Synthesis of Au^I and Au^{III}-bis(NHC) Complexes: The Ligand Influence on the Oxidative Addition to Au(I) Species

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Abstract: The oxidation chemistry of a range of Au(I)-bis(NHC) (NHC = *N*-heterocyclic carbene) complexes with hypervalent iodine(III) oxidants has been explored. Au(I)-bis(NHC) precursors have been synthesized from the reaction of the corresponding [Au(NHC)Cl] derivatives with an imidazoli(di)onium salt in the presence of K₂CO₃. The reactivity of the Au(I) complexes towards PhICl₂ has revealed an influence of the nature of the NHC ligands present in the complex in the oxidation reaction: small and more electron donating NHC ligands favoured the formation of a Au(III) species. Based on these results, a Au(I) complex bearing two 1-butyl-3-methyl-imidazol-2-ylidene (BMIM) ligands has been synthesized. This complex reacted with PhICl₂ and, for the first time in Au-NHC systems, with PhI(OAc)₂ and PhI(OAc)^F, affording stable Au(III)-(NHC)₂ bearing acetate ligands.

Introduction

Homogeneous gold catalysis has witnessed an exponential growth in the last decade.^[1] In this field, the chemistry of gold in oxidation state III has been much developed compared to that of gold in oxidation state I.^[2] The main reason for this is the lack of suitable precursors to explore this chemistry when compared to the number of gold(I) species available in the literature.^[2] Due to the intrinsic high redox potential of gold, gold(III) species have a high tendency to reduce to gold (I) and gold (0) and therefore, tend to decompose or become inactive in catalysis.^[3] In addition, the organo-gold(III) species that have proven to be stable, are typically too stable to be used in catalysis. In this context, much effort is being devoted to the isolation of new stable and

catalytically active gold(III) complexes.^[3a, 4] In addition, a great interest has arisen around the development of gold redox catalysis, and the understanding of the elementary steps involved in the catalytic cycles.^[5] Hypervalent iodine species appear to be a privilege class of oxidants that has allowed for the development of fascinating catalytic reactions.^[5g-i, 6] Oxidative addition from Au(I) to Au(III) is a fundamental step in the redox catalytic cycle and, therefore, the study of reactions of gold(I) complexes with hypervalent iodine oxidants to afford the corresponding gold(III) derivatives and the understanding of the factors that influence this step are of critical importance for the development of new redox catalytic systems.

N-Heterocyclic carbene (NHC) ligands have been extensively used to stabilize organometallic species due to their strong donating properties and tunable steric hindrance.^[7] In the particular case of gold complexes, the use of NHC ligands has allowed for the isolation of unstable species and development of highly active catalysts.^[8] In the context of Au(III) derivatives, a number of Au(III)-NHC derivatives have been reported to date,^[9] e.g. [Au(NHC)Cl₃]^[9a] or [Au(NHC)Br₃]^[9b], which can be obtained by oxidation of the corresponding [Au(I)(NHC)X] (X = Cl, or Br) species. Although these gold(III) compounds can be isolated and fully characterized, they have shown to be typically rather unstable, undergoing relatively facile reductive elimination to afford the Au(I) precursors.

In the search for more stable species, cationic gold(I)-bis(NHC) derivatives attracted our attention, since the presence of a second NHC ligand in the molecule is expected to provide additional stabilization. Stable Au(III) complexes containing bis(diNHC),^[10] benzimidazole^[9g, 11] or less common NHC ligands^[9f, 12] have been successfully synthesised. However, these studies have not been conducted on the most common NHC ligands and Cl₂, Br₂ and I₂ have been the most commonly used oxidants. Due to the relevance of NHC ligands in gold chemistry and the increasing interest of hypervalent iodine oxidants in gold redox catalysis we have now synthesized a series of Au(I)-bis(NHC) complexes bearing the most common NHC ligands, and study their oxidation reactions with PhICl₂, PhIOAc₂ and PhIOAc^F, to afford the corresponding [Au^{III}(NHC)₂X₂] X = Cl, OAc, OAc^F complexes.

Results and Discussion

Synthesis of Au(I)-bis(NHC) derivatives.

Several methodologies have been reported for the preparation of homoleptic Au-bis(NHC) derivatives, usually by transmetallation from the corresponding Ag complex or by using

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free carbenes.^[13] The synthesis of heteroleptic Au(I)-bis(NHC) derivatives can be successfully performed by reacting [Au(NHC)(OH)] complexes with the desired imidazoli(di)onium salt.^[14] In this case, the hydroxide ligand acted as an internal base, deprotonating the salt and affording the Au-bis(NHC) species. Recently, a microwave-assisted protocol for the synthesis of gold-, silver-, and copper- homo- and heteroleptic bis(NHC) complexes has been developed by Cazin and co-workers.^[15] This protocol employed [M(NHC)Cl] (M = Au, Ag, Cu) complexes as precursors and NaOH as external base.

We have recently reported a mild protocol for the preparation of [Au(NHC)Cl] complexes from [Au(DMS)Cl], the corresponding imidazoli(di)onium salt and a weak base (K_2CO_3) in acetone.^[16] This protocol has proven useful in the synthesis of Au(NHC)-acetyl complexes by simply adding extra equivalents of base.^[17] In view of these results, we envisaged that this mild protocol could be also used to promote the formation of a cationic bis-NHC species, by simple addition of another equivalent of imidazolium salt.^[18]

Indeed, when [Au(IPr)Cl]^[19] was reacted with 1 equiv. of IPr·HBF₄ in the presence of 2 equiv. of K_2CO_3 in acetone, at 60 °C, [Au(IPr)₂]BF₄ (**1a**) was obtained (Scheme 1). Following this protocol, **1a** was synthesised on a 2.26 g scale in excellent yield (91%). The synthesis of heteroleptic complexes was then explored. Since IPr is one of the most common ligands in gold chemistry, [Au(IPr)Cl] was selected as precursor, and was reacted with different imidazoli(di)onium salts under the conditions shown in Scheme 1. This methodology allowed for the synthesis of eight Au-bis(NHC) species, containing different ligands and counterions, in moderate to excellent yields (Scheme 2). The NMR data of complexes **1a-1f''** matched the literature values.^[14]

Scheme 1. Alternative synthesis of [Au(NHC)(NHC)]⁺ complexes.

It is worth mentioning that the formation of [Au(IPr)(SIMes)]^[19] (**1c**) from [Au(IPr)Cl] and [SIMes·HBF₄] was found to be much slower than the rest of the complexes and full conversion was not reached even after six days of reaction. We have previously observed a slower reaction for the synthesis of [Au(NHC)Cl] complexes containing saturated NHC ligands, when compared to their unsaturated analogues.^[16] For example, the synthesis of [Au(IMes)Cl]^[19] required 3 h, while the preparation of [Au(SIMes)Cl] required 24 h. In view of these results, and considering that the incorporation of the second NHC is slower than the first one, we modified the procedure and used [Au(SIMes)Cl] as precursor, and reacting it with IPr·HCl, in the presence of K_2CO_3 . Gratifyingly, the reaction reached full

conversion after 72 h and the product was isolated in an excellent yield of 98%.

Scheme 2. [Au(IPr)(NHC)]⁺ synthesized complexes.^[19]

Synthesis of Au(III)-bis(NHC) derivatives.

Once we had this family of complexes in hand, we sought to explore their oxidation chemistry with PhICl₂. This hypervalent iodine reagent has been previously used in the oxidation of gold (I) complexes^[11c, 20] and appears as a safer alternative to chlorine gas. Therefore, complexes **1a-1f''** were reacted with 1.3 – 2.2 equiv. of PhICl₂ in dichloromethane, to afford the corresponding [Au(IPr)(NHC)Cl₂][X] (X = BF₄, PF₆, Cl) complexes, **2a-2f''** (Scheme 3).

Scheme 3. Oxidation of **1a-1f''** with PhICl₂.

Complexes **2a-2f''** were isolated as white solids in good to excellent yields (70 – 95%). The equivalents of oxidant required and the reaction time were found to be dependent on the nature of the ligands present in the complex. The results, including the percent buried volume (%V_{bur})^[21] of the NHC ligands in complexes **1a-1f''**, are summarized in Table 1.

Figure 1. Thermal ellipsoid representation of complexes **2b-2f''** at 50% probability. [BF₄] counterions for complexes **2b-2e** and all hydrogen atoms and are omitted for clarity. Selected distances and %V_{bur} are summarized in Table 3.

Table 1. Oxidation of complexes $[\text{Au}(\text{IPr})(\text{NHC})]^+$ (**1a-1f'**) with PhICl_2 .

entry	NHC (1x)	%V _{bu^c} IPr in 1x	%V _{bu^c} NHC'in 1x	PhICl ₂ (equiv.)	time	yield (%)
1	IPr (1a)	44.0	38.2	2.2	7 d	70
2	IMes (1b)	45.4	35.1	1.3	24 h	92
3	SIMes (1c)	45.6	35.9	1.3	24 h	95
4	I'Bu (1d)	38.4- 39.7	37.9- 37.8	1.3	3.5 h	85
5	ICy (1e)	44.0	27.2	1.3	3.5 h	87
6	BMIM (1f)	42.4	27.6	1.3	3.5 h	93
7	BMIM (1f') ^a	41.7	28.1	1.3	7 h	81
8	BMIM (1f'') ^b	41.6	29.2	1.3	3.5 h	88

[a] Counterion = PF₆⁻. [b] Counterion = Cl⁻. [c] For comparison purposes, structures of complexes **1a-1f**⁺ have been retrieved from the CCDC database and %V_{Bur} recalculated.^[22] SambVca parameters: Bondi radii scaled by 1.17, sphere radius = 3.5 Å, distance to the metal center = Au-C distance obtained in the crystal structure, mesh spacing = 0.1 Å.

