ORGANOMETALLICS

Gold(I) and Gold(III) Complexes of Cyclic (Alkyl)(amino)carbenes

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S *Supporting Information*

ABSTRACT: The chemistry of Au(I) complexes with two types of cyclic (alkyl)(amino)carbene (CAAC) ligands has been explored, using the sterically less demanding dimethyl derivative ^{Me2}CAAC and the 2-adamantyl ligand ^{Ad}CAAC. The conversion of (^{Ad}CAAC)AuCl into (^{Ad}CAAC)AuOH by treatment with KOH is significantly accelerated by the addition of *t*BuOH. (^{Ad}CAAC)AuOH is a convenient starting material for the high-yield syntheses of (^{Ad}CAAC)AuX complexes by acid/base and C−H activation reactions (X = OAryl, CF_3CO_2, $N(Tf)_2$, C_2Ph, C_6F_5, C_6HF_4, $C_6H_2F_3$, $CH_2C(O)C_6H_4OMe$, $CH(Ph)C(O)Ph$, CH_2SO_2Ph), while the cationic complexes $[(^{Ad}CAAC)AuL]^+$ (L = CO, CN^{t}Bu) and (^{Ad}CAAC)AuCN were obtained by chloride substitution from (^{Ad}CAAC)AuCl. The reactivity toward variously substituted fluoroarenes suggests that (^{Ad}CAAC)AuOH is able to react with C−H bonds with pK_a values lower than about 31.5. This, together with the spectroscopic data, confirm the somewhat stronger electron-donor properties of CAAC ligands in comparison to imidazolylidene-type N-heterocyclic carbenes (NHCs). In spite of this, the oxidation of ^{Me2}CAAC and ^{Ad}CAAC gold compounds is much less facile. Oxidations proceed with C−Au cleavage by halogens unless light is strictly excluded. The oxidation of (^{Ad}CAAC)AuCl with $PhICl_2$ in the dark gives near-quantitative yields of (^{Ad}CAAC)AuCl$_3$, while $[Au(^{Me2}CAAC)_2]Cl$ leads to *trans*-$[AuCl_2(^{Me2}CAAC)_2]Cl$. In contrast to the chemistry of imidazolylidene-type gold NHC complexes, oxidation products containing Au−Br or Au−I bonds could not be obtained; whereas the reaction with $CsBr_3$ cleaves the Au−C bond to give mixtures of $[^{Ad}CAAC-Br]^+[AuBr_2]^-$ and $[(^{Ad}CAAC-Br)]^+[AuBr_4]^-$, the oxidation of (^{Ad}CAAC)AuI with I_2 leads to the adduct (^{Ad}CAAC)AuI·I$_2$. Irrespective of the steric demands of the CAAC ligands, their gold complexes proved more resistant to oxidation and more prone to halogen cleavage of the Au−C bonds than gold(I) complexes of imidazole-based NHC ligands.
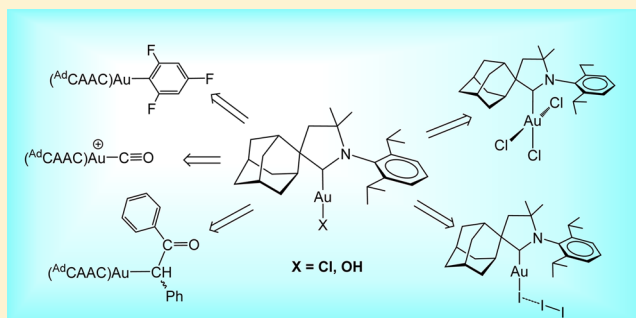
INTRODUCTION

Lappert's pioneering work in the early 1970s established N-donor-stabilized carbenes as remarkably versatile ligands across the Periodic Table, particularly for noble metals, and demonstrated the similarity of the coordination chemistry of N-heterocyclic carbenes (NHCs) and phosphines.[1−3] This work also included the first examples of gold NHC complexes, the dimethylimidazolidinylidene derivatives [Au{C-(NMe)$_2$C$_2$H$_4$}$_2$]X (X = Cl, BF$_4$).[4] Since then, N-heterocyclic carbenes have become one of the most successful and adaptable ligand classes in organometallic chemistry.[5]

A related type of saturated 5-ring carbene ligands is the family of cyclic (alkyl)(amino)carbenes (CAACs) developed by Bertrand et al.,[6] which were inter alia found capable of stabilizing complexes of zerovalent gold,[7] while gold(I) CAAC complexes act as catalysts for a range of interesting transformations.[8] These ligands show electron affinities more negative than those of the more widely used unsaturated imidazolin-2-ylidene type carbenes and higher ligand-to-metal charge transfer ΔN values; i.e., CAAC ligands behave as stronger σ donors.[9]

On the other hand, it is becoming apparent that, even with NHC ligands, the π-acceptor capacity has an important influence on reactivity.[10−13] As Ciancaleoni et al. showed

recently,[14] in contrast to the general description of NHCs as strong σ-donors, in the case of gold they donate less strongly than phosphines, and for this metal in particular there is a significant difference between NHCs with saturated and unsaturated rings; i.e. the π-acceptor capability is likely to play an important role.[11−13] With this in mind, we became interested in exploring the reactivity patterns of CAAC-type carbenes, and their possible differences in comparison to more conventional types of NHCs. We report here an exploration of the reactivity of CAAC gold complexes, including oxidation reactions to Au(III) compounds. Two types of CAAC ligands were employed: the sterically less demanding dimethyl derivative ^{Me2}CAAC and the 2-adamantyl ligand ^{Ad}CAAC (Chart I).[6]
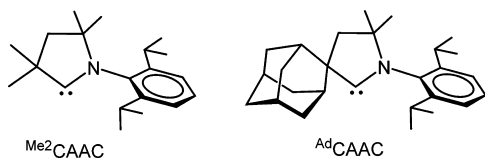
RESULTS AND DISCUSSION

Although gold(I) chloride complexes LAuCl are most commonly employed as entries into ligand exchange reactions and catalytic transformations, often in combination with silver

Chart I

salts, it can be synthetically advantageous to substitute the chloride ligand for a more labile oxygen-containing ligand, so that subsequent reactions benefit from the relative weakness of the Au−O bond.[15] We therefore decided to prepare the corresponding CAAC gold(I) alkoxides, hydroxides, and carboxylates.

Anion Exchange Reactions. The reaction of (^{Ad}CAAC)-AuCl (**1**) with sodium *tert*-butoxide in toluene generates the white alkoxide complex (^{Ad}CAAC)AuO^{t}Bu (**2**) in essentially quantitative yield (Scheme 1).[16] The alkoxide is very sensitive to hydrolysis, and the reaction must be conducted in anhydrous solvents under inert gas. Treatment of **2** with water readily produces the air-stable hydroxide (^{Ad}CAAC)AuOH (**3**). Complex **3** is characterized in its ^{1}H NMR spectrum by a broadened singlet of the OH ligand at δ −0.29 ppm (in C$_6$D$_5$Br).

The same product is also accessible directly from the reaction between the chloride **1** and KOH; however, this reaction proved to be very slow, requiring over 48 h to achieve a 75% conversion. On the other hand, we found that the addition of ^{t}BuOH to the mixture significantly accelerates the rate of chloride substitution and generates the hydroxide **3** cleanly within 24−36 h, evidently due to equilibrium concentrations of strongly nucleophilic ^{t}BuO$^-$, which catalyzes chloride substitution.[17] The use of CsOH, which is often found preferable in gold chloride substitution reactions, is therefore unnecessary. Both complexes **2** and **3** are soluble in polar and aromatic organic solvents (THF, toluene, 1,2-difluorobenzene) and insoluble in hexanes. Chlorinated solvents (CHCl$_3$, CH$_2$Cl$_2$, and 1,2-dichloroethane) should be avoided, because their presence tends to lead to the regeneration of the gold chloride. While the hydroxide **3** can be stored at room temperature in air for months, the *tert*-butoxide **2** is very sensitive to hydrolysis and has to be kept under an inert atmosphere. The carbene-C resonance in the ^{13}C NMR spectra of **2** and **3** is observed at δ

238, slightly upfield from the chloride precursor complex (^{Ad}CAAC)AuCl (δ 239.9).

During reactions of **3** with *p*-methoxyacetophenone (vide infra), a small crop of crystals of a condensation product of **3** was also obtained, the O-bridged cluster [{(^{Ad}CAAC)Au}$_3$(μ_3-O)]$^+$OH$^-$. This compound was identified crystallographically (see the Supporting Information, Figure S9). It is analogous to the well-known Nesmeyanov cation,[18] and its formation indicates that, in spite of the steric bulk of ^{Ad}CAAC, condensation of the hydroxide can still take place.[19]

Both (^{Ad}CAAC)AuO^{t}Bu (**2**) and (^{Ad}CAAC)AuOH (**3**) react cleanly with arylboronic acids in toluene under neutral conditions, i.e. without the addition of external bases, to give the corresponding gold aryls, exemplified here by the quantitative formation of (^{Ad}CAAC)Au(*p*-C$_6$H$_4$F) (**4**; see Scheme 1). Neutral conditions have been shown to be preferable for reactions of boronic acids with both Au(I)[20] and Au(III)[21] hydroxides and to lead cleanly to the corresponding gold organyl complexes in excellent yields.

The reaction of **3** with trifluoroacetic acid (tfaH) affords (^{Ad}CAAC)Au(tfa) (**5**). This product is also accessible directly from (^{Ad}CAAC)AuCl and Ag(tfa). Both methods give essentially quantitative yields; however, the latter approach contaminates the desired complex with traces of silver salts. The carbene carbon resonance is observed at δ(^{13}C) 232.4. This upfield shift of the carbene ^{13}C signal in comparison to that of the chloro complex is observed for all the complexes with Au−O bonds described here but is particularly pronounced for the trifluoroacetate. Complex **5** proved to be temperature sensitive and should be stored at −30 °C to avoid darkening of the sample.

The hydroxide **3** is a convenient starting material for the preparation of gold aryloxides and reacts with 3,5-di-*tert*-butylphenol to give the corresponding gold phenolate complex **6** in high yield. This synthetic method offers advantages over salt metathesis approaches, since reactions can be carried out in air and isolation of analytically pure products is straightforward. Complex **6** was isolated as a white stable solid which can be handled in air for weeks and is stable in toluene solution for months without noticeable decomposition. Like the hydroxide and alkoxide compounds, **6** is sensitive to chlorinated solvents; therefore, such solvents have to be avoided. The ^{13}C carbene-C resonance is observed at δ 236.1 (in C$_6$D$_6$).

Scheme 1
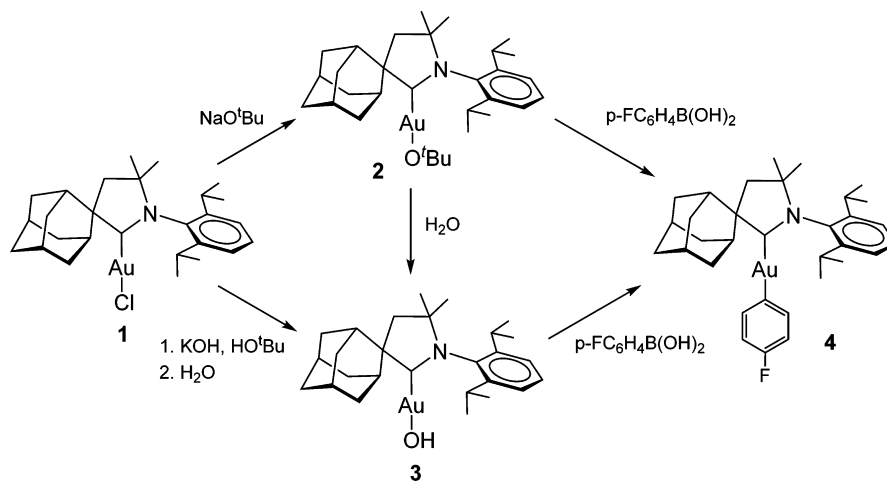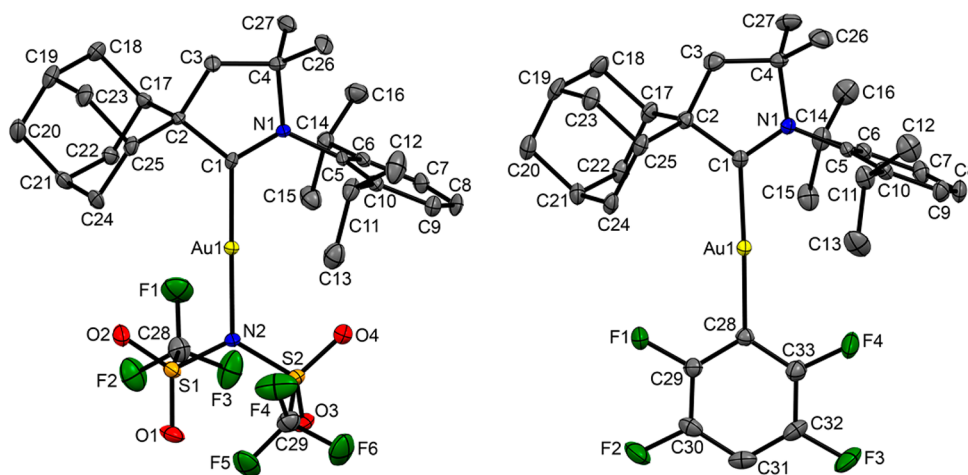
Figure 1. Crystal structures of (left) (^{Ad}CAAC)AuNTf$_2$ (**7**) and (right) (^{Ad}CAAC)AuC$_6$HF$_4$ (**11**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): complex **7**, Au−C(1) 1.977(4), Au−N(2) 2.098(3), N(2)−S(1) 1.627(4), C(1)−C(2) 1.528(5), C(1)−N(1) 1.315(5), C(1)−Au−N(2) 178.64(16), S(1)−N(2)−Au 119.48(19); complex **11**, Au−C(1) 2.018(3), Au−C(28) 2.038(3), C(1)−C(2) 1.528(4), C(1)−N(1) 1.301(4), C(1)−Au−C(28) 177.54(11).

Scheme 2. Syntheses of Gold(I) ^{Ad}CAAC Complexes^a
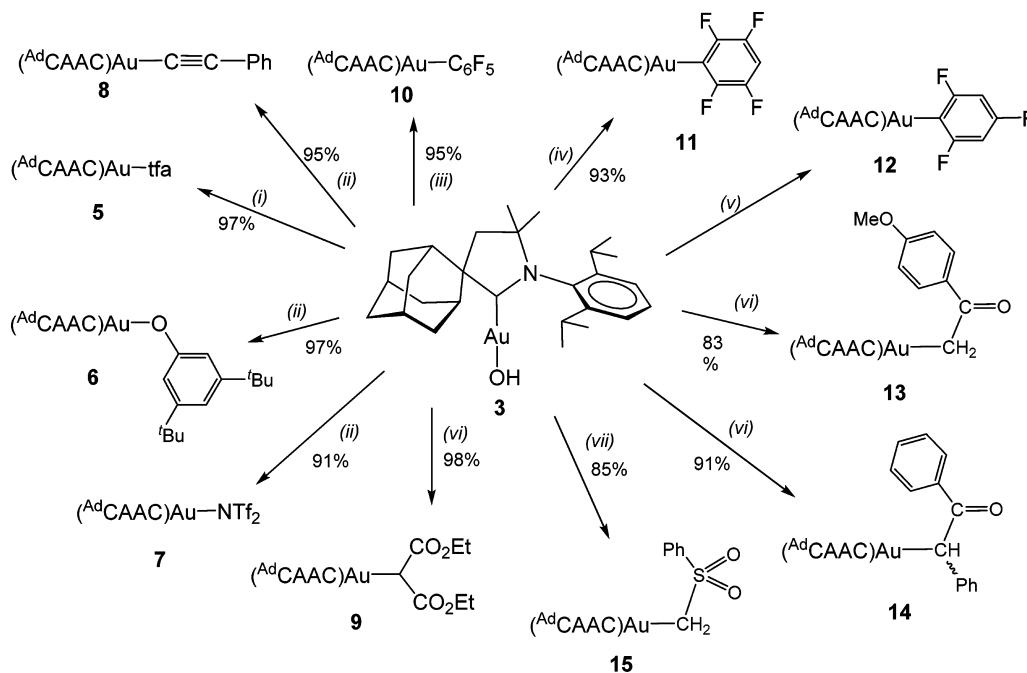
^{a}Reaction conditions: (i) Htfa, toluene, 23 °C, 4 h; (ii) toluene, 23 °C, 18 h; (iii) toluene, 60 °C, 18 h; (iv) toluene, 80 °C, 18 h; (v) 1,4-dioxane, 75 °C, 18 h; (vi) toluene, 70 °C, 12 h; (vii) toluene, 70 °C, 18 h.

