au-CAr = 2.033(2), CNHC-Au-CAr = 178.7(1)), **6** (CNHC-Au = 2.057(5), Au-CAr = 2.033(5), CNHC-Au-CAr = 175.8(2)), **11** (CNHC-Au = 1.952(6), Au-O = 2.044(5), CNHC-Au-O = 176.4(2)), **12** (CNHC-Au = 1.957(3), Au-O = 2.048(2), CNHC-Au-O = 176.6(1)).

**Conclusion**

In conclusion, we have developed efficient, sustainable and operationally simple synthetic routes to a wide range of gold(I)-aryl complexes. The scalability and simplicity of our protocols are remarkable features that will permit further exploration into gold chemistry and catalysis. Notably, this was demonstrated by the promising synthetic uses of **2b**,[26] which we have begun to evaluate as alternatives to more traditional practices in gold chemistry. Further investigations focusing on the uses of these gold-aryl complexes in organometallic chemistry and catalysis are ongoing in our laboratory.

**Experimental Section**

**General information**

All reactions were carried out in air. Solvents and all other reagents were purchased and used as received without further purification unless otherwise stated. [AuCl(DMS)] was prepared from HAuCl4∙nH2O, which was supplied by Umicore. All [Au(NHC)Cl] complexes were synthesized according to known procedures.[16a,20,27] [Au(PPh3)Cl] was purchased from Strem Chemicals, Inc. and was used as received. [Au(IPr)OH] was synthesized using known protocols.[14a,18] Purification of compounds by filtration was performed using basic alumina or celite purchased from Sigma Aldrich. Unless otherwise noted, absolute ethanol, deionized water and freshly crushed potassium carbonate were used. 1H, 13C-{1H} and 19F Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield, Bruker Avance 300 Ultrashield or a Bruker Avance 500 spectrometer at 298 K using the residual solvent peak as reference (CDCl3: δH = 7.26 ppm, δC = 77.16 ppm; CD2Cl2: δH = 5.32 ppm, δC = 54.00 ppm, C6D6: δH = 7.16 ppm, δC = 128.4 ppm). Peaks are assigned as: s (singlet), d (doublet), t (triplet), h (heptuplet) and m (multiplet). The specific rotation of **11** was determined using a Perkin Elmer 241 Polarimeter. All chlorinated solvents were neutralized prior to use by filtration through dried basic alumina. Elemental analyses were either performed at London Metropolitan University 166-220, Holloway Road, London, N7 8DB.

**General synthetic procedures**

**Procedure A**: A 4-mL screwcap vial equipped with a septum cap and a stirring bar was charged with [Au(L)Cl] (50 or 100 mg, 1 equiv.), the boron reagent (1.1 equiv.), K2CO3 (3 equiv.) and ethanol (0.5 or 0.8 mL). The resulting suspension was stirred at 35 °C for 16 h on a metal heating plate. Upon full conversion of [Au(L)Cl] (as judged by NMR analysis of an aliquot), the solvent was removed under vacuum and either dichloromethane, benzene or ethyl acetate was added to the residue. The resulting mixture was filtered through either celite or basic alumina and the filtrate was concentrated to dryness, affording the desired [Au(L)Ar] complex as a microcrystalline solid. Residual solvents or minor impurities present in the obtained solid can be removed by trituration of a saturated dichloromethane solution with pentane or washing with pentane (or diethyl ether) and drying under high vacuum.

**Procedure B**: A 4-mL screwcap vial equipped with a septum cap and a stirring bar was charged with [Au(L)Cl] (1 equiv.), the boron reagent (1.1 equiv.), K2CO3 (3 equiv.), and ethyl acetate/water (1:1). The resulting biphasic suspension was stirred at 35 °C for 16 h on a metal heating plate. Upon full conversion of [Au(L)Cl] (as judged by NMR analysis of an aliquot, or by the formation of a clear organic phase), the reaction mixture was transferred to a separating funnel with ethyl acetate (5 mL) and water (5 mL). The aqueous phase was discarded and the organic phase was washed with water (5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated to dryness, affording the desired [Au(L)Ar] complex as a microcrystalline solid. Residual solvents present in the obtained solid can be removed by trituration with dichloromethane/pentane or washing with pentane (or diethyl ether) and drying under high vacuum.

