

Synthesis and Characterization of Gold(I) Complexes of Dibenzotropyliidene-Functionalized NHC Ligands (Trop-NHCs)

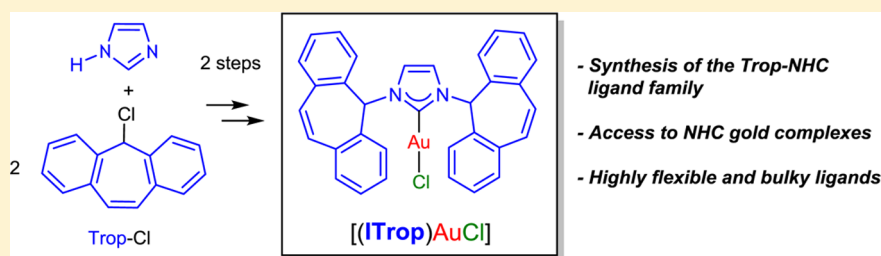
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S Supporting Information



ABSTRACT: Gold(I) complexes of dibenzotropyliidene-functionalized N-heterocyclic carbene ligands (Trop-NHCs) have been prepared in order to investigate their structural features and to reveal possible interactions of the olefin unit with the metal center. The precursor imidazolium chloride salts (**R-1**) were generated in a single step using *N*-substituted imidazoles (R = H, Me, DiPP, Ad) and 1 or 2 equiv of Trop-Cl, generating unsymmetrical and symmetrical NHC-olefin hybrids. The structural parameters of the ligands were determined by synthesis and X-ray diffraction analysis of their corresponding gold(I) chloride complexes, revealing highly flexible steric demands of the Trop unit. Conversion of these complexes with halide-abstracting reagents such as AgNTf₂ and NaBARF₂₄ cleanly gave neutral, NTf₂-coordinated complexes of the type [(NHC)Au(NTf₂)] (**R-3**) and the cationic bis-NHC-coordinated complexes [(NHC)₂Au]BARF₂₄ (**R-4**), respectively. The Gagosz-type complexes **R-3** were further tested in the hydration of diphenylacetylene, showing a clear trend in activity depending on the ligand's sensitivity to hydrolysis.

INTRODUCTION

The use of N-heterocyclic carbenes (NHCs) as ancillary ligands in transition-metal-catalyzed reactions has become—among their many uses in organometallic chemistry¹ or organocatalysis²—one of their main applications.^{3–6} Among these, gold(I)-mediated processes have emerged as one of the most active areas of NHC-based catalysis.⁷ The bulky nature and fan-shaped geometry of the most frequently investigated types of ligands ensure sufficient lifetime of the usually in situ generated gold cations of type [(NHC)Au]⁺. These represent the postulated active species of many gold-mediated organic transformations.⁷ Additionally, the strong σ -donating properties of NHC ligands are believed to play a pivotal role in the stabilization of the low-valent gold center, as reported for many other late-transition-metal-catalyzed processes.^{4b,8}

Numerous labile donors have been investigated to function as stabilizing ligands for isolable, catalytically active gold(I) species of formulas [(L)Au-Y], where L represents either a phosphine or NHC ligand and Y is a commonly used weakly bound neutral or anionic donor such as MeCN and other nitrogen-based donors,^{9,10} TfO⁻ (trifluoromethylsulfonate),¹¹

or NTf₂ (bis(trifluoromethylsulfonyl)imide).^{12,13} A series of complexes in which Y represents an olefin ligand have been reported by Widenhoefer et al.,¹⁴ yet their potential to function as precatalysts has not been fully evaluated to date.^{9a} We set out to develop a cationic (NHC)gold(I) system, which incorporates an olefin group tethered to an NHC ligand, in order to study possible olefin gold(I) bonding as well as its potential in catalysis.

Grützmacher et al. have studied the coordination chemistry 5*H*-dibenzo[*a,d*]cyclohepten-5-yl-substituted phosphorus- and nitrogen-based ligands (a.k.a. “dibenzotropyliidene” or “Trop” ligands).^{15,16} Their studies on coinage-metal complexes of Trop-substituted phosphine ligands (“Tropps”) were able to reveal bonding interactions between the olefin group and Cu or Ag centers in certain cases showing tetrahedral (Cu) or strongly distorted trigonal planar and linear geometries around the metal centers (Ag).^{15b}

Received: November 3, 2014



However, in gold(I) complexes supported by these ligands, no such interaction was observed. Attempts to enforce coordination of the olefin unit to the gold center in complex **I** either by removal of the chloride anion by abstraction with a strong Lewis acid or by replacement with a weakly coordinating ligand were unsuccessful.^{15b} A few years after these reports, NMR and X-ray diffraction analysis of the cationic Trop₃P-ligated complex **II** also did not provide any evidence for an interaction between the more electrophilic gold(I) center and the olefin moiety.¹⁷

We reasoned that Trop-NHC ligands might represent better candidates for obtaining the first chelated gold(I) complexes of olefin-functionalized ligands. In comparison to the Tropp systems, the fan-shaped geometry of the analogous NHC ligands and the additional nitrogen atom between the Trop substituent and the donor atom should accommodate ligands with much larger bite angles. This should then lead to weaker distortions of the preferred linear geometry or the also feasible trigonal-planar geometry in the putative cationic gold(I) complexes **III** and **IV** (bearing the symmetrical Trop-NHC ligand “ITrop”), respectively (Figure 1). The dinuclear,

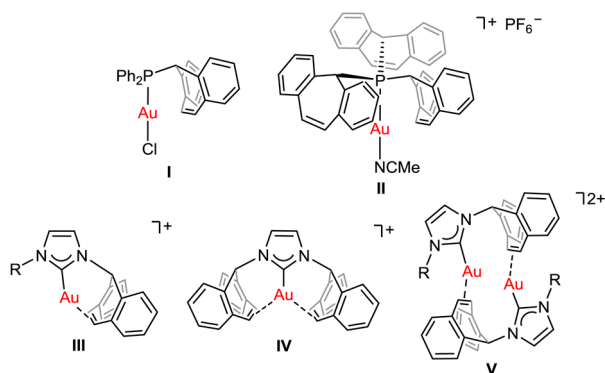


Figure 1. (top) Previously reported Trop-phosphine gold(I) complexes. (bottom) Possible cationic Trop-NHC gold(I) species.

dicationic structure **V**, which represents a common structural motif in the coordination chemistry of coinage metals and bidentate ligands, is also conceivable. This would resemble the bridged analog of the Widenhoefer series of mononuclear NHC olefin complexes.¹⁴

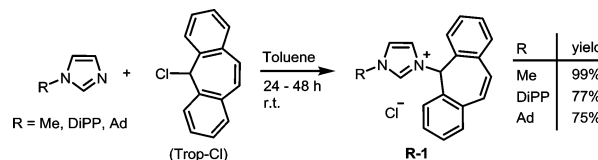
For the single Trop-NHC gold complex reported so far, which one of us reported more than a decade ago, an observation similar to that for the Tropp ligand coordination chemistry was made.¹⁸ The only accessible complex at the time, [(ITrop)Au(PPh₃)]Cl, did not reveal any interaction of the olefin arm with the gold(I) center. However, this complex proved to be resistant toward substitution of the PPh₃ ligand even under harsh conditions. Therefore, neither a complex with a weakly coordinating donor nor a truly naked species of the type [(ITrop)Au]⁺ could be investigated initially.

We now report on the synthesis of gold(I) chloride complexes of a series of new unsymmetrical Trop-NHC ligands and of their previously reported symmetrical congener “ITrop”, for which we have developed a much simpler synthetic access. These complexes provided the opportunity to study the steric properties of the ligands by X-ray diffraction analysis and their reactivity toward halide-abstracting agents containing weakly coordinating or non-coordinating anions with the purpose of investigating possible gold(I)–olefin bonding interactions.

RESULTS AND DISCUSSION

Ligand Synthesis. Due to the high susceptibility of Trop-Cl toward nucleophilic attack, the unsymmetrical ligand precursors **R-1** (R = Me, DiPP, Ad) were obtained easily by stirring solutions of the corresponding *N*-substituted imidazoles and the electrophile in toluene at room temperature for 24–48 h (Scheme 1).¹⁹ As all compounds required multiple washings

Scheme 1. Synthesis of Unsymmetrical Imidazolium Salts



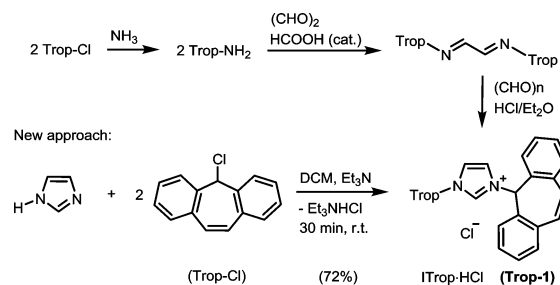
with toluene (R = Me, DiPP) or THF (R = Ad) in order to be obtained in pure form, the lower yields obtained for compounds **DiPP-1** and **Ad-1** are attributable to their higher solubility in comparison to **Me-1**. Since the compounds were hygroscopic and sensitive toward hydrolysis, these were stored under an inert atmosphere until further use.

The symmetrical imidazolium salt **Trop-1** had previously been synthesized following the most common synthetic strategy for symmetrical NHC ligands: Trop-NH₂, which is available from the reaction of Trop-Cl and ammonia at low temperature, can be converted to the corresponding bis-imine of glyoxal, which is then cyclized to the imidazolium salt **Trop-1** with paraformaldehyde in the presence of ethereal HCl.¹⁸ We hoped to introduce a more convenient access using the easily accessible (commercially available) Trop-Cl and imidazole.

Pleasingly, the reaction of 2 equiv of Trop-Cl and imidazole proceeded within minutes in the presence of 1 equiv of triethylamine, forming the imidazolium salt **Trop-1** cleanly. On a preparative scale, the reaction was carried out in dichloromethane, which proceeded smoothly. Removal of the ammonium salt was achieved by extraction of the reaction mixture with water. Pure product was obtained after subsequent washings of the crude product with dry THF and dry diethyl ether. It is important to note that the sensitivity of the imidazolium salt **Trop-1** toward water required the workup to be performed as quickly as possible, before storing the product under an inert atmosphere. Thus, **Trop-1** is now quickly accessible in a single step using commercially available imidazole and Trop-Cl (or in three steps starting from dibenzsuberone) (Scheme 2).