The reaction of the gold hydroxide **3** with HNTf$_2$ in toluene is a high yield route to the Gagosz-type[22] complex (^{Ad}CAAC)-AuNTf$_2$ (**7**), which is of interest for silver-free protocols in gold catalysis.[23] Complex **7** is an air-stable white solid which is soluble in all polar organic solvents. The carbene resonance was observed at δ 233.8. The molecular structure of **7** is shown in Figure 1. The complex is linear; the Au−N and Au−C bond lengths fall in the ranges of 2.077(3)−2.094(3) and 1.969(2)−1.985(2) Å, respectively, similar to those for previously reported (NHC)AuNTf$_2$ complexes.[22]

C−H Activation Reactions. The basicity of (^{Ad}CAAC)-AuOH may be exploited to activate C−H bonds. Phenyl-acetylene and diethyl malonate give the corresponding metalation products (^{Ad}CAAC)AuC≡CPh (**8**) and (^{Ad}CAAC)-

AuCH(CO$_2$Et)$_2$ (**9**), respectively (see Scheme 2). Compounds **8** and **9** are white solids, stable in air at room temperature. Bertrand has previously reported the synthesis of complex **8** in the reaction of (^{Ad}CAAC)AuCl with the lithium salt of phenylacetylene.[8a] The hydroxide route allows the synthesis of **8** by a simpler procedure in air.

The reactivity of **3** toward a series of fluorobenzenes with decreasing degrees of F substitution enables the pK_a value of the gold hydroxide to be estimated. The pK_a values of a range of fluoroarenes have been calculated,[24] with values of 29.0 and 23.1 for C$_6$HF$_5$ and 1,2,4,5-C$_6$H$_2$F$_4$, respectively. As expected, **3** reacts with pentafluorobenzene at 60 °C and with 1,2,4,5-tetrafluorobenzene at 80 °C to give the corresponding aryl complexes (^{Ad}CAAC)AuC$_6$H$_{5−n}$F$_n$ (**10**, n = 5; **11**, n = 4) in

essentially quantitative yields (see Scheme 2). The structure of (^{Ad}CAAC)AuC$_6$HF$_4$ is shown in Figure 1. The Au−C(carbene) and Au−C(aryl) bond lengths are similar to those reported in the analogous complex (NHC)AuC$_6$H$_2$F$_3$ (2.026(3) and 2.044(3) Å).[25]

Prolonged heating with the less C−H acidic 1,3,5-trifluorobenzene (pK_a ≈ 31.5) also leads to the formation of the corresponding gold aryl complex (^{Ad}CAAC)Au(2,4,6-C$_6$H$_2$F$_3$) (**12**); however, the reaction is slow and the product was contaminated with unreacted hydroxide **3**. A higher temperature of 90 °C accelerated the gold arylation, but according to the ^{19}F NMR spectrum this was accompanied by some decomposition. The new set of resonances for fluorine atoms in the ^{19}F NMR spectrum was detected as multiplets centered at δ −84.60 (2F) and −116.86 (1F). To prove that these multiplets corresponded to the desired complex **12**, we performed the auration of 1,3,5-trifluorobenzene with the more basic (^{Ad}CAAC)Au(O^{t}Bu), generated in situ from (^{Ad}CAAC)-AuCl and NaO^{t}Bu (eq 1). These mixtures proved more reactive

$$(^{Ad}CAAC)Au \quad\text{—}\quad \text{(aryl F}_3\text{)} \qquad (1)$$

12, 49%
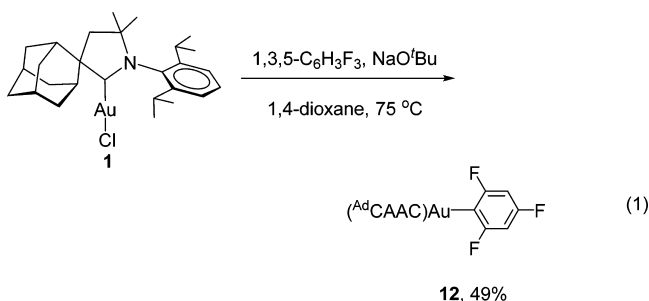
than pure isolated **3** and gave the desired complex **12** in 49% yield. The formation of **12** is accelerated by higher temperatures (75 °C), but since the *tert*-butoxide **2** is somewhat temperature sensitive, its slow decomposition may explain the reduced yield.

The auration of 1,3,5-trifluorobenzene by **3** and (^{Ad}CAAC)-AuCl/NaO^{t}Bu mixtures is in contrast with the lack of reactivity of (IPr)AuOH[23] and is an indication for the enhanced basicity provided by the CAAC ligand. On the other hand, no reaction was observed with 1,2-difluorobenzene and with monofluorobenzene. The reactivity decreases therefore in the sequence shown in Scheme 3;[24] evidently (^{Ad}CAAC)AuOH is sufficiently basic to undergo reactions with C−H bonds with pK_a values of 31.5 or less. This reactivity places the (CAAC)AuOH complexes closer to that of Larossa's systems (^{t}Bu$_3$P)AuCl/AgSbF$_6$ and (R$_3$P)AuCl/NaO^{t}Bu, which also aurate 1,3,5-trifluorobenzene.[25]

The hydroxide **3** is a convenient starting material for the metalation of a series of functionalized C−H compounds. For example, the reaction of (^{Ad}CAAC)AuOH with *p*-methoxyacetophenone, deoxybenzoin, and methyl phenyl sulfone gave the corresponding gold alkyls (^{Ad}CAAC)AuR (R = CH$_2$C(O)-

C$_6$H$_4$OMe (**13**), CH(Ph)C(O)Ph (**14**) and CH$_2$SO$_2$Ph (**15**); see Scheme 2). Related α-keto alkyls have previously been postulated as catalytic intermediates, e.g. Pd−CH(Ph)C(O)Ph species, in the α,α-diarylation of acetophenone en route to tamoxifen precursors.[26] The reaction of **3** with acetophenone has a precedence in the formation of (Ph$_3$P)Au-CH$_2$C(O)Ph from acetophenone and Nesmeyanov's [Au$_3$($μ_3$-O)(PPh$_3$)$_3$]$^+$ cation,[27] while more recent alternative syntheses of gold α-keto alkyls have involved the use of silyl enolates with (Ph$_3$P)AuCl/CsF reagents.[28,29]

The C−H activated products **8−15** were isolated as white air-stable solids which are soluble in all common organic solvents, with the exception of alkanes. Unlike the other compounds, the deoxybenzoin gold complex **14** possesses very low solubility in benzene and toluene. The resonances of the gold methine proton for **9** and **14** and of the gold methylene protons for **13** and **15** are shifted downfield by 1−2 ppm in the ^{1}H NMR spectra in comparison to the signals for the free ligands. The ^{13}C carbene-carbon resonances for **8−15** are shifted upfield relative to those for (^{Ad}CAAC)AuCl and are observed in the range δ 253.2−260.2. The Au-CHR^{1}R^2 center in the C$_1$-symmetric complex **14** is chiral; the complex therefore shows two sets of resonances related to the ^{Ad}CAAC ligand in its ^{1}H NMR spectrum, since the CH$_2$ and CMe$_2$ moieties of the CAAC ligand are diastereotopic (see the Supporting Information). This is illustrated by the crystal structure of complex **14** (Figure 2), which shows that the isopropyl group
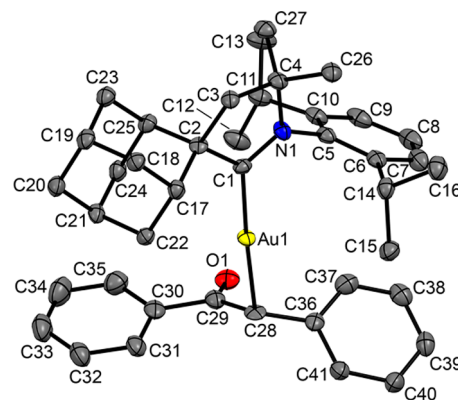
Figure 2. Crystal structure of (^{Ad}CAAC)Au(deoxybenzoinyl) (**14**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−C(1) 2.039(4), Au−C(28) 2.142(4), C(1)−C(2) 1.522(6), C(1)−N(1) 1.308(6), O(1)−C(29) 1.240(6), C(29)−C(28) 1.465(7), C(29)−C(30) 1.527(6), C(28)−C(36) 1.514(6), C(1)−Au−C(2) 176.89(14).
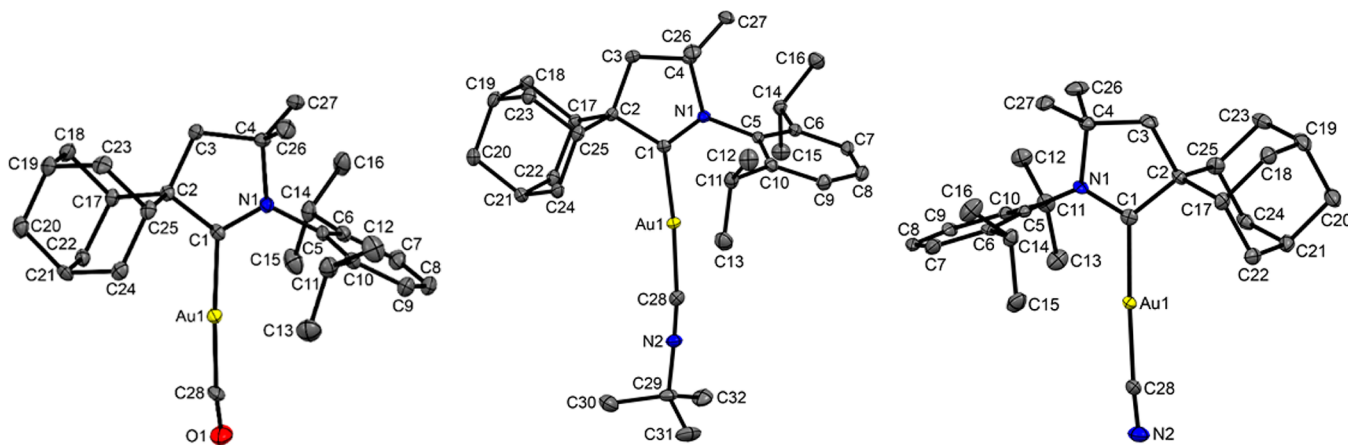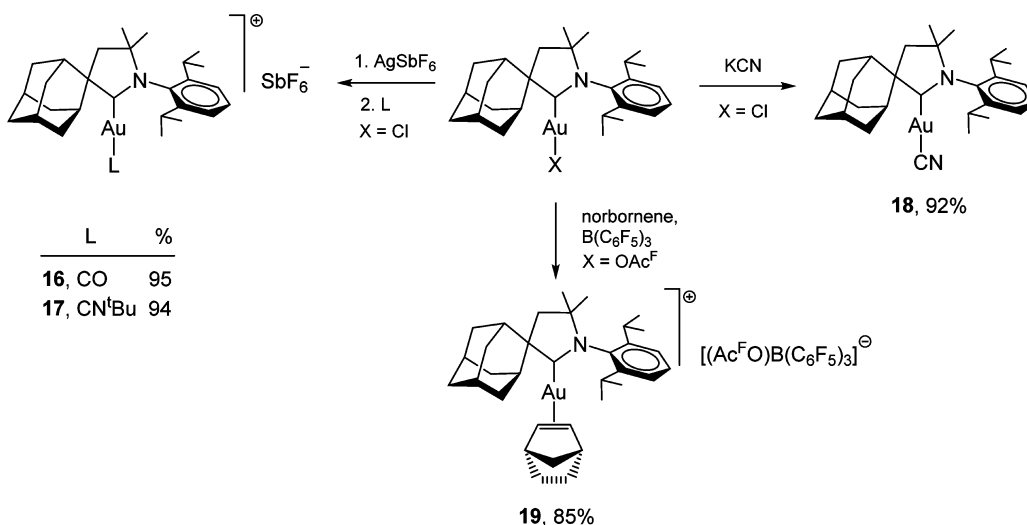
C(14)−C(15)−C(16) occupies a position almost above the phenyl ring of deoxybenzoin (C36−C41), with atom C(15) oriented toward the phenyl ring plane (3.747(8) Å). This

Scheme 3. ^{a}
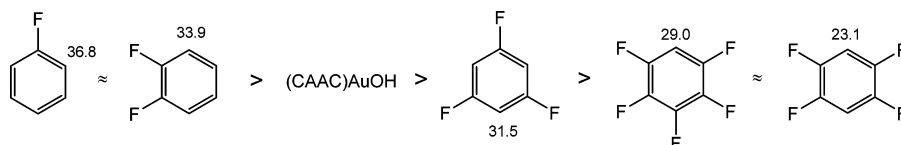
^{a}Values given are calculated pK_a values.[24]

Scheme 4

Figure 3. Solid-state structures of the cations in (left to right) [(^{Ad}CAAC)Au(L)]SbF$_6$ (L = CO (**16**), ^{t}BuNC (**17**)) and (^{Ad}CAAC)AuCN (**18**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **16**, Au−C(1) 2.035(4), Au−C(28) 1.964(5), C(28)−O(1) 1.108(6), C(1)−C(2) 1.519(6), C(1)−N(1) 1.290(5), C(1)−Au−C(28) 173.97(17), Au−C(28)−O(1) 172.9(4); **17**, Au−C(1) 2.022(2), Au−C(28) 1.986(3), C(28)−N(2) 1.143(3), N(2)−C(29) 1.467(3), C(1)−C(2) 1.525(3), C(1)−N(1) 1.304(3), C(1)−Au−C(28) 175.05(9), Au−C(28)−N(2) 174.2(2), C(28)−N(2)−C(29) 177.5(2); **18**, Au−C(1) 2.031(5), Au−C(28) 2.017(5), C(28)−N(2) 1.127(6), C(1)−C(2) 1.516(7), C(1)−N(1)1 1.316(5), C(1)−Au−C(28) 177.33(16), Au−C(28)−N(2) 176.4(5).

spatial orientation of C(15) explains the high-field ^{1}H NMR chemical shift of this methyl group, at δ 0.89, due to magnetic shielding by the aryl.

Functionalized alkyl complexes such as **13−15** should, in principle, provide access to α-keto carbenes, which have been suggested as elusive transient intermediates in a number of organic transformations.[30] Preliminary tests have shown, however, that these complexes do not undergo α-hydride abstraction with standard electrophiles such as CPh$_3^+$ salts. Methods for generating functionalized gold carbene complexes are currently being investigated.

