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# Inner-Sphere versus Outer-Sphere Coordination of $BF_4^-$ in a NHC-Gold(I) Complex

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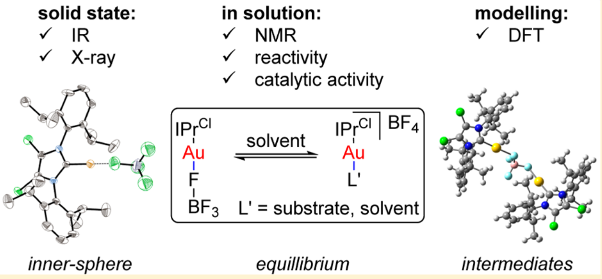
*Supporting Information*

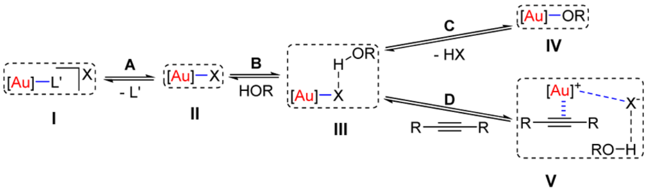
**ABSTRACT:** The role of counterions in chemistry mediated by gold complexes stretches much further than merely providing charge balance to cationic gold species. Interplay between their basicities and coordination strengths influences interactions with both the gold center and substrates in catalysis. Actual monogold(I) active species are generally believed to be monocoordinated species, formed from the abstraction or the decoordination of a second ligand from precursor complexes, but only a small amount of experimental evidence exists to underpin the existence of these transient species. The formation of a bench-stable neutral IPr$^{Cl}$-gold(I) tetrafluoroborate complex is reported herein. Experimental studies by X-ray diffraction analysis and NMR spectroscopy and theoretical studies by DFT calculations were conducted to determine the composition, structure, and behavior of this complex. The absence of an auxiliary ligand resulted in inner-sphere coordination of the counterion in the solid state. In solution, an equilibrium between two conformations was found with the counterion occupying inner-sphere and outer-sphere positions, respectively. Stoichiometric and catalytic reactivity studies with the tetrafluoroborate complex have been conducted. These confirmed the lability of the inner-sphere coordinating counterion that gives the IPr$^{Cl}$-gold(I) fragment behavior similar to that of related systems.



## ■ INTRODUCTION

The use of cationic gold(I) complexes in homogeneous catalysis continues to develop at an impressive rate.[1] Detailed studies are being conducted to gauge the influence of different ligands (L, L′) and (coordinating) counterions (X) in complexes of general composition [Au(L)(L′)][X] (**I**) or [Au(L)(X)] (**II**) on their catalytic activity (Scheme 1).[2] Both N-heterocyclic carbenes (NHCs) and phosphines are widely used as ancillary ligands (L) for these cationic gold catalysts.[3] The most frequently encountered auxiliary ligands (L′) coordinate through nitrogen atoms and include nitriles, amines, and pyridines.[4] The choice of the counterion (X) has been traditionally based on the availability of silver(I) salts AgX (X = OTf, OTs, $BF_4$, $PF_6$, $SbF_6$) that are used to abstract chloride from gold chloride precursors to form cationic gold(I),[5] but with the declining use of these reagents,[6] and the development of silver-free systems,[7] the use of counterions such as phosphate,[8] triflate,[9] and borates[10] has been explored as well.

**Scheme 1. Species Involved in Gold-Catalyzed Addition Reactions to Alkynes**[a]



[a] [Au] = Au(L).

Interaction of the counterion with the gold center has repeatedly been found to play a pivotal role in governing the efficiency of catalysis, and studies of the cornerstone reactions of gold(I) catalysis, addition of (oxygen-based) nucleophiles to alkynes, have provided a useful conceptual framework (Scheme 1).[11] Decoordination of the auxiliary ligand L′ from a species

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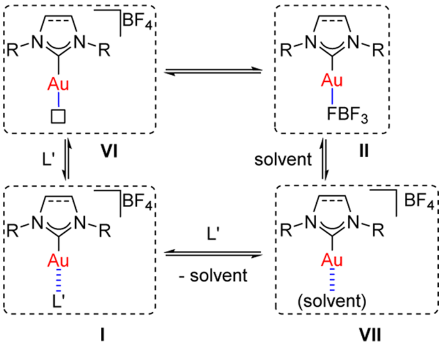
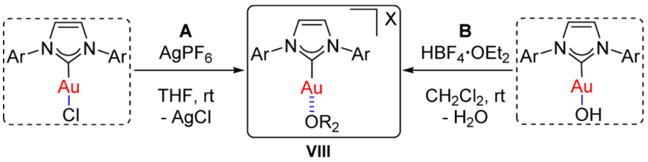
[Au(L)(L′)][X] (**I**) would convert the outer-sphere ion pair to [Au(L)(X)] (**II**), an inner-sphere ion pair. In the presence of water[12] or alcohol[13] and alkyne, the relative basicity of the nucleophile (HOR) and $X^-$ governs the equilibrium between [Au(L)(X)]·HOR (**III**) and catalytically inactive [Au(L)(OR)] (**IV**) and HX. Sufficiently labile counterions would bring **III** and alkyne substrate in equilibrium with the alkyne-coordinated outer-sphere ion pair [Au(L)(alkyne)][X]·HOR (**V**), the starting point for catalysis. The outer-sphere counterion would now be available as a proton shuttle to assist in deprotonation of the nucleophile and later in protodeauration to release the organic addition product.[14]

Active gold(I) catalysts are often postulated to be monocoordinated outer-sphere ion pairs, [Au(L)][X] (**VI**).[15] These structures with an "empty coordination site" on gold are frequently proposed on the basis of the known low dissociation energies of the counterions used,[12,16] without spectroscopic or structural data to support these claims.[17] For these putative species, the second coordination site on the gold(I) center should actually be occupied by any weak ligand such counterions as in [Au(L)(X)] (**II**) or solvents as in [Au(L)(solvent)][X] (**VII**) (Scheme 2).[18] Two examples of gold(I) complexes with weakly coordinating ether ligands, $[Au(L)(OR_2)][X]$ (**VIII**), have been studied previously: $[Au(IPr)(THF)][PF_6]$[19] and $[Au(IPr)(OEt_2)][BF_4]$[20] (Scheme 3). These species were formed through anion metathesis of [Au(IPr)(Cl)] and protonolysis of [Au(IPr)(OH)] with silver salt and acid, respectively. NMR studies revealed that $[Au(IPr)(OEt_2)][BF_4]$ (type **VIII**) existed in equilibrium with $[Au(IPr)][BF_4]$ (of type **VI**) in $CD_2Cl_2$ at 203 K,[20] although this latter species would be indistinguishable from $[Au(IPr)(CH_2Cl_2)][BF_4]$ (of general type **VII**). The low ligand strength of the $BF_4^-$ anion in comparison to the solvent molecules ($Et_2O$ and $CD_2Cl_2$) would prevent its inner-sphere coordination and $[Au(IPr)(FBF_3)]$ (type **II**) would not be likely to exist in solution (Scheme 2).

**Scheme 2. Hypothetical Equilibria of $[Au(NHC)(L)]^+$, $BF_4^-$, and L′ in Solution**



**Scheme 3. Formation of Unstabilized Species [Au(IPr)(solvent)][X]$^a$**



$^a OR_2$ = THF (**A**), $Et_2O$ (**B**). X = $PF_6$, $BF_4$. Ar = 2,6-$^iPr_2C_6H_3$.