**Procedure C**: A 4-mL screwcap vial equipped with a septum cap and a stirring bar was charged with [Au(L)Cl] (1 equiv.), the boron reagent (1.1 equiv.), K2CO3 (3 equiv.), and a 40% v/v aqueous solution of ethanol. The resulting suspension was stirred at 35 °C for 16 h on a metal heating plate. Upon full conversion of [Au(L)Cl] (as judged by NMR analysis of an aliquot),the solvents were evaporated under vacuum and the residue was dissolved and transferred to a separating funnel with ethyl acetate (5 mL) and water (5 mL). The aqueous phase was discarded and the organic phase was washed with water (5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated to dryness, affording the desired [Au(L)Ar] complex as a microcrystalline solid. Residual solvents present in the obtained solid can be removed by trituration with dichloromethane/pentane or washing with pentane (or diethyl ether) and drying under high vacuum.

**Scope of boron reagents**

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](phenyl)gold(I) [Au(IPr)C6H5] (2a):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (50 mg, 0.08 mmol), phenylboronic acid (10.8 mg, 0.089 mmol,1.1 equiv.), K2CO3 (33.4 mg, 0.242 mmol, 3 equiv.) and ethanol (0.5 mL). Purification of the product was carried out by filtration through celite with dichloromethane (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 96% yield (51.2 mg, 0.077 mmol).

**Procedure B**:Synthesized following the general procedure with [Au(IPr)Cl] (50 mg, 0.08 mmol), phenylboronic acid (10.8 mg, 0.089 mmol,1.1 equiv.), K2CO3 (33.4 mg, 0.242 mmol, 3 equiv.) and ethyl acetate (0.25 mL) and water (0.25 mL). Evaporation of the solvent after purification afforded the desired product as a white powder in 94% yield (50.1 mg, 0.076 mmol).

**Procedure C**:Synthesized following the general procedure with [Au(IPr)Cl] (50 mg, 0.08 mmol), phenylboronic acid (10.8 mg, 0.089 mmol,1.1 equiv.), K2CO3 (33.4 mg, 0.242 mmol, 3 equiv.) and 0.5 mL of a 40% v/v aqueous solution of ethanol. Evaporation of the solvent after purification afforded the desired product as a white powder in 92% yield (48.5 mg, 0.076 mmol). **1H NMR (400 MHz, C6D6):** δ (ppm) = 7.52 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.22 (m, 4H, overlapping peaks), 7.08 (d, *J* = 7.8 Hz, 4H), 6.99 (tt, *J* = 7.7, 1.5 Hz, 1H), 6.32 (s, 2H), 2.67 (hept, *J* = 6.8 Hz, 4H), 1.49 (d, *J* = 6.9 Hz, 12H), 1.10 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, C6D6):** δ (ppm) = 198.5, 169.9, 145.9, 141.3, 135.1, 130.5, 127.1, 124.7, 124.2, 122.5, 29.1, 24.8, 23.9. Analytical data obtained are in agreement with reported values.[14a,7a]

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](4-methoxyphenyl)gold(I)** **[Au(IPr)C7H7O] (2b):**

**Procedure A (small scale)**:Synthesized following the general procedure with [Au(IPr)Cl] (50 mg, 0.08 mmol), 4-methoxy-phenylboronic acid (13.5 mg, 0.089 mmol,1.1 equiv.), K2CO3 (33.4 mg, 0.242 mmol, 3 equiv.) and ethanol (0.5 mL). Purification of the product was carried out by filtration through celite with dichloromethane (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 97% yield (54.0 mg, 0.078 mmol).

**Procedure A (large scale)**:Synthesized following the general procedure in a 40 mL scintillation vial equipped with with a septum cap and a stirring bar using [Au(IPr)Cl] (1.00 g, 1.61 mmol,), 4-methoxy-phenylboronic acid (0.257 g, 1.69 mmol,1.05 equiv.), K2CO3 (0.668 mg, 4.83 mmol, 3 equiv.) and ethanol (8 mL). Full conversion had been achieved in 4 hours, as judged by NMR analysis of an aliquot. After concentrating the reaction mixture to dryness, purification of the product was carried out by filtration through celite with dichloromethane (60 mL). Evaporation of the solvent, washing with pentane (3x30 mL) and drying under high vacuum afforded the product as a white powder in 98% yield (1.09 g, 1.58 mmol).