CO, CN, and Alkene Complexes. The reaction of **1** with silver salts in the presence of CO or ^{t}BuNC gives the corresponding cationic complexes [(^{Ad}CAAC)Au(L)]$^+$ (L = CO (**16**); L = ^{t}BuNC (**17**)), which were isolated as SbF$_6^-$ salts in high yields (Scheme 4). Complexes **16** and **17** are white solids, soluble in low-coordinating polar organic solvents (CH$_2$Cl$_2$, 1,2-difluorobenzene). Coordinating solvents such as acetone lead to immediate CO effervescence. All complexes are

stable in air, but the carbonyl **16** has to be stored under a CO atmosphere.

The IR spectrum of **16** shows the CO stretching vibration at 2183 cm^{-1}. As is characteristic for CO complexes of gold ions, the CO stretching frequency is higher than that of free CO (2143 cm^{-1}). The CO stretch of **16** falls within the range observed for CO complexes of Au(I) with phosphine and carbene ligands;[14,31] for instance, the ν(CO) value of **16** is marginally lower than those of [(Mes$_3$P)Au(CO)][SbF$_6$] (Mes = 2,4,6-C$_6$H$_2$Me$_3$) and [(SIDipp)Au(CO)][SbF$_6$], (by 2 and 14 cm^{-1}, respectively).[31] Similarly, the IR spectrum of the isonitrile complex **17** displays a strong vibration at 2241 cm^{-1} which is blue-shifted in comparison to the signal for free *tert*-butyl isocyanide (2135 cm^{-1}) and almost identical with that of [(SIDipp)Au(CN^{t}Bu)][SbF$_6$] (2244 cm^{-1}).[31]

The cyano complex (^{Ad}CAAC)AuCN (**18**) was prepared for comparison with the CO compound, by reaction of the hydroxide (^{Ad}CAAC)AuOH with Me$_3$SiCN or of that of (^{Ad}CAAC)AuCl and KCN. Both approaches lead to almost quantitative yields of complex **18**. The complex shows a ν_{CN}

Scheme 5
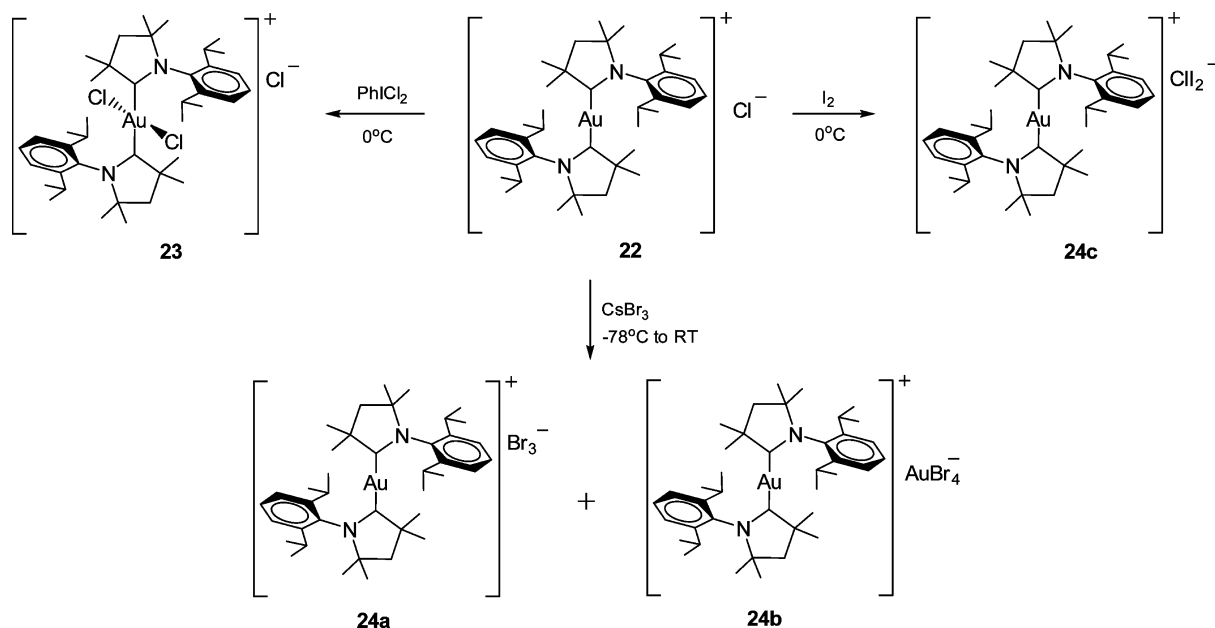
frequency of 2140 cm^{-1}. The C−N frequency of cyanide anions is relatively insensitive to the nature of the ligand in a trans position, and the value is close to that observed for a range of gold(I) CN complexes with phosphine and carbene ligands. There was no ligand rearrangement to give [Au(CN)$_2$]$^-$ salts, as seen for [Au(PMes$_3$)$_2$][Au(CN)$_2$] prepared by the (Mes$_3$P)-AuCl/KCN route.[31] Complex **18** is stable in air and soluble in all polar organic solvents.

The ^{1}H NMR spectra show that the chemical shifts for the CAAC-CH$_2$ protons in the five-membered rings of **16**−**18** are about 0.3−0.8 ppm upfield of that of (^{Ad}CAAC)AuCl. The carbene-C resonances for **16**−**18** are observed at δ 241.1, 246.2, and 253.1, respectively. The CO ^{13}C signal of **16** (δ 182.4) is almost identical with that of [(SIDipp)Au(CO)]-[SbF$_6$] (δ 182.7). The *tert*-butyl isocyanide CNC(CH$_3$)$_3$ ^{13}C shifts of **17** are observed at δ 142.4 and 58.6, broadened by bonding to quadrupolar ^{14}N. **18** shows a ^{13}CN resonance at δ 149.5, slightly shifted upfield of that of (SIDipp)AuCN (δ 152.4).[31] Overall, therefore, these data suggest that the electronic characteristics of CAAC ligands are generally comparable to those of saturated imidazolidinylidene-type NHCs.
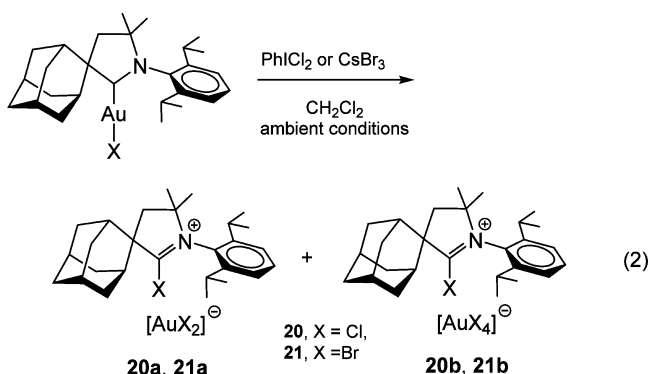
The crystal structures of the CO, ^{t}BuCN, and CN complexes are shown in Figure 3. The carbonyl complex **16** shows the greatest deviation from linear geometry: C(1)−Au−C(28) 172.9(4)°. The Au−C(28) bond trans to the CAAC ligand elongates from 1.964(5) Å for the CO complex **16** to 2.017(5) Å for the cyanide **18**, whereas the carbene−Au distances remain approximately constant throughout this series, deviating only slightly from the value of 2.031(5) Å observed for the cyanide **18**. The isonitrile complex **17** crystallized with a molecule of 1,2-difluorobenzene, which exhibits a T-shaped C−F···π intermolecular interaction between carbon C(28) and one of the fluorine atoms of 1,2-difluorobenzene (C(28)···F(8) 3.090(3) Å), which falls into the range of intermolecular interactions of 2.99−3.53 Å observed for various fluoro-organic compounds.[32]

In view of our earlier observation that ethylene inserts into Au(III)−trifluoroacetate bonds to give the functionalized alkyls

Au−C$_2$H$_4$OAc^F,[33] (^{Ad}CAAC)AuOAc^F was exposed to an atmosphere of ethylene for extended periods of time, either in CH$_2$Cl$_2$ with the addition of AgOAc^F as catalyst or in CH$_2$Cl$_2$/HOAc^F mixtures. However, no insertion of ethylene was observed. The intermediate in this insertion reaction is a cationic alkene complex, and such a complex is indeed easily accessible from the trifluoroacetate precursor if B(C$_6$F$_5$)$_3$ is added as the anion acceptor, as exemplified by the norbornene complex **19** (Scheme 5). The compound is a white, air-stable solid which is soluble in polar organic solvents. The carbene-C signal is observed at δ 246.8.

Oxidation Reactions. Given the electron-donating nature of CAAC ligands, it might be expected that CAAC complexes should be easier to oxidize than compounds of less electron rich NHCs. It is surprising, therefore, that the oxidation chemistry of CAAC complexes does not seem to have been explored.

The oxidation of imidazolylidene-type N-heterocyclic carbene gold(I) complexes with halogens to Au(III) products is of course well precedented and proceeds smoothly in high yields with oxidants such as Br$_2$ and PhICl$_2$, in most cases to give products of the type (NHC)AuX$_3$ (X = Cl, Br, I).[34−41] It was therefore surprising when initial attempts at oxidizing (^{Ad}CAAC)AuX with either PhICl$_2$ or CsBr$_3$ in dichloromethane at room temperature proceeded with Au−C cleavage to give mixtures of products, even when the gold(I) precursor was used in excess (eq 2). The reaction of (^{Ad}CAAC)AuCl with PhICl$_2$ in CH$_2$Cl$_2$ gave a yellow solution from which two types of crystals could be obtained: a small amount of colorless needles which were identified by X-ray crystallography as the dichloroaurate(I) salt [^{Ad}CAAC-Cl][AuCl$_2$] (**20a**), formed by chlorination of the carbene ligand, and a larger component of yellow prisms which turned out to be the product of cocrystallization of two independent molecules of [^{Ad}CAAC-Cl][AuCl$_4$] (**20b**) with one molecule of (^{Ad}CAAC)AuCl$_3$ in the unit cell. The ^{1}H NMR spectrum supported an approximate 2:1 ratio of these products. Lowering the temperature to −78 °C led to recovery of the starting material. The ^{13}C NMR resonance for the iminium carbon atom C−X is shifted upfield

Figure 5. Solid-state structure of the cation in $[AuCl_2(^{Me2}CAAC)_2]Cl$ (**23**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au–Cl(1) 2.2681(7), Au–C(1) 2.064(2), C(1)–C(2) 1.527(3), C(1)–N(1) 1.295(3), C(1)–Au–Cl(1) 87.37(7), C(1)–Au–C(1A) 92.63(7).
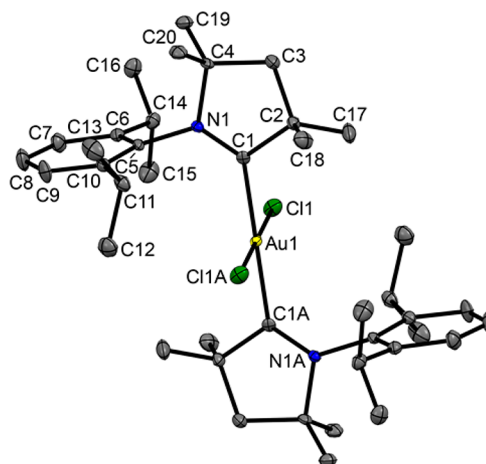
in comparison to the signals for the starting carbene complexes and observed at δ 188.5 and 186.0 for X = Cl, Br, respectively.

The mechanism of Au–C bond cleavage was not studied in detail; however, one plausible explanation may be that the primary oxidation product, $(^{Ad}CAAC)AuCl_3$, partially undergoes photoinduced reductive elimination into Cl_2 and the Au(I) complex $(^{Ad}CAAC)AuCl$. The eliminated chlorine could then react with either $(^{Ad}CAAC)AuCl$ or $(^{Ad}CAAC)AuCl_3$ to give the corresponding salts $[^{Ad}CAAC-Cl][AuCl_2]$ and $[^{Ad}CAAC-Cl][AuCl_4]$, respectively. The photochemical reductive elimination of halogens from $(NHC)AuBr_3$[39a] and from gold(III) phosphine complexes in the presence of olefins as halogen scavengers is known to be facile.[42] In the present case the carbene C–Au bond acts as such a halogen scavenger. Similar cleavage products **21a,b** are obtained using $CsBr_3$ under ambient light conditions (eq 2). The crystal structures of the salts **20a,b** are shown in Figure 4.

However, a different course of this reaction was observed when the oxidation reactions were conducted in the *absence* of ambient light. This aspect was first explored using the sterically less hindered and synthetically more easily accessible $^{Me2}CAAC$ ligand and subsequently extended to $^{Ad}CAAC$ gold compounds.

Stirring a mixture of $[Au(^{Me2}CAAC)_2]Cl$ (**22**) and $PhICl_2$ in dichloromethane in the dark at 0 °C to room temperature for 6 h gave a colorless complex, $[AuCl_2(^{Me2}CAAC)_2]Cl$ (**23**) (Scheme 5). The molecular structure was identified by X-ray diffraction (Figure 5). The gold atom occupies a special position, with the $^{Me2}CAAC$ and Cl ligands being related by an

inversion center. The Au atom possesses the expected square-planar geometry with a trans arrangement of the ligands. The bond length Au–C(1) (2.064(2) Å) is slightly elongated in comparison to those of the analogous imidazolylidene complexes $[AuCl_2(NHC)_2]^+$, while the Au–Cl(1) distance is closely similar.[38b,42]

The crystal structure and elemental analysis show the expected composition of the desired Au(III) product, $[AuCl_2(^{Me2}CAAC)_2]Cl$. At the same time, it is a well-known fact that the ^{13}C NMR resonance of the carbene carbon is usually shifted upfield on oxidation of Au(I) carbene complexes to Au(III).[38b] However, the ^1H and ^{13}C NMR spectra in CD_2Cl_2 of $[AuCl_2(^{Me2}CAAC)_2]Cl$ and its precursor $[Au(^{Me2}CAAC)_2]Cl$ are essentially identical: $\delta(^{13}C)$ 250.6. Therefore, we cannot exclude the possibility that in solution an equilibrium exists between $[AuCl_2(^{Me2}CAAC)_2]Cl$ and its Au(I) isomer, $[Au(^{Me2}CAAC)_2]Cl_3$, which in dichloromethane is predominantly shifted toward the Au(I) complex. It did not prove possible, however, to isolate the trichloride salt, and
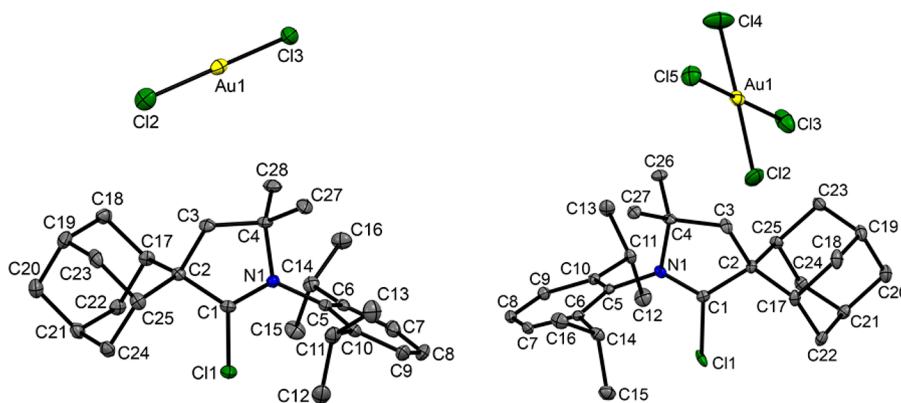
Figure 4. Molecular structures of (left) $[^{Ad}CAAC-Cl]^+[AuCl_2]^-$ (**20a**) and (right) $[^{Ad}CAAC-Cl]^+[AuCl_4]^-$ (**20b**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **20a**, Au–Cl(2) 2.2605(8), Au–Cl(3) 2.2671(8), C(1)–Cl(1) 1.696(3), C(1)–C(2) 1.506(4), C(1)–N(1) 1.288(3), Cl(2)–Au–Cl(3) 175.91(3); **20b**, Au–Cl(2) 2.2828(16), Au–Cl(3) 2.2819(17), Au–Cl(4) 2.2673(13), Au–Cl(5) 2.2813(16), C(1)–Cl(1) 1.718(5), C(1)–C(2) 1.510(6), C(1)–N(1) 1.299(6), Cl(2)–Au–Cl(3) 89.84(7), Cl(2)–Au–Cl(4) 178.86(6).

numerous attempts to pick out different crystals led only to unit cell measurements corresponding to the Au(III) complex [AuCl$_2$(^{Me2}CAAC)$_2$]Cl.