Most of the reactions reached completion within 24 h, in the presence of a slight excess of PhICl_2 . Remarkably, the oxidation of the homoleptic derivative $[\text{Au}(\text{IPr})_2][\text{BF}_4]$ was particularly slow, and full conversion was only reached when 2.2 equiv of the oxidant were reacted with **1a** at room temperature for 7 days (Table 1, entry 1). Presumably, this slower reaction is due to steric hindrance of the two IPr fragments. Oxidation of **1b** and **1c** containing the sterically demanding, *N*-aryl-substituted NHC

ligands IMes and SIMes required 24 h (Table 1, entries 2-3). The use of smaller and more electron donating *N*-alkyl substituted NHC ligands (**1d-1f'**) benefited the reaction, obtaining full conversion in 3.5-7 h (Table 1, entries 4-8). Good to excellent yields were obtained in all the cases. All the complexes were shown to be light stable and stable towards reduction both solution and in the solid state.

Table 2. Carbenic carbon signals observed for Au(I) (**1a-1f'**) and the corresponding Au(III) (**2a-2f'**) complexes in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra^a.

entry		[Au ^I (IPr)(NHC)] ⁺ (1x)		[Au ^{III} (IPr)(NHC)Cl ₂] ⁺ (2x)	
		C _{IPr} (ppm)	C _{NHC} (ppm)	C _{IPr} (ppm)	C _{NHC} (ppm)
1	IPr (a)	184.2	184.2	154.3 ^d	154.3 ^d
2	IMes (b)	186.1	183.1	154.7	152.8
3	SIMes (c)	186.7	205.2	156.0	179.0
4	I ^t Bu (d)	185.5	179.6	156.5	145.9
5	ICy (e)	187.0	178.5	158.8	147.3
6	BMIM (f)	188.0	181.1	159.1	149.6
7	BMIM (f') ^b	188.0	181.3	158.7	150.1
8	BMIM(f'') ^c	188.0	180.6	160.3	148.5

[a] NMR spectra recorded in CDCl_3 unless otherwise stated. [b] Counterion = PF_6^- . [b] Counterion = Cl^- ; [d] NMR spectrum recorded in CD_3OD due to poor solubility of **2a** in CDCl_3

All new complexes were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopies and elemental analyses. The most conspicuous feature of complexes **2a-2f'** is the presence of two

singlets in the low field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, at 150–159 ppm for the unsaturated carbenes and 179 ppm for SIMes. These signals correspond to the carbenic carbon atoms and are shifted ca. 30 ppm towards high field with respect to the gold(I) counterparts (184–188 ppm for the unsaturated ligands and 205 for SIMes), in agreement with a change in the oxidation state of the metal centre.

Complexes **2b–2f'** were unambiguously characterized by X-ray diffraction analyses.^[23] All the complexes presented the expected square planar geometry typical of Au(III) complexes. The NHC ligands occupy mutually trans positions in all the complexes (Figure 1). Au–C_{carbene} distances and calculated percentage buried volume for **2b–2f'** are shown in Table 3.

Table 3. Selected distances and %V_{bur} of the NHC ligands in **2b–2f'**.

entry	NHC (2x)	Au–C _{IPr} (Å)	Au–C _{NHC'} (Å)	%V _{bur} IPr in 2x	%V _{bur} NHC' in 2x
1	IMes (2b)	2.048(3)	2.036(5)	33.5	34.1
2	SIMes (2c)	2.056(7)	2.059(7)	33.2	34.4
3	I'Bu (2d)	2.023(8)	2.066(9)	33.3	36.4
4	ICy (2e)	2.048(17)	1.997(19)	35.4	27.3
5	BMIM (2f)	2.030(10)	2.033(9)	34.9	26.6
6	BMIM (2f') ^a	2.015(19)	2.001(12)	35.6	27.2
7	BMIM (2f'') ^b	2.052(12)	2.053(13)	34.9	26.2

[a] Counterion = PF₆[−]. [b] Counterion = Cl[−]

Synthesis of Au-bis(BMIM) complexes.

In view of the observed effect of steric and electronic properties of the NHC ligands in the oxidation reactions, we sought to synthesize a Au(I)-bis(NHC) derivative bearing two small, *N*-alkyl substituted NHC ligands, to further explore the possibilities in oxidation chemistry. Amongst the *N*-alkyl substituted NHC derivatives tested, BMIM was the ligand of choice, due to its small size and flexibility.

Following the protocol described above, the synthesis of [Au(BMIM)₂][BF₄] in two steps (synthesis of [Au(BMIM)Cl], and subsequent reaction with BMIM·HBF₄) was attempted. Unfortunately, the reaction of [Au(DMS)Cl] with BMIM·HCl and K₂CO₃ reaction afforded a mixture of complexes and [Au(BMIM)Cl] could not be isolated. To overcome this issue, a one-pot reaction was attempted. Gratifyingly, treatment of 1 equiv. of BMIM·HCl and 1 equiv. of BMIM·HBF₄ with [Au(DMS)Cl] in the presence of 2 equiv. of K₂CO₃ afforded the desired complex **3** in high yield and purity (Scheme 4). The reaction was successfully used to prepare 1.8 g of **3** in 95 % yield. Analogous complexes with PF₆ and Cl counterions had been previously reported via multistep syntheses.^[24]

Scheme 4. One-pot synthesis of [Au(BMIM)₂][BF₄] (**3**)

Complex **3** was isolated as a white solid and characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopies and elemental analysis. The ^1H NMR spectrum showed one set of signals for both NHC ligands, in agreement with a symmetrical structure. The low field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** showed one singlet at 183.7 ppm corresponding to the carbenic carbon atoms. This chemical shift is consistent with the values found for the Au(I)-bis(carbene) complexes **1a–1f'** (Table 2).

The structure of **3** was unambiguously characterized by X-Ray diffraction analysis. Suitable crystals were obtained by slow diffusion of pentane into a saturated solution of **3** in dichloromethane at $-20\text{ }^\circ\text{C}$. The linear geometry around the metal centre is the expected coordination for Au(I) complexes (Figure 2). The structure displayed a syn geometry, with the two *n*-butyl groups pointing to the same side, as previously observed for the derivative containing a PF₆ counterion.^[24a] The %V_{bur} of the two BMIM ligands was calculated using the SambVca software^[22] and the obtained values were 27.8 and 27.4 %. As expected, these values are significantly smaller than those obtained for complexes **1a–1f'**, containing the IPr ligand (Table 1).

Figure 2. Thermal ellipsoid representation of **3** at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles ($^\circ$): Au–C1 = 2.010 (8), Au–C11 = 2.008(11), C1–Au–C11 = 178.28° .

The oxidation chemistry of **3** with hypervalent iodine reagents was next explored. Complex **3** reacted smoothly with a slight excess of PhICl₂, affording the corresponding Au(III) derivative, **4**, in 2.5 h at room temperature (Scheme 5). Remarkably, this reaction was found to be faster than the synthesis of any of the complexes **2a–2f'**, bearing a bulky IPr ligand.

Scheme 5. Synthesis of $[\text{Au}(\text{BMIM})\text{Cl}_2][\text{BF}_4]$ (**4**)

Complex **4** was isolated as a white solid in 90 % yield and characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopies, elemental analysis, and X-Ray diffraction analysis. Two set of signals were observed for the BMIM ligands in the ^1H NMR spectrum, presumably due to restricted rotation around the Au-C bond. The carbenic carbon atoms resonate at 153.6 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, in agreement with the values observed for the Au(III) complexes **2a-2f'** (Table 2).

Complex **4** was further characterized by X-ray diffraction analysis (Figure 3). The square planar structure of **4** is analogous to those of complexes **2b-2f'**.

Figure 3. Thermal ellipsoid representation of **4** at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Au1-C1 = 2.032(7), Au1-C11 = 2.023(6), C1-Au1-C11 = 177.37, Cl1-Au1-Cl2 = 178.82

Encouraged by the ease with which **3** underwent oxidative addition with PhI(Cl)_2 , the oxidation of **3** with $\text{PhI}(\text{OAc})_2$ and $\text{PhI}(\text{OAc}^{\text{F}})_2$ (OAc^{F} = trifluoroacetate) was attempted. It should be noted that Au-bis(NHC) derivatives bearing one IPr ligand did not react with these oxidants.

Scheme 6. Synthesis of the Au(III)-bis acetate derivatives **5** and **6**.