Attempts to isolate the NHC-gold(I) ether complexes (**VIII**) or other "monocoordinated" cationic complexes [Au(NHC)][X] (**VI**) bearing either NHC ligands (e.g., $[Au(IPr)][BF_4]$,[20] $[Au(I^tBu)][BF_4]$,[21] and $[Au(ITrop)][BArF_{24}]$[22]) or phosphine ligands (e.g., $[Au(PPh_3)][X]$, X = $BF_4$, $PF_6$, $SbF_6$)[23] have been described to lead to rapid decomposition. Straub and co-workers have reported the formation of $[Au(IPr^{**})][BArF_{24}]$.[10,24] Aldridge and co-workers have explored the abstraction of hydride from less sterically encumbered [Au(6-Dipp)(H)] by $B(C_6F_5)_3$.[25] The transient species $[Au(6\text{-}Dipp)(HB(C_6F_5)_3)]$ proved highly unstable and evolved to $[Au(6\text{-}Dipp)(C_6F_5)]$ and borane $HB(C_6F_5)_2$.

In contrast to the unstable monocoordinated complexes [Au(L)][X] (**VI**), various examples of stable dicoordinated gold(I) complexes with neutral auxiliary ligands, [Au(L)(L′)][X] (**I**), have been studied. Examples include those with coordinating molecules of acetonitrile such as $[Au(IPr)(NCCH_3)][PF_6]$[26] and $[Au(PR_3)(NCCH_3)][SbF_6]$[27] or those with coordinating molecules of substrate such as $[Au(IPr)(3\text{-}hexyne)][BF_4]$,[28] $[Au(PR_3)(alkene)]$, $[Au(PR_3)(alkyne)]$,[29,30] or $[Au(PR_3)(allene)]$.[31,32] Structural data obtained from X-ray diffraction studies unambiguously confirmed the outer-sphere coordination of the counterions in these complexes, and $^{19}F,^1H$-HOESY and $^1H$-DOSY NMR experiments have been used to further assess the dynamic behavior of the ion pairs in solution.[28]

Examples of inner-sphere coordination of $BF_4^-$ anions exists for transition metals other than gold, with literature examples for cobalt,[33] nickel,[34] copper,[35] zinc,[36] rhodium,[37] silver,[38] and platinum.[39] The few reported complexes $[M(L)_n(X)_n]$ that bear at least one NHC ligand are non-coinage-metal species, with palladium ($n$ = 1, X = $FBF_3$),[40] ruthenium ($n$ = 2, X = $FBF_3$)[41] and indium ($n$ = 1, X = $FSbF_5$)[42] centers instead. Monocoordinated *neutral* complexes of copper(I) and silver(I) with an anionic aryl ligand, $[M(2,4,6\text{-}Ph_3C_6H_2)]$ (M = Cu, Ag), have been characterized in the solid state,[43] but to the best of our knowledge, evidence for monocoordinated complexes of gold(I) is lacking.

Despite the challenges associated with the isolation of [Au(L)(X)] (**II**) or [Au(L)][X] (**VI**) with weakly coordinating counterions (X), various cationic gold(I) species with a 1:1 ratio of $[Au(L)]^+$ and $X^-$ without auxiliary ligand L′ have been isolated (Figure 1). For example, attempts to grow crystals of the norbonadiene-stabilized complex $[Au(IPr)(nbd)][PF_6]$ have been described to produce $[\{Au(IPr)\}_2(\mu\text{-}PF_4)][PF_4]$ instead (Figure 1a).[19] This remarkable complex contains both inner- and outer-sphere $PF_4^-$ fragments. The digold(I) complexes $[\{Au(X)\}_2(DTBM\text{-}Segphos)]$ (X = $FBF_3$, $OClO_3$, Figure 1b)[44] and a (C^N)-cyclometalated gold(III) congener (Figure 1c)[45] constitute other examples of inner-sphere coordination of the counterions. Coordination of these counterions in the inner coordination sphere of gold proceeds via the formation of an apparent gold−halide bond.[46] Indeed, gold−fluorine bond distances (2.0−2.3 Å) measured in solid-state structures are comparable to those obtained in gold(I) complexes [Au(NHC)(F)] (Figure 1d, 2.071(2) Å)[47] and $[\{Au(SIPr)\}_2(\mu\text{-}F)][BF_4]$ (Figure 1e, 2.060(1) Å)[48] and gold(III) complexes bearing NHC ($[Au(IPr)(CH_3)(\mu\text{-}F)]_2[F]_2$, Figure 1f, 2.034(3) and 2.124(3) Å),[49] phosphine (2.024(5) Å),[50] or pincer ligands (2.264(3) Å).[51]

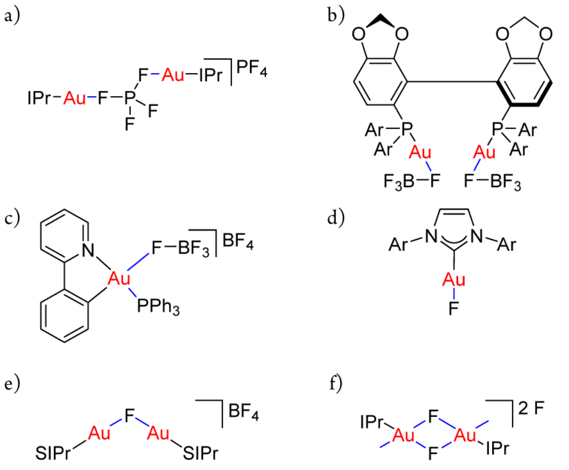


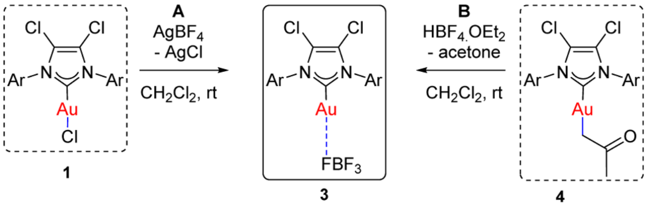
**Figure 1.** Selected gold(I) complexes. Au–F bond distances (Å): (a) $[\{Au(IPr)\}_2(\mu\text{-}PF_4)][PF_4]$, 2.055(4) and 2.042(4);[19] (b) $[\{Au(FBF_3)\}_2$(DTBM-Segphos)], 2.101(15) and 2.095(15), Ar = 3,5-di-*tert*-butyl-4-methoxyphenyl;[44] (c) [Au(C^N)(PPh$_3$)(FBF$_3$)][BF$_4$], 2.095(4).[45] (d) [Au(NHC)(F)], NHC = IPr, 2.071(2);[47] NHC = SIPr, 2.0281(17);[52] (e) $[\{Au(SIPr)\}_2(\mu\text{-}F)][BF_4]$, 2.060(1);[48] (f) $[Au(IPr)(CH_3)(\mu\text{-}F)]_2[F]_2$, 2.034(3) and 2.124(3).[49]

None of the reported gold complexes containing inner-sphere coordinating counterions (Figure 1a–c) have been studied in great detail. The observation of $[\{Au(IPr)\}_2(\mu\text{-}PF_4)][PF_4]$[19] and $[\{Au(FBF_3)\}_2$(DTBM-Segphos)][44] in the solid state suggested that the judicious choice of a NHC ligand and fluorinated counterion would permit access to a "monocoordinated" species [Au(NHC)(X)] (of type **II**) or [Au(NHC)][X] (of type **VI**) without a specified auxiliary ligand L′.