**Procedure B (large scale)**: Synthesized following the general procedure in a 100 mL round bottom flask equipped with with a septum and a stirring bar using [Au(IPr)Cl] (6.00 g, 9.66 mmol,), 4-methoxy-phenylboronic acid (1.5 g, 9.85 mmol,1.02 equiv.), K2CO3 (4.01 g, 29.0 mmol, 3 equiv.) and ethyl acetate (30 mL) and water (30 mL). Full conversion had been achieved after 16 hours, as judged by the evolution of a completely clear, biphasic solution. The reaction mixture was transferred to a 1.0 L separation funnel using 220 mL of ethyl acetate and 220 mL of water. After vigorous mixing of the two phases, the aqueous phase was separated and extracted with 50 mL of ethyl acetate which was subsequently added to the organic phase. The organic phase was washed with 50 mL of water, dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The product was precipitated by the addition of pentane (200 mL) to the obtained saturated solution, filtered on a sintered glass crucible, washed with pentane (2x100 mL) and dried under high vacuum. The product was isolated as a white solid in 95% yield (6.37 g, 9.19 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.45 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 4H), 7.13 (s, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.65 (s, 3H), 2.67 (hept, *J* = 6.9 Hz, 4H), 1.40 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 197.3, 156.9, 145.9, 140.8, 134.8, 130.2, 124.0, 122.9, 122.8, 112.8, 55.1, 28.9, 24.7, 24.1. **Elemental analysis** calcd (%) for C34H43AuN2O: C 58.95, H 6.26, N 4.04; found: C 58.97, H 6.38, N 3.91. Analytical data obtained are in agreement with reported values.[14c]

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](2,4,6-trimethylphenyl)gold(I) [Au(IPr)C9H13] (2c):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), 2,4,6-trimethylphenylboronic acid (29.1 mg, 0.177 mmol,1.1 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 83% yield (94.0 mg, 0.134 mmol). **1H NMR (400 MHz, C6D6):** δ (ppm) = 7.27 (t, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 4H), 6.98 (s, 2H), 6.36 (s, 2H), 2.66 (hept, *J* = 6.8 Hz, 4H), 2.28 (s, 3H), 2.24 (s, 6H), 1.44 (d, *J* = 6.9 Hz, 12H), 1.10 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, C6D6):** δ (ppm) = 201.0, 167.1, 146.6, 146.2, 135.3, 133.1, 130.4, 128.3, 128.1, 127.8, 126.1, 124.1, 122.31, 29.1, 26.4, 24.7, 24.1, 21.5. Analytical data obtained are in agreement with reported values.[7a]

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene)](1,1’-napthalenyl)gold(I)** **[Au(IPr)C10H7] (2d):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), naphthalene-1-boronic acid (30.4 mg, 0.177 mmol,1.1 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 96% yield (94.0 mg, 0.154 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.59 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.38 (t, *J* = 4.7 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 4H), 7.21 (s, 2H), 7.19 (t, *J* = 1.4 Hz, 1H), 7.16 (m, 2H), 7.01 (ddd, *J* = 8.2, 6.7, 1.4 Hz, 1H), 2.83 – 2.65 (m, 4H), 1.39 (d, *J* = 6.9 Hz, 12H), 1.26 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 197.9, 173.1, 146.1, 143.8, 136.7, 134.8, 134.8, 133.9, 130.3, 127.7, 125.1, 124.1, 123.9, 123.71, 122.9, 122.7, 29.0, 24.6, 24.2. Analytical data obtained are in agreement with reported values.[14c]

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene)](3,4-dichlorophenyl)gold(I)** **[Au(IPr)C6H3Cl2] (2e):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), 3,4-dichlorophenylboronic acid (33.8 mg, 0.177 mmol,1.1 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 94% yield (110 mg, 0.150 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.49 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.15 (s, 2H), 7.10 (d, *J* = 1.0 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 7.7, 1.0 Hz, 1H), 2.63 (hept, *J* = 6.9 Hz, 4H), 1.37 (d, *J* = 6.9 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 195.4, 170.0, 145.9, 141.2, 139.3, 134.5, 130.9, 130.5, 128.2, 127.5, 124.1, 123.0, 28.9, 24.7, 24.1. Analytical data obtained are in agreement with reported values.[14c]

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene)](4-fluorophenyl)gold(I)** **[Au(IPr)C6H4F] (2f):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), 4-fluorophenylboronic acid (24.8 mg, 0.177 mmol,1.1 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 91% yield (100 mg, 0.147 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.47 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 4H), 7.14 (s, 2H), 7.04 – 6.96 (m, 2H), 6.76 – 6.69 (m, 2H), 2.66 (hept, *J* = 6.8 Hz, 4H), 1.39 (d, *J* = 6.9 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 196.6 (s), 164.3 (s), 161.0 (d, *JCF* = 240.9 Hz), 145.9 (s), 140.9 (d, *JCF* = 5.0 Hz), 134.7 (s), 130.3 (s), 124.1 (s), 122.9 (s), 113.4 (d, *JCF* = 17.2 Hz), 28.9 (s), 24.7 (s), 24.1 (s). **19F NMR (471 MHz, CDCl3)** δ (ppm) = -119.06 (m). Analytical data obtained are in agreement with reported values.[14c,28]