In dichloromethane at room temperature, complex **3** slowly reacted with $\text{PhI}(\text{OAc})_2$, affording a new stable species which was characterized as $[\text{Au}(\text{BMIM})_2(\text{OAc})_2][\text{BF}_4]$ (**5**). Under these conditions full conversion to **5** was not obtained. However, replacing dichloromethane by dichloroethane and increasing the temperature to 60 °C resulted in full conversion of **4** to **5** after 14 h. Complex **5** was isolated as a white microcrystalline solid in excellent yield (93%) (Scheme 6). Under these optimized conditions, **4** was reacted with $\text{PhI}(\text{OAc}^{\text{F}})_2$, affording $[\text{Au}(\text{BMIM})_2(\text{OAc}^{\text{F}})_2][\text{BF}_4]$ (**6**), which was isolated as a white-yellow solid in excellent yield (96%) (Scheme 6). To the best of our knowledge, **4** and **5** are the first examples of Au(III)-NHC complexes bearing acetate ligands.

As observed for **3**, and in contrast to **4**, complexes **5** and **6** showed a single set of signals for the BMIM ligands in the ^1H NMR spectra. The low field region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** and **6** contained two signals corresponding to the C=O group of the acetate ligands and the carbenic carbon atoms. These signals appeared as a singlet at 174.9 ppm (C=O) and a singlet at 152.9 ppm (carbene) for **5**, and a quartet at 160.4 ppm (C=O, C-F coupling with CF_3) and a singlet at 149.0 ppm (carbene) for **6**. Solid state IR of complexes **5** and **6** showed bands corresponding to C-O stretching. These have been assigned as follows: 1666.4 ($\nu_{\text{asym}} \text{ CO}$) and 1251 cm^{-1} ($\nu_{\text{sym}} \text{ CO}$) for **5**; and 1730.1 ($\nu_{\text{asym}} \text{ CO}$) and 1145.7 cm^{-1} ($\nu_{\text{sym}} \text{ CO}$) for **6**. The large separations between the asymmetric and symmetric stretching bands ($\Delta(\nu_{\text{asym}}-\nu_{\text{sym}}) = 415 \text{ cm}^{-1}$ for **5** and $\Delta(\nu_{\text{asym}}-\nu_{\text{sym}}) = 584 \text{ cm}^{-1}$) are consistent with monodentate coordination of the acetate ligands.^[25]

Complex **5** was further characterized by X-ray diffraction analysis. Suitable single crystals for analysis were obtained by slow diffusion of pentane into a saturated acetone solution of **5** at -20 °C. **5** presented the expected square planar geometry with the NHC ligands occupying mutually trans positions and the acetate ligands coordinated in a monodentate fashion. In contrast to the structure found for **3** and **4**, complex **5** presented an anti geometry with regard to the orientation of the two BMIM ligands. (Figure 4)

Figure 4. Thermal ellipsoid representation of **5** at 50% probability. Hydrogen atoms and $[\text{BF}_4]$ counterion are omitted for clarity. Selected distances (Å) and angles ($^\circ$): Au1-C1 = 2.020(7), Au1-O11 = 2.001(3), Au1-O13 = 2.895, C1-Au1-C1 = 180.

The reactivity of **4**, **5**, and **6** was studied. Unfortunately all attempted reactions to exchange the chloride or acetate ligands led to complex mixtures of products, decomposition or reduction to the corresponding gold (I) complexes. This reactivity was attributed to the presence of two possible reactive positions, e.g. two chloride or two acetate ligands. For example, when the substitution of a single Cl ligand of **4** by an acetate ligand was attempted by reaction of **4** with 1 equivalent of AgOAc , a mixture of three products was obtained. This mixture contained unreacted starting material **4**; complex **5**, where the two chloride ligands had been replaced by acetates; and a new complex, tentatively assigned to the desired product $[\text{Au}(\text{BMIM})_2(\text{OAc})(\text{Cl})]$ complex (Scheme 7).

Scheme 7. Reactivity of **4** with AgOAc

In view of these results, we sought to synthesize a new Au(I)-bis(NHC) complex with a different geometry. In this context, bis-NHC pincer ligands attracted our attention. Bis-NHC ligands can coordinate to metal centers in a bridge or chelate mode (Figure 5). The chelate coordination mode appears to be favoured with bulky R groups and short linkers or small R groups and longer linkers. In addition, the presence of halides in the media promotes bridging coordination of the ligand.^[26] Although the coordination of pincer bis-NHC ligands to gold typically affords bridging species^[10c, 26-27] some examples of Au with chelating bis-NHC pincer ligands have been reported.^[10c, 26, 28]

Figure 5. Coordination modes of pincer-NHC ligands.

With this in mind, bis-imidazolium salt **g**· $(\text{HBF}_4)_2$, containing a rigid phenyl linker and flexible R groups was synthesized following a reported procedure (Scheme 8).^[29]

Scheme 8. Synthesis of the pincer salt **g**· $(\text{HBF}_4)_2$.

A single product was obtained from the reaction of salt **g**· $(\text{HBF}_4)_2$ with $[\text{Au}(\text{DMS})\text{Cl}]$ and K_2CO_3 in acetone (Scheme 9). The ^1H NMR spectrum of this species showed a single set of signals for ligand **g**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contained a signal corresponding to the carbenic carbon atoms at 183.7 ppm, in agreement with the formation of a Au(I)-bis(NHC) complex. However, as confirmed by X-ray diffraction analysis, **7** was not the targeted chelated-bis NHC complex. Instead, a digold complex containing two pincer ligand units acting as bridging ligands was obtained (Scheme 9 and Figure 6).

Scheme 9. Synthesis of **7**

The formation of complex **7** is in agreement with complexes bearing the *N*-methyl analogous ligand to **g**, recently reported species by Tubaro and co-workers^[10e, 27b], and with the bis-Ag complex bearing ligand **g** reported by de Frémont and co-workers.^[30]

Figure 6. Thermal ellipsoid representation of **7** at 50% probability. Hydrogen atoms and $[\text{BF}_4]$ counterions are omitted for clarity. Selected distances (Å) and angles ($^\circ$): Au1-C16 = 2.034(13), Au1-C16 = 2.060(12), C1-Au-C16 = 176.72.

Although the desired chelating coordination was not obtained, the reactivity of complex **7** towards PhICl_2 and $\text{PhI}(\text{OAc})_2$ was explored. While reaction with the latter did not afford any Au(III) species and unreacted starting material was recovered, reaction with the former under the conditions described in Scheme 10 afforded a new species. This new complex was characterized as the digold Au(III)-Au(III) complex **8** shown in Scheme 10.

Scheme 10. Oxidation of **7** with PhICl_2

Complex **8** was characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopies, and elemental analysis. As for **7**, a single set of signals was observed for each ligand in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. A single signal was observed for the carbenic carbon atoms at 153.0 ppm, in agreement with the presence of gold(III) centers. Unfortunately, all the attempts to obtain suitable crystals of **8** were unsuccessful, presumably due to the low solubility of this complex in common organic solvents.

Conclusions

In conclusion, we have presented an alternative protocol for the synthesis of a range of homo- and heteroleptic Au(I)-bis(NHC) complexes bearing NHC ligands with different electronic and steric properties. Their reactivity towards hypervalent iodine (III) oxidants to afford the corresponding Au(III) species, which is a key elemental step in gold redox catalysis, has been studied. Complexes of the formula $[\text{Au}^{\text{I}}(\text{IPr})(\text{NHC})]\text{X}$ underwent oxidative addition when reacted with PhICl_2 affording the corresponding $[\text{Au}^{\text{III}}(\text{IPr})(\text{NHC})_2\text{Cl}_2]\text{X}$ complexes. Analysis of the steric and

electronic properties of the ligands employed revealed that oxidation of the Au(I) center was favoured with small and more electron donating NHC ligands, providing important information about the ligand requirements to favour the oxidative addition of Au(I) species to Au(III) with hypervalent iodine oxidants. This study allowed for the design of a new system where oxidation of the metal centre appears to be more facile. Complex $[\text{Au}(\text{BMIM})_2][\text{BF}_4]$ was synthesized in multi-gram scale via a one-pot reaction from $[\text{Au}(\text{DMS})\text{Cl}]$, BMIM-HCl, and BMIM-HBF₄. This complex reacted with PhICl_2 and, for the first time with NHC systems, with $\text{PhI}(\text{OAc})_2$ and $\text{PhI}(\text{OAc}^{\text{F}})_2$, obtaining the corresponding Au(III)-dichloride, bis-acetate and bis-trifluoroacetate complexes. Finally, a digold complex bearing a pincer NHC ligand bridging the two gold centers has been synthesized. Reaction with PhICl_2 afforded the corresponding digold(III) complex. Further reactivity studies of the gold(III) complexes are currently being conducted.

Experimental Section

General information. All reactions were carried out under air and technical grade solvents were used. PhICl_2 was prepared following reported procedures.^[31] Commercial products were used as obtained. Deuterated solvents were purchased from Sigma Aldrich and Acros and dried over activated molecular sieves. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded at ambient temperature in CDCl_3 , CDCl_2 or CD_3OD on a Bruker-500 MHz, 400 MHz or 300 MHz spectrometer. Chemical shifts are expressed in parts per million and are referenced to residual solvent peaks. Elemental analyses were performed by the analytical services at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.