## RESULTS AND DISCUSSION

**Synthesis of [Au(IPr$^{Cl}$)(FBF$_3$)]/[Au(IPr$^{Cl}$)(L)][BF$_4$] (3).** On the basis of our experience with NHC-monogold[19,53] and (hydroxide bridged) NHC-digold[54] complexes containing BF$_4$ counterions, the synthesis of [Au(NHC)(FBF$_3$)]/[Au(NHC)(L)][BF$_4$]/ (type **II**/**VI**) was targeted. The synthesis was first approached by performing metathesis reactions of [Au(NHC)(Cl)] with AgBF$_4$ in CH$_2$Cl$_2$, a poorly coordinating solvent. The use of various NHC ligands (e.g., IPr, IAd, I$^t$Bu, IDD, SIPr, IPent$^{Cl}$, and IMes$^{Cl}$) did not allow isolation of well-defined complexes, and the formation of [Au(IMes)$_2$][BF$_4$][55] was observed in the reaction from [Au(IMes)(Cl)].[56,57] With [Au(IPr$^{Cl}$)(Cl)] (**1**) as the starting material, however, the air- and moisture-stable solid product [Au(IPr$^{Cl}$)(FBF$_3$)]/[Au(IPr$^{Cl}$)(L)][BF$_4$] (**3**) was obtained (Scheme 4, reaction A).[58] No trace of the dicoordinated cationic side product [Au(IPr$^{Cl}$)$_2$][BF$_4$] was observed. Complex **3** could also be accessed from the recently developed NHC-gold(I) acetonyl [Au(IPr$^{Cl}$)(CH$_2$COCH$_3$)] (**4**) complex to avoid the use of silver salts (Scheme 4, reaction B).[59]

**Scheme 4. Synthetic Access to 3$^a$**



$^a$Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$.

Complex **3** proved stable in CDCl$_3$ solution, and decomposition was not observed after 15 days at room temperature according to $^1$H and $^{19}$F{$^1$H} NMR analyses. The solution remained clear, and the formation of precipitate was not observed, indicating that decomposition to gold(0) had not occurred.[60] Additionally, **3** was found to be soluble in C$_6$D$_6$, toluene-$d_8$, and DMSO-$d_6$. Solutions of **3** in C$_6$D$_6$ or toluene-$d_8$ could be heated to 120 °C without observable decomposition in $^1$H and $^{19}$F{$^1$H} NMR spectra.[61] Heating of CDCl$_3$ or DMSO-$d_6$ solutions to 60 °C, however, resulted in decomposition. The formation of [Au(IPr$^{Cl}$)(Cl)] (**1**) in the former solvent was attributed to release of Cl$^-$ from chloroform. In the latter solvent, the well-defined species that formed was tentatively assigned to [Au(IPr$^{Cl}$)$_2$][BF$_4$].

**IR and X-ray Studies of 3 in the Solid State.** The presence of a BF$_4^-$ ion in the isolated complex was initially supported by the observation of a characteristic B–F stretching band (at 1059 cm$^{-1}$) in the solid-state IR spectrum of **3**.[62] The diffraction study confirmed the expected stoichiometry and charge balance in **3** (Figure 2).[63] One of the fluorine atoms of the BF$_4$ unit pointed to the gold atom of the IPr$^{Cl}$-Au fragment, while another fluorine points to a chlorine atom of the backbone of a second IPr$^{Cl}$-Au fragment. The gold–fluorine distance of 2.027(7) Å was significantly shorter than the sum of the van der Waals radii of 3.13 Å for gold and fluorine atoms[64] and similar to that of the previously reported complexes with gold–fluorine linkages (Figure 1). In the solid state, **3** was thus found to be best described as the inner-sphere complex [Au(IPr$^{Cl}$)(FBF$_3$)] (**3**-in), rather than as the outer-sphere complex [Au(IPr$^{Cl}$)(L)][BF$_4$] (**3**-out). The BF$_4$ moiety was found to be no longer tetrahedral, and the B1–F1 distance (1.495(18) Å) is longer than the other B–F bonds (average of 1.38 Å). The carbenic carbon–gold distance of 1.960(9) Å is close to that of [Au(IPr$^{Cl}$)(NTf$_2$)] (**9**) (1.967(4) Å)[7c] and similar to that of other cationic NHC-gold complexes.[26] Torsion angles C3–N2–C1–Au1 and C4–N5–C1–Au1 of −179.1(6) and 179.6(6)° and different angles N2–C1–Au1

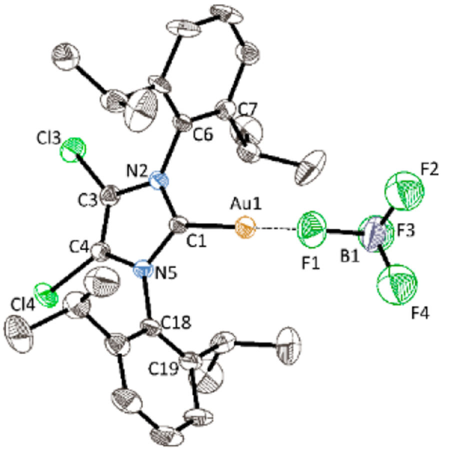


**Figure 2.** Solid-state structure of **3**·(CH$_3$)$_2$CO. One fragment of [Au(IPr$^{Cl}$)(FBF$_3$)] (**3**-in) from the unit cell is shown. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, a molecule of acetone, and the minor component of disorder in F2, F3, and F4 are omitted for clarity.

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and N5−C1−Au1 of 128.5(6) and 125.8(6)° as well as different torsion angles C1−N2−C6−C7 and C1−N5−C18−C19 of 88.8(10) and −79.6(11)° are all indicative of a slightly unsymmetrically twisted geometry of the $IPr^{Cl}$ ligand. A cocrystallized molecule of acetone was found in the crystal lattice, but large distances of the constituting atoms to **3** (at least 3 Å) indicated that interactions with the gold complex were absent. An alternative assignment of $[Au(IPr^{Cl})(FBF_3)]$ (**3**-in) as the isoelectronic hydroxyfluoroborate complex $[Au(IPr^{Cl})(HOBF_3)]$ (**5**-in) could be refuted.[61]

**NMR Studies of 3 in Solution.** The behavior and reactivity of **3** in $CDCl_3$ solution were studied by means of NMR spectroscopy at ambient temperature (295 K). $^1H$ NMR and $^{19}F\{^1H\}$ NMR spectra of isolated **3** and of crystals $\mathbf{3}\cdot(CH_3)_2CO$ matched, confirming that the crystals had the same composition as the isolated material. The $^1H$ NMR spectra showed two sets of isopropyl methyl groups with nonequivalent intensities, indicative of an equilibrium between different species. Similarly, two distinct sets of signals were present in both $^{19}F\{^1H\}$ NMR and $^{11}B$ NMR spectra (Figure 3),[65] suggesting that the $BF_4^-$ occupied different sites in solution as in $[Au(IPr^{Cl})(FBF_3)]$ (**3**-in) and $[Au(IPr^{Cl})(L)][BF_4]$ (**3**-out). No other signals (e.g., that expected for gold fluoride) were detected.