Spectroscopically, the most salient feature of the imidazolium salts is a strongly varying chemical shift value observed for the 2*H*-imidazolium proton signals in the ¹H NMR spectra. While

Scheme 2. Old and Improved Syntheses of ITrop·HCl (**Trop-1**)

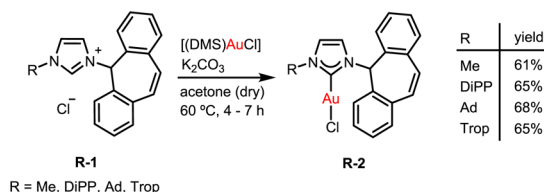


these protons resonate in the expected region above 9 ppm in the *N*-Me- and *N*-Ad-substituted compounds (9.21 and 9.56 ppm, respectively), the corresponding signal in **DiPP-1** is found at 8.11 ppm and—more surprisingly—at 6.82 ppm for **Trop-1**. It is likely that this discrepancy in chemical shifts is caused by the shielding effect of the Trop substituent aryl moieties. These chemical shifts should not be regarded as indicative of the acidity of these protons, since the following complexation reactions did not show substantial differences in reaction times (see below). All resonances of the Trop unit are observed as sharp signals, indicating that only one of the possible endo and exo conformations of the carbocycle is present in solution, as previously reported for Tropp-type ligands. As this working hypothesis was confirmed for the following metal complexes of the Trop-NHC ligands, the spectroscopic characteristics of the Trop unit will be discussed in greater detail in the following section.

Synthesis and Steric Features of Gold(I) Chloride Complexes. Next, we targeted the synthesis of gold(I) chloride complexes. These complexes should serve as models for the characterization of the NHC steric properties and as suitable starting materials for the conversion into cationic gold(I) complexes.

As reported by Grützmacher and co-workers, the isolation of the free ligands is impossible in these systems due to a rapidly occurring rearrangement proceeding most likely via nucleophilic attack of the carbene lone pair on the double bond of the Trop substituent.^{18,19} Therefore, a suitable protocol for the in situ generation/complexation of the ligand had to be found. We sought to apply a mild and convenient protocol for the synthesis of the desired gold(I) chloride complexes, which has recently been introduced by us.²⁰ It involves potassium carbonate as the base at 60 °C using technical grade acetone as solvent under non-inert conditions (Scheme 3).

Scheme 3. Synthesis of Trop-NHC Gold(I) Chloride Complexes



The yields obtained by applying this procedure ranged between 55 and 61% after filtering the crude mixtures through a pad of silica gel. Due to the sensitivity of the starting imidazolium salts toward hydrolysis (vide supra), we were hoping to obtain better yields under dry reaction conditions. Unfortunately, these improved only slightly under otherwise identical conditions. However, it was revealed that the sensitivity of the starting materials toward hydrolysis indeed affected the reactions slightly, as the formation of Trop-OH was observed when the crude products were analyzed by NMR spectroscopy. We also examined yields following two other common in situ protocols used in the synthesis of NHC-metal complexes: formation of silver adducts followed by subsequent transmetalation²¹ and the addition of a solution of KHMDS to a mixture of the imidazolium salt and the metal precursor at low temperature.²² Both procedures proved to be suitable alternatives yet produced similar yields. Therefore, the least

expensive and silver-free protocol involving K_2CO_3 as base remains our method of choice for the preparation of these complexes. Despite the moderate yields, all compounds were obtained in analytical purity and did not show any sensitivity toward moisture, which most likely is due to the fact that the neutral imidazolylidene heterocycle represents a poorer leaving group than its imidazolium counterpart in the compounds **R-1**.

The 1H NMR spectra of the new complexes show the expected patterns, displaying the most characteristic resonances such as the olefinic group as a singlet between 6.86 and 6.97 ppm, the benzylic proton as a singlet between 6.78 and 6.82 ppm, and the aromatic proton of the Trop unit positioned closest to the imidazole heterocycle as a broad doublet between 7.75 and 7.90 ppm ($J \approx 7.3$ Hz). The other aromatic signals of the Trop substituent appear as overlapping multiplets between 7.56 and 7.35 ppm. Only in the case of the *N*-adamantyl-substituted complex **Ad-2** is a significant difference with respect to the other compound signals observed for the benzylic proton, which resonates at some 0.3 ppm higher field (7.12 ppm). In comparison to the Trop unit signals of the imidazolium salts **R-1**, the most significant difference in chemical shift is found not unexpectedly for the benzylic protons, which here are shifted 0.3–1.4 ppm toward lower field.

A comparison of the chemical shifts of the carbene $^{13}C\{^1H\}$ NMR signals of the series **DiPP-2**, **Me-2**, **Trop-2**, and **Ad-2**, which appear at 173.4, 171.0, 169.7, and 168.1 ppm, respectively, reveals that the Trop unit (secondary C atom as *N*-substituent) possesses the expected electron-donating influence, since the chemical shift of the carbene carbon atom of **Trop-2** fits well between those of the *N*-Me ($N-C^{prim}$) and *N*-Ad-substituted compounds ($N-C^{tert}$).

In order to gain insight into the steric characteristics of the ligands, all gold(I) chloride complexes were characterized by X-ray diffraction analysis of crystals obtained in each case by slow vapor diffusion of pentane into concentrated solutions of the compounds in chloroform (Figure 2). The different substitution patterns appear to have little influence on the Au–C^{carbene} and Au–Cl bond lengths, which range between 1.97 and 1.99 Å and between 2.27 and 2.30 Å, respectively, and compare well to other gold(I) chloride complexes of the literature.²³ The Trop substituent adopts two major conformations with respect to the rotation around the N–C^{benz} bond in the solid-state structures. This situation leads to important variations in steric shielding of the metal center by the Trop unit aryl moieties. While in one of the conformations the benzylic C–H bond is oriented nearly perpendicular to the NHC plane, as seen in **Me-2** and **DiPP-2**, **Ad-2** contains the C–H bond nearly within the NHC plane (called “in plane” orientation in the following) while the hydrogen atom is facing in the direction of the metal center. The structural data of **Trop-2** further reveal—in addition to two independent molecules in the unit cell of the crystal lattice—intermediate orientations between both described rotameric forms. In one of these molecules the torsional angles defined by the atoms C^{carbene}–N–C^{benz}–H measure 23.1 and 67.4°, while the other shows significantly larger values of 44.9 and 92.5°, thus reflecting the much stronger steric shielding of the latter metal center and the flexible steric nature of the system. Notably, the “in plane” orientation of the C–H bond while the hydrogen atom faces the opposite direction of the metal center, which would place the olefin donor next to the gold center, was not observed in either structure.

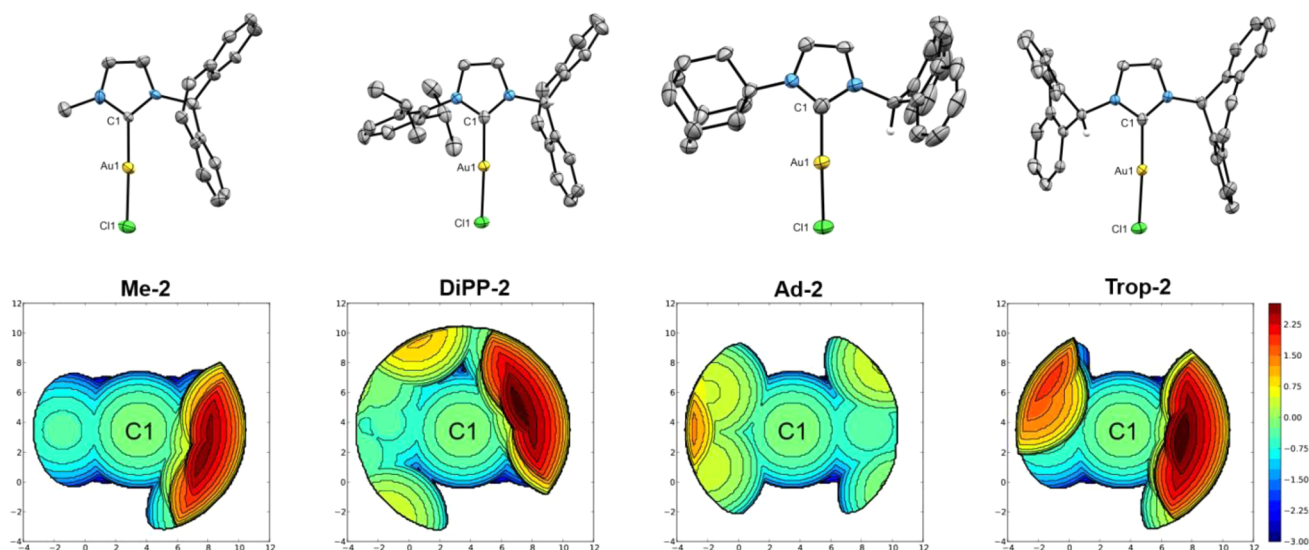


Figure 2. (Top row, from left to right) ORTEP plots of the solid-state structures of the gold(I) chloride complexes **Me-2**, **DiPP-2**, **Ad-2**, and **Trop-2** (only one of the independent molecules found in the unit cell is shown). All hydrogen atoms except for those located at the benzylic positions of the Trop substituents are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. (Bottom row) Steric mapping corresponding to the structures depicted above with a view along the Au–C^{carbene} bond axis.

The variable steric influences of the Trop unit further impose slight distortions of the linear geometry in such a way that the C1–Au1–Cl1 angles diminish slightly toward the opposite side of the more bulky substituent (R = Me, 178.09°; R = DiPP, 177.99°; R = Ad, 178.26°; R = Trop, 176.89°). The “more bulky” substituent (in the solid state) can be identified best by calculating a steric mapping of each structure using the SambVca software developed in the Cavallo group (Figure 2).^{24,25} Furthermore, the software also permits calculation of the “percent buried volume” (%V_{bur}), a quantitative measure for the steric bulk of a ligand, which was introduced by us in collaboration with the Cavallo group.²⁶

As expected, the different orientations of the Trop substituent arising from the rotation around the N–C^{benz} bond create drastic variations in the steric shielding of the metal center. The solid-state structures containing the Trop substituents with the C–H bond oriented perpendicular to the NHC plane thus correspond to steric mappings where large parts of two quadrants residing on the same side of the steric map are severely hindered (**Me-2**, **DiPP-2**, **Trop-2**). In the case of the **DiPP-2** and **Trop-2** structures, which contain an additional bulky substituent as opposed to the N-Me group in **Me-2**, significantly crowded situations are obtained with %V_{bur} values ranging between 43.4 and 51.1.

Comparison of these values with those reported in the literature for two popularly investigated ligands, IPr and its much bulkier analogue IPr* (1,3-bis(2,6-diphenylmethyl-4-methylphenyl)imidazol-2-ylidene),²⁷ reveal that, in fact, similarly bulky steric environments around the metal center are being created by these Trop ligands (see Table 1)—at least according to the %V_{bur} values of the solid state. Surprisingly, the value calculated for **DiPP-2** even slightly exceeds that of IPr*.

However, the limit of the buried volume model, which strictly relies on the solid-state structure of metal complexes, becomes evident on comparison of these values to those of **Ad-2**, which contains the least sterically shielding conformation of the Trop substituent with respect to the metal center (“in plane” conformation with the C^{benz}–H bond directed toward the metal center). A value of %V_{bur} even lower than in the case

Table 1. Comparison of R-2 with [(NHC)AuCl] Analogues

[(NHC)AuCl]	Au–C ^{carbene} (Å)	%V _{bur} ^a
NHC = IMe ^{me,b,c}	1.987(8)	26.2
Me-2	1.992(18)	40.2
NHC = IAd ^c	1.989(2)	39.8
Ad-2	1.993(11)	37.5
NHC = IPr ^c	1.942(3)	44.5
DiPP-2	1.972(3)	51.1
NHC = IPr* ^d	1.987(7)	50.4
Trop-2	1.986(3)/1.990(3)	43.4/49.4

^aParameters used in SambVca calculations: sphere radius, 3.50 Å; Au–Cl, 2.00 Å; mesh spacing, 0.05; Bondi radius, 1.17. H atoms excluded.