General procedure for the synthesis of $[\text{Au}(\text{IPr})(\text{NHC})][\text{X}]$ ($\text{X} = \text{BF}_4$, PF_6 , Cl) complexes. A vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$, the corresponding NHC-HX salt (1.05 equiv), K_2CO_3 (2 equiv) and acetone. The mixture was stirred at 60 $^\circ\text{C}$ until full conversion to the final product was observed by ^1H NMR analysis of an aliquot of the reaction mixture. After this time, the mixture was filtered through a pad of silica and rinsed with dichloromethane. The solvent was concentrated and n-pentane was added to obtain the final complex which was washed with further portions of n-pentane and dried under vacuum.

Synthesis of $[\text{Au}(\text{IPr})_2][\text{BF}_4]$ (1a**).** Following the general procedure, a 50 mL round bottom flask equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (1459 mg, 2.35 mmol), IPr-HBF₄ (1120 mg, 2.35 mmol, 1 equiv), K_2CO_3 (650 mg, 4.7 mmol, 2 equiv) and acetone (10 mL). The mixture was stirred at 60 $^\circ\text{C}$ for 72 hours. White solid obtained. Yield: 2.26 g, 91%. ^1H NMR (500 MHz, CDCl_3): δ 7.45 (t, $^3J_{\text{HH}} = 7.7$ Hz, 4H, $\text{CH}_{\text{P-Ar}}$ IPr), 7.11 (d, $^3J_{\text{HH}} = 7.7$ Hz, 8H, $\text{CH}_{\text{m-Ar}}$ IPr), 7.09 (s, 4H, $\text{CH}^{\text{A},5}$), 2.27 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.04 (d, $^3J_{\text{HH}} = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 0.92 (d, $^3J_{\text{HH}} = 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$) ppm. The NMR data is in agreement with the reported characterization data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{IMes})][\text{BF}_4]$ (1b**).** Following the general procedure, a vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (45.5 mg, 0.073 mmol), IMes-HBF₄ (31.09 mg, 0.080 mmol, 1.1 equiv), K_2CO_3 (20.6 mg, 0.149 mmol, 2 equiv) and acetone (1.5 mL). The mixture was stirred at 60 $^\circ\text{C}$ for 24 h. White solid obtained. Yield: 38 mg, 52%. ^1H NMR (500 MHz, CDCl_3): δ 7.53 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{\text{P-Ar}}$ IPr), 7.23 (s, 2H, $\text{CH}^{\text{A},5}$ IPr), 7.15 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{\text{m-Ar}}$ IPr), 7.02 (s, 2H,

$\text{CH}^{4,5}$ IMes), 6.77 (s, 4H, $\text{CH}_{m\text{-Ar}}$ IMes), 2.38 (s, 6H, $\text{CH}_{3,p\text{-Ar}}$ IMes), 2.27 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.67 (s, 12H, $\text{CH}_{3,o\text{-Ar}}$ IMes), 1.12 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.85 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{SiMes})][\text{BF}_4]$ (1c). 1c was prepared following a slight variation of the general protocol. A vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{SiMes})\text{Cl}]$ (100.2 mg, 0.186 mmol) and $\text{IPr}\cdot\text{HBF}_4$ (92.8 mg, 0.195 mmol, 1.05 equiv), K_2CO_3 (51.3 mg, 0.371 mmol, 2 equiv) and acetone (1.5 mL). The mixture was stirred at 60 °C for 48 h. Yield: 180 mg, 98 %. ^1H NMR (500 MHz, CDCl_3): δ 7.56 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.19 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.17 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 6.71 (s, 4H, $\text{CH}_{m\text{-Ar}}$ SiMes), 3.85 (s, 4H, $\text{CH}_2^{4,5}$ SiMes), 2.34 (s, 6H, $\text{CH}_{3,p\text{-Ar}}$ SiMes), 2.26 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.91 (s, 12H, $\text{CH}_{3,o\text{-Ar}}$ SiMes), 1.12 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.87 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{tBu})][\text{BF}_4]$ (1d). Following the general procedure, a vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (66.0 mg, 0.106 mmol) and $\text{tBu}\cdot\text{HBF}_4$ (33.2 mg, 0.117 mmol, 1.1 equiv), K_2CO_3 (29.3 mg, 0.212 mmol, 2 equiv) and acetone (1.5 mL). The mixture was stirred at 60 °C for 72 h. Yield: 69 mg, 82%. ^1H NMR (400 MHz, CDCl_3): δ 7.54 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.45 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.34 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 7.11 (s, 2H, $\text{CH}^{4,5}$ tBu), 2.65 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.27 (s, 18H, $\text{C}(\text{CH}_3)_3$ tBu), 1.25 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{ICy})][\text{BF}_4]$ (1e). Following the general procedure, a vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (96.1 mg, 0.155 mmol), $\text{ICy}\cdot\text{HBF}_4$ (54.5 mg, 0.170 mmol, 1.1 equiv) and K_2CO_3 (42.8 mg, 0.309 mmol, 2 equiv). Acetone (1.5 mL) was added and the mixture was stirred at 60 °C for 16 h. Yield: 106 mg, 73%. ^1H NMR (400 MHz, CDCl_3): δ 7.59 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.40 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.38 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 7.03 (s, 2H, $\text{CH}^{4,5}$ ICy), 3.53–3.44 (m, 2H, CH ICy), 2.58 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.75–1.66 (m, 4H, CH_2 ICy), 1.65–1.56 (m, 6H, CH_2 ICy), 1.47–1.34 (m, 4H, CH_2 ICy), 1.29 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.29 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.18–1.08 (m, 2H, CH_2 ICy), 1.00–0.87 (m, 4H, CH_2 ICy) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{BMIM})][\text{BF}_4]$ (1f). Following the general procedure, a 25 mL round bottom flask equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (1550 mg, 2.50 mmol), $\text{BMIM}\cdot\text{HBF}_4$ (621.6 mg, 2.75 mmol, 1.1 equiv) and K_2CO_3 (691.1 mg, 5.00 mmol, 2 equiv). Acetone (10 mL) was added and the mixture was stirred at 60 °C for 20 h. Yield: 1.95 g, 96%. ^1H NMR (500 MHz, CDCl_3): δ 7.54 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.41 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.33 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 7.07 (d, $^3J_{\text{HH}} = 1.7$ Hz, 1H, CH BMIM), 6.91 (d, $^3J_{\text{HH}} = 1.7$ Hz, 1H, CH BMIM), 3.50 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H, $\text{CH}_{2,N\text{-Butyl}}$ BMIM), 3.12 (s, 3H, CH_3 BMIM), 2.54 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.32–1.26 (m, 2H, CH_2 BMIM), 1.28 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.92–0.84 (m, 2H, CH_2 BMIM), 0.73 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_3 BMIM) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{BMIM})][\text{PF}_6]$ (1f'). Following the general protocol, a vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (85.9 mg, 0.137 mmol), $\text{BMIM}\cdot\text{HPF}_6$ (42.9 mg, 0.151 mmol, 1.1 equiv) and K_2CO_3 (37.9 mg, 0.274 mmol, 2 equiv). Acetone (1 mL) was added

and the mixture was stirred at 60 °C for 72 h. Yield: 96 mg, 79%. ^1H NMR (500 MHz, CDCl_3): δ 7.55 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.39 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.34 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 6.97 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1H, CH BMIM), 6.87 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1H, CH BMIM), 3.50 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H, $\text{CH}_{2,N\text{-Butyl}}$ BMIM), 3.11 (s, 3H, $\text{CH}_3,N\text{-Methyl}$ BMIM), 2.54 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.33–1.26 (m, 2H, CH_2 BMIM), 1.28 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.93–0.84 (m, 2H, CH_2 BMIM), 0.74 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, CH_3 BMIM) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

Synthesis of $[\text{Au}(\text{IPr})(\text{BMIM})][\text{Cl}]$ (1f''). A vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})\text{Cl}]$ (92.1 mg, 0.147 mmol), $\text{BMIM}\cdot\text{HCl}$ (28.3 mg, 0.162 mmol, 1.1 equiv) and K_2CO_3 (40.6 mg, 0.294 mmol, 2 equiv). Acetone (1 mL) was added and the mixture was stirred at 60 °C for 22 h. Yield: 69 mg, 62%. ^1H NMR (400 MHz, CDCl_3): δ 7.55 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.54 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1H, CH BMIM), 7.40 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.34 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 7.03 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1H, CH BMIM), 3.53 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H, $\text{CH}_{2,N\text{-Butyl}}$ BMIM), 3.22 (s, 3H, $\text{CH}_3,N\text{-Methyl}$ BMIM), 2.54 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.34–1.27 (m, 2H, CH_2 BMIM), 1.28 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.95–0.84 (m, 2H, CH_2 BMIM), 0.73 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H, CH_3 BMIM) ppm. The NMR data is in agreement with the reported characterisation data.^[14]

General procedure for the synthesis of $[\text{Au}(\text{IPr})(\text{NHC})\text{Cl}_2][\text{X}]$ ($\text{X} = \text{BF}_4$, PF_6 , Cl) complexes. A vial equipped with a stir bar was charged, under air, with the corresponding $[\text{Au}(\text{IPr})(\text{NHC})][\text{X}]$ complex (**1-1f''**), PhICl_2 (1.1 – 2.5 equiv) and dichloromethane. The mixture was stirred at room temperature until full conversion to the final product was observed by ^1H NMR analysis of an aliquot of the reaction mixture. After this time, the mixture was filtered through a pad of Celite® and rinsed multiple times with dichloromethane. The solvent was concentrated and *n*-pentane or diethyl ether was added to obtain the final complex as a white to yellow-white solid which was washed with further portions of *n*-pentane and dried under vacuum.