The quality of the product strongly depends on the absence of the light during the reaction and on storage. For instance, the colorless solution of [AuCl$_2$(^{Me2}CAAC)$_2$]Cl slowly turned yellow (within ca. 24 h) if left exposed to ambient light, while the ^{1}H and ^{13}C NMR spectra of the sample remained unchanged. The products of this reaction could not be unequivocally determined but seemed likely to contain [AuCl$_4$]$^-$ salts.

The oxidation of **22** with CsBr$_3$ as selective brominating agent took a somewhat different course. Under ambient conditions [Au(^{Me2}CAAC)$_2$]Cl reacts with CsBr$_3$ to give a mixture of orange prisms of [Au(^{Me2}CAAC)$_2$]Br$_3$ (**24a**) and of red crystals of [Au(^{Me2}CAAC)$_2$]AuBr$_4$ (**24b**) (Scheme 5). In contrast, the attempted oxidation of [Au(^{Me2}CAAC)$_2$]Cl with iodine gave the Au(I) diiodochloride salt [Au(^{Me2}CAAC)$_2$]ClI$_2$ (**24c**). Since ^{1}H and ^{13}C NMR spectra are not informative, the nature of these products was confirmed by X-ray crystallography (see the Supporting Information).

In none of these reactions did we observe the formation of gold(III) bromo or iodo complexes. The reactivity of CAAC complexes therefore differs significantly from that of unsaturated NHC complexes, where oxidation with Br$_2$ has been shown to generate complexes of the type (NHC)AuBr$_3$ and [AuBr$_2$(NHC)$_2$]$^+$ [35a,38b,39b] and where oxidation with iodine has given rise to compounds of the types (NHC)AuBrI$_2$, [AuI$_2$(NHC)$_2$]$^+$, and (NHC)AuI$_3$.[38,39a]

A similar reactivity pattern was observed in the oxidation reactions of the more bulky monocarbene complexes (^{Ad}CAAC)AuX (X = Cl, Br, I). As was observed for the bis-carbene cation [Au(^{Me2}CAAC)$_2$]$^+$, carbene complexes of Au(III) are only obtained if ambient light is excluded. Thus, the reaction of (^{Ad}CAAC)AuCl with PhICl$_2$ over the temperature range from 0 °C to room temperature for 6 h in the dark led to the isolation of (^{Ad}CAAC)AuCl$_3$ (**25**) as a light yellow solid in almost quantitative yield (eq 3). There was no reaction at −78 °C.

(3)
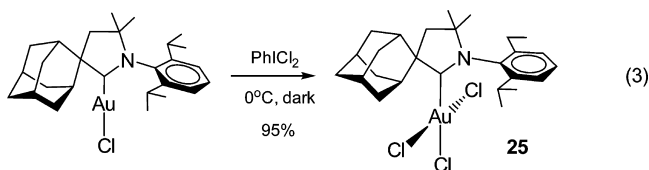
The ^{13}C NMR spectrum of **25** shows the carbene carbon signal at δ 218.8, substantially downfield of the ^{13}C carbene signals of imidazolidine-type (NHC)AuCl$_3$ complexes, which are typically observed in the range of δ 130−170.[35−40] In comparison to Au(I) CAAC complexes, which show ^{13}C carbene chemical shifts of ca. δ 235−240,[6c] the Au(III) complexes are shifted upfield by about 20 ppm. Such changes have previously been explained on the basis of increased Lewis acidity of the Au(III) center and shielding effects of the *cis*-halide ligands.[38b,39a] There was no evidence for ligand rearrangement, e.g. to [AuCl$_2$(^{Ad}CAAC)$_2$][AuCl$_4$], and the solid-state structure is retained in solution. The structure of the complex is shown in Figure 6. The Au(III) atom possesses square-planar geometry. The bond lengths Au−C(1) (2.018(4) Å) and Au−Cl(2) (2.3170(13) Å in position trans to the
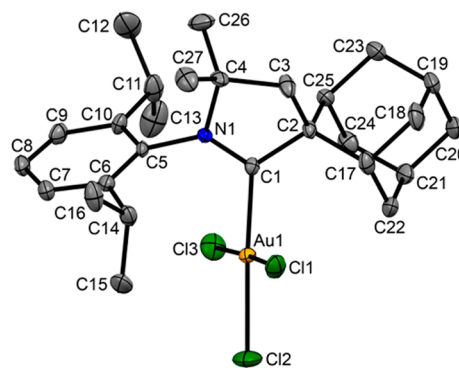
Figure 6. Crystal structure of (^{Ad}CAAC)AuCl$_3$ (**25**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−Cl(1) 2.2972(13), Au−Cl(2) 2.3170(13), Au−Cl(3) 2.2632(13), Au−C(1) 2.018(4), C(1)−C(2) 1.537(6), C(1)−N(1) 1.295(6), C(1)−Au−Cl(2) 174.25(13), C(1)−Au−Cl(1) 85.64(13), C(1)−Au−Cl(2) 95.83(13), Cl(1)−Au−Cl(2) 88.79(6).

carbene carbon) are almost identical with those observed in numerous (NHC)AuCl$_3$ complexes.[35−40]

In contrast, the reaction of (^{Ad}CAAC)AuI with iodine in dichloromethane under various reaction conditions (i.e., either protected from light or unprotected, low or ambient temperature) gave a dark red solution from which crystals of the dark red iodine adduct (^{Ad}CAAC)AuI·I$_2$ (**26**) were isolated (eq 4).

(4)
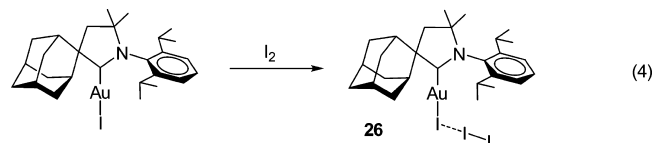
This is in contrast to the oxidative addition of iodine observed with other types of NHC complexes, which form gold(III) iodides.[38b,45] The formation of triiodides and iodine adducts has previously been observed for phosphine and isonitrile Au(I) complexes.[43,44] Indications for the redox equilibrium LAu^I(I$_3$) ⇌ LAu^{III}(I)$_3$ were not detected.

The structure of **26** is shown in Figure 7. According to the Cambridge Structural Database the only closely analogous
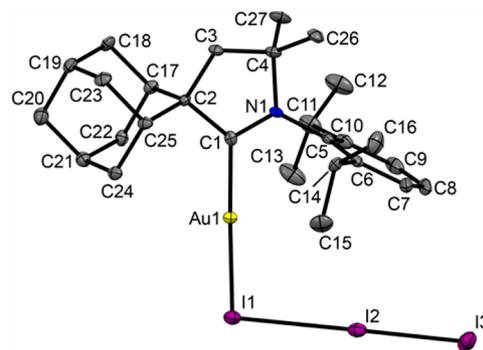
Figure 7. Crystal structure of (^{Ad}CAAC)AuI·I$_2$ (**26**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−I(1) 2.5684(4), Au−C(1) 2.024(4), I(1)−I(2) 3.1655(5), I(2)−I(3) 2.7626(5), C(1)−C(2) 1.517(6), C(1)−N(1) 1.299(6); C(1)−Au−I(1) 177.36(12), Au−I(1)−I(2) 93.56(1), I(1)−I(2)−I(3) 177.28(2).

compound with a triiodide moiety is $[(^tBuNC)_2Au][AuI_2]\cdot I_2$, reported by Schmidbaur.[43] The Au−I(1) and I(2)−I(3) bond lengths for the complex (^AdCAAC)AuI·I_2 (2.5684(4) and 2.7626(5) Å) are almost identical with those for $[(^tBuNC)_2Au][AuI_2]\cdot I_2$ (2.553(1) and 2.738(1) Å, respectively), but the I(1)−I(2) distance is significantly shorter: 3.1655(5) vs 3.311(1) Å. At the same time the I···I distance is in accordance with typical values for polyiodide complexes.[46] Analysis of intermolecular contacts shows neither aurophilic interactions (the shortest distance between gold atoms is 7.521 Å) nor polyiodide chain formation.

■ CONCLUSION

The ^AdCAAC ligand produces a gold(I) hydroxide with slightly increased basicity in comparison to the imidazolylidene-type complex (NHC)AuOH. It is a convenient starting material for the synthesis of a wide range of acid/base and C−H activation reactions and gives gold aryls even with 1,3,5-trifluorobenzene. Arylgold complexes of less acidic arenes are obtainable by the reactions of the corresponding arylboronic acids under neutral conditions in toluene. The oxidation reactions of CAAC-supported gold(I) complexes by halogens, on the other hand, did not conform to the expectations for electron-rich complexes, and only stronger oxidants, such as PhICl_2, afforded gold(III) CAAC complexes. In bromine oxidations the CAAC ligand proved to be a halide scavenger, while iodine formed a gold(I) triiodide. The halide complexes readily decompose under the influence of light, and exclusion of light is required if cleavage of the Au−carbene bond by halogens is to be avoided. With such precautions, the first examples of gold(III) CAAC complexes could be prepared in almost quantitative yields. The reaction patterns of CAAC-type carbenes provide therefore an interesting contrast to those of more strongly π-accepting[13i] imidazole-based NHC carbenes.

■ EXPERIMENTAL SECTION

General Considerations. Unless stated otherwise, all reactions were carried out in air. Solvents were distilled and dried as required. Pentafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3,5-trifluorobenzene, sodium *tert*-butoxide, diethyl malonate, trimethylsilyl cyanide, triethoxysilane, triflimide, *tert*-butyl alcohol, ^tBuNC, KCN, and norbornene were purchased from Sigma-Aldrich and used as received. (^AdCAAC)AuCl[6c] and ^Me2CAAC[47] were obtained according to a literature procedure. ^1H, ^13C{^1H}, and ^19F NMR spectra were recorded using a Bruker Avance DPX-300 MHz NMR spectrometer. ^1H NMR spectra (300.13 MHz) and ^13C{^1H} (75.47 MHz) were referenced to CD_2Cl_2 at δ 5.32 (^13C, δ 54.0), C_6D_6 at δ 7.16 (^13C, δ 128.4), CDCl_3 at δ 7.26 (δ ^13C 77.2), or C_6D_5Br at δ 7.30 for the most downfield signal (^13C, δ 122.5 for the most upfield signal) ppm. ^19F NMR spectra (282.4 MHz) were referenced externally to CFCl_3 and internally to C_6F_6 (δ_F −164.9). IR spectra were recorded using a PerkinElmer Spectrum One FT-IR spectrometer equipped with a diamond ATR attachment. Elemental analyses were performed by the London Metropolitan University.

Synthesis of (^AdCAAC)AuO^tBu (2). An oven-dried 25 mL Schlenk flask was equipped with a stirring bar and charged with (^AdCAAC)-AuCl (303 mg, 0.5 mmol) and sodium *tert*-butoxide (48 mg, 0.5 mmol) under an argon atmosphere. Anhydrous toluene (15 mL) was added, and the resulting white suspension was stirred in the dark for 5 h and filtered through a Celite pad (2 cm), which was washed with an additional 10 mL of toluene. The volatiles were evaporated under vacuum, affording a white solid: yield 307 mg (0.475 mmol, 95.5%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.43 (t, J = 7.6 Hz, 1H, CH-aromatic), 7.27 (d, J = 7.6 Hz, 2H, CH-aromatic), 4.12 (br d, J = 13.2 Hz, 2H, CH_2), 2.77 (sept, J = 6.6 Hz, 2H, CH(CH_3)_2), 2.32−1.75 (m,

14H, adamantyl CH and CH_2), 1.44 (d, J = 6.6 Hz, 6H, CH(CH_3)_2), 1.31 (s, 6H, 2CH_3), 1.28 (d, J = 6.6 Hz, 6H, CH(CH_3)_2), 0.91 (s, 9H, OC(CH_3)_3) ppm. ^13C{^1H} NMR (75 MHz, CD_2Cl_2): δ 238.1 (C carbene), 144.9 (o-C), 136.4 (Ar, C_{ipso}), 129.0 (Ar, p-C), 124.8 (Ar, m-C), 75.9 (C_q), 70.2 (C_q, OC(CH_3)_3), 63.7 (C_q), 48.7 (CH_2), 39.0 (CH_2), 36.8, 34.9 (OC(CH_3)_3), 34.8, 34.4 (CH_2), 29.0 (CH), 28.9, 27.7, 27.3, 26.5, 22.9 (CH_3) ppm. IR (ATR, cm^{−1}): 2900, 2846, 1493, 1447, 1343, 1188, 958, 802, 765, 587. Anal. Calcd for C_{31}H_{48}AuNO (647.68): C, 57.49; H, 7.47; N, 2.16. Found: C, 57.58; H, 7.50; N, 2.18.

Synthesis of (^AdCAAC)AuOH (3). *Method A.* A 50 mL Schlenk flask was charged with (^AdCAAC)AuCl (303 mg, 0.5 mmol), freshly ground KOH (285 mg, 5 mmol), and 10 mL of THF. To the stirred suspension was added *tert*-butyl alcohol (0.02 mL, 0.2 mmol), and stirring was continued for 36 h at room temperature. The dark suspension was filtered through a Celite pad (3 cm) and washed with additional THF (2 × 5 mL). Water (4 mL) was added to the THF solution, after which it was concentrated to ca. 7 mL. Water (10 mL) was added to the cloudy suspension. All volatiles were removed under vacuum (30 °C, 20 mbar). If any coloration of the solid remained, it could be redissolved in THF/H_2O (4:1) and passed through Celite. The white residue was washed with hexanes (2 × 5 mL) and dried under vacuum for 1 day. Yield: 282 mg (0.48 mmol, 96%).

Method B. An excess of distilled water (5 mL) was added to the stirred solution of (^AdCAAC)AuO^tBu (194 mg, 0.30 mmol) in 1 mL of THF. The milky suspension was stirred for 15 min, and the volatiles were removed under vacuum. The white residue was washed with hexanes (5 mL) and dried under vacuum for 1 day. Yield: 171 mg (0.29 mmol, 97%).