^bIMe^{me} = 1,3,4,5-tetramethylimidazol-2-ylidene. ^cTaken from ref 23.

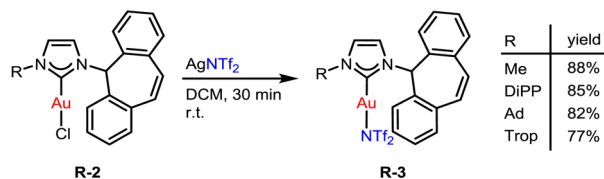
^dTaken from ref 27c.

of **Me-2** was calculated (37.5 vs 40.2, respectively), although the spatial requirements of an adamantyl group are certainly substantially higher than those of a methyl group.

With the main characteristics of the individual ligands being elucidated, we set out to convert the gold(I) chloride complexes into compounds incorporating a more electrophilic gold(I) center in order to facilitate gold–olefin interactions. For this study we chose two halide-abstracting agents containing weakly coordinating anions with largely differing abilities to coordinate to the metal center: NaBARF₂₄ (practically not coordinating)²⁸ and AgNTf₂ (giving rise to weakly bound N-metalated complexes).¹²

In accordance with the reported procedure, the neutral complexes **R-3** were obtained in good yields by stirring equimolar mixtures of the gold(I) chloride complexes **R-2** and AgNTf₂ in dichloromethane at room temperature for 15–30 min (Scheme 4).¹² All compounds proved to be crystalline, air-stable materials which were obtained analytically pure. In the case of **Me-3**, slow decomposition was observed in CDCl₃ solution over the course of a few days and in the solid state over several weeks. The coordination of the NTf₂ anion to the gold(I) center was confirmed for all compounds by X-ray

Scheme 4. Synthesis of Gagosz-Type Complexes R-3



diffraction analysis of crystals obtained by slow vapor diffusion of pentane into concentrated chloroform solutions.

In agreement with the NMR data, which do not show any significant shifts of the olefin unit in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra in comparison to the signals of **R-2**, an interaction between the olefin moiety and the metal center was not detected. In fact, the Trop unit signals in the ^1H NMR spectra appear at nearly the same chemical shifts as in **R-2**, while only the imidazolylidene protons experience minor low-field shifts of about 0.1 ppm, indicating the more electrophilic nature of the gold(I) center. However, a profound steric influence of the Trop substituent on the bulky anion is noticeable in the solid-state structures of these complexes (Figure 3). As a function of the conformation of the Trop unit, different torsion angles between the NHC plane and the NTf_2^- are observed. This can be quantified roughly by the torsional angles defined by the sulfur atoms of the NTf_2^- anion and the heterocycle nitrogen

atoms (for details, see Table 2). Thus, in the structure of **Ad-3**, in which the Trop substituent again adopts the “least bulky” conformation as in its chloride analogue **Ad-2** ($\text{C}^{\text{benz}}-\text{H}$ bond within the NHC plane), the NTf_2^- is twisted only slightly with respect to the NHC plane. The other solid-state structures show the Trop substituent in the “more bulky” conformations, leading to notable distortions of the complex geometry due to steric interaction with the NTf_2^- unit. While in **DiPP-3**, again containing the “most bulky” Trop orientation ($\text{C}^{\text{benz}}-\text{H}$ bond perpendicular to the NHC plane), the NTf_2^- is oriented nearly perpendicular to the NHC plane (as exemplified by the torsional angle defined by the atoms $\text{S1}-\text{S2}-\text{N5}-\text{N2}$ of 93.47°), the “intermediately bulky conformations” in **Me-3** and **Trop-3** lead to smaller distortions (130.48 and 123.73° , respectively; see Table 2 for details).²⁹ While these repulsive interactions between the expansive Trop moiety and the NTf_2^- ligand do not seem to significantly affect the Au–N bond distances, the deviation from the ideal linear geometry indeed is greatest in the **DiPP-3** and **Trop-3** complexes (5.2 and 4.9° , respectively), which possess the smallest torsional angles (see Table 2).

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the same decreasing order of chemical shift values of the carbene carbon signals was observed for the series **DiPP-3**, **Me-3**, **Trop-3** and **Ad-3**, as seen before for the corresponding chloride complexes **R-2** (Table 2), which

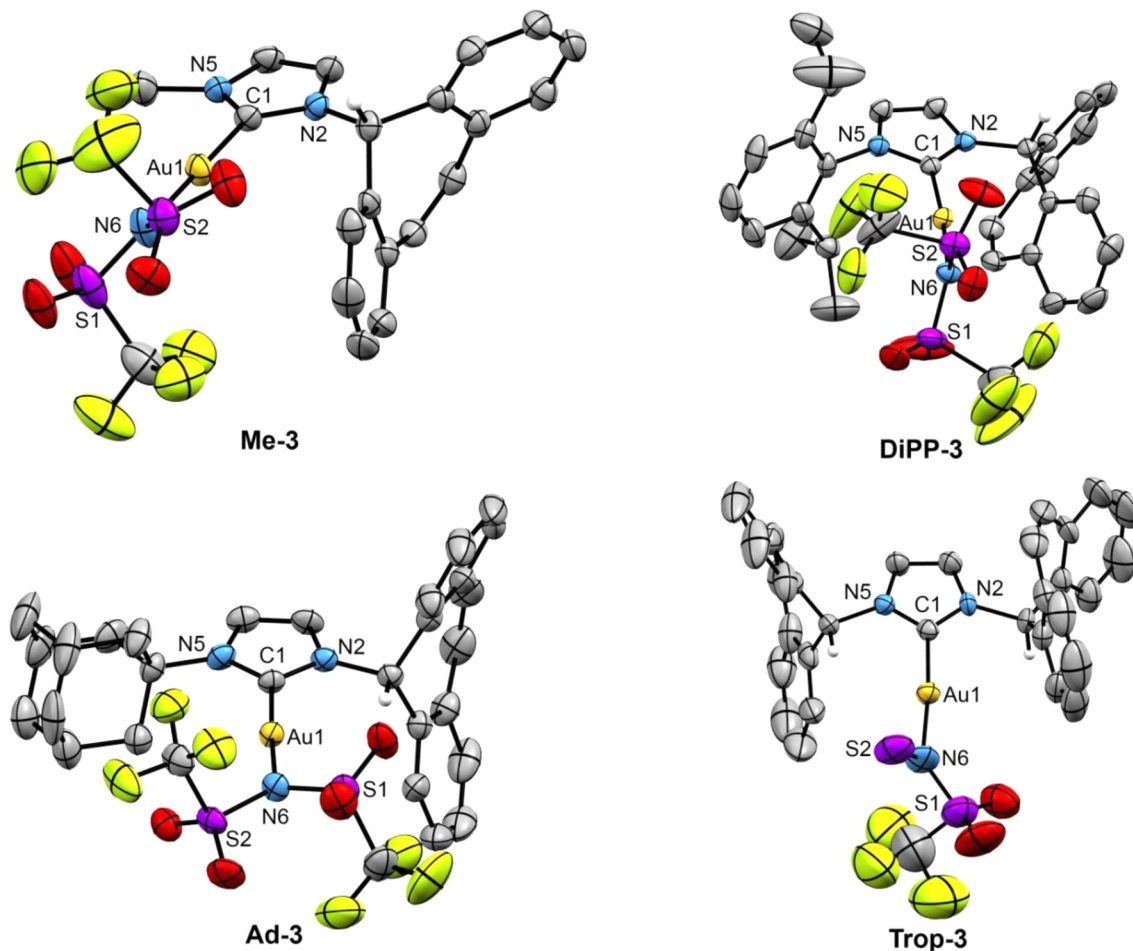


Figure 3. ORTEP plot of the solid-state structures of **Me-3** (top left), **DiPP-3** (top right), **Ad-3** (bottom left), and **Trop-3** (the CF_3 group at S2 showed disorder and is omitted for clarity) gold complexes. Solvent molecules and hydrogen atoms except for those located at the benzylic positions of the Trop substituents are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Important Spectroscopic and Structural Parameters of the Gold(I) Compounds of This Study

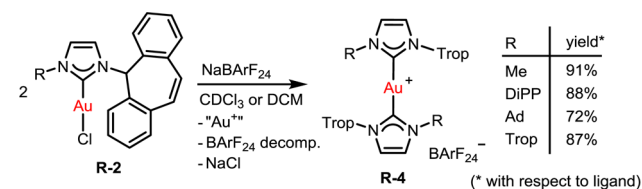
compound	Au1–C1/Å	Au1–Y ^a /Å	$\delta(^{13}\text{C}^{\text{carbene}})^b$ /ppm	C1–Au–Y/deg	torsion ^c /deg
[(Me-NHC-Trop)AuCl]	1.992(18)	2.299(5)	171.02	178.1(5)	
[(Me-NHC-Trop)AuNTf ₂]	1.976(6)	2.090(6)	163.27	177.1(2)	130.48 ^d
[(Me-NHC-Trop) ₂ Au]BArF ₂₄	2.021(6)	2.021(6)	184.30	179.25(15)	92.68 ^e
[(DiPP-NHC-Trop)AuCl]	1.972(3)	2.2732(9)	173.43	177.99(8)	
[(DiPP-NHC-Trop)AuNTf ₂]	1.975(3)	2.096(3)	166.28	174.81 (13)	93.47 ^f
[(DiPP-NHC-Trop) ₂ Au]BArF ₂₄			182.90		
[(Ad-NHC-Trop)AuCl]	1.993(11)	2.273(3)	168.11	178.2(3)	
[(Ad-NHC-Trop)AuNTf ₂]	1.973(7)	2.088(7)	159.37	176.9(3)	166.33 ^g
[(Ad-NHC-Trop) ₂ Au]BArF ₂₄	2.037(5)	2.037(5)	180.46	175.1(2)	114.58 ^h
[(Trop-NHC-Trop)AuCl]	1.986(3)/1.990(3)	2.2902(13)/2.3007(10)	169.68	177.34(10)/176.89(10)	
[(Trop-NHC-Trop)AuNTf ₂]	1.977(7)	2.081(8)	161.57	175.4(3)	123.73 ⁱ
[(Trop-NHC-Trop) ₂ Au]BArF ₂₄			184.29		

^aY = Cl, N6, C^{carbene}. ^bMeasured in CDCl₃. ^cTorsion angles are defined in footnotes d–i. ^dS1–S2–N5–N2. ^eN2–N5–N2¹–N5¹. ^fS1–S2–N5–N2. ^gS1–S2–N2–N5. ^hN2–N5–N32–N35. ⁱS1–S2–N2–N5.

corroborates their classification as being as fairly electron rich N-alkyl-substituted NHC donors.