Synthesis of $[\text{Au}(\text{IPr})_2\text{Cl}_2][\text{BF}_4]$ (2a). Following the general procedure, a vial equipped with a stir bar was charged, under air, with $[\text{Au}(\text{IPr})_2][\text{BF}_4]$ (**1a**) (107.4 mg, 0.101 mmol), PhICl_2 (62.2 mg, 0.226 mmol, 2.2 equiv.) and dichloromethane (1.5 mL). The mixture was stirred at room temperature for 7 d. Yield: 79 mg, 70 %. ^1H NMR (400 MHz, CD_3OD): δ 7.75 (s, 4H, $\text{CH}^{4,5}$), 7.56 (t, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.22 (d, $^3J_{\text{HH}} = 7.8$ Hz, 8H, $\text{CH}_{m\text{-Ar}}$ IPr), 2.53 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 1.00 (d, $^3J_{\text{HH}} = 6.8$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 0.98 (d, $^3J_{\text{HH}} = 6.8$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_3OD): δ –155.0 (s, $^{19}\text{BF}_4$), –155.0 (s, $^{11}\text{BF}_4$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3OD): δ 154.3 (s, $\text{C}_{\text{carbene}}$), 146.9 (s, s, Co-Ar), 133.9 (s, CN-Ar), 132.9 (s, s, $\text{CH}_{p\text{-Ar}}$), 129.2 (s, $\text{CH}^{4,5}$), 126.0 (s, $\text{CH}_{m\text{-Ar}}$), 30.1 (s, $\text{CH}(\text{CH}_3)_2$), 26.5 (s, $\text{CH}(\text{CH}_3)_2$), 23.0 (s, $\text{CH}(\text{CH}_3)_2$) ppm. Anal. Calcd for $\text{C}_{54}\text{H}_{72}\text{AuCl}_2\text{F}_4\text{N}_4$: C, 57.30; H, 6.41; N, 4.95. Found: C, 57.16; H, 6.35; N, 4.85.

Synthesis of $[\text{Au}(\text{IPr})(\text{IMes})\text{Cl}_2][\text{BF}_4]$ (2b). Following the general procedure, $[\text{Au}(\text{IPr})(\text{IMes})][\text{BF}_4]$ (**1b**) (100 mg, 0.102 mmol) and PhICl_2 (30.8 mg, 0.112 mmol, 1.1 equiv) were dissolved in dichloromethane (1 mL) and stirred at room temperature for 24 h. Yield: 98 mg, 92%. ^1H NMR (400 MHz, CDCl_3): δ 7.61 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $\text{CH}_{p\text{-Ar}}$ IPr), 7.35 (s, 2H, $\text{CH}^{4,5}$ IPr), 7.20 (s, 2H, $\text{CH}^{4,5}$ IMes), 7.19 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, $\text{CH}_{m\text{-Ar}}$ IPr), 6.71 (s, 4H, $\text{CH}_{m\text{-Ar}}$ IMes), 2.51 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 2.39 (s, 6H, CH_3 IMes), 1.84 (s, 12H, CH_3 IMes), 1.01 (d, $^3J_{\text{HH}} = 6.7$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3): δ –154.4 (s, $^{19}\text{BF}_4$), –154.5 (s, $^{11}\text{BF}_4$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 154.7 (s, $\text{C}_{\text{carbene}}$ IPr), 152.8 (s, $\text{C}_{\text{carbene}}$ IMes), 146.3 (s, Co-Ar IPr), 139.8 (s, Co-Ar IMes), 134.7 (s, Co-Ar IMes), 132.5 (s, CN-Ar IMes), 132.0 (s, CN-Ar IPr), 131.6 (s, $\text{CH}_{p\text{-Ar}}$ IPr), 130.1 (s, $\text{CH}_{m\text{-Ar}}$ IMes), 127.0 (s, $\text{CH}^{4,5}$ IPr), 126.5

(s, CH^{4.5} IMes), 124.3 (s, CH *m*-Ar IPr), 29.0 (s, CH(CH₃)₂), 26.8 (s, CH(CH₃)₂), 21.8 (s, CH(CH₃)₂), 21.4 (s, CH₃ IMes), 18.2 (s, CH₃ IMes) ppm. Anal. Calcd for C₄₈H₆₀AuBCl₂F₄N₄: C, 55.03; H, 5.77; N, 5.35. Found: C, 55.14; H, 5.81; N, 5.28.

Synthesis of [Au(IPr)(SIMes)Cl₂][BF₄] (2c). Following the general procedure, a vial equipped with a stir bar was charged, under air, with [Au(IPr)(SIMes)][BF₄] (1c) (13.8 mg, 0.014 mmol) and PhICl₂ (5.0 mg, 0.018 mmol, 1.3 equiv) and dichloromethane (1 mL). The mixture was stirred at room temperature for 24 h. Yield: 14 mg, 95%. ¹H NMR (400 MHz, CDCl₃): δ 7.55 (t, ³J_{HH} = 7.8 Hz, 2H, CH_{*p*-Ar} IPr), 7.25 (s, 2H, CH^{4.5} IPr), 7.14 (d, ³J_{HH} = 7.8 Hz, 4H, CH_{*m*-Ar} IPr), 6.62 (s, 4H, CH_{*m*-Ar} SIMes), 4.02 (s, 4H CH₂^{4.5} SIMes), 2.47 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 2.33 (s, 6H, CH₃_{*p*-Ar} SIMes), 2.06 (s, 12H, CH₃_{*o*-Ar} SIMes), 1.01 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 0.97 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂) ppm. ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -154.3 (s, ¹⁰BF₄), -154.3 (s, ¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 179.0 (s, C_{carbene} SIMes), 156.0 (s, C_{carbene} IPr), 146.1 (s, C_o-Ar IPr), 138.7 (s, C_p-Ar SIMes), 135.5 (s, CH_{*p*-Ar} IPr), 132.2 (s, CH_{*m*-Ar} SIMes), 131.9 (s, C_N-Ar IPr), 131.5 (s, CH_{*p*-Ar} IPr), 130.4 (s, CH_{*m*-Ar} SIMes), 126.8 (s, CH^{4.5} IPr), 124.2 (s, CH_{*m*-Ar} IPr), 53.1 (s, CH₂^{4.5} SIMes), 28.9 (s, CH(CH₃)₂), 26.8 (s, CH(CH₃)₂), 21.9 (s, CH₃_{*p*-Ar} SIMes), 21.3 (s, CH(CH₃)₂), 18.4 (s, CH₃_{*o*-Ar} SIMes) ppm. Anal. Calcd for C₄₈H₆₂AuBCl₂F₄N₄: C, 54.92; H, 5.95; N, 5.34. Found: C, 54.87; H, 5.86; N, 5.41.

Synthesis of [Au(IPr)(*i*Bu)Cl₂][BF₄] (2d). Following the general procedure, a vial equipped with a stir bar was charged, under air, with [Au(IPr)(*i*Bu)][BF₄] (1d) (45.5 mg, 0.059 mmol), PhICl₂ (21.2 mg, 0.077 mmol, 1.3 equiv) and dichloromethane (1 mL). The mixture was stirred at room temperature for 3.5 h. Yield: 42 mg, 85%. ¹H NMR (400 MHz, CDCl₃): δ 7.63 (t, ³J_{HH} = 7.6 Hz, 2H, CH aromatic IPr), 7.56 (s, 2H, CH imidazole IPr), 7.50 (s, 2H, CH imidazole *i*Bu), 7.41 (d, ³J_{HH} = 2.0 Hz, 4H, CH aromatic IPr), 2.86 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 1.33 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.31 (s, 18H, C(CH₃)₃), 1.15 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -154.1 (s, ¹¹BF₄), -154.2 (s, ¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 156.5 (s, C_{carbene} IPr), 146.9 (s, s, C_o-Ar IPr), 145.9 (s, C_{carbene} *i*Bu), 133.0 (s, C_N-Ar IPr), 132.3 (s, CH_{*p*-Ar} IPr), 127.5 (s, CH^{4.5} IPr), 125.0 (s, CH_{*m*-Ar} IPr), 123.2 (s, CH^{4.5} *i*Bu), 61.1 (s, C_N-alkyl *i*Bu), 31.6 (s, CH₃ *i*Bu), 29.2 (s, CH(CH₃)₂), 27.0 (s, CH(CH₃)₂), 22.4 (s, CH(CH₃)₂) ppm. Anal. Calcd for C₃₈H₅₆AuBCl₂F₄N₄: C, 49.42; H, 6.11; N, 6.07; Found: C, 49.29; H, 5.93; N, 5.90.