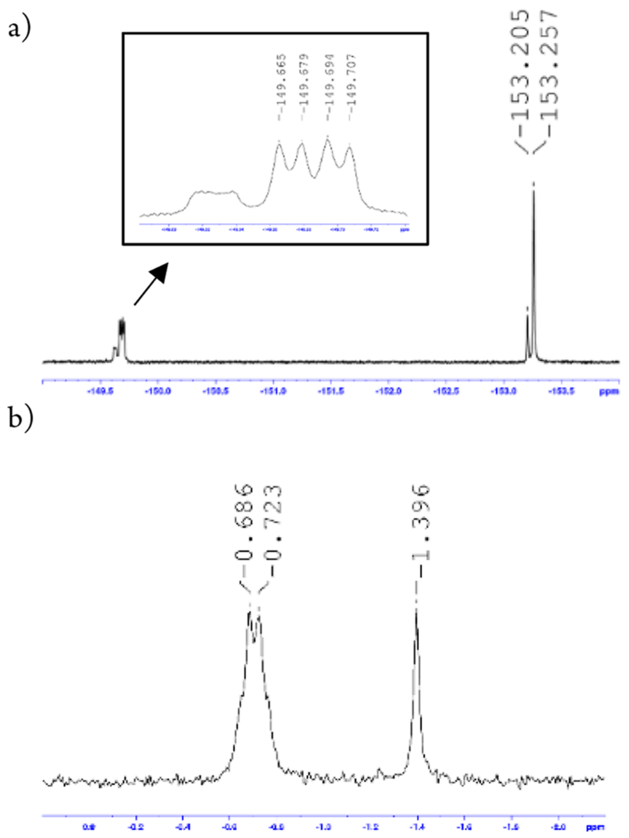


**Figure 3.** NMR spectra of **3** in $CDCl_3$ (4 mM) at ambient temperature: (a) $^{19}F\{^1H\}$ NMR spectrum (inset shows area between −149.6 and −149.8 ppm); (b) $^{11}B$ NMR spectrum in $CDCl_3$ (12 mM) at ambient temperature.

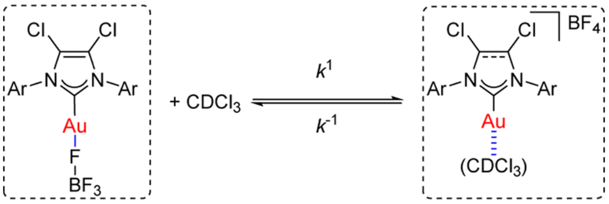
Both sets of fluorine signals displayed the characteristic split with a 1:4 ratio expected from the natural abundance of $^{10}B$:$^{11}B$. Furthermore, characteristic splitting patterns for heteronuclear coupling to these nuclei with spins 3 and 3/2 (5.2 Hz), respectively, in the signals at lower field confirm bonding between fluorine and boron. Likewise, in the $^{11}B$ NMR spectrum, a broadened set of signals was observed for the signals around −0.7 ppm (about 4.7 Hz), while the resonance at −1.4 ppm appeared as a sharp singlet (Figure 3b). Observation of coupling for the lower field signals and not for the higher field signals supported the assignment of the signals around −1.4 and −0.7 ppm to outer- and inner-sphere coordination, respectively.[66] Additional coupling was not observed in addition to the heteronuclear F−B coupling. Chemical shifts of the signals at higher field in both $^{11}B$ NMR (−1.4 ppm) and $^{19}F\{^1H\}$ NMR (−153.2 ppm) spectra (Figure 3) similar to those of $[Au(IPr)(NCCH_3)][BF_4]$ (−1.1 and −153.7 ppm, in $CDCl_3$ at ambient temperature)[19] also supported the assignment of these signals to outer-sphere coordinating $BF_4^-$ (**3**-out). The absence of an auxiliary ligand L′ in the $CDCl_3$ solution of **3** would suggest that **3**-out actually exists as the solvent-separated ion pair $[Au(IPr^{Cl})(CDCl_3)][BF_4]$ (**6**) (Scheme 2).

The carbenic carbon $^{13}C$ NMR chemical shifts are indicative of the environment around [Au(NHC)(L)] fragments and have been used to predict the Lewis acidity of gold complexes.[67,68] Correspondingly, a shift from 175.1 ppm (in $CDCl_3$) for $[Au(IPr^{Cl})(Cl)]$ (**1**)[69] to higher fields of 166.4 ppm (in $CDCl_3$) for $[Au(IPr^{Cl})(NCCH_3)][BF_4]$ (**7**), 163.0 ppm (in $CD_2Cl_2$) for $[\{Au(IPr^{Cl})\}_2(\mu\text{-}OH)][BF_4]$ (**8**), or 168.4 ppm (in $CDCl_3$) for $[Au(IPr^{Cl})(NTf_2)]$ (**9**)[70] agreed nicely with the known Lewis acidity of the last three cationic complexes.[22,53,71] Carbenic $^{13}C$ chemical shifts of [Au(NHC)(Cl)] (for SIPr, $\delta$ 196.4 ppm in $CD_2Cl_2$)[72] shift only by about 2−5% in comparison to the corresponding [Au(NHC)(F)] (for IPr $\delta$ 172.7[73] and for SIPr $\delta$ 185.9,[52] both in $CD_2Cl_2$). While not determined experimentally, a carbenic $^{13}C$ chemical shift for $[Au(IPr^{Cl})(F)]$ would thus be expected to reside in the range of 166−172 ppm. The carbenic $^{13}C$ chemical shift of **3** appeared at 163.2 ppm and indicated that this complex would be more Lewis acidic than **7**, consistent with a gold complex containing a loosely bound $BF_4^-$ ion rather than one with tightly bound fluoride as in $[Au(IPr^{Cl})(F)]$.

**Dynamic Behavior of 3 in Solution.** The presumed existence of **3** in $CDCl_3$ as a mixture of species with inner-sphere coordinating and outer-sphere coordinating $BF_4^-$ anions raised the question as to whether these species existed as monomeric entities and whether they would interconvert. The presence of chlorine substituents in $IPr^{Cl}$ ruled out the option to perform $^{19}F,^1H$-HOESY NMR spectroscopy that might have supported the outer-sphere coordination of $BF_4^-$ (close to the NHC backbone) in $[Au(IPr^{Cl})(L)][BF_4]$ (**3**-out) or $[Au(IPr^{Cl})(CDCl_3)][BF_4]$ (**6**). $^1H$-DOSY NMR experiments were performed to permit assignment of the single set of $IPr^{Cl}$ proton resonances in the $^1H$ NMR spectrum to either a monomeric or multinuclear species.[61] On the basis of the resonance of the C−H isopropyl signal (at 1.29 ppm), a diffusion constant of 8.87 × $10^{10}$ $m^2$ $s^{-1}$ was measured (in $CDCl_3$), which was on the same order of magnitude as that previously reported for [Au(IPr)(OH)] (8.86 × $10^{10}$ $m^2$ $s^{-1}$, in THF-$d_8$).[74] These values correspond to a hydrodynamic radius of 7.0 Å, clearly in agreement with mononuclear NHC-gold species.

The presumed reversible displacement of $BF_4^-$ from $[Au(IPr^{Cl})(FBF_3)]$ (**3**-in) by a solvent molecule in a $CDCl_3$ solution of **3** to form the solvent-separated ion pair $[Au(IPr^{Cl})(CDCl_3)][BF_4]$ (**6**) was studied by variable-temperature $^{19}F$-EXSY NMR experiments. Cross peaks between the signals around −149 and −152 ppm confirmed the reversibility of this process, and both the associated thermodynamic and kinetic parameters were determined from relative signal intensities at different temperatures (Table 1). The van't Hoff analysis gave negative values for $\Delta H$ and $\Delta S$ (Table 1, entries 1 and 2), corresponding to a Gibbs free energy change $\Delta G$ of only 1.0 kcal mol$^{-1}$ at 298.15 K. These values were indicative of slightly more favorable inner-sphere coordination of $BF_4^-$ in comparison to outer-sphere coordination in lieu of a stronger auxiliary ligand. The negative entropy of activation could be explained by the higher order in the state with two solvated ions $[Au(IPr^{Cl})]^+$ and $BF_4^-$ rather than in the case of one larger polarized but overall neutral species **3**-in. The Eyring analysis gave similar activation parameters for the forward ($k^1$) and backward ($k^{-1}$) processes (Table 1, entries 4−6), indicating that dissociation and association might proceed through the same transition state. The highly positive entropy indicated that dissociation of $BF_4^-$ might be a mononuclear process rather than an associative one. The average values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ corresponded to a modest Gibbs free energy change $\Delta G^\ddagger$ of about 17.4 kcal mol$^{-1}$.