^1H NMR (300 MHz, C_6D_5Br): δ 7.21 (t, J = 7.9 Hz, 1H, CH-aromatic), 7.06 (d, J = 7.9 Hz, 2H, CH-aromatic), 4.21(br d, J = 13.2 Hz, 2H, CH_2), 2.69 (sept, J = 6.6 Hz, 2H, CH(CH_3)_2), 1.98−1.52 (m, 14H, adamantyl CH and CH_2), 1.46 (d, J = 6.6 Hz, 6H, CH(CH_3)_2), 1.16 (d, J = 6.6 Hz, 6H, CH(CH_3)_2), 0.99 (s, 6H, 2CH_3), −0.29 (br s, 1H, OH) ppm. ^13C{^1H} NMR (75 MHz, C_6D_5Br): δ 238.2 (C carbene), 145.1 (o-C), 136.0 (C_{ipso}), expected signal at ca. 129.0 (p-C) overlaps with solvent peak of C_6D_5Br, 125.1 (m-C), 75.8 (C_q), 63.8 (C_q), 48.6 (CH_2), 39.3 (CH_2), 37.1, 35.3, 34.7 (CH_2), 29.2(CH), 29.0, 28.0, 27.6, 27.0, 23.3 (CH_3) ppm. IR (ATR, cm^{−1}): 3671, 3605 (br), 2960, 2900, 1500, 1448, 1358, 1098, 945, 803, 778, 540. Anal. Calcd for C_{27}H_{40}AuNO (591.57): C, 54.82; H, 6.81; N, 2.37. Found: C, 54.71; H, 6.84; N, 2.41.

Synthesis of (^AdCAAC)Au(p-C_6H_4F)] (4). *Method A.* Under an argon atmosphere, an oven-dried 25 mL Schlenk flask was charged with a stirring bar, (^AdCAAC)AuO^tBu (97 mg, 0.15 mmol), and p-fluorophenylboronic acid (22 mg, 0.15 mmol). Anhydrous toluene (5 mL) was added, and the resulting suspension was stirred overnight. The reaction mixture was filtered through a Celite pad (2 cm), which was washed with another 8 mL of toluene. The volatiles were removed under vacuum to give an off-white product, which was washed with hexanes (2 × 4 mL) and dried under vacuum. Yield: 92 mg (0.14 mmol, 92%).

Method B. A scintillation vial was charged in air with a stirring bar, (^AdCAAC)AuOH (60 mg, 0.10 mmol) and p-fluorophenylboronic acid (15 mg, 0.10 mmol). Toluene (4 mL) was added and the resulting suspension was stirred overnight. The mixture was filtered through a Celite pad (2 cm) which was washed with another 8 mL of toluene. All volatiles were removed under vacuum to give an off white product which was washed with hexanes (2 × 4 mL) and dried under vacuum. Yield: 65.5 mg (0.097 mmol, 97%).

^1H NMR (300 MHz, CD_2Cl_2): δ 7.45 (t, J = 7.6 Hz, 1H, CH-aromatic), 7.29 (d, J = 7.6 Hz, 2H, CH-aromatic), 6.99 and 6.72 (dd, 4H, J_{AB} = ca. 9.7 Hz, ^3J_{Ha-F} = ca. 7.9 Hz, ^4J_{Hb-F} = ca. 5.1 Hz, p-C_6H_4), 4.21(br d, J = 12.6 Hz, 2H, CH_2), 2.86 (sept, J = 6.7 Hz, 2H, CH(CH_3)_2), 2.31−1.81 (m, 14H, adamantly CH and CH_2), 1.45 (d, J = 6.7 Hz, 6H, CH(CH_3)_2), 1.35 (s, 6H, 2CH_3), 1.31 (d, J = 6.7 Hz, 6H, CH(CH_3)_2).^19F NMR (282 MHz, CD_2Cl_2): δ −119.9. ^13C{^1H} NMR (75 MHz, CD_2Cl_2): δ 263.9 (C carbene), 163.4 (d, ^4J_{C−F} = 3.9 Hz, Au-C_q, p-C_6H_4F), 160.9 (d, ^1J_{C−F} = 239 Hz, CF, p-C_6H_4F), 145.2 (Ar, o-C), 141.2 (d, ^3J_{C−F} = 5.5 Hz, CH, p-C_6H_4F), 135.6 (C_{ipso}), 129.0

(p-C), 124.6 (m-C), 112.8 (d, $^2J_{C-F}$ = 17.1 Hz, CH, p-C$_6$H$_4$F), 77.1 (C$_q$), 65.2 (C$_q$), 48.8 (CH$_2$), 39.0 (CH$_2$), 37.1, 35.3, 34.4 (CH$_2$), 29.0 (CH), 28.99 (almost overlapping with signal at 29.0), 28.2, 27.4, 26.1, 22.8 (CH$_3$) ppm. Anal. Calcd for C$_{28}$H$_{39}$AuN$_2$ (669.66): C, 59.19; H, 6.47; N, 2.09. Found: C, 59.01; H, 6.46; N, 2.13.

Synthesis of (^AdCAAC)Au(OAc^F)] (5). *Method A.* A Schlenk flask was charged with (^AdCAAC)AuOH (59 mg, 0.10 mmol) and a trifluoroacetic acid solution (9 μL, 0.11 mmol) in toluene (1 mL). The resulting solution was stirred for 4 h. All volatiles were removed under vacuum. The residue was washed with hexanes (2 × 2 mL) and dried under vacuum to give a white solid. Yield: 66.5 mg (0.096 mmol, 96%).

Method B. A Schlenk flask was charged with (^AdCAAC)AuCl (59 mg, 0.1 mmol), silver trifluoroacetate (23 mg, 0.10 mmol), and CH$_2$Cl$_2$ (2 mL). The resulting suspension was stirred for 30 min in the dark. The mixture was filtered through a Celite pad (2 cm), which was washed with another 8 mL of CH$_2$Cl$_2$. All volatiles were removed under vacuum to leave an off-white product, which was dried under vacuum. Yield: 63.5 mg (0.092 mmol, 92%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.49 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.30 (d, J = 7.7 Hz, 2H, CH-aromatic), 4.00 (br d, J = 12.6 Hz, 2H, CH_2), 2.74 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.39−1.81 (m, 14H, adamantyl CH and CH$_2$), 1.38 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.35 (s, 6H, 2CH$_3$),1.31 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −74.5 ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 232.4 (C carbene), 160.7 (quart. $^2J_{C-F}$ = 37.8 Hz, CO$_2$), 144.8 (o-C), 135.4 (C$_{ipso}$), 129.8 (p-C), 125.0 (m-C), 117.7 (quart. $^1J_{C-F}$ = 293 Hz, CF$_3$), 77.2 (C$_q$), 63.6 (C$_q$), 48.2 (CH$_2$), 38.9 (CH$_2$), 37.0, 35.1, 34.4 (CH$_2$), 29.0 (CH), 28.9, 27.7, 27.2, 26.3, 22.6 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2968, 2908, 1701, 1527, 1450, 1407, 1372, 1187, 1135, 1097, 841, 804, 727, 609, 520. Anal. Calcd for C$_{29}$H$_{39}$AuF$_3$NO$_2$ (687.58): C, 50.66; H, 5.72; N, 2.04. Found: C, 50.72; H, 5.80; N, 2.02.

Synthesis of (^AdCAAC)Au(3,5-di-*tert*-butylphenolate) (6). A scintillation vial was charged with a stirring bar, (^AdCAAC)AuOH (59 mg, 0.10 mmol), and 3,5-di-*tert*-butylphenol (21 mg, 0.102 mmol). Toluene (3 mL) was added and the resulting yellow solution was stirred overnight. All volatiles were evaporated under vacuum, affording the product as a white solid, which was washed with hexanes (2 × 4 mL) and dried under vacuum. Yield: 75.5 mg (0.097 mmol, 97%).

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.18 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.01 (d, J = 7.7 Hz, 2H, CH-aromatic), 6.98 (br d, J = 1.7 Hz, 2H, CH, phenolate), 6.93 (br t, J = 1.7 Hz, 1H, CH, phenolate), 4.40 (br d, J = 12.2 Hz, 2H, CH_2), 2.67 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.15−1.60 (m, 14H, adamantyl CH and CH$_2$), 1.51 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.40 (s, 18H, two ^{t}Bu groups), 1.09 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.79 (s, 6H, 2CH$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 236.1 (C carbene), 168.6 (O-C phenolate), 150.4 (C$_{meta}$ phenolate), 144.8 (C$_o$ aromatic), 135.3 (C$_{ipso}$ aromatic), 129.9 (CH$_p$ aromatic), 113.9 (CH$_o$ phenolate), 108.7 (CH$_{para}$ phenolate), 75.5 (C$_q$), 63.5 (C$_q$), 48.0 (CH$_2$), 38.9 (CH$_2$), 36.9, 35.1, 34.7 (C(CH$_3$)$_3$), 34.4 (CH$_2$), 31.9 (C(CH$_3$)$_3$), 29.1(CH), 28.3, 27.6, 27.3, 26.7, 22.6 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2962, 2897, 1576, 1509, 1463, 1422, 1320, 1098, 973, 804, 705, 643, 582, 474. Anal. Calcd for C$_{41}$H$_{60}$AuNO (779.88): C, 63.14; H, 7.75; N, 1.80. Found: C, 63.23; H, 7.81; N, 1.85.

Synthesis of (^AdCAAC)Au(NTf$_2$) (7). A Schlenk flask was charged with a stirring bar, (^AdCAAC)AuOH (59 mg, 0.10 mmol), and HNTf$_2$ (30 mg, 0.105 mmol) under argon. Toluene (1 mL) was added, and the resulting suspension was stirred overnight. The product was precipitated with hexanes (10 mL) and dried under vacuum. The residue was washed with hexanes (2 × 2 mL) and dried under vacuum. The microcrystalline product contains half a molecule of toluene, while precipitation from dichloromethane with hexanes gives the CH$_2$Cl$_2$ solvate: yield 86 mg (0.091 mmol, 91%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.45 (t, J = 7.8 Hz, 1H, CH-aromatic), 7.28 (d, J = 7.8 Hz, 2H, CH-aromatic), 3.82 (br d, J = 13.2 Hz, 2H, CH_2), 2.71 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.40−1.81 (m, 14H, adamantyl CH and CH$_2$), 1.39 (s, 6H, 2CH$_3$),1.36 (d, J = 6.7 Hz,

6H, CH(CH_3)$_2$), 1.30 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −75.3 ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 233.8 (C carbene), 144.5 (o-C), 135.5 (C$_{ipso}$), 129.8 (p-C), 125.2 (m-C), 119.1 (quart. $^1J_{C-F}$ = 323.3 Hz, CF$_3$), 77.8 (C$_q$), 63.8 (C$_q$), 48.3 (CH$_2$), 38.8 (CH$_2$), 37.0, 34.7, 34.4 (CH$_2$), 29.2 (CH), 29.0, 27.5, 27.1, 26.0, 23.0 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2907, 2852, 1532, 1450, 1397, 1375, 1192, 1131, 1053, 955, 830, 654, 607, 567, 507. Anal. Calcd for C$_{29}$H$_{39}$AuF$_6$N$_2$O$_4$S$_2$·CH$_2$Cl$_2$ (939.64): C, 38.35; H, 4.40; N, 2.98. Found: C, 38.05; H, 4.23; N, 3.18.

Synthesis of (^AdCAAC)Au(CH(CO$_2$Et)$_2$) (8). A scintillation vial was charged with a stirring bar, (^AdCAAC)AuOH (59 mg, 0.10 mmol), and diethyl malonate (16 mg, 0.1 mmol). Toluene (2 mL) was added, and the resulting suspension was stirred overnight. All volatiles were evaporated under vacuum, affording the product as a white solid, which was washed with hexanes (2 × 2 mL) and dried under vacuum. Yield: 72 mg (0.098 mmol, 98%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.21 (d, J = 7.7 Hz, 2H, CH-aromatic), 3.91 (br d, J = 12.4 Hz, 2H, CH_2) overlapping with 3.88 (q, J = 7.3 Hz, 2H, OCH_2CH$_3$),3.76 (q, J = 7.3 Hz, 2H, OCH_2CH$_3$), 3.41 (s, 1H, CH(CO$_2$Et)$_2$), 2.69 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.27−1.74 (m, 14H, adamantyl CH and CH$_2$), 1.37 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.31 (s, 6H, 2CH$_3$), 1.26 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.05 (t, J = 7.3 Hz, 6H, OCH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 253.2 (C carbene), 172.7 (C=O malonate), 145.0 (o-C), 135.2 (C$_{ipso}$), 129.3 (p-C), 124.7 (m-C), 77.1 (C$_q$, overlapping with signal from CDCl$_3$), 64.4 (C$_q$), 58.4 (OCH$_2$-malonate) 48.6 (CH$_2$), 42.3 (CH-malonate), 39.0 (CH$_2$), 37.0, 35.2, 34.5 (CH$_2$), 29.2 (CH), 29.0, 27.8, 27.1, 26.6, 23.1 (CH$_3$), 14.5 (CH$_3$-malonate) ppm. Anal. Calcd for C$_{34}$H$_{50}$AuNO$_4$ (733.73): C, 55.66; H, 6.87; N, 1.91. Found: C, 55.54; H, 6.95; N, 1.94.

Synthesis of (^AdCAAC)AuC≡CPh (9). A scintillation vial was charged with a stirring bar, (^AdCAAC)AuOH (59 mg, 0.10 mmol), and phenylacetylene (17 mg, 0.166 mmol). Toluene (2 mL) was added, and the resulting suspension was stirred overnight. All volatiles were evaporated under vacuum, affording the product as a white solid, which was washed with hexanes (2 × 2 mL) and dried under vacuum. Yield: 64 mg (0.095 mmol, 95%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.40 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.33 (br d, J = 7.6 Hz, 2H, CH, phenylacetylide), 7.24 (d, J = 7.7 Hz, 2H, CH-aromatic), 7.12 (br t, J = 7.6 Hz, 2H, CH, phenylacetylide),7.05 (br tt, ^3J = 7.6 Hz,^4J = 1.4 Hz, 1H, CH, phenylacetylide), 4.02 (br d, J = 12.4 Hz, 2H, CH_2), 2.77 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.28−1.78 (m, 14H, adamantyl CH and CH$_2$), 1.47 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.31 (s, 6H, 2CH$_3$), 1.29 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 257.5 (C carbene), 144.9 (o-C), 134.8 (C$_{ipso}$ aromatic), 132.3 (Ph acetylide), 129.4 (p-C), 127.5 (Ph acetylide), 127.0 (C acetylide), 126.2 (C aromatic acetylide), 125.7 (Ph acetylide), 124.8 (m-C), 106.8 (C acetylide), 77.1 (C$_q$), 65.2 (C$_q$), 48.7 (CH$_2$), 39.0 (CH$_2$), 37.0, 35.6, 34.5 (CH$_2$), 29.1(CH), 29.0, 27.6, 27.2, 27.0, 23.0 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2968, 2892, 2115 (C≡C), 1508, 1447, 1368, 1098, 910, 805, 754, 693, 527. Anal. Calcd for C$_{35}$H$_{44}$AuN (675.69): C, 62.21; H, 6.56; N, 2.07. Found: C, 62.13; H, 6.62; N, 2.18.