**Synthesis of** **[***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](4-nitrophenyl)gold(I)** **[Au(IPr)C6H4NO2] (2g):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), 4-nitrophenylboronic acid (29.6 mg, 0.177 mmol,1.1 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a bright yellow powder in 88% yield (100 mg, 0.141 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.79 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 7.18 (s, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 2.64 (hept, *J* = 6.8 Hz, 2H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 195.2, 182.2, 145.9, 145.3, 140.3, 134.5, 130.5, 124.2, 123.2, 120.5, 28.9, 24.7, 24.1. Analytical data obtained are in agreement with reported values.[14c]

**Synthesis of** **[***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](4-(phenylethynyl)phenyl)gold(I)** **[Au(IPr)C6H4CCC6H4] (2h):**

**Procedure A**:Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), 4-(phenylethynyl)phenylboronic acid pinacol ester (53.8 mg, 0.177 mmol,1.1 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through basic alumina with benzene (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a light yellow solid in 73% yield (100 mg, 0.118 mmol). **1H NMR (400 MHz, C6D6):** δ (ppm) = 7.56 (d, *J* = 8.0 Hz, 2H, HAr), 7.49 (d, *J* = 8.0 Hz, 2H, HAr), 7.38 (dd, *J* = 7.8, 1.6 Hz, 2H, HAr), 7.23 (t, *J* = 7.8 Hz, 2H, HAr(IPr)), 7.07 (d, *J* = 7.8 Hz, 4H, HAr(IPr)), 6.97 – 6.87 (m, 3H, HAr), 6.32 (s, 2H, HImid), 2.65 (hept, *J* = 6.8 Hz, 4H, C*H*(CH3)2(IPr)), 1.46 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPr)), 1.10 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPr)). **13C {1H} NMR (101 MHz, C6D6):** δ (ppm) = 197.6 (N*C*N), 172.4 (CAr-Au), 145.9 (CAr(IPr)), 141.0 (*C*HAr-CAr-Au), 134.9 (N*C*Ar(IPr)), 131.9 (CHAr), 130.6 (CHAr(IPr)), 130.0 (Au-C=CH-*C*HAr), 128.3 (CHAr, seen in HSQC), 127.4 (CHAr), 125.2 (CAr), 124.2 (CHAr(IPr)), 122.6 (CHImid), 119.2 ((Au-C=CH-CHAr-CHAr-*C*Ar-CC), 92.6 (*C*C, close to Au), 88.3 (C*C*), 29.1 (*C*H(CH3)2(IPr)), 24.8 (CH(*C*H3)2(IPr)), 23.9 (CH(*C*H3)2(IPr)). **Elemental analysis** calcd (%) for C41H45AuN2: C 64.56, H 5.95, N 3.67; found: C 64.61, H 5.87, N 3.61.

**Synthesis of** **[***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](furan-2-yl)gold(I)** **[Au(IPr)C4H3O] (2i):**

**Procedure A**: Synthesized following the general procedure with [Au(IPr)Cl] (100 mg, 0.161 mmol), 2-furanylboronic acid (19.8 mg, 0.225 mmol,1.4 equiv.), K2CO3 (66.8 mg, 0.484 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in >99% yield (105 mg, 0.161 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.49 (d, *J* = 1.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 7.14 (s, 2H), 6.24 (dd, *J* = 2.9, 1.7 Hz, 1H), 5.80 (d, *J* = 2.9 Hz, 1H), 2.64 (hept, *J* = 6.8 Hz, 4H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 194.6, 192.3, 145.8, 143.9, 134.6, 130.4, 124.2, 123.1, 117.9, 107.7, 28.9, 24.7, 24.1. Analytical data obtained are in agreement with reported values.[15a]

**Scope of ligands**

**Synthesis of [***N*,*N***-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene](4-methoxyphenyl)gold(I)** **[Au(SIPr)C7H7O] (3):**

**Procedure A**: Synthesized following the general procedure with [Au(SIPr)Cl] (50.15 mg, 0.08 mmol), 4-methoxyphenylboronic acid (13.5 mg, 0.089 mmol,1.1 equiv.), K2CO3 (33.44 mg, 0.242 mmol, 3 equiv.) and ethanol (0.5 mL). Purification of the product was carried out by filtration through celite with dichloromethane (6 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 74% yield (41.4 mg, 0.060 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.37 (t, *J* = 7.8 Hz 2H), 7.22 (d, *J* = 7.8 Hz, 4H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4Hz, 2H), 4.00 (s, 4H), 3.64 (s, 3H), 3.15 (hept, *J* = 6.9 Hz, 4H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.35 (d, *J* = 6.8 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 216.8, 161.0, 156.9, 146.9, 140.8, 134.9, 129.5, 124.4, 112.7, 55.1, 53.9, 29.1, 25.2, 24.2. Analytical data obtained are in agreement with reported values.[8]