Our investigations into the conversion of the gold(I) chloride complexes with NaBArF₂₄ began by monitoring the reactions by in situ NMR spectroscopy in CDCl₃ (Scheme 5). Addition

Scheme 5. Formation of Cationic Gold Complexes R-4



of the solvent to a mixture of NaBArF₂₄ and Me-2 immediately led to the formation of a purple coloration and a black precipitate. ¹H NMR spectroscopy recorded shortly thereafter indicated the formation of a new NHC-containing species (imidazolylidene signals at higher field: 6.58 and 6.27 ppm) next to multiple new signals in the BArF₂₄[−] region at field lower than 7.5 ppm. In accordance with this, ¹⁹F NMR spectroscopy showed several new fluorine-containing species close to the BArF₂₄ resonance, which roughly integrated to the same value

as the new signals combined (see the Supporting Information). Washing of the crude product with pentane was able to reduce these fluoride-containing by-products to trace amounts and made it clear that the new compound consisted of a ligand to BArF₂₄[−] ratio of 2:1. Therefore, it seemed most likely that the corresponding cationic bis-NHC complex had formed under loss of half an equivalent of highly reactive, “naked” cationic gold(I), which presumably is responsible for the immediate reaction with the BArF₂₄ anion until all of it is consumed. The occurrence of the carbene signal in the ¹³C{¹H} NMR spectrum at 184.3 ppm was also in accordance with the formation of a cationic, bis-NHC-coordinated complex.³⁰ Olefin-coordinated species were not detected.

Further purification of the compound was achieved by filtration through silica gel using dichloromethane. This further treatment permitted us to obtain pure material, as gauged by elemental analysis, and also allowed single crystals to be grown for X-ray diffraction analysis by slow vapor diffusion of pentane into a solution of the compound in CHCl₃, revealing the expected cationic structure (Figure 4).

For the more bulky complexes of the series, we hoped that possible olefin-stabilized cationic gold species would be more favored over the bimolecular decomposition products. However, similar in situ ¹H and ¹⁹F NMR spectra were obtained,

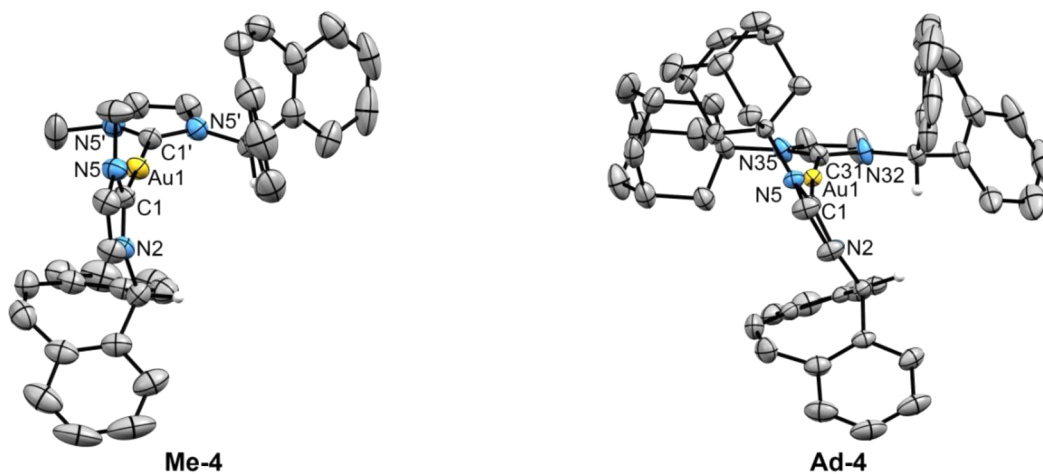


Figure 4. ORTEP plot of the solid-state structures of Me-4 (left) and Ad-4 (right). All hydrogen atoms (except for those located at the benzylic positions of the Trop substituents), counterions, and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

showing the decomposition products of the BARF_{24} anion in nearly the same ratios as before. Notably, full conversion of the starting complexes was only obtained after stirring at room temperature overnight, but intermediate species were again not detected. The larger scale reactions were carried out in dichloromethane as solvent, and workup proceeded in each case similarly to the method used for **Me-1**. All compounds were obtained in good to high yields (with respect to the starting ligand) and were fully characterized by NMR spectroscopy and by elemental analysis.

Obviously, bimolecular decomposition is strongly favored over the formation of ligand-chelated structures—at least in the case of metal complexes bearing NHC ligands which do not exceed buried volumes of approximately 50%. It can only be postulated that a much greater steric demand of the second *N*-substituent is required in order to sufficiently stabilize a possible olefin-coordinated species. Even though bimolecular decomposition is well-known to accompany the formation of cationic (NHC)gold(I) complexes,³¹ clean and quantitative formation of these complexes was nevertheless surprising to us (no NHC-containing side products were observed). The lower than theoretical yields are simply a consequence of the extensive purification (washing, filtration, and—if needed—recrystallization) required in order to remove the decomposition products of the BARF_{24} anion.

In order to exclude the notion that the formation of these by-products is not just specific to the Trop-NHC systems of this study, a control experiment was conducted using $[\text{Au}(\text{IAd})\text{Cl}]$. In situ NMR spectroscopy in CDCl_3 revealed an identical signal pattern for the formed fluorinated aryl compounds in the ^{19}F NMR, and the ^1H NMR spectrum again showed the clean formation of the corresponding cationic bis-NHC complex, next to the same new signals at low field below 7.5 ppm. It must therefore be assumed that the “naked” gold fragments formed in activations of (NHC)Au^I chloride complexes by NaBARF_{24} are rapidly reduced to colloidal gold by reaction with the borate salt. The cleavage of a C–B bond of the BARF_{24} anion by a cationic gold fragment has recently been reported by Straub and co-workers and supports this conclusion.³² Due to the extreme steric bulk of the NHC ligand employed in their study, the bond activation proceeds only slowly over several days.

For complex **Ad-4**, we were again able to grow crystals suitable for X-ray diffraction analysis by layering a CHCl_3 solution of the compound with pentane (Figure 4). While in the previous solid-state structures the complex geometry was governed mainly by the Trop substituent expansive orientation toward the metal center, the bis-NHC-ligated complexes reveal that the second *N*-substituent can also have a significant impact. Figure 4 shows the solid-state structures of **Me-4** and **Ad-4**, which demonstrate that the presence of the large *N*-Ad group leads to a repulsion with the Trop substituents of the opposing NHC ligand. Consequently, a nearly perpendicular orientation of the NHC planes as in **Me-4** is not feasible in **Ad-4**, leading to an increase in the angle between the NHC planes to some 115° . This steric interaction further becomes apparent in the lengthening of the $\text{C}^{\text{carbene}}\text{—Au}$ bonds from ca. 2.02 Å in **Me-4** to 2.04 Å in **Ad-4**.

Preliminary Catalytic Study. Although the ligands have so far not been able to reveal olefin–gold interactions, their strongly variable steric demands maintained our interest in investigating their application in catalysis. Keeping the significant influence of the Trop moiety on the opposing coordinating NTf_2^- unit in mind, a beneficial influence on

catalysis was envisaged for the Gagosz-type complexes **R-3**. It has been postulated that a substantial steric congestion of the NHC ligand leads to more facile dissociation of the NTf_2^- anion, thus leading to higher activities due to the increase in concentration of the catalytically active gold cation $[\text{AuL}]^+$.³³

As a typical benchmark reaction, the hydration of alkynes—more specifically of diphenylacetylene—was chosen.³⁴ Quickly it became clear that only precatalyst **DiPP-3** was considerably active in this reaction, showing full conversion at 2.5 mol % catalyst loading after 24 h (Table 3, entry 5). The reactions

Table 3. Hydration of Diphenylacetylene^a

entry	$[\text{Au}(\text{NHC})(\text{NTf}_2)]$	loading (mol %)	conversn (%) ^a
1	Me-3	5	0
2	NHC = IAd ^b	5	9
3	Ad-3	5	9
4	NHC = IPr ^c	0.25	88 ^d
5	DiPP-3	2.5	>99
6	DiPP-3	2.0	86
7	Trop-3	5	0

^aDetermined by GC; averaged values of two runs. ^bPrepared according to ref 12b. ^cPrepared according to ref 13. ^dAfter 3 h reaction time.

involving the other precatalysts indicated rapid decomposition of the complexes by the formation of black precipitates within the first few minutes. Thus, even at 5 mol % catalyst loading complexes **Me-3** and **Trop-3** showed no conversion of the substrate, while **Ad-3** showed little catalytic activity (9% conversion after 24 h).

Interestingly, the parent systems to the DiPP- and Ad-substituted Trop ligands of this study, $[\text{Au}(\text{IPr})(\text{NTf}_2)]$ and $[\text{Au}(\text{IAd})(\text{NTf}_2)]$, provided some insights into the nature of this reactivity trend. As the IAd-based precatalyst performs similarly to **Ad-3** (also 9% conversion) but not as poorly as **Me-3** and **Trop-3**, it seems that even very bulky tertiary alkyl *N*-substituents are not well tolerated in water-inclusive gold(I) catalysis. The systems bearing *N*-substituents which are most susceptible to hydrolysis, **Me-3** and **Trop-3**, therefore do not show any catalytic activity. In this regard, it is not surprising that **DiPP-2**, bearing one hydrolysis-resistant *N*-substituent, shows drastically enhanced catalytic activity over **Ad-3** but is far less effective than its parent catalyst system $[\text{Au}(\text{IPr})(\text{NTf}_2)]$ (Table 3, entry 4).

CONCLUSION

In summary, a series of new gold(I) complexes bearing dibenzotropyliene-functionalized NHC ligands have been accessed starting from the corresponding imidazolium chloride salts (**R-1**), which are accessible in a single step from *N*-substituted imidazoles (*N*-alkyl, *N*-aryl or *N*-H) and Trop-Cl. The steric features of the ligands were evaluated in the solid-state structures of the gold(I) chloride complexes **R-2**, which revealed drastically varying steric shielding of the metal center depending on the orientation of the Trop moiety. This was visualized by calculating the steric mapping of these complexes and quantified by the $\%V_{\text{bur}}$ values. The most bulky ligand showed a surprisingly high $\%V_{\text{bur}}$ of 51.1%, thus surpassing

even the value calculated for one of the most commonly used ligands, the very bulky NHC species IPr*.

Reacting the gold(I) chloride complexes (**R-2**) with halide abstractors such as AgNTf₂ and NaBarF₂₄ led to the formation of the Gagosz-type complexes (**R-3**) and cationic bis-NHC-ligated complexes of the type [Au(NHC)₂]BarF₂₄ (**R-4**), respectively. Unfortunately, an interaction between the olefin unit of the ligands and the gold center was never observed; however, the Trop unit's significant steric effects on the NTf₂ ligands implicated its potential application in catalysis.