Synthesis of [Au(IPr)(ICy)Cl₂][BF₄] (2e). Following the general protocol, a vial equipped with a stir bar was charged, under air, with [Au(IPr)(ICy)][BF₄] (1e) (59.7 mg, 0.066 mmol), PhICl₂ (27.0 mg, 0.099 mmol, 1.5 equiv) and dichloromethane (1 mL). The mixture was stirred at room temperature for 3.5 h. Yield: 56 mg, 87%. ¹H NMR (400 MHz, CDCl₃): δ 7.63 (t, ³J_{HH} = 7.8 Hz, 2H, CH_{*p*-Ar} IPr), 7.55 (s, 2H, CH^{4.5} IPr), 7.43 (d, ³J_{HH} = 7.8 Hz, 4H, CH_{*m*-Ar} IPr), 7.27 (s, 2H, CH^{4.5} ICy), 3.43–3.33 (m, 2H, CH₂ ICy), 2.82 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 1.76–1.68 (m, 8H, CH₂ ICy), 1.64–1.55 (m, 4H, CH₂ ICy), 1.52–1.39 (m, 4H, CH₂ ICy), 1.34 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.18 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 0.95–0.81 (m, 4H, CH₂ ICy) ppm. ¹⁹F{¹H} NMR (282 Hz, CDCl₃): δ -153.6 (s, BF₄) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 158.4 (s, C_{carbene} IPr), 147.5 (s, C_{carbene} ICy), 146.8 (s, C_{aromatic} IPr), 132.5 (s, C_{aromatic} IPr), 132.0 (s, CH_{aromatic} IPr), 127.1 (s, CH imidazole IPr), 124.8 (s, CH_{aromatic} IPr), 121.1 (s, CH imidazole ICy), 61.0 (s, N-CH₂ ICy), 33.2 (s, CH₂ ICy), 29.3 (s, CH(CH₃)₂), 26.7 (s, CH(CH₃)₂), 25.0 (s, CH₂ ICy), 24.5 (s, CH₂ ICy), 22.7 (s, CH₂ ICy) ppm. Anal. Calcd for C₄₂H₆₀AuBCl₂F₄N₄: C, 51.71; H, 6.20; N, 5.74. Found: C, 51.81; H, 6.03; N, 5.62.

Synthesis of [Au(IPr)(BMIM)Cl₂][BF₄] (2f). Following the general protocol, a vial equipped with a stir bar was charged, under air, with [Au(IPr)(BMIM)][BF₄] (1f) (205.2 mg, 0.25 mmol), PhICl₂ (91.8 mg, 0.33 mmol, 1.3 equiv) and dichloromethane (1.5 mL) was added and the mixture was stirred at room temperature for 3.5 h. Yield: 205 mg, 93%. ¹H NMR (400 MHz, CDCl₃): δ 7.59 (t, ³J_{HH} = 7.8 Hz, 2H, CH_{aromatic} IPr), 7.54 (s, 2H, CH imidazole IPr), 7.39 (d, ³J_{HH} = 7.8 Hz, 4H, CH_{aromatic} IPr), 7.35 (d, ³J_{HH} = 1.6 Hz, 1H, CH imidazole BMIM), 7.08 (d, ³J_{HH} = 1.6 Hz, 1H, CH imidazole BMIM), 3.58 (t, ³J_{HH} = 7.4 Hz, 2H, N-CH₂ butyl BMIM), 3.24 (s, 3H, N-CH₃ BMIM), 2.79 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 1.40–1.34 (m, 2H, CH₂ BMIM), 1.35 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.16 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.00–0.91 (m, 2H, CH₂ butyl BMIM), 0.74 (t, ³J_{HH} = 7.2 Hz, 3H, butyl BMIM). ¹⁹F{¹H} NMR (376 Hz, CDCl₃): δ -153.2 (s, BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 159.51 (s, C_{carbene} IPr), 149.6 (s, C_{carbene} BMIM), 146.6 (s, C_{aromatic} IPr), 132.3 (s, C_{aromatic} IPr), 132.0 (s, CH imidazole IPr), 126.8 (s, CH_{aromatic} IPr), 125.8 (s, CH_{aromatic} IPr), 124.6 (s, CH imidazole BMIM), 123.6 (s, CH imidazole BMIM), 50.3 (s, N-CH₂ BMIM), 36.7 (s, N-CH₃ BMIM), 32.2 (s, CH₂ BMIM), 29.3 (s, CH(CH₃)₂), 27.0 (s, CH(CH₃)₂), 22.4 (s, CH(CH₃)₂), 19.5 (s, CH₂ BMIM), 13.6 (s, CH₃ butyl BMIM) ppm. Anal. Calcd for C₃₅H₅₀AuBCl₂F₄N₄: C, 47.69; H, 5.72; N, 6.36. Found: C, 47.59; H, 5.75; N, 6.27.

Synthesis of [Au(IPr)(BMIM)Cl₂][PF₆] (2f'). Following the general procedure, a vial equipped with a stir bar was charged, under air, with [Au(IPr)(BMIM)][PF₆] (1f') (40.0 mg, 0.046 mmol), PhICl₂ (16.5 mg, 0.059 mmol, 1.3 equiv) and dichloromethane (1 mL). The mixture was stirred at room temperature for 7 h. Yield: 29 mg, 81%. ¹H NMR (400 MHz, CDCl₃): δ 7.59 (t, ³J_{HH} = 7.8 Hz, 2H, CH_{*p*-Ar} IPr), 7.54 (s, 2H, CH^{4.5} IPr), 7.39 (d, ³J_{HH} = 7.8 Hz, 4H, CH_{*m*-Ar} IPr), 7.19 (d, ³J_{HH} = 2.1 Hz, 1H, CH⁴ BMIM), 7.03 (d, ³J_{HH} = 2.1 Hz, 1H, CH⁵ BMIM), 3.58 (t, ³J_{HH} = 7.4 Hz, 2H, CH₂ *N*-Butyl BMIM), 3.22 (s, 3H, CH₃ *N*-Methyl BMIM), 2.79 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 1.41–1.34 (m, 2H, CH₂ BMIM), 1.35 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.16 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.00–0.90 (m, 2H, CH₂ BMIM), 0.74 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃ BMIM) ppm. ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -73.2 (d, ¹J_{FP} = 712.2 Hz, 6F, PF₆) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 158.7 (s, C_{carbene} IPr), 150.1 (s, C_{carbene} BMIM), 146.6 (s, C_o-Ar IPr), 132.3 (s, C_N-Ar IPr), 132.0 (s, CH_{*p*-Ar} IPr), 126.8 (s, CH^{4.5} IPr), 125.4 (s, CH⁴ BMIM), 124.6 (s, CH_{*m*-Ar} IPr), 123.6 (s, CH⁵ BMIM), 50.4 (s, CH₂ *N*-Butyl BMIM), 36.7 (s, CH₃ *N*-Methyl BMIM), 32.2 (s, CH₂ BMIM), 29.4 (s, CH(CH₃)₂), 26.9 (s, CH(CH₃)₂), 22.4 (s, CH(CH₃)₂), 19.5 (s, CH₂ BMIM), 13.6 (s, CH₃ BMIM) ppm. ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -144.4 (sept, ¹J_{PF} = 712.2 Hz, 1P, PF₆) ppm. Anal. Calcd for C₃₅H₅₀AuCl₂F₆N₄P: C, 44.74; H, 5.36; N, 5.96. Found: C, 44.63; H, 5.43; N, 5.94.

Synthesis of [Au(IPr)(BMIM)Cl₂][Cl] (2f''). Following the general protocol, a vial equipped with a stir bar was charged, under air, with [Au(IPr)(BMIM)][Cl] (1f'') (40.0 mg, 0.053 mmol), PhICl₂ (18.8 mg, 0.068 mmol, 1.3 equiv) and dichloromethane (1 mL). The mixture was stirred at room temperature for 3.5 h. Yield: 39 mg, 88%. ¹H NMR (500 MHz, CDCl₃): δ 8.09 (d, ³J_{HH} = 1.8 Hz, 1H, CH⁴ BMIM), 7.59 (t, ³J_{HH} = 7.8 Hz, 2H, CH_{*p*-Ar} IPr), 7.51 (s, 2H, CH^{4.5} IPr), 7.39 (d, ³J_{HH} = 7.8 Hz, 4H, CH_{*m*-Ar} IPr), 7.23 (d, ³J_{HH} = 1.8 Hz, 1H, CH⁵ BMIM), 3.62 (t, ³J_{HH} = 7.4 Hz, 2H, CH₂ *N*-Butyl BMIM), 3.38 (s, 3H, CH₃ *N*-Methyl BMIM), 2.80 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 1.40–1.35 (m, 2H, CH₂ BMIM), 1.35 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.16 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.00–0.92 (m, 2H, CH₂ *N*-Butyl BMIM), 0.74 (t, ³J_{HH} = 7.4 Hz, 3H, CH₃ *N*-Butyl BMIM) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 160.3 (s, C_{carbene} IPr), 148.5 (s, C_{carbene} BMIM), 146.5 (s, C_o-Ar IPr), 132.2 (s, C_N-Ar IPr), 132.1 (s, CH_{*p*-Ar} IPr), 126.8 (s, CH⁴ BMIM), 126.4 (s, CH^{4.5} IPr), 124.6 (s, CH_{*m*-Ar} IPr), 123.4 (s, CH⁵ BMIM), 50.3 (s, CH₂ *N*-Butyl BMIM), 36.9 (s, CH₃ *N*-Methyl BMIM), 32.3 (s, CH₂ BMIM), 29.4 (s, CH(CH₃)₂), 27.0 (s, CH(CH₃)₂), 22.4 (s, CH(CH₃)₂), 19.6 (s, CH₂ BMIM), 13.6 (s, CH₃ BMIM) ppm. Anal. Calcd

for $C_{35}H_{50}AuCl_3N_4$: C, 50.64; H, 6.07; N, 6.75. Found: C, 50.52; H, 6.05; N, 6.61.