**Synthesis of [4,5-dichloro-***N*,*N***-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](4-methoxyphenyl)gold(I)** **[Au(IPrCl)C7H7O] (4):**

**Procedure A**: Synthesized following the general procedure with [Au(IPrCl)Cl] (100 mg, 0.145 mmol), 4-methoxyphenylboronic acid (24.22 mg, 0.159 mmol,1.1 equiv.), K2CO3 (60.1 mg, 0.435 mmol, 3 equiv.) and ethanol (0.8 mL). Purification of the product was carried out by filtration through basic alumina with benzene (6 mL, ethyl acetate can also be used). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white powder in 91% yield (100 mg, 0.131 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.51 (t, *J* = 7.8 Hz, 2H, HAr(IPrCl)), 7.30 (d, *J* = 7.8 Hz, 4H, HAr(IPrCl)), 6.95 (d, *J* = 8.4 Hz, 2H, HAr), 6.63 (d, *J* = 8.4 Hz, 2H, HAr), 3.65 (s, 3H,OC*H*3), 2.56 (hept, *J* = 6.9 Hz, 4H, C*H*(CH3)2(IPrCl)), 1.40 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPrCl)), 1.27 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPrCl)). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 197.3 (N*C*N), 158.9 (CAr-Au), 157.1 (CAr-OMe), 146.4 (CAr(IPrCl)), 140.8 (CHAr), 131.7 (N*C*Ar(IPrCl)), 131.2 (CHAr(IPrCl)), 124.3 (CHAr(IPrCl)), 118.8 (CImid-Cl), 112.8 (CHAr), 55.1 (O*C*H3), 29.3 (*C*H(CH3)2(IPrCl)), 24.7 (CH(*C*H3)2(IPrCl)), 23.6 (CH(*C*H3)2(IPrCl)). **Elemental analysis** calcd (%) for C34H41AuCl2N2O: C 53.62, H 5.43, N 3.68; found: C 53.55, H 5.44, N 3.61.

**Synthesis of [***N*,*N***-Bis(adamantyl)imidazol-2-ylidene](phenyl)gold(I)** **[Au(IAd)C6H5] (5):**

**Procedure A**: Synthesized following the general procedure with [Au(IAd)Cl] (45.8 mg, 0.08 mmol), phenylboronic acid (10.8 mg, 0.089 mmol,1.1 equiv.), K2CO3 (33.4 mg, 0.242 mmol, 3 equiv.) and ethanol (0.5 mL). Purification of the product was carried out by filtration through celite with dichloromethane (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white, microcrystalline solid in 81% yield (39.8 mg, 0.065 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.60 (dd, *J* = 7.8, 1.5 Hz, 2H, HAr), 7.23 (t, *J* = 7.5 Hz, 2H, HAr), 7.05 (s, 2H, NC*H*), 7.04 – 6.99 (m, 1H, HAr), 2.68 (m, 12H, NCC*H*2), 2.29 (s, 6H, C*H*Alk), 1.82 (m, 12H, C*H*2). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 191.9 (N*C*N), 166.8 (CAr-Au), 141.6 (CHAr), 127.3 (CHAr), 124.6 (CHAr), 115.0 (N*C*H=*C*HN), 58.8 (NCAlk), 44.5 (NC*C*H2), 36.23 (CH2), 30.2(CHAlk). **Elemental analysis** calcd (%) for C29H37AuN2: C 57.05, H 6.11, N 4.59; found: C 57.18, H 6.23, N 4.45.