However, it was revealed that—at least for water-inclusive gold(I) catalysis—the catalysts lack sufficient stability for efficient catalysis (as another common symmetrical *N*-alkyl-substituted NHC ligand did as well). Full conversion was only achieved for the *N*-aryl-substituted precatalyst DiPP-3, presumably due to its decreased sensitivity toward hydrolysis under the reaction conditions. We are currently exploring the activity of these complexes in non-water-inclusive catalytic reactions.

Due to the highly flexible nature of the Trop-NHC system, our future efforts will be directed toward the design of new ligands with restricted rotation around the N–C^{Trop} bonds in order to preorganize chelation of the ligand. We believe the simple synthetic access to the Trop-substituted imidazolium salts will be key in finding suitable alternatives.

EXPERIMENTAL SECTION

General Information on reagents and synthetic details, X-ray diffraction data, and details of data collection can be found in the Supporting Information.

Preparation of (Me-NHC-Trop)·HCl (Me-1). Under an inert gas atmosphere, *N*-methylimidazole (2.19 g 26.7 mmol) was added slowly to a solution of Trop-Cl (5.50 g, 24.3 mmol) in dry toluene (150 mL) in a 250 mL round-bottom flask. The mixture was stirred for 24 h, leading to the precipitation of a white solid which was collected on a frit under inert conditions, washed with toluene (5 × 100 mL), and then dried under vacuum at 50 °C for 72 h. **Me-1** was obtained as a very hygroscopic white powder (7.4 g, 99% yield). ¹H NMR (500.13 MHz, CDCl₃): 9.21 (s, NCHN), 7.91 (bd, ³J_{HH} = 7.3 Hz, 2H, C^{benz}C^{quart}C^{Ar}H), 7.58–7.48 (m, 6H, C^{Ar}H), 7.20 (d, ³J_{HH} = 1.5 Hz, 1H, MeNCHCHN), 7.06 (s, 1H, C^{benz}H), 6.94 (s, 2H, C^{olef}H), 6.56 (d, ³J_{HH} = 1.7 Hz, 1H, MeNCHCHN), 3.95 (s, 3H, MeN). ¹³C{¹H} DEPTQ NMR (125.76 MHz, CDCl₃): 137.43 (NCHN), 134.21 (C^{quart} trop), 132.32 (C^{quart} trop), 131.44 (C^{benz}C^{quart}C^{Ar}H), 130.84 + 130.79 (C^{olef}H + C^{Ar}H), 130.23 (C^{Ar}H), 130.09 (C^{Ar}H), 122.21 (s, MeNCHCHN), 121.47 (s, MeNCHCHN), 69.33 (C^{benz}H), 36.95 ((H₃C)N). MS (ESI⁺, MeCN): calcd, 273.14 (M – Cl⁺), 191.09 (dibenzotropylium cation); found, 273.21, 191.14.

Preparation of (DiPP-NHC-Trop)·HCl (DiPP-1). Under argon, a solution of Trop-Cl (227 mg, 1.00 mmol) in dry toluene (4 mL) was added slowly to a solution of *N*-DiPP-imidazole (251 mg, 1.10 mmol) in dry toluene (6 mL). The mixture was stirred for 2 days, leading to the precipitation of a white solid which was collected on a frit and washed with dry toluene (2 × 5 mL) and then with dry diethyl ether (3 × 10 mL). The solid remaining on the frit was dried under a stream of nitrogen (to avoid formation of a sticky oil due to the hygroscopic behavior of the substance) and then under vacuum at 80 °C for 3 days to give the title compound as a white powder (350 mg, 77% yield). ¹H NMR (500.13 MHz, CDCl₃): 8.38 (ps-d, J_{HH} = 7.6 Hz, 2H, C^{benz}C^{quart}C^{Ar}H), 8.22 (s, 1H, C^{benz}H), 8.11 (s, 1H, NCHN), 7.60–7.55 (m, 2H, C^{Ar}H), 7.50–7.42 (m, 5H, 4C^{Ar}H + *p*-C^{DiPP}H), 7.21 (d, ³J_{HH} = 7.9 Hz, 2H, *m*-C^{DiPP}H), 7.07 (t, ³J_{HH} = 1.7 Hz, 1H, DiPP-NCHCHN), 6.97 (t, ³J_{HH} = 1.8 Hz, 1H, DiPP-NCHCHN), 6.94 (s, 2H, C^{olef}H), 2.30 (sept, ³J_{HH} = 6.8 Hz, 2H, CH(CH₃)₂), 1.09 (d, ³J_{HH} = 6.6 Hz, 12H, 2 × CH(CH₃)₂). ¹³C{¹H} DEPTQ NMR (125.76 MHz, CDCl₃): 145.70 (C^{DiPP}-N), 137.00 (NCHN), 134.08 (C^{quart} trop), 133.17 (C^{quart} trop), 132.69 (C^{benz}C^{quart}C^{Ar}H), 131.83 (*p*-C^{DiPP}H),

130.72 (C^{olef}H), 130.52 (C^{Ar}H), 130.17 (C^{Ar}H), 129.80 (C^{Ar}H), 124.72 (*m*-C^{DiPP}H), 123.14 (s, DiPP-NCHCHN), 122.54 (s, DiPP-NCHCHN), 68.51 (C^{benz}H), 28.51 (CH(CH₃)₂), 24.55 (CH(CH₃)₂(CH₃)^b), 24.38 (CH(CH₃)₂(CH₃)^b). MS (ESI⁺, MeCN): calcd, 419.25 (M – Cl⁺), 191.09 (dibenzotropylium cation); found 419.24, 191.08.

Preparation of (Ad-NHC-Trop)·HCl (Ad-1). Under argon, a solution of Trop-Cl (227 mg, 1.00 mmol) in dry toluene (4 mL) was added slowly to a solution of *N*-Ad-imidazole (222 mg, 1.10 mmol) in dry toluene (6 mL). The mixture was stirred for 24 h, leading to the precipitation of a sticky white solid which was triturated with dry THF (2 × 5 mL), a mixture of dry THF and diethyl ether (2/1, 1 × 5 mL), and finally dry diethyl ether (1 × 5 mL). The solid was dried under vacuum at 50 °C for 3 days to give the title compound as a white powder (322 mg, 75% yield). ¹H NMR (400.30 MHz, CDCl₃): 9.56 (s, 1H, NCHN), 8.23 (ps-d, J_{HH} = 7.5 Hz, 2H, C^{benz}C^{quart}C^{Ar}H), 7.83 (s, 2H, C^{benz}H), 7.58–7.50 (m, 2H, C^{Ar}H), 7.49–7.42 (m, 4H, C^{Ar}H), 7.11 (s, 1H, C^{limi}H), 6.96 (s, 1H, C^{olef}H), 6.87 (bs, 1H, C^{limi}H), 2.23 (s, 3H, C^{Ad}H), 2.00 (s, 6H, C^{Ad}H₂), 1.71 (s, 6H, C^{Ad}H₂). ¹³C{¹H} DEPTQ NMR (100.66 MHz, CDCl₃): 134.62 (NCHN), 134.30 (C^{quart} trop), 133.35 (C^{quart} trop), 132.60 (C^{benz}C^{quart}C^{Ar}H), 131.03 (C^{olef}H), 130.41 (C^{Ar}H), 130.36 (C^{Ar}H), 129.64 (C^{Ar}H), 121.69 (s, C^{limi}H), 116.80 (s, C^{limi}H), 68.26 (C^{benz}H), 60.36 (C^{quart}-N), 42.75 (C^{Ad}H₂), 35.39 (C^{Ad}H₂), 29.45 (C^{Ad}H). MS (ESI⁺, MeCN): calcd, 393.23 (M – Cl⁺), 191.09 (dibenzotropylium cation); found, 393.20, 191.04.

Preparation of (Trop-NHC-Trop)·HCl (Trop-1). Under argon, a solution of Trop-Cl (499 mg, 2.20 mmol) in dry DCM (5 mL) was added slowly to a solution of imidazole (68.1 mg, 1.00 mmol) and NEt₃ in dry DCM (15 mL). The mixture was stirred for 30 min and was then washed with water (2 × 5 mL), dried over MgSO₄, and evaporated to dryness as quickly as possible. The residue was triturated with dry THF (3 × 5 mL) and then dry diethyl ether (2 × 10 mL). Drying under vacuum at 80 °C for 3 days (which was required for fully removing all of the solvent from the solid) led to a pale yellow coloration of the compound (349 mg, 72%). ¹H NMR (500.13 MHz, CDCl₃): 7.86 (dd, ³J_{HH} = 7.3 Hz, ³J_{HH} = 1.5 Hz, 4H, C^{benz}C^{quart}C^{Ar}H), 7.45–7.34 (m, 12H, C^{Ar}H), 7.14 (s, 2H, C^{benz}H), 6.82 (s, 1H, NCHN), 6.75 (s, 2H, C^{olef}H), 6.39 (d, ⁴J_{HH} = 1.7 Hz, 2H, CH^{limi}). ¹³C{¹H} DEPTQ NMR (125.76 MHz, CDCl₃): 134.68 (NCN), 133.92 (C^{quart} trop), 132.62 (C^{quart} trop), 131.47 (C^{benz}C^{quart}C^{Ar}H), 130.50 (C^{olef}H), 130.16 (C^{Ar}H), 130.04 (C^{Ar}H), 129.72 (C^{Ar}H), 120.98 (s, C^{limi}H), 68.40 (C^{benz}H). MS (ESI⁺, MeCN): calcd, 449.20 (M – Cl⁺), 191.09 (dibenzotropylium cation); found, 449.19, 191.09.

Preparation of [(Me-NHC-Trop)AuCl] (Me-2). Me-1 (61.7 mg, 200 μmol), [(DMS)AuCl] (58.9 mg, 200 μmol), and K₂CO₃ (55.3 mg, 400 μmol) were suspended in dry acetone (3 mL) and were stirred at 60 °C for 4 h. The mixture was filtered through a pad of Celite (glass pipet: one-third filled), and the filtrate was evaporated to dryness on a rotary evaporator. After the crude product was filtered quickly through a pad of silica gel (glass pipet: one-third filled) and the pad was rinsed with dichloromethane (3 × 1.5 mL), the filtrate was reduced to approximately 1 mL and the product was precipitated by slow addition of pentane with vigorous stirring. After the mother liquor was decanted, the precipitate was washed with pentane (2 × 2 mL) and then dried under vacuum to give **Me-2** as a microcrystalline white solid (61.7 mg, 61% yield). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of **Me-2** in CHCl₃. Anal. Calcd for C₁₉H₁₆AuClN₂ (504.76 g/mol): C, 45.21; H, 3.19; N, 5.55. Found: C, 45.20; H, 3.36; N, 5.38. ¹H NMR (400.13 MHz, CDCl₃): 7.81 (ps-d, ³J_{HH} = 7.3 Hz, 2H, C^{benz}C^{quart}C^{Ar}H), 7.53–7.47 (m, 2H, C^{Ar}H), 7.46–7.43 (m, 4H, C^{Ar}H), 6.95 (s, 2H, C^{olef}H), 6.78 (s, 1H, C^{benz}H), 6.62 (d, ³J_{HH} = 2.0 Hz, 1H, MeNCHCHN), 6.58 (d, ³J_{HH} = 2.0 Hz, 1H, MeNCHCHN), 3.68 (s, 3H, MeN). ¹³C{¹H} DEPTQ NMR (100.61 MHz, CDCl₃): 171.02 (NCN), 134.55 (C^{quart} trop), 134.40 (C^{quart} trop), 131.57 (C^{benz}C^{quart}C^{Ar}H), 131.07 (C^{olef}H), 130.47 (C^{Ar}H), 129.93 (C^{Ar}H), 129.19 (C^{Ar}H), 120.96 (s, MeNCHCHN), 120.00 (s, MeNCHCHN), 70.84 (C^{benz}H) 38.93 ((H₃C)N).