Synthesis of $[Au(BMIM)_2][BF_4]$ (3). A 100 mL round bottom flask equipped with a stir bar was charged, under air, with $[Au(DMS)Cl]$ (1342 mg, 4.56 mmol), BMIM-HCl (1081 mg, 4.78 mmol, 1.05 equiv), BMIM-HBF₄ (845 mg, 4.85 mmol, 1.06 equiv) and K₂CO₃ (1261 mg, 9.12 mmol, 2 equiv). Acetone (25 mL) was added and the mixture was stirred at 60 °C for 6 h. After this time, the mixture was filtered through a pad of silica on a frit and rinsed with dichloromethane (3 x 15 mL). The solution was concentrated and *n*-pentane was added to obtain a white microcrystalline solid which was washed with further portions of *n*-pentane and dried under vacuum. Yield: 1.81 g, 95%. ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, ³J_{HH} = 1.9 Hz, 2H, CH⁴), 7.12 (d, ³J_{HH} = 1.9 Hz, 2H, CH⁵), 4.16 (t, ³J_{HH} = 7.2 Hz, 4H, CH₂, *N*-butyl), 3.89 (s, 6H, CH₃, *N*-Methyl), 1.89–1.80 (m, 4H, CH₂), 1.41–1.29 (m, 4H, CH₂), 0.94 (t, ³J_{HH} = 7.4 Hz, 6H, CH₃) ppm. ¹⁹F{¹H} (470 MHz, CDCl₃): δ –153.3 (s, ¹⁰BF₄), –153.4 (s, ¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): 183.7 (s, *C*_{carbene}), 123.3 (s, CH⁴), 121.7 (s, CH⁵), 51.1 (s, CH₂, *N*-Butyl), 38.1 (s, CH₃, *N*-Methyl), 33.6 (s, CH₂), 19.8 (s, CH₂), 13.8 (s, CH₃) ppm. Anal. Calcd for C₁₆H₂₈AuBF₄N₄: C, 34.13; H, 5.04; N, 10.00. Found: C, 34.42; H, 5.15; N, 9.95.

Synthesis of $[Au(BMIM)_2Cl_2][BF_4]$ (4). A vial equipped with a stir bar was charged, under air, with $[Au(BMIM)_2]BF_4$ (3) (416.7 mg, 0.744 mmol), PhICl₂ (248.2 mg, 0.903 mmol, 1.3 equiv) and dichloromethane (2.5 mL). The mixture was stirred at room temperature for 2.5 h and then was filtered over Celite® and rinsed with dichloromethane (3 x 2 mL). The solvent was concentrated and first diethyl ether (1 mL), then *n*-pentane (2 mL) was added to obtain the product as a pale yellow-white microcrystalline solid which was washed with further portions of pentane (2 x 1 mL) and dried under vacuum. Yield: 424 mg, 90%. ¹H NMR (500 MHz, CDCl₃): δ 7.44 (d, ³J_{HH} = 1.9 Hz, 1H, CH⁴), 7.40 (d, ³J_{HH} = 1.9 Hz, 1H, CH⁴), 7.33 (d, ³J_{HH} = 1.9 Hz, 2H, CH⁵), 4.27–4.21 (m, 4H, CH₂, *N*-butyl), 4.01 (s, 3H, CH₃, *N*-Methyl), 3.99 (s, 3H, CH₃, *N*-Methyl), 2.02–1.89 (m, 4H, CH₂), 1.40–1.34 (m, 4H, CH₂), 0.97 (t, ³J_{HH} = 7.3 Hz, 6H, CH₃) ppm. ¹⁹F{¹H} (376 MHz, CDCl₃): δ –152.3 (s, ¹⁰BF₄), –152.4 (s, ¹¹BF₄) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): 153.6 (s, *C*_{carbene}), 125.5 (s, CH⁴), 123.8 (s, CH⁵), 123.7 (s, CH⁵), 50.8 (s, CH₂, *N*-Butyl), 50.8 (s, CH₂, *N*-Butyl), 37.8 (s, CH₃, *N*-Methyl), 37.6 (s, CH₃, *N*-Methyl), 32.9 (s, CH₂), 32.9 (s, CH₂), 19.9 (s, CH₂), 19.9 (s, CH₂), 13.7 (s, CH₃) ppm. Anal. Calcd for C₁₆H₂₈AuCl₂F₄N₄: C, 30.45; H, 4.47; N, 8.88. Found: C, 30.36; H, 4.56; N, 8.85.

Synthesis of $[Au(BMIM)_2(OAc)_2][BF_4]$ (5). A vial equipped with a stir bar was charged, under air, with $[Au(BMIM)_2]BF_4$ (3) (202.4 mg, 0.361 mmol), PhI(OAc)₂ (152.2 mg, 0.472 mmol, 1.31 equiv) and dichloroethane (2 mL). The mixture was stirred at 60 °C for 72 h and then was filtered over Celite® and rinsed with dichloromethane (3 x 2 mL). The solvent was concentrated and diethyl ether (3 mL) was added to obtain the product as a white microcrystalline solid which was washed with further portions of *n*-pentane and dried under vacuum. Yield: 228 mg, 93%. ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, ³J_{HH} = 2.0 Hz, 2H, CH⁴), 7.28 (d, ³J_{HH} = 2.0 Hz, 2H, CH⁵), 4.33 (t, ³J_{HH} = 7.2 Hz, 4H, CH₂, *N*-butyl), 4.08 (s, 6H, CH₃, *N*-Methyl), 1.98–1.89 (m, 4H, CH₂), 1.90 (s, 6H, CH₃, OAc), 1.49–1.38 (m, 4H, CH₂), 1.00 (t, ³J_{HH} = 7.4 Hz, 6H, CH₃) ppm. ¹⁹F{¹H} (376 MHz, CDCl₃): δ –152.8 (s, ¹⁰BF₄), –152.9 (s, ¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): 174.9 (s, CO₂CH₃), 152.9 (s, *C*_{carbene}), 125.1 (s, CH⁴), 122.7 (s, CH⁵), 50.7 (s, CH₂, *N*-Butyl), 37.2 (s, CH₃, *N*-Methyl), 32.7 (s, CH₂), 20.2 (s, CO₂CH₃), 20.0 (s, CH₂), 13.7 (s, CH₃) ppm. ATR-IR (cm^{–1}): ν 1666.4 (vs, CO_{asym} stretch), 1251.8 (vs, CO_{sym} stretch). Anal. Calcd for C₂₀H₃₄AuBF₄N₄O₄: C, 35.42; H, 5.05; N, 8.26. Found: C, 35.58; H, 4.96; N, 8.14.

Synthesis of $[Au(BMIM)_2(OAc)_2][BF_4]$ (6). A vial equipped with a stir bar was charged, under air, with $[Au(BMIM)_2]BF_4$ (4) (566.0 mg, 1.01 mmol), PhI(OAc)₂ (478.2 mg, 1.11 mmol, 1.1 equiv) and dichloroethane (2 mL). The mixture was stirred at 60 °C for 6 h and then was filtered over Celite® and rinsed with dichloromethane (3 x 2 mL). The solvent was removed and the yielding solid was dissolved in dichloromethane (0.5 mL), diethyl ether (2 mL) and *n*-pentane were added to obtain the product as a white-yellow microcrystalline solid which was washed with further portions of pentane and dried under vacuum. Yield: 765 mg, 96%. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, ³J_{HH} = 1.9 Hz, 2H, CH⁴), 7.38 (d, ³J_{HH} = 1.9 Hz, 2H, CH⁵), 4.32 (t, ³J_{HH} = 7.7 Hz, 4H, CH₂, *N*-butyl), 4.11 (s, 6H, CH₃, *N*-Methyl), 1.97–1.89 (m, 4H, CH₂), 1.47–1.36 (m, 4H, CH₂), 0.98 (t, ³J_{HH} = 7.4 Hz, 6H, CH₃) ppm. ¹⁹F{¹H} (470 MHz, CDCl₃): δ –71.8 (s, CO₂CF₃), –152.2 (s, ¹⁰BF₄), –152.3 (s, ¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): 160.4 (q, ²J_{CF} = 41.2 Hz, CO₂CF₃), 149.0 (s, *C*_{carbene}), 126.0 (s, CH⁴), 123.6 (s, CH⁵), 113.2 (q, ¹J_{CF} = 288 Hz, CO₂CF₃) 50.8 (s, CH₂, *N*-Butyl), 37.1 (s, CH₃, *N*-Methyl), 32.6 (s, CH₂), 19.8 (s, CH₂), 13.3 (s, CH₃) ppm. ATR-IR (cm^{–1}): ν 1730.1 (vs, CO_{asym} stretch), 1145.7 (vs, CO_{sym} stretch). Anal. Calcd for C₂₀H₂₈AuBF₄N₄O₄: C, 30.55; H, 3.59; N, 7.13. Found: C, 30.65; H, 3.64; N, 7.07.