**Synthesis of [***N*,*N***-Bis(*tert*-butyl)imidazol-2-ylidene](4-methoxyphenyl)gold(I)** **[Au(ItBu)C7H7O] (6):**

**Procedure A**: Synthesized following the general procedure with [Au(ItBu)Cl] (100 mg, 0.242 mmol), 4-methoxyphenylboronic acid (32.5 mg, 0.266 mmol,1.1 equiv.), K2CO3 (50.2 mg, 0.363 mmol, 3 equiv.) and ethanol (0.7 mL). Purification of the product was carried out by filtration through basic alumina with dichloromethane (6 mL). That solution was filtered again though celite and the filter cake was washed with dichloromethane (4 mL) The filtrate was concentrated and pentane (4 mL) was added, leading to precipitation of a white solid. Filtration, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white, microcrystalline solid in 77% yield (90 mg, 0.186 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.51 (d, *J* = 8.4 Hz, 2H, HAr), 7.04 (s, 2H, NC*H*), 6.86 (d, *J* = 8.4 Hz, 2H, HAr), 3.78 (s, 3H, OC*H*3), 1.94 (s, 18H, NC(C*H*3)3). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 193.3 (N*C*N), 157.7 (CAr-Au), 157.3 (CAr-OMe), 141.5 (CHAr), 116.0 (N*C*H=*C*HN), 113.3 (CHAr), 58.6 (NCAlk), 55.2 (O*C*H3), 32.0 (C*C*H3). **Elemental analysis** calcd (%) for C18H27AuN2O: C 44.63, H 5.62, N 5.78; found: C 44.82, H 5.70, N 5.65.

**Synthesis of [Triphenylphosphine](phenyl)gold(I)** **[Au(PPh3)C6H5] (7):**

**Procedure A**: Synthesized following the general procedure with [Au(PPh3)Cl] (50.0 mg, 0.101 mmol), phenylboronic acid (13.6 mg, 0.111 mmol,1.1 equiv.), K2CO3 (42.0 mg, 0.304 mmol, 3 equiv.) and ethanol (0.5 mL). Purification of the product was carried out by filtration through basic alumina with dichloromethane (4 mL). Evaporation of the solvent, washing with pentane (3x3 mL) and drying under high vacuum afforded the product as a white, microcrystalline solid in 82% yield (44.0 mg, 0.082 mmol). **1H NMR (400 MHz, C6D6):** δ (ppm) = 8.13 (m, 2H), 7.52 (td, *J* = 7.7, 1.6 Hz, 2H), 7.46 – 7.38 (m, 6H), 7.27 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.00 – 6.89 (m, 9H). **13C {1H} NMR (101 MHz, C6D6):** δ (ppm) = 173.7 (d, *JCP* = 117.7 Hz), 140.4 (s), 134.6 (d, *JCP* = 13.7 Hz), 131.7 (d, *J* = 48.2 Hz), 131.0 (d, *J* = 2.2 Hz), 129.2 (d, *J* = 10.6 Hz), 126.3 (s). **31P NMR (162 MHz, C6D6):** δ (ppm) = 56.85. **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.65 – 7.54 (m, 8H), 7.52 – 7.42 (m, 9H), 7.31 – 7.26 (m, 2H), 7.11 – 7.06 (m, 1H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 172.1 (d, *J* = 116.9 Hz), 139.7 (s), 134.5 (d, *J* = 13.7 Hz), 131.3 (d, *J* = 2.2 Hz), 131.3 (d, *J* = 2.2 Hz), 129.2 (d, *J* = 10.7 Hz), 127.7 (d, *J* = 6.0 Hz), 126.0 (s). **31P NMR (162 MHz, CDCl3):** δ (ppm) = 43.53.Analytical data obtained are in agreement with reported values.[9a]

**Reactivity of 2b**

**Synthesis of** **[Au(IPr)(MeCN)][****BF4] (8):**

A 4-mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (50 mg, 0.072 mmol, 1 equiv.) and acetonitrile (0.5 mL). To the resulting solution was added HBF4•Et2O (13 mg, 0.079 mmol, 1.1 equiv.) *via* a micropipette. After stirring at room temperature for 5 minutes, the solvent was removed under vacuum and diethyl ether was added to the residue. The resulting mixture was filtered, and the solid product was washed with diethyl ether and dried under vacuum. The product was obtained as a white, microcrystalline solid in 94% yield (48.4 mg, 0.068 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.57 (t, *J* = 7.8 Hz, 2H), 7.40 (s, 2H), 7.34 (d, *J* = 7.8 Hz, 4H), 2.44 (hept, *J* = 6.9 Hz, 4H), 2.39 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 166.4, 145.6, 133.1, 131.6, 125.0, 124.7, 121.2, 29.0, 24.8, 24.1, 2.8. **19F NMR (471 MHz, CDCl3):** δ (ppm) = -153.59, -153.64.Analytical data obtained are in agreement with reported values.[22]

**Synthesis of** **[Au(IPr)(OTs)] (9):**

A 4 mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (20 mg, 0.029 mmol, 1 equiv.), *p*-toluenesulfonic acid monohydrate (8.2 mg, 0.043 mmol, 1.5 equiv.) and benzene (0.6 mL). This solution was stirred overnight at 50 °C. Afterwards, dichloromethane was added and the mixture was pushed through a microfilter, in order for a clear solution to be obtained. The solvent was evaporated, and the white residue was washed with diethyl ether (2x3 mL) and pentane. The product was obtained as a white solid in 64% yield (14 mg, 0.019 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.55 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.21 (s, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 2.55 – 2.42 (hept, *J* = 6.8 Hz, 4H), 2.32 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (75 MHz, CDCl3):** δ (ppm) = 164.6, 145.7, 133.8, 131.0, 128.8, 126.4, 124.5, 123.6, 29.0, 24.4, 24.3, 21.5.Analytical data obtained are in agreement with reported values.[29]