**Table 1. Thermodynamic and Kinetic Parameters for the Equilibrium between 3-in and 6**[a]



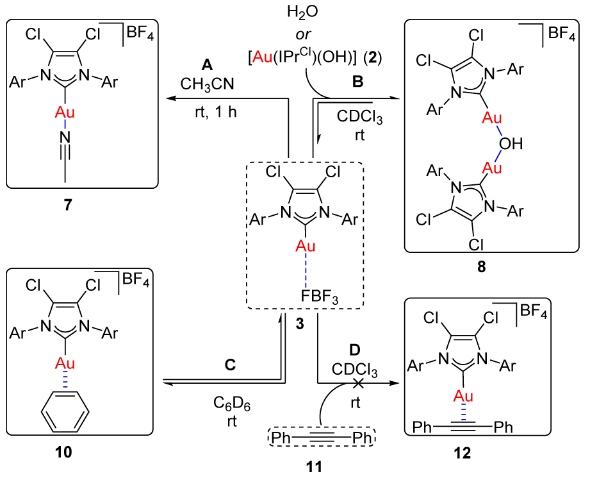
**3-in** **6**

| entry | direction | param | value | units |
|---|---|---|---|---|
| 1 | $k^1$ | $\Delta H$ | −22.8 ± 2.2 | kcal/mol |
| 2 | $k^1$ | $\Delta S$ | −5.7 ± 1.0 | kcal/(mol K) |
| 3 | $k^1$ | $\Delta H^\ddagger$ | 29.9 ± 4.0 | kcal/mol |
| 4 | $k^1$ | $\Delta S^\ddagger$ | 40.8 ± 6.0 | kcal/(mol K) |
| 5 | $k^{-1}$ | $\Delta H^\ddagger$ | 28.6 ± 7.0 | kcal/mol |
| 6 | $k^{-1}$ | $\Delta S^\ddagger$ | 38.6 ± 11.0 | kcal/(mol K) |

[a] Obtained from measurements of **3** in $CDCl_3$ at 12 mM concentration over a temperature range of 285−310 K (with 5 K intervals).

**Stoichiometric Reactivity of 3.** The reactivity of **3** was studied by subjecting it to different substrates that are known to coordinate to electron-deficient gold(I) centers (Scheme 5).[61] Acetonitrile was found to smoothly displace the $BF_4^-$ to form $[Au(IPr^{Cl})(NCCH_3)][BF_4]$ (**7**) (Scheme 5, reaction A). The formation of $[\{Au(IPr^{Cl})\}_2(\mu\text{-}OH)][BF_4]$ (**8**) from hydrolysis of **3** was studied (Scheme 5, reaction B). The reaction of metal tetrafluoroborate complexes (e.g., of Mn, Re, W, Cr, Fe, Os, Pt, Zr, and Ti) with water had been described to form the metal-aqua complexes $[M(L)_n(OH_2)_m][BF_4]$,[15b] and the intermediacy of aquo species $[Au(NHC)(OH_2)][BF_4]$ with subsequent formation of $\{Au(NHC)\}_2(\mu\text{-}OH)][BF_4]$ has been computed to be a favorable pathway.[14] As expected from this precedent, an equilibrium situation was observed between **3** and **8** when water was added to a sample of **3** in $CDCl_3$.[75] When **3** was mixed with $[Au(IPr^{Cl})(OH)]$ (**2**),[7b] complex **8** formed predominantly, consistent with the 2:1 stoichiometry of gold to $BF_4^-$ in the mixture.

**Scheme 5. Displacement of $BF_4^-$ from 3**



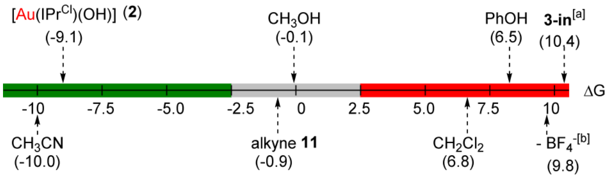
Coordination of arenes to cationic phosphine-gold[27] and NHC-gold complexes has previously been achieved as in $[Au(L)(\eta\text{-arene})][X,]$[76] and the complex $[Au(IPr)(\pi\text{-}PhC{\equiv}CPh)][BF_4]$ has been demonstrated to be an air-stable compound.[77] The facile displacement of $BF_4^-$ from **3** (by neutral solvent molecules) prompted us to test whether $\eta$-arene and $\pi$-alkyne complexes could be formed from reactions of **3** as well. The expected species $[Au(IPr^{Cl})(\eta\text{-benzene})][BF_4]$ (**10**) was found to be in equilibrium with **3**-in when **3** was dissolved in benzene (Scheme 5, reaction C). The signal in the $^{19}F\{^1H\}$ NMR spectrum assigned to **10**, however, was not observed when a stoichiometric amount of benzene was added to a solution of **3** in $CDCl_3$. Addition of a stoichiometric amount of diphenylacetylene (**11**) to a $CDCl_3$ solution of **3**, however, did not form $[Au(IPr^{Cl})(\pi\text{-}PhC{\equiv}CPh)][BF_4]$ (**12**) (Scheme 5, reaction D). A protonolysis reaction of **4** with in $HBF_4{\cdot}OEt_2$ the presence of **11** in $CDCl_3$ gave a mixture that appeared to contain **12**, but it was found to rapidly decompose to 1,2-diphenylethan-1-one (**14**), demonstrating the higher reactivity of the $[Au(IPr^{Cl})]^+$ fragment in comparison to the $[Au(IPr)]^+$ analogue.

**Catalytic Activity of $[Au(IPr^{Cl})][BF_4]$.** The predicted high Lewis acidity of **3** (from the $^{13}C$ NMR chemical shift of the carbene) and its facile conversion to both acetonitrile complex $[Au(IPr^{Cl})(NCCH_3)][BF_4]$ (**7**) and digold hydroxide complex $[\{Au(IPr^{Cl})\}_2(\mu\text{-}OH)][BF_4]$ (**8**) suggested that it could be used as a catalyst in transformations that are known to be mediated by those complexes. Various reactions that proceed through $\pi$ activation of triple bonds or by $\sigma$ activation of benzylic alcohols were selected: alkyne hydration, hydroalkoxylation with various alcohols, and dehydrative etherification. Next to comparison of the activities of complexes **3**, **7**, and **8** with $BF_4^-$ counterions the neutral triflimide complex $[Au(IPr^{Cl})(NTf_2)]$ (**9**) was also tested to allow for comparison of results of complexes with different anions.[7a,23] The catalyst system $AgBF_4/[Au(IPr^{Cl})(Cl)]$ (**1**) was included in the benchmarking studies to provide an example of an in situ generated species.[61] The catalytic activity of complex **3** in all of these transformations confirmed the catalytic relevance of this gold(I) species with an inner-sphere coordinating counterion. Additional stoichiometric reactions of **3** seemed to indicate that $BF_4^-$ was a better ligand for $[Au(IPr^{Cl})]^+$ than alcohols and $[Au(IPr^{Cl})(OHR)][BF_4]$ species were not observed.