Synthesis of (^AdCAAC)Au(C$_6$F$_5$) (10). A Schlenk flask was charged with (^AdCAAC)AuOH (118 mg, 0.2 mmol) and a pentafluorobenzene solution (42 μL, 0.4 mmol) in toluene (2 mL). The resulting mixture was heated to 60 °C for 18 h. The slightly pink solution was filtered through a Celite pad (1 cm) which was washed with an additional 6 mL of toluene. The solution was concentrated to ca. 0.3 mL under vacuum and the white residue precipitated with hexanes (10 mL). The resulting suspension was centrifuged. The solid was washed with hexanes (2 × 4 mL) and dried under vacuum to give an off-white solid. Yield: 140 mg (0.19 mmol, 95%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.44 (t, J = 7.8 Hz, 1H, CH-aromatic), 7.25 (d, J = 7.8 Hz, 2H, CH-aromatic), 4.09 (br d, J = 13.2 Hz, 2H, CH_2), 2.79 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.33−1.81 (m, 14H, adamantyl CH and CH$_2$), 1.38 (s, 6H, 2CH$_3$), 1.36 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.29 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$)ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ −115.3 to −115.5 (m, 2F), −160.5 (t, J =

20.7 Hz, 1F), −163.43 to −163.70 (m, 2F) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$): δ (Au−C from C$_6$F$_5$ was not observed) 258.5 (C carbene), 150.5−147.3 (d m,$^1J_{C-F}$ = 226 Hz, CF), 144.9 (C$_o$ aromatic), 139.6−136.5 (d m, $^1J_{C-F}$ = 239 Hz, CF), 138.2−134.9 (d m, $^1J_{C-F}$ = 252 Hz, CF), 135.2 (C$_{ipso}$), 129.4 (p-C), 124.8 (m-C), 77.2 (C$_q$), 64.9 (C$_q$), 48.9 (CH$_2$), 39.0 (CH$_2$), 37.2, 35.2, 34.5 (CH$_2$), 29.3 (CH), 29.0, 27.8, 27.2, 26.3, 23.2 (CH$_3$) ppm. Anal. Calcd for C$_{33}$H$_{39}$AuF$_5$N (741.62): C, 53.44; H, 5.30; N, 1.89. Found: C, 53.59; H, 5.39; N, 1.93.

Synthesis of (^{Ad}CAAC)Au(p-C$_6$HF$_4$) (11). The compound was made in a fashion similar to that for **10** from (^{Ad}CAAC)AuOH (59 mg, 0.10 mmol), and 1,2,4,5-tetrafluorobenzene (22 μL, 0.20 mmol) solution in toluene (2 mL). The resulting solution was heated to 80 °C for 18 h. The slightly pink solution was filtered through Celite pad (1 cm) which was washed with an additional with 6 mL of toluene. Concentration and precipitation with hexanes gave an off-white solid. Yield: 67 mg (0.093 mmol, 93%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.46 (t, J = 7.6 Hz, 1H, CH-aromatic), 7.29 (d, J = 7.6 Hz, 2H, CH-aromatic), 6.55 (tt, J_{H-F} = 9.5 and 6.9 Hz, 1H), 4.09 (br d, J = 12.9 Hz, 2H, CH$_2$), 2.83 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.35−1.83 (m, 14H, adamantyl CH and CH$_2$), 1.38 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.38 (s, 6H, 2CH$_3$),1.31 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$) ppm. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −117.4 to −117.6 (m, 2F), −141.9 to −142.1 (m, 2F) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD$_2$Cl$_2$): δ 258.4 (C carbene), 151.0−146.7 (d m, $^1J_{C-F}$ = 228 Hz, CF), 145.1 (o-C), 147.1−143.4 (d m, $^1J_{C-F}$ = 250 Hz, CF), 140.4 (t m, $^2J_{C-F}$ = 59 Hz, C tetrafluoroaryl), 135.4 (C$_{ipso}$), 129.2 (p-C), 124.7 (m-C), 102.0 (t, $^2J_{C-F}$ = 23.7 Hz, CH tetrafluoroaryl), 77.5 (C$_q$), 65.0 (C$_q$), 48.7 (CH$_2$), 39.0 (CH$_2$), 37.2, 35.2, 34.4 (CH$_2$), 29.1 (CH), 29.0, 28.1, 27.4, 26.0, 22.9 (CH$_3$) ppm. Anal. Calcd for C$_{33}$H$_{40}$AuF$_4$N (723.63): C, 54.77; H, 5.57; N, 1.94. Found: C, 55.17; H, 5.78; N, 2.09.

Reaction of (^{Ad}CAAC)Au(OH) with 1,3,5-Trifluorobenzene. A J. Young NMR tube was loaded with (^{Ad}CAAC)AuOH (30 mg, 0.05 mmol) and 1,3,5-trifluorobenzene (15 μL, 0.152 mmol) solution in toluene-d_8 (0.4 mL) and sealed. The resulting solution was heated to 90 °C for 18 h. The first signals for the product appear after 2 h of heating. The yellow solution with some black precipitate was cooled to room temperature. The major product crystallizing from the solution after 8 h was the O-bridged cluster [(AdCAAC)$_3$Au$_3$(μ-O)]OH (identified by X-ray crystallography as the C$_6$H$_3$F$_3$ solvate) (11 mg). The yellow solution was decanted and filtered through a pipet filled with Celite (1 cm), which was washed with an additional 4 mL of toluene. Concentration and precipitation with hexanes gave a yellow solid (11 mg) as a mixture of products. Attempts to increase the reaction time to 48 h led to significant formation of decomposition products. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −84.60 (m, 2F), −116.81 to −116.92 (m, 1F) ppm.

Synthesis of (^{Ad}CAAC)Au(2,4,6-C$_6$H$_2$F$_3$) (12). A Schlenk flask was loaded with (^{Ad}CAAC)AuCl (60 mg, 0.1 mmol), 1,3,5-trifluorobenzene (60 μL, 0.608 mmol), NaO^{t}Bu (29 mg, 0.3 mmol), and 1,4-dioxane (0.8 mL) and sealed. The resulting suspension was heated to 75 °C for 18 h. After the suspension was cooled to room temperature, the solid was extracted with CH$_2$Cl$_2$ and the extract filtered through a pad of Celite (1 cm). The solution was concentrated, the product precipitated with hexanes, and the solvent decanted. All volatiles were evaporated to give an off-white solid. An analytically pure sample was obtained after flash chromatography (CH$_2$Cl$_2$/hexane 30/70). Evaporation of all volatiles gave a white solid: yield 34 mg (0.049 mmol, 49%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.44 (t, J = 7.6 Hz, 1H, CH-aromatic), 7.27 (d, J = 7.6 Hz, 2H, CH-aromatic), 6.40−6.34 (m, 2H, C$_6$H$_2$F$_3$), 4.13 (br d, J = 12.0 Hz, 2H, CH$_2$), 2.82 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.33−1.81 (m, 14H, adamantyl CH and CH$_2$), 1.37 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.35 (s, 6H, 2CH$_3$), 1.29 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$) ppm. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −84.60 (m, 2F), −116.81 to −116.92 (m, 1F) ppm. ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ (C-F from C$_6$H$_2$F$_3$ was not observed) 259.7 (C carbene), 170.6−169.9 (m, Au-C$_q$, trifluoroaryl), 145.1 (o-C), 135.4 (C$_{ipso}$), 129.1 (p-C), 124.6 (m-C), 97.6 (ddd, J_{C-F} = 36.5, 23.3, 4.8 Hz, CH

trifluoroaryl), 77.3 (C$_q$), 65.0 (C$_q$), 48.7 (CH$_2$), 39.1 (CH$_2$), 37.2, 35.1, 34.3 (CH$_2$), 29.05 (CH), 29.0, 28.1, 27.4, 26.0, 22.6 (CH$_3$) ppm. Anal. Calcd for C$_{33}$H$_{41}$AuF$_3$N (705.64): C, 56.17; H, 5.86; N, 1.98. Found: C, 56.39; H, 5.98; N, 1.87.

Synthesis of (^{Ad}CAAC)Au(CH$_2$C(O)-p-methoxyphenyl) (13). A scintillation vial was charged with (^{Ad}CAAC)AuOH (59 mg, 0.10 mmol) and p-methoxyacetophenone (20 mg, 0.13 mmol) in toluene (2 mL). The resulting mixture was heated to 70 °C for 12 h. The slightly yellow solution was filtered through a Celite pad (1 cm) which was washed with an additional 6 mL of toluene. The solution was concentrated to ca. 0.3 mL under vacuum and the white residue precipitated with hexanes (10 mL). The resulting suspension was centrifuged. The solid was washed with hexanes (2 × 4 mL) and dried under vacuum to give an off-white solid. Yield: 60 mg (0.083 mmol, 83%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 8.21 (d, 2H, AA'BB', J_{AB} = ca. 8.2 Hz, p-C$_6$H$_4$), 7.13 (t, J = 7.6 Hz, 1H, CH-aromatic), 6.95 (d, J = 7.6 Hz, 2H, CH-aromatic), 6.76 (d, 2H, AA'BB', J_{AB} = ca. 8.2 Hz, p-C$_6$H$_4$), 4.17 (br d, J = 12.9 Hz, 2H, CH$_2$), 3.31 (s, 3H, OCH$_3$), 3.25 (s, 2H, CH$_2$Au), 2.63 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 1.97−1.54 (m, 14H, adamantyl CH and CH$_2$), 1.48 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.08 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 0.79 (s, 6H, 2CH$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD$_2$Cl$_2$): δ 260.2 (C carbene), 200.9 (C═O), 161.1 (MeOC$_{ipso}$ methoxyphenyl), 144.7 (o-C), 135.3 (C$_{ipso}$), 134.1 (C$_{ipso}$ methoxyphenyl), 129.9 (m-C methoxyphenyl), 129.4 (p-C), 124.7 (m-C), 112.6 (o-C methoxyphenyl), 76.3 (C$_q$), 64.5 (C$_q$), 54.5 (CH$_3$O methoxyphenyl), 48.3 (CH$_2$), 38.9 (CH$_2$), 37.0, 35.0, 34.3 (CH$_2$), 33.8 (CH$_2$Au), 29.0 (CH), 28.4, 27.8, 27.3, 26.3, 22.9 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2968, 2904, 1625 (C═O), 1598, 1507, 1464, 1369, 1306, 1245, 1163, 1097, 1023, 840, 805, 589. Anal. Calcd for C$_{36}$H$_{49}$AuNO$_2$ (724.74): C, 59.66; H, 6.81; N, 1.93. Found: C, 59.75; H, 6.92; N, 1.95.

Synthesis of (^{Ad}CAAC)Au(deoxybenzoinyl) (14). A scintillation vial was charged with (^{Ad}CAAC)AuOH (76 mg, 0.128 mmol) and deoxybenzoin (28 mg, 0.142 mmol) in toluene (2 mL). The resulting mixture was heated to 70 °C for 12 h. All volatiles were removed from the gray suspension. The product was extracted with CH$_2$Cl$_2$ and passed through a Celite pad (1 cm) which was washed with an additional 6 mL of CH$_2$Cl$_2$. The solution was concentrated to ca. 0.3 mL under vacuum and the white residue precipitated with hexanes (10 mL). The resulting suspension was centrifuged. The residue was washed with hexanes (2 × 4 mL) and dried under vacuum to give a white solid. Yield: 87 mg (0.116 mmol, 92%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.73−7.70 (m, 2H, C$_6$H$_5$), 7.41 (t, J = 7.6 Hz, 1H, CH-aromatic), 7.31 (tt, J = 7.6 and 1.8 Hz, 1H, C$_6$H$_5$), 7.24 (d, J = 7.6 Hz, 2H, CH-aromatic) overlapping with 7.22−7.20 (m, 1H, C$_6$H$_5$), 7.12−7.70 (m, 5H, C$_6$H$_5$), 6.84 (tt, J = 7.6 and 1.8 Hz, 1H, C$_6$H$_5$), 4.80 (s, 1H, Au-CH), diastereotopic signals for carbene ligand 3.75 (br d, J = 12.9 Hz, 1H, CH$_2$), 3.43 (br d, J = 12.9 Hz, 1H, CH$_2$), 2.64 (sept, J = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 2.57 (sept, J = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 2.22−1.55 (m, 14H, adamantyl CH and CH$_2$), 1.29 (d, J = 6.7 Hz, 3H, CH(CH$_3$)$_2$), 1.26 (s, 3H, C-CH$_3$), 1.25 (d, J = 6.7 Hz, 3H, CH(CH$_3$)$_2$) overlapping with 1.25 (s, 3H, C−CH$_3$), 1.16 (d, J = 6.7 Hz, 3H, CH(CH$_3$)$_2$), 0.89 (d, J = 6.7 Hz, 3H, CH(CH$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD$_2$Cl$_2$): δ 254.6 (C carbene), 194.9 (C═O), 144.7 (o-C$_o$ aromatic), 144.6, 144.5, 141.2, 135.6 (C$_{ipso}$), 129.4 (p-C), 129.3, 128.2, 127.5, 126.9, 126.9, 124.9 (m-C),124.8, 121.2, 77.0 (C$_q$), 64.2 (C$_q$), 56.3 (CH-Au), 48.6 (CH$_2$), 38.9 (CH$_2$), 37.0, 36.8, 34.9, 34.6, 34.3 (CH$_2$), 34.2 (CH$_2$), 29.0 (CH), 28.9, 28.8, 27.7, 27.2, 26.0, 25.4, 22.9 and 22.7(CH$_3$) ppm. IR (ATR, cm^{-1}): 2968, 2900, 1614 (CO), 1574, 1519, 1449, 1368, 1282, 1195, 1097, 1039, 931, 847, 807, 695, 579. Anal. Calcd for C$_{39}$H$_{50}$AuNO (745.78): C, 62.81; H, 6.76; N, 1.88. Found: C, 62.95; H, 6.86; N, 1.93.

Synthesis of (^{Ad}CAAC)Au(CH$_2$SO$_2$Ph) (15). A scintillation vial was charged with (^{Ad}CAAC)AuOH (94 mg, 0.16 mmol) and methyl phenyl sulfone (30 mg, 0.19 mmol) in toluene (2 mL). The resulting mixture was heated to 70 °C overnight. The slightly yellow solution was filtered through a Celite pad (1 cm) which was washed with an additional 6 mL of toluene. The solution was concentrated to ca. 0.3 mL under vacuum and the white residue precipitated with hexanes (10

mL). The resulting suspension was centrifuged. The solid was washed with hexanes (2 × 4 mL) and dried under vacuum to give an off-white solid. Yield: 98 mg (0.134 mmol, 85%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.77−7.74 (m, 2H, sulfone C$_6$H$_5$), 7.43 (t, J = 7.8 Hz, 1H, CH-aromatic) overlapping with 7.42−7.36 (m, 3H, sulfone C$_6$H$_5$), 7.26 (d, J = 7.8 Hz, 2H, CH-aromatic), 4.05 (br d, J = 12.0 Hz, 2H, CH$_2$), 2.79 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.55 (s, 2H, CH$_2$Au), 2.34−1.80 (m, 14H, adamantyl CH and CH$_2$), 1.37 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.32 (s, 6H, 2CH$_3$), 1.29 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 258.2 (C carbene), 147.5 (C$_{ipso}$ sulfone Ph), 145.1 (o-C), 135.3 (C$_{ipso}$), 130.7 (p-C sulfone), 129.2 (p-C), 128.3 (m-C sulfone), 125.9 (o-C sulfone), 124.6 (m-C), 77.3 (C$_q$), 65.1 (C$_q$), 49.7 (CH$_2$Au, sulfone), 48.6 (CH$_2$), 39.0 (CH$_2$), 37.1, 35.2, 34.4 (CH$_2$), 29.0 (CH), 28.9, 27.9, 27.4, 26.3, 22.7 (CH$_3$) ppm. Anal. Calcd for C$_{34}$H$_{46}$AuNSO$_2$ (729.76): C, 55.96; H, 6.35; N, 1.92. Found: C, 56.13; H, 6.47; N, 1.99.