Preparation of [(DiPP-NHC-Trop)AuCl] (DiPP-2). DiPP-1 (91.0 mg, 200 μmol), [(DMS)AuCl] (58.9 mg, 200 μmol), and K_2CO_3 (55.3 mg, 400 μmol) were suspended in dry acetone (3 mL) and were stirred at 60 $^\circ\text{C}$ for 7 h. The mixture was filtered through a pad of silica (glass pipet: one-third filled) and the filtrate was evaporated to dryness on a rotary evaporator. After the crude product was filtered through a pad of silica gel (glass pipet: one-third filled) and the pad was rinsed with dichloromethane (3 \times 1.5 mL), the filtrate was evaporated to dryness. Slow vapor diffusion of pentane (2.5 mL) into a solution of the crude product in CHCl_3 provided DiPP-2 as colorless plates (80 mg, 68% yield) which were suitable for X-ray diffraction analysis. Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{AuClN}_2$ (651.00 g/mol): C, 55.35; H, 4.64; N, 4.30. Found: C, 55.23; H, 4.62; N, 4.36. ^1H NMR (500.13 MHz, CDCl_3): 7.83 (ps-d, $J_{\text{HH}} = 7.5$ Hz, 2H, $\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 7.56–7.51 (m, 2H, C^{ArH}), 7.50–7.47 (m, 4H, C^{ArH}), 7.37 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H, $p\text{-C}^{\text{DiPP}}\text{H}$), 7.14 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, $m\text{-C}^{\text{DiPP}}\text{H}$), 6.97 (s, 2H, C^{olefH}), 6.78 (s, 1H, C^{benzH}), 6.63 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 1H, C^{ImiH}), 6.61 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 1H, C^{ImiH}), 2.23 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.17 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, $2 \times \text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$), 1.04 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, $2 \times \text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 173.43 (NCN), 145.53 ($\text{C}^{\text{DiPP-N}}$), 134.94 ($\text{C}^{\text{quart trop}} + o\text{-C}^{\text{DiPP}}$), 134.32 ($\text{C}^{\text{quart trop}}$), 131.21 ($\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 130.79 (C^{olefH}), 130.44 ($p\text{-C}^{\text{DiPP}}\text{H}$), 130.27 (C^{ArH}), 129.93 (C^{ArH}), 129.20 (C^{ArH}), 124.14 ($m\text{-C}^{\text{DiPP}}\text{H}$), 121.11 (s, C^{ImiH}), 120.96 (s, C^{ImiH}), 70.60 (C^{benzH}), 28.33 ($\text{CH}(\text{CH}_3)_2$), 24.40 ($\text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$), 24.29 ($\text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$).

Preparation of [(Ad-NHC-Trop)AuCl] (Ad-2). Ad-1 (85.8 mg, 200 μmol), [(DMS)AuCl] (58.9 mg, 200 μmol) and K_2CO_3 (55.3 mg, 400 μmol) were suspended in dry acetone (3 mL) and were stirred at 60 $^\circ\text{C}$ for 7 h. The mixture was filtered through a pad of Celite (glass pipet: one-third filled) and the filtrate was evaporated to dryness on a rotary evaporator. After the crude product was filtered quickly through a pad of silica gel (glass pipet: one-third filled) and the pad was rinsed with dichloromethane (3 \times 1.5 mL), the filtrate was evaporated to dryness. Trituration of the residue with pentane (2 \times 2 mL) and drying under vacuum gave Ad-2 as a white solid (85 mg, 68% yield). Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{AuClN}_2$ (624.96 g/mol): C, 53.81; H, 4.52; N, 4.48. Found: C, 53.68; H, 4.61; N, 4.51. ^1H NMR (300.06 MHz, CDCl_3): 7.90 (ps-d, $J_{\text{HH}} = 7.3$ Hz, 2H, $\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 7.52–7.44 (m, 2H, C^{ArH}), 7.44–7.41 (m, 4H, C^{ArH}), 7.15 (s, 1H, C^{benzH}), 6.97 (s, 2H, C^{olefH}), 6.79 (d, $^3J_{\text{H,H}} = 2.2$ Hz, 1H, C^{ImiH}), 6.74 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 1H, C^{ImiH}), 2.39 (d, $^3J_{\text{HH}} = 3.1$ Hz, 6H, C^{AdH_2}), 2.18 (s, C^{AdH}), 1.69 (t, $J_{\text{HH}} = 2.9$ Hz, 6H, C^{AdH_2}). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (75.45 MHz, CDCl_3): 168.11 (NCN), 134.83 ($\text{C}^{\text{quart trop}}$), 134.48 ($\text{C}^{\text{quart trop}}$), 132.99 ($\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 131.27 (C^{olefH}), 130.57 (C^{ArH}), 129.93 (C^{ArH}), 129.06 (C^{ArH}), 118.68 (s, C^{ImiH}), 116.42 (s, C^{ImiH}), 72.26 (C^{benzH}), 59.41 ($\text{C}^{\text{quart-N}}$), 44.21 (C^{AdH_2}), 35.84 (C^{AdH_2}), 29.93 (C^{AdH}).

Preparation of (Trop-NHC-Trop)AuCl (Trop-2). Trop-1 (91.0 mg, 200 μmol), [(DMS)AuCl] (58.9 mg, 200 μmol) and K_2CO_3 (55.3 mg, 400 μmol) were suspended in dry acetone (3 mL) and were stirred at 60 $^\circ\text{C}$ for 7 h. The mixture was filtered through a pad of Celite (glass pipet: one-third filled), and the filtrate was evaporated to dryness on a rotary evaporator. After the crude product was filtered through a pad of silica gel (glass pipet: one-third filled) and the pad was rinsed with dichloromethane (3 \times 1.5 mL), the solvent was removed and the product was triturated with pentane (2 \times 2 mL). A white powder was obtained after drying under vacuum (83 mg, 65% yield). Colorless needles of Trop-1 suitable for X-ray diffraction analysis were grown by slow vapor diffusion of pentane into a concentrated solution of the compound in CHCl_3 . Anal. Calcd for $\text{C}_{33}\text{H}_{24}\text{AuClN}_2$ (680.99 g/mol): C, 58.20; H, 3.55; N, 4.11. Found: C, 58.05; H, 3.49; N, 4.02. ^1H NMR (500.13 MHz, CDCl_3): 7.75 (ps-d, $J_{\text{HH}} = 7.4$ Hz, 4H, $\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 7.43 (dt, $J = 10.8$ Hz, $J = 1.9$ Hz, 4H, C^{ArH}), 7.40–7.35 (m, 8H, C^{ArH}), 6.86 (s, 4H, C^{olefH}), 6.82 (d, $^3J_{\text{H,H}} = 2.2$ Hz, 2H, C^{benzH}), 6.39 (s, 2H, C^{ImiH}). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 169.68 (NCN), 134.48 ($\text{C}^{\text{quart trop}}$), 134.39 ($\text{C}^{\text{quart trop}}$), 131.80 ($\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 131.13 (C^{olefH}), 130.43 (C^{ArH}), 129.85 (C^{ArH}), 129.05 (C^{ArH}), 119.31 (s, C^{ImiH}), 71.29 (C^{benzH}).

Preparation of [(Me-NHC-Trop)Au(NTf₂)] (Me-3). Gold complex Me-2 (25.2 mg, 50.0 μmol) and AgNTf_2 (23.3 mg, 60.0 μmol) were dried under vacuum for 15 min. Under an atmosphere of argon, dry dichloromethane (3 mL) was added and the mixture was stirred in the dark for 10 min. The suspension was filtered through a pad of Celite (glass pipet: one-third filled), which was subsequently rinsed with dichloromethane (3 \times 1 mL), and the filtrate was concentrated to approximately 0.2 mL. After the addition of pentane (2 mL) the product slowly precipitated as a microcrystalline material which was further washed with pentane (2 \times 1 mL). The product was obtained as a white solid after drying under vacuum (33 mg, 88% yield). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of Me-3 in CHCl_3 . Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{AuF}_6\text{N}_3\text{O}_4\text{S}_2$ (749.45 g/mol): C, 33.66; H, 2.15; N, 5.61. Found: C, 33.74; H, 1.97; N, 5.68. ^1H NMR (500.13 MHz, CDCl_3): 7.81 (ps-d, $^3J_{\text{HH}} = 7.4$ Hz, 2H, $\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 7.54–7.49 (m, 2H, C^{ArH}), 7.48–7.44 (m, 4H, C^{ArH}), 6.98 (s, 2H, C^{olefH}), 6.77 (s, 1H, C^{benzH}), 6.70 (d, $^3J_{\text{H,H}} = 2.1$ Hz, 1H, MeNCHCHN), 6.68 (d, $^3J_{\text{HH}} = 2.1$ Hz, 1H, MeNCHCHN), 3.71 (s, 3H, MeN). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 163.27 (NCN), 134.37 ($\text{C}^{\text{quart trop}}$), 134.11 ($\text{C}^{\text{quart trop}}$), 131.66 ($\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 131.21 (C^{olefH}), 130.65 (C^{ArH}), 130.10 (C^{ArH}), 129.42 (C^{ArH}), 121.77 (s, MeNCHCHN), 120.67 (s, MeNCHCHN), 119.56 (q, $J_{\text{CF}} = 321.1$ Hz, CF_3), 71.54 (C^{benzH}), 39.09 ($(\text{H}_3\text{C})\text{N}$).