**Computational Modeling Studies.** To support the experimental observations, modeling studies using DFT implemented in the Gaussian09 package[78] with the BP86

GGA functional[79] were conducted.[61] Benchmarking studies established that the important consideration of solvent effects with the charged species involved through use of the PCM solvation model for $CH_2Cl_2$ permitted predictions to be made with an accuracy of approximately 5 kcal $mol^{-1}$. Negative Gibbs free energy values of −10.0 and −9.1 kcal $mol^{-1}$ for displacement of $BF_4^-$ from **3**-in by acetonitrile or $[Au(IPr^{Cl})(OH)]$ (**2**) to form $[Au(IPr^{Cl})(NCCH_3)][BF_4]$ (**7**) or $[\{Au(IPr^{Cl})\}_2(\mu\text{-}OH)][BF_4]$ (**8**) were in agreement with the experimental observations (Scheme 6). Small absolute Gibbs free energy values (<1.0 kcal $mol^{-1}$) for reactions of **3**-in with diphenylacetylene (**11**) or methanol could not be used to support the corresponding experimental results. A large positive Gibbs free energy value of 6.5 kcal $mol^{-1}$ for displacement of $BF_4^-$ from **3**-in by phenol agreed with the experimental result.

**Scheme 6. Reactions of 3-in with Various Compounds**



[a]Association of two molecules of **3**-in. [b]Dissociation of $BF_4^-$ from **3**-in. Free energy changes (PCM, dichloromethane) are given in kcal $mol^{-1}$ in parentheses. Shaded areas highlight spontaneous reactions (green), nonspontaneous reactions (red), and reactions where a firm assignment could not be made (gray).

The favorable existence of **3** as $[Au(IPr^{Cl})(FBF_3)]$ (**3**-in) rather than as an outer-sphere species such as $[Au(IPr^{Cl})(L)][BF_4]$ (**3**-out) or solvent-separated ion pair $[Au(IPr^{Cl})(CH_2Cl_2)][BF_4]$ (**15**) also followed from positive calculated Gibbs free energy values of 9.8 and 6.8 kcal $mol^{-1}$.[80] This first value was nearly as large as the calculated Gibbs free energy value for association of 2 equiv of **3**-in to form $[\{Au(IPr^{Cl})\}_2(BF_4)][BF_4]$ (**13**) of 10.4 kcal $mol^{-1}$. Even though dissociation of $BF_4^-$ from **3**-in remained disfavored, coordination of a solvent molecule incurred some stability relative to **3**-out with an empty coordination site on gold. These data were in qualitative agreement with the experimental results that predicted a slightly unfavorable reaction of **3**-in to $[Au(IPr^{Cl})(CDCl_3)][BF_4]$ (**6**) ($\Delta G$ = 1.0 kcal $mol^{-1}$) and the existence of the $[Au(IPrCl)]^+$ fragment as a monomeric species in solution.

## CONCLUSIONS

Having capitalized on the apparently remarkably more stable gold(I) complexes bearing the $IPr^{Cl}$ ligand in comparison to those bearing other NHC ligands, we found a stable species containing the $[Au(IPr^{Cl})]^+$ fragment to exist in the presence of a tetrafluoroborate counterion as the stable species $[Au(IPr^{Cl})(FBF_3)]/[Au(IPr^{Cl})(L)][BF_4]$ (**3**) without the need for an auxiliary stabilizing ligand. Even though this complex resembled a neutral gold fluoride in the solid state, the $BF_4^-$ anion remained labile and complex **3** could be considered an equilibrium between neutral and cationic gold species in solution. A series of NMR experiments and computational modeling studies have unveiled a process that interconverts inner-sphere and outer-sphere coordinating counterions in these two conformations and confirmed the favorable coordination of solvent molecules in the coordinatively unsaturated complex where the $BF_4^-$ anion resided in the outer sphere. Both stoichiometric and catalytic studies have shown that the $[Au(IPr^{Cl})]^+$ fragment in complex **3** retained a behavior similar to that known for other gold(I) complexes that bear that $IPr^{Cl}$ ligand. The ability of a weakly coordinating counterion to coordinate to a cationic gold(I) fragment in the absence of better auxiliary ligands should be considered in the design of future catalyst systems. Future studies will be devoted to gaining an understanding of the stability of the complex bearing the $IPr^{Cl}$ ligand relative to congeners bearing other NHC ligands. The mechanism of activation of different types of substrates such as alkynes and alcohols by complex **3** is the subject of extended investigations as well.

## EXPERIMENTAL SECTION

**Procedure for Synthesis of 3.** To a stirred solution of $[Au(IPr^{Cl})(CH_2COCH_3)]$ (**4**) in dichloromethane (1.4 M) was added, at room temperature in air, a solution of $HBF_4·OEt_2$ (50% in diethyl ether, 1.05 equiv). After 30 min, the solution was filtered over $MgSO_4$ with additional dichloromethane (3 times the initial reaction volume). Part of the solvent was removed under vacuum (about half of the initial reaction volume remained), and the product was precipitated by addition of pentane (about the initial reaction volume). The product was collected by filtration, washed with additional pentane (about 2 times the initial reaction volume), and dried under high vacuum to give a microcrystalline solid in quantitative yield. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.60 (t, $^3J(H,H)$ = 7.7 Hz, 2H; *p*-PhC), 7.36 (d, $^3J(H,H)$ = 7.7 Hz, 4H; *m*-PhC), 2.39 (h, $^3J(H,H)$ = 6.8 Hz, 4H; C*H*), 1.34 (d, $^3J(H,H)$ = 6.8 Hz, 12H; $CH_3$), 1.27 (d, $^3J(H,H)$ = 6.8 Hz, 12H; $CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta$ 163.2 (1C; $C_{carb}$), 146.1 (4C; *o*-PhC), 132.1 (4C; *i*-PhC), 130.8 (2C; *p*-PhC), 124.9 (4C; *m*-PhC), 119.6 (2C; *C*), 29.3 (4C; CH), 24.5 (4C; $CH_3$), 23.7 (4C; $CH_3$). $^{11}B$ NMR (128 MHz, $CDCl_3$): $\delta$ −0.70 (br), −1.40 (s). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): $\delta$ −149.6 (br), −149.7 (q, $^1J(F,B)$ = 5.2 Hz), −153.2 (s), −153.3 (s). Anal. Calcd for $C_{29}H_{37}AuBCl_2F_4N_3$: C, 43.75; H, 4.62; N, 3.78. Found: C, 43.64; H, 4.70; N, 3.74. FTIR (ATR): $\tilde{\nu}$ 1059 $cm^{-1}$ (B−F).

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00345.

General information, crystallographic information, characterization data for stoichiometric and catalytic experiments, and DFT calculations (PDF)
Cartesian coordinates for calculated structures (XYZ)
Cartesian coordinates for calculated structures (XYZ)

### Accession Codes

CCDC 1514529 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

$BArF_{24}$ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate; COSY = correlation spectroscopy; 6-Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidinylidene; DOSY = diffusion-ordered spectroscopy; DTBM-Segphos = 5,5′-bis[bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole; EXSY = exchange spectroscopy; HOESY = heteronuclear NOESY; IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene; $I^{t}Bu$ = 1,3-di-*tert*-butylimidazol-2-ylidene; $IPr^{Cl}$ = 4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IPr** = 1,3-bis{2,6-bis[bis(4-*tert*-butylphenyl)methyl]-4-methylphenyl}-2,3-dihydro-1*H*-imidazol-2-ylidene; IMe = 1,3-dimethylimidazol-2-ylidene; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; ITrop = 1,3-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)imidazol-2-ylidene; nbd = norbornadiene; NMR = nuclear magnetic resonance; NHC = N-hetereocyclic carbene; NOESY = NOE spectroscopy; NOE = nuclear Overhauser effect; SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; Tf = trifluoromethanesulfonate; TFA = trifluoroacetic acid; Ts = tosylate

## ■ REFERENCES

(1) (a) Hashmi, A. S. K. *Gold Bull.* **2004**, *37*, 51−65. (b) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896−7936. (c) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180−3211. (d) Raubenheimer, H. G.; Cronje, S. *Chem. Soc. Rev.* **2008**, *37*, 1998−2011. (e) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561−3598. (f) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448−2462. (g) Leyva-Pérez, A.; Corma, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 614−635. (h) Raubenheimer, H. G.; Schmidbaur, H. *J. Chem. Educ.* **2014**, *91*, 2024−2036. (i) Hashmi, A. S. K. *Acc. Chem. Res.* **2014**, *47*, 864−876. (j) Friend, C. M.; Hashmi, A. S. K. *Acc. Chem. Res.* **2014**, *47*, 729−730. (k) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028−9072. (l) Pflästerer, D.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2016**, *45*, 1331−1367.