Synthesis of [(^{Ad}CAAC)Au(CO)]SbF$_6$ (16). A Schlenk flask was charged with (^{Ad}CAAC)AuCl (60.5 mg, 0.1 mmol), AgSbF$_6$ (35 mg, 0.1 mmol), and CH$_2$Cl$_2$ (2 mL). The resulting suspension was stirred for 1 h in the dark. The mixture was filtered through a Celite pad (2 cm), which was washed with another 8 mL of CH$_2$Cl$_2$. The colorless solution was concentrated to ca. 3 mL, cooled to −20 °C, and saturated by bubbling with CO for 1 min followed by stirring at room temperature for 2 h. Precipitating with an excess of hexanes (15 mL), decanting the solvents, and removing volatiles under vacuum for 0.5 min afforded the product as a white solid. Yield: 80.0 mg, 0.095 mmol, 95%. The compound was stored under an atmosphere of CO.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.57 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.38 (d, J = 7.7 Hz, 2H, CH-aromatic), 3.23 (br d, J = 12.7 Hz, 2H, CH$_2$), 2.70 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.47−1.85 (m, 14H, adamantyl CH and CH$_2$), 1.44 (s, 6H, 2CH$_3$), 1.35 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.33 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 241.1 (C carbene), 182.4 (s, CO), 144.7 (o-C), 134.2 (C$_{ipso}$), 131.2 (p-C), 125.7 (m-C), 80.8 (C$_q$), 65.4 (C$_q$), 47.9 (CH$_2$), 38.4 (CH$_2$), 36.9, 36.8, 33.8 (CH$_2$), 29.1 (CH), 29.0, 27.7, 27.1, 26.6, 22.7 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2968, 2903, 2183 (C≡O), 1541, 1450, 1387, 1262, 1195, 1097, 805, 651, 610, 583. Anal. Calcd for C$_{28}$H$_{39}$AuF$_6$NOSb (838.33): C, 40.12; H, 4.69; N, 1.67. Found: C, 40.01; H, 4.59; N, 1.63.

Synthesis of [(^{Ad}CAAC)Au(CN^{t}Bu)]SbF$_6$ (17). A Schlenk flask was charged with (^{Ad}CAAC)AuCl (60.5 mg, 0.1 mmol), AgSbF$_6$ (35 mg, 0.10 mmol), and CH$_2$Cl$_2$ (2 mL). The resulting suspension was stirred for 1 h in the dark. The mixture was filtered through a Celite pad (2 cm), which was washed with another 8 mL of CH$_2$Cl$_2$. The colorless solution was concentrated to ca. 2 mL, and an excess of ^{t}BuNC (22 µL, 0.2 mmol) was added, followed by stirring at room temperature for 2 h. The product was precipitated with an excess of hexanes (15 mL), centrifuged, and washed with hexanes (5 mL). All volatiles were removed under vacuum to give the complex as a white solid. Yield: 83.5 mg (0.094 mmol, 94%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.52 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.33 (d, J = 7.7 Hz, 2H, CH-aromatic), 3.42 (br d, J = 12.6 Hz, 2H, CH$_2$), 2.71 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.40−1.83 (m, 14H, adamantyl CH and CH$_2$), 1.48 (s, 9H, C(CH_3)$_3$), 1.39 (s, 6H, 2CH$_3$), 1.33 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.31 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 246.2 (C carbene), 144.8 (o-C), 142.4 (br s, CN^{t}Bu) 134.5 (C$_{ipso}$), 130.4 (p-C), 125.3 (m-C), 79.5 (C$_q$), 65.1 (C$_q$), 58.6 (br s, CNCMe$_3$), 48.0 (CH$_2$), 38.5 (CH$_2$), 36.9, 36.1, 34.0 (CH$_2$), 29.5 (CNC(CH$_3$)$_3$), 29.0 (CH), 28.9, 27.8, 26.8, 26.6, 22.7 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2973, 2899, 2241 (CN^{t}Bu), 1538, 1450, 1373, 1194, 1147, 1097, 803, 776, 654, 523. Anal. Calcd for C$_{32}$H$_{48}$AuF$_6$N$_2$Sb (893.45): C, 43.02; H, 5.41; N, 3.14. Found: C, 43.13; H, 5.49; N, 3.19.

Synthesis of (^{Ad}CAAC)AuCN (18). *Method A.* Trimethylsilyl cyanide (20 µL, 0.150 mmol) was added to the solution of (^{Ad}CAAC)AuOH (59 mg, 0.1 mmol) in 2 mL of toluene. The mixture was stirred at room temperature overnight and concentrated under vacuum. The white residue was precipitated with hexanes (6 mL). The resulting suspension was centrifuged. The solid was washed

with hexanes (3 × 5 mL) and dried under vacuum to give a while solid. Yield: 57.5 mg, 0.095 mmol, 95%.

Method B. (^{Ad}CAAC)AuCl (45 mg, 0.075 mmol), KCN (5 mg, 0.076 mmol) and 10 mL of ethanol were charged in a scintillation vial and stirred overnight. All volatiles were evaporated, and the white residue was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined extracts were filtered through a glass frit and concentrated to ca. 0.5 mL. The product was precipitated with hexanes (10 mL) and dried under vacuum. Yield: 42 mg (0.07 mmol, 92%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.49 (t, J = 7.8 Hz, 1H, CH-aromatic), 7.30 (d, J = 7.8 Hz, 2H, CH-aromatic), 3.71 (br d, J = 13.1 Hz, 2H, CH$_2$), 2.72 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.32−1.79 (m, 14H, adamantyl CH and CH$_2$), 1.37 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.34 (s, 6H, 2CH$_3$), 1.30 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 253.1 (C carbene), 149.5 (CN), 144.9 (o-C), 134.8 (C$_{ipso}$), 129.8 (p-C), 124.9 (m-C), 78.0 (C$_q$), 64.9 (C$_q$), 48.3 (CH$_2$), 38.8 (CH$_2$), 37.0, 35.6, 34.2 (CH$_2$), 29.0 (CH), 28.9, 27.8, 27.1, 26.4, 22.7 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2969, 2900, 2140 (C≡N), 1530, 1447, 1370, 1097, 934, 808, 727. Anal. Calcd For C$_{28}$H$_{39}$AuN$_2$ (600.58): C, 56.00; H, 6.54; N, 4.66. Found: C, 56.16; H, 6.61; N, 4.72.

Synthesis of [(^{Ad}CAAC)Au(norbornene)][tfaB(C$_6$F$_5$)$_3$] (19). A Schlenk flask was charged with (^{Ad}CAAC)AuOAc^f (60 mg, 0.088 mmol), B(C$_6$F$_5$)$_3$ (90 mg, 0.176 mmol), norbornene (16.5 mg, 0.176 mmol), and dry CH$_2$Cl$_2$ (2 mL) under an argon atmosphere. The resulting suspension was stirred for 1 h at −78 °C and left to warm to room temperature while stirring overnight. The mixture was filtered through a Celite pad (1 cm), which was washed with another 8 mL of CH$_2$Cl$_2$. The colorless solution was concentrated to ca. 1 mL and the oily residue precipitated with an excess of hexanes (15 mL). The solvents were decanted, and the residue was dissolved in 0.5 mL of CH$_2$Cl$_2$ and precipitated with hexane (15 mL). The oily colorless residue after decantation was dried under vacuum to afford a white powder which was additionally dried under vacuum overnight. Yield: 96 mg (0.074 mmol, 85%).
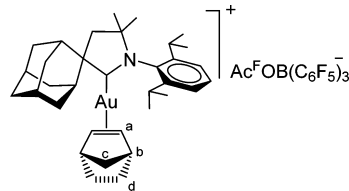
^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.50 (t, J = 7.8 Hz, 1H, CH-aromatic), 7.33 (d, J = 7.7 Hz, 2H, CH-aromatic), 5.83 (br s, 2H, H$_a$ norbornene), 3.27 (br d, J = 12.2 Hz, 2H, CH$_2$), 3.00 (br s, 2H, H$_b$ norbornene), 2.71 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.42−1.75 (m, 18H, adamantyl CH and CH$_2$ overlapping with 4H$_d$ norbornene), 1.44 (s, 6H, 2CH$_3$), 1.32 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.29 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.60 (br d, 1H, ^1J = 10.2 Hz, H$_c$ norbornene), 0.39 (br d, 1H, ^1J = 10.2 Hz, H$_c$ norbornene) ppm. ^{19}F NMR (282 MHz, CD$_2$Cl$_2$): δ −76.9 (s, 3F, CF$_3$), −135.09 (br d, 6F, $J_{F−F}$ = 19.5 Hz, o-C$_6$F$_5$), −161.7 (br t, 3F, $J_{F−F}$ = 19.5 Hz, p-C$_6$F$_5$), −166.7 (br t, 6F, $J_{F−F}$ = 19.5 Hz, m-C$_6$F$_5$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ (B−C$_{ipso}$ from C$_6$F$_5$ and C=O signals were not observed) 246.8 (C carbene), 149.5−146.3 (d m,$^1J_{C−F}$ = 248 Hz, CF), 144.6 (o-C), 140.6−137.3 (d m, $^1J_{C−F}$ = 248 Hz, CF), 138.2−135.0 (d m, $^1J_{C−F}$ = 252 Hz, CF), 135.3 (C$_{ipso}$), 130.7 (p-C), 125.5 (m-C), 123.7 (CH$_a$, norbornene), 115.4 (quart. $^1J_{C−F}$ = 288 Hz, CF$_3$), 79.6 (C$_q$), 64.5 (C$_q$), 48.3 (CH$_2$), 44.6 (CH$_b$, norbornene), 43.9 (CH$_{2c}$, norbornene), 38.4 (CH$_2$), 36.9, 35.8, 33.9 (CH$_2$), 29.1 (CH), 29.0, 27.8, 26.7, 26.5, 23.7 (CH$_{2d}$, norbornene), 22.8 (CH$_3$) ppm. IR (ATR, cm^{-1}): 2906, 1749 (C=O), 1643 (C=C norbornene), 1514, 1465, 1374, 1281, 1187, 1153, 1093, 977, 851, 807, 680. Anal. Calcd for C$_{54}$H$_{49}$AuBF$_{18}$NO$_2$ (1293.71): C, 50.13; H, 3.82; N, 1.08. Found: C, 50.32; H, 3.61; N, 1.01.

Reaction of (^{Ad}CAAC)AuCl with PhICl$_2$ at 20 °C without Light Protection. A mixture of (^{Ad}CAAC)AuCl (61 mg, 0.10 mmol) and PhICl$_2$ (30 mg, 0.11 mmol) in 5 mL of CH$_2$Cl$_2$ was stirred overnight at room temperature. The yellow solution was concentrated to ca. 0.3

mL. Adding Et_2O (10 mL) gave a yellow precipitate, which was washed with Et_2O (2 × 5 mL) and dried under vacuum: yield 63 mg. Crystallization by layering a CH_2Cl_2 solution with hexanes led to the formation of two types of crystals, the structures of which were confirmed by X-ray diffraction. A small amount of colorless needles was identified as the dichloroaurate(I) salt $[(^{Ad}CAAC-Cl)][AuCl_2]$ (**20a**), while the major component of yellow prisms turned out to be the cocrystallization product $\{2[(^{Ad}CAAC-Cl)][AuCl_4]\cdot(^{Ad}CAAC)\text{-}AuCl_3\}$. NMR spectroscopy showed two sets of ligand signals in an approximate 2:1 ratio, which were assigned on the basis of the known signals for the pure salt $[(^{Ad}CAAC-Cl)]AuCl_4$ (**20b**) and the complex $^{Ad}CAACAuCl_3$ (**25**). The ^1H and ^{13}C NMR spectra of the two salts $[(^{Ad}CAAC-Cl)]AuCl_2$ and $[(^{Ad}CAAC-Cl)]AuCl_4$ are essentially identical. Elemental analysis was not carried out due to formation of a product mixture.

Synthesis of $[(^{Ad}CAAC-Cl)][AuCl_4]$ (20b). A solution of $(^{Ad}CAAC)AuCl$ (61 mg, 0.1 mmol) and $PhICl_2$ (58 mg, 0.21 mmol) in 5 mL of CH_2Cl_2 was stirred for 3 h without light protection. A yellow solution resulted, which was concentrated to ca. 0.3 mL. The addition of Et_2O (10 mL) gave a yellow precipitate, which was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 74 mg, 0.098 mmol, 98%.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.66 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.46 (d, J = 7.7 Hz, 2H, CH-aromatic, 2.92 (s, 2H, CH_2, adamantyl), 2.67 (br d, J = 13.0 Hz, 2H, CH_2), 2.45 (sept, J = 6.7 Hz, 2H, $CH(CH_3)_2$), 2.39−1.89 (m, 12H, adamantyl CH and CH_2), 1.58 (s, 6H, $2CH_3$), 1.38 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.20 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 188.5 (C−Cl), 143.8 (o-C), 132.7 (p-C), 128.0 (C_{ipso}), 126.5 (m-C), 79.2 (C_q), 60.8 (C_q), 47.8 (CH_2), 38.0 (CH_2), 37.1, 34.1, 32.1 (CH_2), 29.9 (CH), 28.5, 26.4, 25.8, 23.1 (CH_3) ppm. Anal. Calcd for $C_{27}H_{39}AuCl_5N$ (751.83): C, 43.13; H, 5.23; N, 1.86. Found: C, 42.96; H, 5.28; N, 2.00.

Synthesis of $(^{Ad}CAAC)AuBr$. A suspension of $(^{Ad}CAAC)AuCl$ (61 mg, 0.10 mmol) and LiBr (88 mg, 1 mmol) in 10 mL of acetone was stirred for 24 h at room temperature. The solvent was removed under vacuum. The white residue was extracted with CH_2Cl_2 (2 × 10 mL) and filtered through Celite (1 cm). All volatiles were removed under vacuum to give an off-white solid with one solvate molecule of CH_2Cl_2. Yield: 72.5 mg (0.098 mmol, 98%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.24 (d, J = 7.7 Hz, 2H, CH-aromatic), 5.29 (s, 2H, solvent molecule CH_2Cl_2), 4.02 (br d, J = 12.6 Hz, 2H, CH_2), 2.74 (sept, J = 6.7 Hz, 2H, $CH(CH_3)_2$), 2.35−1.78 (m, 14H, adamantyl CH and CH_2), 1.42 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.34 (s, 6H, $2CH_3$), 1.29 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 242.6 (C carbene), 144.8 (o-C), 135.1 (C_{ipso}), 129.7 (p-C), 124.9 (m-C), 76.7 (C_q), 63.7 (C_q), 53.4 (solvent molecule CH_2Cl_2), 48.6 (CH_2), 38.9 (CH_2), 37.0, 35.1, 34.5 (CH_2), 29.1 (CH), 29.0, 27.5, 27.1, 26.8, 23.0 (CH_3) ppm. Anal. Calcd for $C_{27}H_{39}AuBrN\cdot CH_2Cl_2$ (739.40): C, 45.48; H, 5.59; N, 1.89. Found: C, 45.57; H, 5.67; N, 2.01.