Preparation of [(DiPP-NHC-Trop)Au(NTf₂)] (DiPP-3). Gold complex DiPP-2 (35.0 mg, 53.8 μmol) and AgNTf_2 (20.9 mg, 53.8 μmol) were dried under vacuum for 10 min. Under an atmosphere of argon, dichloromethane (3 mL) was quickly added and the mixture was stirred in the dark for 20 min. The suspension was filtered through a pad of Celite (glass pipet: one-third filled), which was subsequently rinsed with dichloromethane (3 \times 1 mL), and the filtrate was concentrated to approximately 0.3 mL. The slow addition of pentane (~2 mL) led to the precipitation of the product as colorless needles which were further washed with pentane (2 \times 1 mL) and dried under vacuum (41 mg, 85% yield). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of DiPP-3 in CHCl_3 . Anal. Calcd for $\text{C}_{32}\text{H}_{30}\text{AuF}_6\text{N}_3\text{O}_4\text{S}_2$ (895.68 g/mol): C, 42.91; H, 3.38; N, 4.69. Found: C, 43.02; H, 3.41; N, 4.75. ^1H NMR (500.13 MHz, CDCl_3): 7.81 (ps-d, $J_{\text{HH}} = 7.6$ Hz, 2H, $\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 7.57–7.52 (m, 2H, C^{ArH}), 7.51–7.47 (m, 4H, C^{ArH}), 7.42 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H, $p\text{-C}^{\text{DiPP}}\text{H}$), 7.18 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, $m\text{-C}^{\text{DiPP}}\text{H}$), 6.96 (s, 2H, C^{olefH}), 6.73 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 1H, C^{ImiH}), 6.72 (s, 1H, C^{benzH}), 6.63 (d, $^3J_{\text{H,H}} = 2.0$ Hz, 1H, C^{ImiH}), 2.17 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, $^3J_{\text{HH}} = 6.5$ Hz, 6H, $2 \times \text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$), 1.04 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, $2 \times \text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 166.28 (NCN), 145.45 ($\text{C}^{\text{DiPP-N}}$), 134.62 ($o\text{-C}^{\text{DiPP}}\text{H}$), 134.56 ($\text{C}^{\text{quart trop}}$), 134.17 ($\text{C}^{\text{quart trop}}$), 131.13 ($\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 130.77 (C^{olefH}), 130.64 ($p\text{-C}^{\text{DiPP}}\text{H}$), 130.38 (C^{ArH}), 129.97 (C^{ArH}), 129.41 (C^{ArH}), 124.14 ($m\text{-C}^{\text{DiPP}}\text{H}$), 121.78 (s, C^{ImiH}), 121.50 (s, C^{ImiH}), 119.21 (q, $J_{\text{CF}} = 323.2$ Hz, CF_3), 70.78 (C^{benzH}), 28.41 ($\text{CH}(\text{CH}_3)_2$), 24.62 ($\text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$), 24.58 ($\text{CH}(\text{CH}_3)^{\text{a}}(\text{CH}_3)^{\text{b}}$).

Preparation of [(Ad-NHC-Trop)Au(NTf₂)] (Ad-3). Gold complex Ad-2 (25.0 mg, 40.0 μmol) and AgNTf_2 (15.5 mg, 40.0 μmol) were dried under vacuum for 10 min. Under an atmosphere of argon, dichloromethane (2 mL) was quickly added and the mixture was stirred in the dark for 10 min. The suspension was filtered through a pad of Celite (glass pipet: one-third filled), which was subsequently rinsed with dichloromethane (3 \times 1 mL), and the filtrate was evaporated to dryness. The crude product was filtered once again through Celite and was concentrated to approximately 0.5 mL. The product was precipitated by the addition of pentane (~3 mL), washed with pentane (2 mL), and dried under vacuum (32 mg, 92% yield). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of Ad-3 in CHCl_3 . Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{AuF}_6\text{N}_3\text{O}_4\text{S}_2$ (869.65 g/mol): C, 41.43; H, 3.25; N, 4.83. Found: C, 41.52; H, 3.34; N, 4.86. ^1H NMR (500.13 MHz, CDCl_3): 7.87 (ps-d, $J_{\text{HH}} = 7.5$ Hz, 2H, $\text{C}^{\text{benz}}\text{C}^{\text{quart}}\text{C}^{\text{ArH}}$), 7.52–7.47 (m, 2H, C^{ArH}), 7.47–7.42 (m, 4H, C^{ArH}), 7.19 (s, 1H, C^{benzH}), 7.01 (d, $J_{\text{HH}} = 1.0$ Hz, 2H, C^{olefH}), 6.99 (t, $^3J_{\text{H,H}} = 2.1$ Hz, 1H,

AdNCHCHN), 6.74 (t, $^3J_{\text{HH}} = 1.7$ Hz, 1H, AdNCHCHN), 2.35 (d, $^3J_{\text{HH}} = 2.8$ Hz, 6H, C^{AdH_2}), 2.22 (s, C^{AdH}), 1.72 (t, $J_{\text{HH}} = 2.9$ Hz, 6H, C^{AdH_2}). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 159.37 (NCN), 134.48 ($\text{C}^{\text{quart trop}}$), 134.43 ($\text{C}^{\text{quart trop}}$), 131.90 ($\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 131.48 (C^{olefH}), 130.87 (C^{ArH}), 130.07 (C^{ArH}), 129.30 (C^{ArH}), 119.66 (q, $^1J_{\text{CF}} = 323.9$ Hz, CF_3), 119.14 (s, AdNCHCHN), 117.81 (s, AdNCHCHN), 73.31 (C^{benzH}), 59.89 ($\text{C}^{\text{quart-N}}$), 44.24 (C^{AdH_2}), 35.62 (C^{AdH_2}), 29.99 (C^{AdH}).

Preparation of [(Trop-NHC-Trop)Au(NTf₂)] (Trop-3). Gold complex **Trop-2** (40.9 mg, 60.0 μmol) and AgNTf_2 (23.3 mg, 60.0 μmol) were dried under vacuum for 10 min. Under an atmosphere of argon, dichloromethane (3 mL) was quickly added and the mixture was stirred in the dark for 20 min. The suspension was filtered through a pad of Celite (glass pipet: one-third filled), which was subsequently rinsed with dichloromethane (3×1 mL), and the filtrate was concentrated to approximately 0.3 mL. The slow addition of pentane (~2 mL) led to the precipitation of the product as colorless needles which were further washed with pentane (2×1 mL) and dried under vacuum (40 mg, 72% yield). Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of **Trop-3** in CHCl_3 . Anal. Calcd for $\text{C}_{35}\text{H}_{24}\text{AuF}_6\text{N}_3\text{O}_4\text{S}_2$ (925.67 g/mol): C, 45.41; H, 2.61; N, 4.54. Found: C, 45.28; H, 2.68; N, 4.58. ^1H NMR (500.13 MHz, CDCl_3): 7.75 (ps-d, $J_{\text{HH}} = 7.4$ Hz, 4H, $\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 7.48–7.43 (m, 4H, C^{ArH}), 7.43–7.36 (m, 8H, C^{ArH}), 6.88 (s, 4H, C^{olefH}), 6.76 (d, $^3J_{\text{HH}} = 2.2$ Hz, 4H, C^{benzH}), 6.49 (s, 4H, C^{limiH}). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 161.57 (NCN), 134.36 ($\text{C}^{\text{quart trop}}$), 134.07 ($\text{C}^{\text{quart trop}}$), 131.83 ($\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 131.23 (C^{olefH}), 130.51 (C^{ArH}), 129.96 (C^{ArH}), 129.26 (C^{ArH}), 119.56 (q, $^1J_{\text{CF}} = 323.9$ Hz, CF_3), 120.06 (s, C^{limiH}), 71.88 (C^{benzH}).

Preparation of [(Me-NHC-Trop)₂Au]BARF₂₄ (Me-4). Solid NaBARF_{24} (15.5 mg, 17.5 μmol) was added to a solution of **Me-2** (7.5 mg, 15 μmol) in dry CDCl_3 (0.6 mL) in a J. Young NMR tube. The solution was mixed by rotating the NMR tube for 90 min at ~30 rpm, leading to the precipitation of a black solid. At this point in situ ^1H and ^{19}F spectroscopy indicated complete conversion of the starting material to the corresponding **Me-4** and three to four new fluoride-containing species likely arising from the decomposition of the BARF_{24} anion. The suspension was filtered through a pad of Celite (glass pipet, one-third filled) and the solvent was removed from the filtrate under vacuum. After the residue was washed with pentane and dried under vacuum the product was obtained as a white solid (11 mg, 91% yield with respect to the starting quantity of ligand). Crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of pentane into a solution of **Me-3** in CHCl_3 . Anal. Calcd for $\text{C}_{70}\text{H}_{44}\text{AuBF}_4\text{N}_4$ (1604.86 g/mol): C, 52.39; H, 2.76; N, 3.49. Found: C, 52.27; H, 2.75; N, 3.57. ^1H NMR (500.13 MHz, CDCl_3): 7.70 (ps-t, $J = 2.2$ Hz, 4H, $\text{o-C}^{\text{BARF}_{24}}\text{H}$), 7.54–7.49 (m, 10H, 4 $\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}} + 4 \text{C}^{\text{olefC}^{\text{quart}}\text{C}^{\text{ArH}}} + 2 \text{p-C}^{\text{BARF}_{24}}\text{H}$), 7.40 (dt, $J = 11.3$ Hz, $J = 1.3$ Hz, 4H, C^{ArH}), 7.38 (dt, $J = 11.2$ Hz, $J = 1.4$ Hz, 4H, C^{ArH}), 6.95 (s, 4H, C^{olefH}), 6.58 (d, $^3J_{\text{HH}} = 2.0$ Hz, 2H, MeNCHCHN), 6.27 (d, $^3J_{\text{HH}} = 2.0$ Hz, 2H, MeNCHCHN), 6.24 (s, 2H, C^{benzH}), 3.44 (s, 6H, MeN). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 184.30 (NCN), 161.82 (q, $^1J_{\text{CB}} = 49.8$ Hz, $\text{B-C}^{\text{BARF}_{24}}$), 134.93 ($\text{o-C}^{\text{BARF}_{24}}$), 134.73 ($\text{C}^{\text{quart trop}}$), 134.60 ($\text{C}^{\text{quart trop}}$), 130.78 ($\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 130.58, 130.39 ($\text{C}^{\text{olefH}} + \text{C}^{\text{olefC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 129.28 (C^{ArH}), 129.16 (C^{ArH}), 128.9 (m, $\text{m-C}^{\text{BARF}_{24}}$), 124.67 (q, $^1J_{\text{CF}} = 272.8$ Hz), 121.92 (s, MeNCHCHN), 119.78 (s, MeNCHCHN), 117.60 ($\text{p-C}^{\text{BARF}_{24}}$), 70.24 (C^{benzH}) 38.98 ($(\text{H}_3\text{C})\text{N}$).