(2) (a) Zuccaccia, D.; Belpassi, L.; Rocchigiani, L.; Tarantelli, F.; Macchioni, A. *Inorg. Chem.* **2010**, *49*, 3080−3082. (b) Biasiolo, L.; Del Zotto, A.; Zuccaccia, D. *Organometallics* **2015**, *34*, 1759−1765.

(3) (a) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776−1782. (b) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351−3378. (c) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676. (d) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. *Acc. Chem. Res.* **2012**, *45*, 778−787.

(4) Nun, P.; Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 9113.

(5) (a) Peone, J.; Vaska, L. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 511−512. (b) Bond, G. C. *Gold Bull.* **1972**, *5*, 11−13. (c) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405−6406. (d) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405−408. (e) Preisenberger, M.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1645−1650.

(6) Jia, M.; Bandini, M. *ACS Catal.* **2015**, *5*, 1638−1652.

(7) (a) Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704−4707. (b) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 2742−2744. (c) Patrick, S. R.; Gómez-Suárez, A.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2014**, *33*, 421−424. (d) Ramón, R. S.; Gaillard, S.; Poater, A.; Cavallo, L.; Slawin, A. M. Z.; Nolan, S. P. *Chem. - Eur. J.* **2011**, *17*, 1238−1246.

(8) Gaillard, S.; Rix, D.; Slawin, A. M. Z.; Lacour, J.; Nolan, S. P. *Dalton Trans.* **2012**, *41*, 8235.

(9) (a) Hirner, J. J.; Faizi, D. J.; Blum, S. A. *J. Am. Chem. Soc.* **2014**, *136*, 4740−4745. (b) Jaroschik, F.; Simonneau, A.; Lemière, G.; Cariou, K.; Agenet, N.; Amouri, H.; Aubert, C.; Goddard, J.-P.; Lesage, D.; Malacria, M.; Gimbert, Y.; Gandon, V.; Fensterbank, L. *ACS Catal.* **2016**, *6*, 5146−5160.

(10) Weber, S. G.; Zahner, D.; Rominger, F.; Straub, B. F. *Chem. Commun.* **2012**, *48*, 11325.

(11) Biasiolo, L.; Trinchillo, M.; Belanzoni, P.; Belpassi, L.; Busico, V.; Ciancaleoni, G.; D'Amora, A.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D. *Chem. - Eur. J.* **2014**, *20*, 14594−14598.

(12) Trinchillo, M.; Belanzoni, P.; Belpassi, L.; Biasiolo, L.; Busico, V.; D'Amora, A.; D'Amore, L.; Del Zotto, A.; Tarantelli, F.; Tuzi, A.; Zuccaccia, D. *Organometallics* **2016**, *35*, 641−654.

(13) Ciancaleoni, G.; Belpassi, L.; Zuccaccia, D.; Tarantelli, F.; Belanzoni, P. *ACS Catal.* **2015**, *5*, 803−814.

(14) Gatto, M.; Belanzoni, P.; Belpassi, L.; Biasiolo, L.; Del Zotto, A.; Tarantelli, F.; Zuccaccia, D. *ACS Catal.* **2016**, *6*, 7363−7376.

(15) (a) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331. (b) Beck, W.; Suenkel, K. *Chem. Rev.* **1988**, *88*, 1405−1421. (c) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942. (d) Macchioni, A. *Chem. Rev.* **2005**, *105*, 2039−2074.

(16) Kovács, G.; Ujaque, G.; Lledós, A. *J. Am. Chem. Soc.* **2008**, *130*, 853−864.

(17) (a) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232−5241. (b) Ranieri, B.; Escofet, I.; Echavarren, A. M. *Org. Biomol. Chem.* **2015**, *13*, 7103−7118.

(18) Bartolomé, C.; Ramiro, Z.; Peñas-Defrutos, M. N.; Espinet, P. *ACS Catal.* **2016**, *6*, 6537−6545.

(19) de Frémont, P.; Marion, N.; Nolan, S. P. *J. Organomet. Chem.* **2009**, *694*, 551−560.

(20) Gaillard, S.; Bosson, J.; Ramón, R. S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P. *Chem. - Eur. J.* **2010**, *16*, 13729−13740.

(21) Baker, M. V.; Barnard, P. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2005**, 37−43.

(22) Brill, M.; Collado, A.; Cordes, D. B.; Slawin, A. M. Z.; Vogt, M.; Grützmacher, H.; Nolan, S. P. *Organometallics* **2015**, *34*, 263−274.

(23) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133−4136.

(24) The NMR studies showed that $BArF_{24}^{-}$ remained outer sphere and stabilization of the cationic gold center was described to originate from the interaction of the encapsulating ligand instead.

(25) Phillips, N.; Dodson, T.; Tirfoin, R.; Bates, J. I.; Aldridge, S. *Chem. - Eur. J.* **2014**, *20*, 16721−16731.

(26) de Frémont, P.; Stevens, E. D.; Fructos, M. R.; Mar Díaz-Requejo, M.; Pérez, P. J.; Nolan, S. P. *Chem. Commun.* **2006**, 2045−2047.

(27) Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem.* **2006**, *118*, 5581−5585; *Angew. Chem., Int. Ed.* **2006**, *45*, 5455−5459.

(28) (a) Akana, J. A.; Bhattacharyya, K. X.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 7736−7737. (b) Ciancaleoni, G.; Biasiolo, L.; Bistoni, G.; Macchioni, A.; Tarantelli, F.; Zuccaccia, D.; Belpassi, L. *Organometallics* **2013**, *32*, 4444−4447.

(29) Shapiro, N. D.; Toste, F. D. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 2779−2782.