Synthesis of salt g-(HBF₄)₂:

1,3-di(1H-imidazol-1-yl)benzene (I). A 100 mL flask equipped with a stir bar was charged, under air, with 1,3-dibromobenzene (2.5 mL, 21 mmol), imidazole (3.5 g, 51 mmol, 2.4 equiv), K₂CO₃ (7.2 g, 52 mmol, 2.5 equiv), CuO (0.6 g, 8.6 mmol, 0.4 equiv) and DMSO (20 mL). The flask was sealed with a septum and the mixture was heated to 150 °C for 72 h. Then, the DMSO was distilled off under reduced pressure and the crude was filtered over silica and rinsed with a 10:1 mixture of dichloromethane/methanol. Drying over MgSO₄ and removal of the volatiles led to a yellow white solid which was further dried under vacuum. Yield: 3.23 g, 78%. ¹H NMR (400 MHz, CDCl₃): δ 7.91 (s, 2 H), 7.64–7.58 (m, 1H), 7.43 (s, 2H), 7.42–7.39 (m, 1H), 7.33 (s, 2H), 7.26–7.25 (m, 2H) ppm. The NMR data is in agreement with the reported characterisation data.^[29]

1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazolium) bromide (II). A vial equipped with a stir bar was charged, under air, with 1,3-di(1H-imidazol-1-yl)benzene (I) (264.0 mg, 1.26 mmol), *n*-butyl bromide (172.4 mg, 12.6 mmol, 10 equiv) and acetonitrile (1 mL). The mixture was heated to 80 °C for 3 h. After the volatiles were removed, the product was further dried under vacuum to obtain an off-white solid. Yield: 562 mg, 92%. ¹H NMR (400 MHz, CDCl₃): δ = 11.40 (s, 2H, CH²_{imidazol}), 9.11 (t, ³J_{HH} = 1.9 Hz, 2H, CH⁴_{imidazol}), 8.97 (t, ⁴J_{HH} = 2.2 Hz, 1H, CH²_{Ar}), 8.33 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 2.2 Hz, 2H, CH^{4,6}_{Ar}), 7.65–7.59 (m, 3H, CH⁵_{imidazol}, CH⁵_{Ar}), 4.45 (t, ³J_{HH} = 7.3 Hz, 4H, CH₂, *N*-butyl), 2.06–1.96 (m, 4H, CH₂), 1.48–1.37 (m, 4H, CH₂), 0.97 (t, ³J_{HH} = 7.3 Hz, 6H, CH₃) ppm. The NMR data is in agreement with the reported characterisation data.^[29]

Synthesis of 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazolium) tetrafluoroborate (g-(HBF₄)₂). A vial equipped with a stir bar was charged, under air, with 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazolium) bromide (51) (283 mg, 0.584 mmol) and H₂O (1 mL). Then, HBF₄/H₂O (48 w%, 120 mg, 0.679 mmol, 1.2 equiv) was added dropwise and the resulting suspension was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over Na₂SO₄, concentrated in vacuum and *n*-pentane was added to obtain the product as a white solid which was further dried under vacuum. Yield: 165 mg, 56 %. ¹H NMR (400 MHz, CD₃OD): δ = 8.22–8.17 (m, 3H), 8.00–7.96 (m, 2H), 7.95–7.88 (m, 3H), 4.36 (t, ³J_{HH} = 7.6 Hz, 4H, CH₂, *N*-butyl), 2.05–1.95 (m, 4H, CH₂), 1.52–1.42 (m, 4H, CH₂), 1.03 (t, ³J_{HH} = 7.4 Hz, 6H, CH₃) ppm. ¹⁹F{¹H} NMR (377 MHz, MeOD): δ -153.6 (s, ¹⁰BF₄), -153.6 (s, ¹¹BF₄) ppm. Anal.

Calcd for $C_{20}H_{28}B_2F_8N_4$: C, 48.23; H, 5.67; N, 11.25. Found: C, 48.35; H, 5.55; N, 11.17.^[29]

Synthesis of 7. A vial equipped with a stir bar was charged, under air, with $[Au(DMS)Cl]$ (88.7 mg, 0.301 mmol, 1.0 equiv), salt **g**·(HBf_4)₂ (150 mg, 0.301 mmol, 1.0 equiv.), and K_2CO_3 (166.4 mg, 1.204 mmol, 4 equiv). Acetone (2 mL) was added and the mixture was stirred at 60 °C for 16 h. After this time, the suspension was filtered through silica and rinsed with methanol. The filtrate was concentrated and pentane added to obtain a white solid that was washed with further portions of pentane. Yield: 131.2 mg, 72%. ¹H NMR (400 MHz, CD_3OD): δ 7.72 (dd, J_{HH} = 7.8, 1.9 Hz, 4H, CH aromatic Ph), 7.68 (t, J_{HH} = 1.9 Hz, 2H, CH aromatic Ph), 7.64 (d, J_{HH} = 2.0 Hz, 4H, CH imidazole), 7.61 (d, J_{HH} = 2.0 Hz, 4H, CH imidazole), 7.48 (t, J_{HH} = 7.8 Hz, 2H, CH aromatic Ph), 4.40 (t, J_{HH} = 7.2 Hz, 8H, N-CH₂ butyl), 2.01 (pent, J_{HH} = 7.4 Hz, 8H, CH(CH₃)₂), 1.53–1.42 (m, 8H, CH₂ butyl), 1.04 (t, J_{HH} = 7.3 Hz, 12H, butyl). ¹⁹F{¹H} NMR (376 Hz, CD_3OD): δ -154.5 (¹⁰BF₄), -154.6 (¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CD_3OD): δ 183.7 (s, C_{carbene}), 141.2 (s, N-C), 131.7 (s, CH aromatic Ph), 126.9 (s, CH aromatic Ph), 124.0 (s, CH imidazole), 123.9 (s, CH imidazole), 122.8 (br, CH aromatic Ph), 52.5 (s, N-CH₂), 34.6 (s, CH₂ butyl), 20.9 (s, CH₂ butyl), 14.1 (s, CH₃ butyl) ppm. Anal. Calcd for $C_{40}H_{52}Au_2B_2F_8N_4$: C, 39.69; H, 4.32; N, 9.24. Found: C, 39.67; H, 4.27; N, 9.17.

Synthesis of $[Au_2(g)_2Cl_2][BF_4]$ (8). A vial equipped with a stir bar was charged, under air, with **7** (100 mg, 0.0824 mmol, 1.0 equiv), and $PhICl_2$ (58.9 mg, 0.214 mmol, 2.6 equiv). Dichloromethane (2 mL) was added and the mixture was stirred at room temperature for 16 h. After this time, the suspension was filtered through silica and rinsed with dichloromethane. The filtrate was concentrated and pentane added to obtain a white solid that was washed with further portions of pentane. Yield: 97 mg, 87%. ¹H NMR (400 MHz, CD_3COCD_3): δ 8.30 (t, J_{HH} = 7.8 Hz, 2H, CH aromatic Ph), 7.99 (d, J_{HH} = 2.0 Hz, 4H, CH imidazole), 7.94 (d, J_{HH} = 2.0 Hz, 4H, CH imidazole), 7.89 (dd, J_{HH} = 8.0, 2.1 Hz, 4H, CH aromatic Ph), 7.72 (t, J_{HH} = 2.1 Hz, 2H, CH aromatic Ph), 4.72–4.50 (m, 8H, N-CH₂ butyl), 2.14 (pent, J_{HH} = 7.6 Hz, 8H, CH(CH₃)₂), 1.59–1.44 (m, 8H, CH₂ butyl), 1.01 (t, J_{HH} = 7.4 Hz, 12H, butyl). ¹⁹F{¹H} NMR (376 Hz, CD_3COCD_3): δ -151.1 (¹⁰BF₄), -151.2 (¹¹BF₄) ppm. ¹³C{¹H} NMR (101 MHz, CD_3COCD_3): δ 153.0 (s, C_{carbene}), 139.2 (s, N-C), 134.6 (s, CH aromatic Ph), 128.3 (s, CH aromatic Ph), 127.0 (s, CH imidazole), 125.8 (s, CH imidazole), 125.7 (s, CH aromatic Ph), 51.9 (s, N-CH₂), 33.4 (s, CH₂ butyl), 20.5 (s, CH₂ butyl), 14.0 (s, CH₃ butyl) ppm. Anal. Calcd for $C_{40}H_{52}Au_2B_2Cl_2F_8N_4$: C, 35.48; H, 3.87; N, 8.27. Found: C, 35.62; H, 3.84; N, 8.18.

Experimental details including copy of the spectra of all the compounds and crystallographic information can be found in the Supporting Information file. CCDC 1483138 (**2b**), 1483139 (**2c**), 1483140 (**2d**), 1483141 (**2e**), 1483142 (**2f**), 1483143 (**2f'**), 1483144 (**2f''**), 1483145 (**3**), 1483146 (**4**), 1483147 (**5**), and 1483148 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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