**Synthesis of** **[Au(IPr)(OMs)] (10):**

A 4 mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (100 mg, 0.144 mmol, 1 equiv.), chloroform (3.0 mL) and methanesulfonic acid (10.0 µL, 0.159 mmol, 1.1 equiv.). This solution was stirred overnight at room temperature. Afterwards, dichloromethane was added and the mixture was filtered through a microfilter, in order for a clear solution to be obtained. The solvent was evaporated, and the white residue was washed with diethyl ether (2x5 mL) and dried under vacuum. The product was obtained as a white solid in 88% yield (84 mg, 0.123 mmol). **1H NMR (400 MHz, CD2Cl2):** δ (ppm) = 7.57 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 4H), 7.29 (s, 2H), 2.52 (hept, *J* = 6.9 Hz, 4H), 2.36 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (75 MHz, CD2Cl2):** δ (ppm) = 164.5, 146.4, 134.3, 131.4, 124.9, 124.4, 39.6, 29.4, 24.7, 24.4.Analytical data obtained are in agreement with reported values.[30]

**Synthesis of [Au(IPr)(OCs)] (11):**

A 4 mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (100 mg, 0.144 mmol, 1 equiv.), (+)-camphorsulfonic acid (37 mg, 0.159 mmol, 1.1 equiv.) and chloroform (3 mL). This solution was stirred overnight at room temperature. Afterwards, dichloromethane was added and the mixture was pushed through a microfilter, in order for a clear solution to be obtained. The solvent was evaporated, and the white residue was washed with diethyl ether (2x5 mL) and dried under vacuum. The product was obtained as a white solid in 82% yield (97 mg, 0.019 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.51 (t, *J* = 7.8 Hz, 2H, HAr(IPr)), 7.31 – 7.28 (m, 4H, HAr(IPr)), 7.22 (s, 2H, HImid), 3.21 (d, *J* = 15.1 Hz, 1H, C*H*H(OCs)), 2.60 (d, *J* = 15.1 Hz, 1H, CH*H*(OCs)), 2.56 – 2.38 (m, 5H, overlapping peaks C*H*(CH3)2(IPr), C*H*(OCs)), 2.28 – 2.25 (m, 1H, C*H*H(OCs)), 2.23 – 2.20 (m, 1H, C*H*H(OCs)) 1.91 (t, *J* = 4.3 Hz, 1H, CH*H*(OCs)), 1.85 – 1.71 (m, 3H, overlapping peaks CHH(OCs)), 1.34 (dd, *J* = 6.9, 1.2 Hz, 12H, CH(C*H3*)2(IPr)), 1.21 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPr)), 0.95 (s, 3H, C*H*3(OCs)), 0.70 (s, 3H, C*H*3(OCs)). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 215.8 (*C*=O), 164.6 (N*C*N), 145.7 (CAr(IPr)), 133.8 (CAr(IPr)), 131.0 (*C*HAr(IPr)), 124.5 (*C*HAr(IPr)), 123.6 (N*C*H), 58.4 (C(OCs)), 47.5 (C(OCs)), 47.4 (*C*HH(OCs)), 43.0 (*C*HH(OCs)), 42.7 (*C*HH(OCs)), 29.0 (*C*H(CH3)2(IPr)), 27.1 (*C*HH(OCs)), 24.7 (*C*H(OCs)), 24.5 (CH(*C*H3)2(IPr)), 24.2 (CH(*C*H3)2(IPr)), 20.5 (*C*H3(OCs)), 19.9 (*C*H3(OCs)). **Elemental analysis** calcd (%) for C37H51AuN2O4S: C 54.40, H 6.29, N 3.43; found: C 54.29, H 6.43, N 3.62. **[*α*]D20** = +14.7 (*c* = 1.0 in chloroform).