Reaction of $(^{Ad}CAAC)AuBr$ with $CsBr_3$. A suspension of $(^{Ad}CAAC)AuBr\cdot CH_2Cl_2$ (74 mg, 0.10 mmol) and $CsBr_3$ (38 mg, 0.10 mmol) in 5 mL of CH_2Cl_2 was stirred for 20 min at −78 °C and warmed to room temperature with stirring for 1 h. The suspension was filtered through a glass frit and the filtrate concentrated to ca. 0.3 mL. An orange solid was precipitated with hexanes (10 mL) and dried under vacuum. Yield: 80 mg. Recrystallization by layering a CH_2Cl_2 solution with hexanes led to the formation of two types of crystals, which were identified by X-ray diffraction: a larger amount of colorless prisms of $[(^{Ad}CAAC-Br)]^+[AuBr_2]^-$ (**21a**) and a small amount of red prisms of $[(^{Ad}CAAC-Br)]^+[AuBr_4]^-$ (**21b**). Both give identical ^1H and ^{13}C NMR spectra.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.65 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.46 (d, J = 7.7 Hz, 2H, CH-aromatic), 2.93 (s, 2H, CH_2, adamantyl) overlapping with 2.91 (br d, J = 13.0 Hz, 2H, CH_2), 2.44 (sept, J = 6.7 Hz, 2H, $CH(CH_3)_2$), 2.36−1.89 (m, 12H, adamantyl CH and CH_2), 1.59 (s, 6H, $2CH_3$), 1.38 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.26 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz,

CD_2Cl_2): δ 186.0 (C−Br), 143.6 (o-C), 132.5 (p-C), 130.4 (C_{ipso}), 126.7 (m-C), 80.8 (C_q), 62.7 (C_q), 48.0 (CH_2), 38.3 (CH_2), 37.1, 34.3, 31.9 (CH_2), 29.8 (CH), 28.7, 26.5, 25.9, 23.5 (CH_3) ppm. Elemental analysis was not carried out due to formation of a product mixture.

Synthesis of $[(^{Me2}CAAC)_2Au]Cl$ (22). A Schlenk flask was charged with $^{Me2}CAAC$ (0.39 g, 1.36 mmol), $(Me_2S)AuCl$ (0.195 g, 0.66 mmol), and 20 mL of THF under an argon atmosphere. The mixture was stirred at room temperature for 18 h. All volatiles were removed under vacuum and the residue was washed with hexanes (3 × 10 mL). The product was dissolved in CH_2Cl_2 (3 mL) and precipitated with hexanes (40 mL). All volatiles were evaporated. The residue was dried under vacuum to give a white solid. Yield: 510 mg (0.635 mmol, 96%).

^1H NMR (300 MHz, CD_2Cl_2): δ 7.42 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.23 (d, J = 7.7 Hz, 2H, CH-aromatic), 2.59 (sept, J = 6.7 Hz, 2H, $CH(CH_3)_2$), 2.04 (br s, 2H, CH_2), 1.31 (s, 6H, $2CH_3$), 1.24 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.20 (s, 6H, $2CH_3$), 1.01 (br d, J = 6.7 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 250.6 (C carbene), 144.6 (o-C), 133.5 (C_{ipso}), 130.1 (p-C), 125.1 (m-C), 82.3 (C_q), 54.6 (C_q), 49.3 (CH_2), 28.9 (CH), 28.8, 28.4, 26.7, 22.6 (CH_3). Anal. Calcd for $C_{40}H_{62}AuClN_2$ (803.35): C, 59.80; H, 7.78; N, 3.49. Found: C, 59.49; H, 7.57; N, 3.31.

Synthesis of $[AuCl_2(^{Me2}CAAC)_2]Cl$ (23). A mixture of $[Au(^{Me2}CAAC)_2]Cl$ (80 mg, 0.10 mmol) and $PhICl_2$ (28 mg, 0.10 mmol) in 5 mL of CH_2Cl_2 was stirred in the dark for 6 h at 0 °C and warmed to room temperature. The colorless solution was concentrated to ca. 0.3 mL. Addition of Et_2O (10 mL) gave an off-white precipitate, which was washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 91 mg (0.94 mmol, 94%). Crystallization by layering a CH_2Cl_2 solution with hexanes in the dark led to the formation of large colorless prisms and negligible amounts of yellow prisms, which were identified by X-ray diffraction: the colorless prisms as $[AuCl_2(^{Me2}CAAC)_2]Cl\cdot CH_2Cl_2$ (**23**·CH_2Cl_2) and yellow prisms as $[Au(^{Me2}CAAC)_2]AuCl_4$.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.42 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.23 (d, J = 7.7 Hz, 2H, CH-aromatic), 2.58 (sept, J = 6.7 Hz, 2H, $CH(CH_3)_2$), 2.04 (br s, 2H, CH_2), 1.31 (s, 6H, $2CH_3$), 1.23 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.19 (s, 6H, $2CH_3$), 1.01 (br s, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 250.6 (C carbene), 144.6 (o-C), 133.4 (C_{ipso}), 130.1 (p-C), 125.1 (m-C), 82.3 (C_q), 54.6 (C_q), 49.3 (CH_2), 28.9 (CH), 28.8, 28.4, 26.7, 22.6 (CH_3) ppm. Anal. Calcd for $C_{40}H_{62}AuCl_3N_2\cdot CH_2Cl_2$ (959.18): C, 51.34; H, 6.73; N, 2.92. Found: C, 51.64; H, 6.96; N, 3.14.

Reaction of $[Au(^{Me2}CAAC)_2]Cl$ with $CsBr_3$ at −78 °C. A mixture of $[Au(^{Me2}CAAC)_2]Cl$ (89 mg, 0.10 mmol) and $CsBr_3$ (38 mg, 0.10 mmol) in 5 mL of CH_2Cl_2 was stirred for 20 min at −78 °C and warmed to room temperature with stirring for 1 h. The orange-red solution was concentrated to ca. 0.3 mL. An orange solid was precipitated with hexanes (10 mL) and dried under vacuum. Yield: 95 mg. Crystallization by layering a CH_2Cl_2 solution with hexanes gave two type of crystals, which were identified by X-ray diffraction as orange prisms of $[Au(^{Me2}CAAC)_2]Br_3$ (**24a**) and red prisms of $[Au(^{Me2}CAAC)_2]AuBr_4$ (**24b**). Both give identical ^1H NMR spectra.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.43 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.25 (d, J = 7.7 Hz, 2H, CH-aromatic), 2.61 (sept, J = 6.7 Hz, 2H, $CH(CH_3)_2$), 2.06 (br s, 2H, CH_2), 1.33 (s, 6H, $2CH_3$), 1.26 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.22 (s, 6H, $2CH_3$), 1.03 (br d, J = 6.7 Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 250.6 (C carbene), 144.6 (o-C), 133.5 (C_{ipso}), 130.1 (p-C), 125.1 (m-C), 82.4 (C_q), 54.6 (C_q), 49.5 (CH_2), 28.9 (CH), 28.8, 28.5, 26.7, 22.6 (CH_3) ppm. Elemental analysis was not carried out due to formation of a product mixture.

Synthesis of $[Au(^{Me2}CAAC)_2]ClI_2$ (24c). A solution of $[Au(^{Me2}CAAC)_2]Cl$ (80 mg, 0.10 mmol) and I_2 (26 mg, 0.10 mmol) in 3 mL of CH_2Cl_2 was stirred for 1 h at 0 °C and warmed to room temperature with stirring for 1 h. Addition of hexanes (15 mL) led to the precipitation of a brown product, which was centrifuged, washed with 5 mL of Et_2O, and dried under vacuum. Yield: 102.5 mg (0.097 mmol, 97%).

^1H NMR (300 MHz, CD_2Cl_2): δ 7.44 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.24 (d, J = 7.7 Hz, 2H, CH-aromatic), 2.59 (sept, J = 6.7

Hz, 2H, CH(CH$_3$)$_2$), 2.06 (br s, 2H, CH$_2$), 1.32 (s, 6H, 2CH$_3$), 1.25 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.21 (s, 6H, 2CH$_3$), 1.02 (br d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 250.6 (C carbene), 144.6 (o-C), 133.5 (C$_{ipso}$), 130.1 (p-C), 125.1 (m-C), 82.4 (C$_q$), 54.6 (C$_q$), 49.4 (CH$_2$), 28.9 (CH), 28.8, 28.5, 26.7, 22.6 (CH$_3$) ppm. Anal. Calcd for C$_{40}$H$_{62}$AuClI$_2$N$_2$ (1057.16): C, 45.45; H, 5.91; N, 2.65. Found: C, 45.37; H, 5.83; N, 2.59.

Synthesis of (^{Ad}CAAC)AuCl$_3$ (25). All operations have to be performed with minimum exposure to light. A scintillation vial was charged with (^{Ad}CAAC)AuCl (61 mg, 0.10 mmol) and PhICl$_2$ (29 mg, 0.105 mmol) and wrapped in aluminum foil. Chilled CH$_2$Cl$_2$ (5 mL) was added and resulting solution stirred for 6 h at 0 °C in the dark. A slightly yellow solution resulted, which was concentrated to ca. 0.3 mL. The addition of Et$_2$O (15 mL) gave a pale yellow precipitate which was washed with Et$_2$O (2 × 5 mL) and dried under vacuum. Yield: 64 mg (0.095 mmol, 95%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.52 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.38 (d, J = 7.7 Hz, 2H, CH-aromatic), 3.33 (br d, J = 13.2 Hz, 2H, CH$_2$), 3.04 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.54−1.82 (m, 14H, adamantyl CH and CH$_2$), 1.55 (s, 6H, 2CH$_3$), 1.48 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.27 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 218.8 (C carbene), 146.2 (o-C), 133.5 (p-C), 130.9 (C$_{ipso}$), 126.7 (m-C), 82.1 (C$_q$), 69.1 (C$_q$), 47.6 (CH$_2$), 38.0 (CH$_2$), 37.7, 35.3, 34.5 (CH$_2$), 30.1 (CH), 29.0, 27.1, 26.6, 26.1 (CH$_3$). Anal. Calcd for C$_{27}$H$_{39}$AuCl$_3$N (680.92): C, 47.62; H, 5.77; N, 2.06. Found: C, 47.69; H, 5.72; N, 2.12.

Synthesis of (^{Ad}CAAC)AuI. A mixture of [Au(AdCAAC)(Cl)] (61 mg, 0.10 mmol) and NaI (150 mg, 1 mmol) in 10 mL of acetone was stirred for 24 h at room temperature. The solvent was removed under vacuum. The white residue was extracted with CH$_2$Cl$_2$ (2 × 10 mL) and the solution filtered through Celite (1 cm). All volatiles were removed under vacuum to give an off-white solid with 0.5 CH$_2$Cl$_2$ as a solvate molecule. Yield: 73.5 mg (0.098 mmol, 98%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.48 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.29 (d, J = 7.7 Hz, 2H, CH-aromatic), 5.33 (s, 1H, solvent molecule 0.5CH$_2$Cl$_2$) 3.98 (br d, J = 12.6 Hz, 2H, CH$_2$), 2.78 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.38−1.81 (m, 14H, adamantyl CH and CH$_2$), 1.41 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.36 (s, 6H, 2CH$_3$), 1.30 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 247.5 (C carbene), 144.9 (o-C), 135.1 (C$_{ipso}$), 129.6 (p-C), 124.8 (m-C), 77.1 (C$_q$), 63.9 (C$_q$),, 48.4 (CH$_2$), 38.8 (CH$_2$), 37.0, 34.9, 34.3 (CH$_2$), 29.0 (CH), 28.9, 27.8, 27.2, 26.4, 22.8 (CH$_3$) ppm. Anal. Calcd for C$_{27}$H$_{39}$AuIN·0.5CH$_2$Cl$_2$ (743.94): C, 44.40; H, 5.42; N, 1.88. Found: C, 44.33; H, 5.48; N, 1.93.

Synthesis of (^{Ad}CAAC)AuI·I$_2$ (26). A mixture of (^{Ad}CAAC)AuI· 0.5CH$_2$Cl$_2$ (74 mg, 0.10 mmol) and I$_2$ (26 mg, 0.10 mmol) in 5 mL of CH$_2$Cl$_2$ was stirred for 20 min at −78 °C and warmed to room temperature with stirring for 2 h to give a dark red solution. The solvent was removed under vacuum and the residue washed with hexanes (3 × 6 mL) and dried under vacuum to afford a dark red solid. Yield: 92 mg (0.097 mmol, 97%).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.50 (t, J = 7.7 Hz, 1H, CH-aromatic), 7.29 (d, J = 7.7 Hz, 2H, CH-aromatic), 3.96 (br d, J = 12.6 Hz, 2H, CH$_2$), 2.77 (sept, J = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 2.38−1.82 (m, 14H, adamantyl CH and CH$_2$), 1.41 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$), 1.36 (s, 6H, 2CH$_3$), 1.30 (d, J = 6.7 Hz, 6H, CH(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 246.6 (C carbene), 144.8 (o-C), 135.1 (C$_{ipso}$), 129.8 (p-C), 125.0 (m-C), 77.2 (C$_q$), 63.9 (C$_q$), 48.4 (CH$_2$), 38.8 (CH$_2$), 37.0, 35.1, 34.3 (CH$_2$), 29.0 (CH), 28.9, 27.8, 27.2, 26.5, 22.8 (CH$_3$) ppm. Anal. Calcd for C$_{27}$H$_{39}$AuI$_3$N (955.28): C, 33.95; H, 4.11; N, 1.47. Found: C, 33.81; H, 4.02; N, 1.39.

X-ray Crystallography. Crystals suitable for X-ray study were obtained by layering of a CH$_2$Cl$_2$ solution with hexanes, with the exception of complex **17** (1,2-difluorobenzene/hexanes). Crystals were mounted in oil on glass fibers and fixed in the cold nitrogen stream on a diffractometer. X-ray diffraction experiments were carried out with an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 140 K. Data were processed using the CrystalisPro-CCD and -RED software.[48] The principal crystallographic data and refinement

parameters are given in Table S1 (Supporting Information). The CH$_2$ (C3 atom) and methyl groups (C17 and C18 atoms) were disordered over two positions with occupancies of 0.65/0.35 and 0.62/0.38, respectively. The Cl1 and I2 atoms for complex **24c** were disordered into two positions linked by a center of inversion with equal occupancies. The complex [{(^{Ad}CAAC)Au}$_3$(μ_3-O)]$^+$OH$^-$ crystallizes with two independent molecules and half of a benzene molecule. The oxygen atoms of the hydroxide counteranion for [{(^{Ad}CAAC)Au}$_3$(μ_3-O)]$^+$OH$^-$ were not refined anisotropically, due to disorder problems masked by the presence of the disordered solvent molecules. For the final refinement, the contribution of severely disordered CH$_2$Cl$_2$ molecules in crystals of **7**, **14**, and [{(^{Ad}CAAC)-Au}$_3$(μ_3-O)]$^+$OH$^-$ were removed from the diffraction data with PLATON/SQUEEZE.[49,50] The structures were solved by direct methods and refined by the full-matrix least squares against F^2 in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in an isotropic approximation in the "riding" model with the U_{iso}(H) parameters equal to 1.2[U_{eq}(C$_i$)] and for methyl groups equal to 1.5[U_{eq}(C$_{ii}$)], where U(C$_i$) and U(C$_{ii}$) are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. The hydrogen atom of the hydroxide counteranion in [{(^{Ad}CAAC)Au}$_3$(μ_3-O)]$^+$OH$^-$ was not located. All calculations were performed using the SHELXTL software.[51] Intensities for complex **14** and [{(^{Ad}CAAC)Au}$_3$(μ_3-O)]$^+$OH$^-$ were collected at 100(2) K on a Bruker-Nonius Roper CCD diffractometer, equipped with Mo Kα radiation and a graphite monochromator at the EPSRC National Crystallography service, Southampton, U.K.[52] Data were processed using CrystalClear-SM Expert 3.1 b21 (Rigaku, 2012) programs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF files giving crystallographic data for compounds **7**, **11**, **14**, **16−18**, **20a/24**, **20b**, **21a,b**, **23**, **24a−c**, **26**, (^{Ad}CAAC)AuX (X = Br, I), and [{(^{Ad}CAAC)Au}$_3$(μ_3-O)]$^+$OH$^-$ and ^{1}H and ^{13}C{^{1}H} NMR spectra for complex **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ DEDICATION

Dedicated to the memory of Professor Michael F. Lappert, a superbly inventive pioneer of organometallic chemistry and a much-missed friend.

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