DOI: 10.1021/acs.organomet.7b00345
*Organometallics* XXXX, XXX, XXX−XXX

(30) The alkyne-tethered phosphine ligand diphenyl(4-(triisopropylsilyl)but-3-yn-1-yl)phosphane coordinates to two distinct gold centers, producing an A-frame type complex. The alkene-tethered phosphine ligand (4-methylpent-3-en-1-yl)diphenylphosphane also coordinates to two distinct gold centeres, producing linkage polymers.
(31) Brown, T. J.; Sugie, A.; Dickens, M. G.; Widenhoefer, R. A. *Organometallics* **2010**, *29*, 4207−4209.
(32) $PR_3$ = (2-biphenyl)di-*tert*-butylphosphine, allene = 3-methylbuta-1,2-diene.
(33) Flörke, U.; Hoffmann, A.; Henkel, G. *CCDC 1452942: Experimental Crystal Structure Determination* **2016**, DOI: 10.5517/cc1krx3b.
(34) Herbert, D. E.; Lara, N. C.; Agapie, T. *Chem. - Eur. J.* **2013**, *19*, 16453−16460.
(35) Rossin, A.; Tuci, G.; Giambastiani, G.; Peruzzini, M. *ChemPlusChem* **2014**, *79*, 406−412.
(36) Döring, A.; Flörke, U.; Hoffmann, A.; Jones, M. D.; Kuckling, D.; Michaelis de Vasconcellos, J.; Herres-Pawlis, S. *Z. Anorg. Allg. Chem.* **2015**, *641*, 2147−2156.
(37) Salem, H.; Milstein, D.; Shimon, L. J. W. *CCDC 668208: Experimental Crystal Structure Determination* **2007**, DOI: 10.5517/ccdc.csd.ccqfb3k.
(38) Maier, J. M.; Li, P.; Hwang, J.; Smith, M. D.; Shimizu, K. D. *J. Am. Chem. Soc.* **2015**, *137*, 8014−8017.
(39) Friedemann, R.; Seppelt, K. *Eur. J. Inorg. Chem.* **2013**, *2013*, 1197−1206.
(40) Chernyshova, E. S.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2007**, *26*, 3236−3251.
(41) Fawcett, J.; Harding, D. A. J.; Hope, E. G.; Singh, K.; Solan, G. A. *Dalton Trans.* **2009**, 6861.
(42) Michelet, B.; Colard-Itté, J.-R.; Thiery, G.; Guillot, R.; Bour, C.; Gandon, V. *Chem. Commun.* **2015**, *51*, 7401−7404.
(43) Lingnau, R.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 436−436.
(44) Abadie, M.-A.; Trivelli, X.; Medina, F.; Capet, F.; Roussel, P.; Agbossou-Niedercorn, F.; Michon, C. *ChemCatChem* **2014**, *6*, 2235−2239.
(45) Tlahuext-Aca, A.; Hopkinson, M. N.; Daniliuc, C. G.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 11587−11592.
(46) Krossing, I.; Raabe, I. *Chem. - Eur. J.* **2004**, *10*, 5017−5030.
(47) Mankad, N. P.; Toste, F. D. *Chem. Sci.* **2012**, *3*, 72−76.
(48) Wyss, C. M.; Tate, B. K.; Bacsa, J.; Wieliczko, M.; Sadighi, J. P. *Polyhedron* **2014**, *84*, 87−95.
(49) Mankad, N. P.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 12859−12861.
(50) Winston, M. S.; Wolf, W. J.; Toste, F. D. *J. Am. Chem. Soc.* **2015**, *137*, 7921−7928.
(51) Kumar, R.; Linden, A.; Nevado, C. *Angew. Chem., Int. Ed.* **2015**, *54*, 14287−14290.
(52) Laitar, D. S.; Müller, P.; Gray, T. G.; Sadighi, J. P. *Organometallics* **2005**, *24*, 4503−4505.
(53) Veenboer, R. M. P.; Nolan, S. P. *Green Chem.* **2015**, *17*, 3819−3825.
(54) (a) Gómez-Suárez, A.; Oonishi, Y.; Meiries, S.; Nolan, S. P. *Organometallics* **2013**, *32*, 1106−1111. (b) Biannic, B.; Aponick, A. *Eur. J. Org. Chem.* **2011**, *2011*, 6605−6617. (c) Veenboer, R. M. P.; Dupuy, S.; Nolan, S. P. *ACS Catal.* **2015**, *5*, 1330−1334. (d) Dupuy, S.; Gasperini, D.; Nolan, S. P. *ACS Catal.* **2015**, *5*, 6918−6921.
(55) Möhlmann, L.; Wendt, O. F.; Johnson, M. T. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *67*, m719−m720.
(56) (a) Marion, N.; Ramón, R. S.; Nolan, S. P. *J. Am. Chem. Soc.* **2009**, *131*, 448−449. (b) Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653−2656.
(57) Such complexes are known to be catalytically inactive, and their facile formation under these general conditions explains why IMes ligands are only rarely used in homogeneous catalysis in comparison to the slightly larger IPr ligand.
(58) Cordón, J.; López-de-Luzuriaga, J. M.; Monge, M. *Organometallics* **2016**, *35*, 732−740.
(59) Gasperini, D.; Collado, A.; Goméz-Suárez, A.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P. *Chem. - Eur. J.* **2015**, *21*, 5403−5412.
(60) Kumar, M.; Jasinski, J.; Hammond, G. B.; Xu, B. *Chem. - Eur. J.* **2014**, *20*, 3113−3119.
(61) Full results and details are given in the Supporting Information.
(62) Amster, R. L.; Taylor, R. C. *Spectrochim. Acta* **1964**, *20*, 1487−1502.
(63) Hydrolysis of $BF_4^-$ anions to afford $HOBF_3$ units is known. In order to rule out the formation of this species, further analyses were carried out. See the Supporting Information for a detailed discussion.
(64) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.
(65) No additonal splitting of signals was detected in non-proton-decoupled fluorine NMR spectra.
(66) It could be assumed that the more symmetrical environment of the boron nucleus in the outer coordination sphere would impede the quadrupole relaxation that enabled the observation of heteronuclear coupling in the inner-sphere coordinating counterion.
(67) (a) Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, *501*, C1−C4. (b) de Frémont, P.; Singh, R.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2007**, *26*, 1376−1385. (c) Tapu, D.; Dixon, D. A.; Roe, C. *Chem. Rev.* **2009**, *109*, 3385−3407.
(68) Upfield shifts indicate a lower electron density at the carbenic carbon atom associated with a higher net charge transfer of the ligand to the gold atom, as dictated by the electron deficiency of the more Lewis acidic gold atom.
(69) Gaillard, S.; Slawin, A. M. Z.; Bonura, A. T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2010**, *29*, 394−402.
(70) Müller, R. S. R. Homogeneous gold catalysts: development of applications for gold(I) catalysts bearing *N*-heterocyclic carbene ligands. University of St Andrews, 2011.
(71) Gómez-Suárez, A.; Gasperini, D.; Vummaleti, S. V. C.; Poater, A.; Cavallo, L.; Nolan, S. P. *ACS Catal.* **2014**, *4*, 2701−2705.
(72) Collado, A.; Gómez-Suárez, A.; Martin, A. R.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2013**, *49*, 5541−5543.
(73) Meiries, S.; Nolan, S. *Synlett* **2014**, *25*, 393−398.
(74) Brulé, E.; Gaillard, S.; Rager, M.-N.; Roisnel, T.; Guérineau, V.; Nolan, S. P.; Thomas, C. M. *Organometallics* **2011**, *30*, 2650−2653.
(75) Formation of **8** would coincide with formation of 1 equiv of $HBF_4$ from deprotonation of water by the second equivalent of $BF_4^-$ in **3**. For dedicated experiments that show a shift of this equilibrium in the presence of excess $HBF_4$, see: Gaillard, S.; Bosson, J.; Ramón, R. S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P. *Chem. - Eur. J.* **2010**, *16*, 13729−13740.
(76) (a) Fu, M.-C.; Shang, R.; Cheng, W.-M.; Fu, Y. *ACS Catal.* **2016**, *6*, 2501−2505. (b) Zuccaccia, D.; Belpassi, L.; Tarantelli, F.; Macchioni, A. *J. Am. Chem. Soc.* **2009**, *131*, 3170−3171.
(77) Oonishi, Y.; Gómez-Suárez, A.; Martin, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 9767−9771.
(78) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian09 Revision B.01*; Gaussian Inc., Wallingford, CT.
(79) (a) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822−8824. (b) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater.*

*Phys.* **1986**, *34*, 7406−7406. (c) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547−2553.

(80) The energy of **3**-out has been calculated as the sum of separate $[Au(IPr^{Cl})]^+$ and $BF_4^-$ fragments.