**Synthesis of** **[Au(IPr)(OMess)] (12):**

A 4 mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (53.3 mg, 0.077 mmol, 1 equiv.), mesitylene sulfonic acid dihydrate (20 mg, 0.085 mmol, 1.1 equiv.) and benzene (1.6 mL). This solution was stirred overnight at 50 °C. After evaporation of the solvent under vacuum, dichloromethane was added (3 mL) and the mixture was pushed through celite, in order for a clear solution to be obtained. The solvent was evaporated, and the white residue was washed with diethyl ether (2x3 mL) and pentane. The product was obtained as a white solid in 62% yield (37.2 mg, 0.047 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.52 (t, *J* = 7.8 Hz, 2H, HAr(IPr)), 7.27 (d, *J* = 7.8 Hz, 4H, HAr(IPr)), 7.18 (s, 2H, HImid), 6.67 (s, 2H, HAr(OMess)), 2.51 – 2.40 (hept, *J* = 6.9 Hz, 4H, C*H*(CH3)2(IPr)), 2.33 (s, 6H, C*H3*(OMess)), 2.20 (s, 3H, C*H3*(OMess))), 1.26 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPr)), 1.19 (d, *J* = 6.9 Hz, 12H, CH(C*H3*)2(IPr)). **13C {1H} NMR (75 MHz, CDCl3):** δ (ppm) = 164.9 (N*C*N), 145.6 (CAr(IPr)), 133.8 (CAr(IPr)), 131.1 (*C*HAr(IPr)), 131.0 (*C*HAr(OMess)), 124.4 (*C*HAr(IPr)), 123.5 (N*C*H), 29.0 (*C*H(CH3)2(IPr)), 24.4 (CH(*C*H3)2(IPr)), 24.2 (CH(*C*H3)2(IPr)), 23.0 (*C*H3(OMess)), 21.0 (*C*H3(OMess)). Certain signals attributed to the anion could not be detected. This is consistent with the literature.[10] **Elemental analysis** calcd (%) for C36H47AuN2O3S: C 55.09, H 6.04, N 3.57; found: C 55.42, H 6.09, N 3.38.

**Synthesis of** **[Au(IPr)CCPh] (13):**

A 4 mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (20.0 mg, 0.029 mmol, 1 equiv.), benzene (0.6 mL) and phenylacetylene (3.6 μL, 0.032 mmol, 1.1 equiv.). This solution was stirred for 16 hours at 80 °C. The solvent was evaporated under vacuum and the white residue was washed with diethyl ether (2x2 mL) and dried The product was obtained as a white solid in 92% yield (18 mg, 0.027 mmol). **1H NMR (400 MHz, CDCl3):** δ (ppm) = 7.49 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 6H), 7.12 (s, 2H), 7.11 – 7.01 (m, 3H), 2.70 – 2.51 (hept, *J* = 6.9 Hz, 4H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CDCl3):** δ (ppm) = 191.2, 145.8, 134.5, 132.4, 130.6, 129.3, 127.6, 126.1, 125.9, 124.3, 123.3, 103.9, 28.9, 24.8, 24.2.Analytical data obtained are in agreement with reported values.[14a,16c]

**Synthesis of** **[Au(IPr)Cbz] (14):**

A 4 mL screwcap vial equipped with a septum cap and a stirring bar was charged with **2b** (80.0 mg, 0.092 mmol, 1 equiv.), carbazole (19.2 mg, 0.092 mmol, 1.0 equiv.) and benzene (0.6 mL). This solution was stirred for 16 hours at 80 °C. The solvent was evaporated under vacuum and the white residue was washed with diethyl ether (3x3 mL) and dried The product was obtained as a white solid in 91% yield (62.9 mg, 0.084 mmol). **1H NMR (400 MHz, CD2Cl2):** δ (ppm) = 7.88 (ddd, *J* = 7.7, 1.2, 0.7 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 4H), 7.35 (s, 1H), 7.03 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 2H), 6.86 (ddd, *J* = 7.9, 7.1, 1.0 Hz, 2H), 6.73 (dt, *J* = 8.2, 0.8 Hz, 2H), 2.72 (hept, *J* = 6.9 Hz, 4H), 1.38 (d, *J* = 6.9 Hz, 12H), 1.29 (d, *J* = 6.9 Hz, 12H). **13C {1H} NMR (101 MHz, CD2Cl2):** δ (ppm) = 179.2, 149.9, 146.7, 134.9, 131.2, 124.8, 124.0, 123.9, 123.9, 119.6, 116.2, 114.0, 29.5, 24.7, 24.5. Analytical data obtained are in agreement with reported values.[24]

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**Keywords:** Synthetic methodology • Sustainability • Gold synthon • Catalysts • N-Heterocyclic carbenes

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**Entry for the Table of Contents**



**Gilded arylation**: New methods for the transmetallation of organoboranes to gold(I) centers allow for the synthesis of a plethora of organogold complexes. The scalability of the synthetic methods, in combination with a diversity of reactivity, sets the stage for the use of these complexes in catalytic and synthetic applications.