Preparation of [(DiPP-NHC-Trop)₂Au]BARF₂₄ (DiPP-4). Solid NaBARF_{24} (15.5 mg, 17.5 μmol) was added to a solution of **DiPP-2** (7.5 mg, 15 μmol) in dry CDCl_3 (0.6 mL) in a J. Young NMR tube. The solution was mixed by rotating the NMR tube overnight at ~30 rpm, leading to the precipitation of a black solid. In situ ^1H and ^{19}F spectroscopy indicated complete conversion of the starting material to the bis(NHC) complex and three to four new fluoride-containing species likely arising from the decomposition of the BARF_{24} anion. The suspension was filtered through a pad of Celite (glass pipet, one-third filled), which was subsequently rinsed with dichloromethane, and the solvent was removed from the filtrate under vacuum. The residue was

filtered through a pad of silica (glass pipet, one-third filled) using DCM. After the solvent was removed from the filtrate under vacuum and the residue washed with pentane, the colorless oil was dried under vacuum and solidified over time (18 mg, 88% yield with respect to the starting quantity of ligand). Anal. Calcd for $\text{C}_{92}\text{H}_{72}\text{AuBF}_4\text{N}_4$ (1897.32 g/mol): C, 58.24; H, 3.82; N, 2.95. Found: C, 58.11; H, 3.76; N, 3.16. ^1H NMR (500.13 MHz, CDCl_3): 7.72 (ps-t, $J = 2.2$ Hz, 4H, $\text{o-C}^{\text{BARF}_{24}}\text{H}$), 7.51 (s, 2H, $\text{p-C}^{\text{BARF}_{24}}\text{H}$), 7.49–7.44 (m, 6H, $4\text{C}^{\text{ArH}} + 2 \text{p-C}^{\text{DiPPH}}$), 7.41 (dt, $J = 11.2$ Hz, $J = 1.2$ Hz, 4H, C^{ArH}), 7.32–7.28 (m, 6H, 4 $\text{C}^{\text{ArH}} + 2 \text{DiPP-NCHCHN}$), 7.21 (d, $^3J_{\text{HH}} = 7.85$ Hz, 4H, $\text{m-C}^{\text{DiPPH}}$), 7.21 (4H, $\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$ covered by signal of $\text{m-C}^{\text{DiPPH}}$), 7.04 (s, 4H, C^{olefH}), 6.81 (s, 2H, C^{benzH}), 6.72 (d, $^3J_{\text{HH}} = 1.9$ Hz, 2H, DiPP-NCHCHN), 2.14 (sept., $^3J_{\text{HH}} = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 0.95 (ps-t, $J_{\text{HH}} = 7.1$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 182.90 (NCN), 161.84 (q, $^1J_{\text{CB}} = 50.0$ Hz, $\text{B-C}^{\text{BARF}_{24}}$), 145.60 ($\text{C}^{\text{DiPP-N}}$), 134.96 ($\text{o-C}^{\text{BARF}_{24}}$), 134.49 ($\text{C}^{\text{quart trop}}$), 134.32 ($\text{C}^{\text{quart trop}}$), 134.27 (o-C^{DiPP}), 131.59 + 131.46 ($\text{C}^{\text{olefH}} + \text{C}^{\text{olefC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 131.06 ($\text{p-C}^{\text{DiPPH}}$), 130.09 ($\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 129.66 (C^{ArH}), 129.49 (C^{ArH}), 129.03 (q, $^2J_{\text{CF}} = 30.5$ Hz, $\text{m-C}^{\text{BARF}_{24}}$), 124.70 (q, $^1J_{\text{CF}} = 272.8$ Hz, CF_3), 124.55 ($\text{m-C}^{\text{DiPPH}}$), 124.45 (s, DiPP-NCHCHN), 121.28 (s, DiPP-NCHCHN), 117.58 (t, $J = 4.0$ Hz, $\text{p-C}^{\text{BARF}_{24}}$), 71.26 (C^{benzH}), 28.49 ($\text{CH}(\text{CH}_3)_2$), 24.55 ($\text{CH}(\text{CH}_3)_2$), 24.22 ($\text{CH}(\text{CH}_3)_2$), 24.22 ($\text{CH}(\text{CH}_3)_2$).

Preparation of [(Ad-NHC-Trop)₂Au]BARF₂₄ (Ad-4). At 0 °C, a solution of **Ad-2** (18.7 mg, 30.0 μmol) in DCM (1 mL) was added dropwise to a suspension of NaBARF_{24} (31.9 mg, 36.0 μmol) in DCM (1.5 mL). The mixture was stirred at 0 °C for 15 min before removing the cooling bath and stirring at room temperature overnight. Then, the suspension was filtered through a pad of Celite and the filtrate was concentrated on a rotary evaporator before filtering through a pad of silica (glass pipet, one-third filled) which was subsequently rinsed with DCM (3×1 mL). The residue was concentrated to approximately 0.2 mL, and the product was obtained by the addition of pentane (3 mL) as an oil. After the solution was decanted, the product solidified upon drying under vacuum to give a white powder (20 mg, 72% yield with respect to the starting quantity of ligand). Crystals suitable for X-ray diffraction analysis were obtained by layering a solution of **Ad-3** in CHCl_3 with pentane. Anal. Calcd for $\text{C}_{88}\text{H}_{68}\text{AuBF}_4\text{N}_4$ (1845.25 g/mol): C, 57.28; H, 3.71; N, 3.04. Found: C, 57.19; H, 3.60; N, 3.10. ^1H NMR (500.13 MHz, CDCl_3): 7.72 (br.s, 4H, $\text{o-C}^{\text{BARF}_{24}}\text{H}$), 7.62–7.57 (m, 2H, $\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 7.52 (s, 2H, $\text{p-C}^{\text{BARF}_{24}}\text{H}$), 7.43–7.38 (m, 2H, $\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 7.35–7.30 (m, 4H, C^{ArH}), 7.00 (s, 3H, 2 $\text{C}^{\text{olefH}} + 2\text{Ad-NCHCHN}$), 6.83 (d, $^3J_{\text{HH}} = 2.0$ Hz, 2H, Ad-NCHCHN), 6.80 (s, 2H, C^{benzH}), 2.24 (d, $J = 2.1$ Hz, 6H, C^{AdH_2}), 2.08 (s, 3H, C^{AdH}), 1.66 (d, $^2J_{\text{HH}} = 12.5$ Hz, 3H, $\text{C}^{\text{AdH}^{\text{H}^{\text{b}}}}$), 1.51 (d, $^2J_{\text{HH}} = 12.0$ Hz, 3H, $\text{C}^{\text{AdH}^{\text{H}^{\text{b}}}}$). $^{13}\text{C}\{^1\text{H}\}$ DEPTQ NMR (125.76 MHz, CDCl_3): 180.46 (NCN), 161.84 (q, $^1J_{\text{CB}} = 49.9$ Hz, $\text{B-C}^{\text{BARF}_{24}}$), 135.15 ($\text{C}^{\text{quart trop}}$), 134.95 ($\text{o-C}^{\text{BARF}_{24}}$), 134.44 ($\text{C}^{\text{quart trop}}$), 131.23 (C^{olefH}), 130.49, 129.38, 129.34, 129.07 + $\text{C}^{\text{olefC}^{\text{quart}}\text{C}^{\text{ArH}}}$, ($\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), (C^{ArH}), (C^{ArH}), 129.87 (m, $\text{m-C}^{\text{BARF}_{24}}$), 124.69 (q, $^1J_{\text{CF}} = 272.7$ Hz, CF_3), 120.58 (s, Ad-NCHCHN), 117.59 (br. s, $\text{p-C}^{\text{BARF}_{24}}$), 116.83 (s, Ad-NCHCHN), 71.34 (C^{benzH}), 59.37 ($\text{C}^{\text{quart-N}}$), 44.66 ($\text{N-C}^{\text{AdH}_2}$), 35.58 (C^{AdH_2}), 29.83 (C^{AdH}).

Preparation of [(Trop-NHC-Trop)₂Au]BARF₂₄ (Trop-4). A mixture of NaBARF_{24} (42.6 mg, 48.0 μmol) and **Trop-2** (27.2 mg, 40 μmol) was dried under vacuum for approximately 10 min, dissolved in 2 mL of dry DCM, and stirred at room temperature overnight. A black precipitate formed, and the suspension was filtered through a pad of Celite (glass pipet, one-third filled) which was subsequently rinsed with DCM (3×1 mL). The filtrate was concentrated on a rotary evaporator to approximately 0.3 mL and filtered through a pad of silica (glass pipet, half filled) which was subsequently rinsed with DCM (3×1 mL). After the filtrate was evaporated to dryness, the residue was triturated with pentane (3×2 mL) and dried in vacuo to give the product as a white powder (34 mg, 87% yield with respect to the starting quantity of ligand). Anal. Calcd for $\text{C}_{98}\text{H}_{60}\text{AuBF}_4\text{N}_4$ (1957.29 g/mol): C, 60.14; H, 3.09; N, 2.86. Found: C, 60.04; H, 3.01; N, 3.02. ^1H NMR (500.13 MHz, CDCl_3): 7.74 (br s, 8H, $\text{o-C}^{\text{BARF}_{24}}\text{H}$), 7.58–7.48 (m, 20H, $16\text{C}^{\text{ArH}} + 4\text{p-C}^{\text{BARF}_{24}}\text{H}$), 7.27 (dt, $J = 11.0$ Hz, $J = 1.5$ Hz, 8H, C^{ArH}), 7.00 (br s, 8H, $\text{C}^{\text{benzC}^{\text{quart}}\text{C}^{\text{ArH}}}$), 6.98

(br.s, 8H, C^{olef}H), 6.05 (s, 4H, C^{imi}H), 5.68 (s, 4H, C^{benz}H). ¹³C{¹H} DEPTQ NMR (125.76 MHz, CDCl₃): 184.30 (NCN), 161.88 (q, ¹J_{CB} = 49.8 Hz, B-C^{BArF₂4}), 135.22 (C^{quart trop}), 134.96 (o-C^{BArF₂4}), 134.73 (C^{quart trop}), 131.13 (C^{benz}C^{quart}C^{Ar}H), 130.89 (C^{olef}H), 129.09 (C^{Ar}H), 129.93 (C^{Ar}H), 129.49 (C^{Ar}H), ~129.0 (m-C^{BArF₂4}, parts of the quartet are overlaid and not clearly visible), 124.71 (q, ¹J_{CF} = 272.8 Hz, CF₃), 118.81 (s, C^{imi}H), 117.59 (bs, p-C^{BArF₂4}), 69.20 (C^{benz}H).

General Procedure for the Hydration of Diphenylacetylene.

In air, 2 mL of a mixture of 1,4-dioxane and water (2/1) was added to a 3 mL glass vial charged with the catalyst R-3 (2.5–5 mol %) and diphenylacetylene (89.1 mg, 500 μmol). The vessel was sealed and heated to 80 °C for 24 h. After it was cooled to room temperature, the mixture was diluted with pentane and a sample of the organic layer was analyzed via GC.

■ ASSOCIATED CONTENT

● Supporting Information

Text, figures, tables, and CIF files giving general information on synthetic procedures, NMR spectra, and X-ray diffraction data. This material is available free of charge via the Internet at <http://pubs.acs.org>. In addition, data have been deposited with the Cambridge Crystallographic Data Center with the following file numbers: CCDC 1029001 (Me-2), 1028999 (DiPP-2), 1028996 (Ad-2), 1028994 (Trop-2), 1029002 (Me-3), 1029000 (DiPP-3), 1028997 (Ad-3), 1028995 (Trop-3), 1029003 (Me-4), 1028998 (Ad-4). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The ERC (Advanced Investigator Award-FUNCAT), Syngenta, and the EPSRC are gratefully thanked for support of this work. Umicore AG is thanked for generous donations of auric acid. S.P.N. is a Royal Society Wolfson Research Merit Award holder. Mr. Enrico Marelli is thanked for helpful discussions regarding the synthesis of the imidazolium salts.

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