Gold(I) and Gold(III) Complexes of Cyclic (Alkyl)(amino)carbenes
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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 \( \text{Me}_2\text{CAAC} \) and the 2-adamantyl ligand \( \text{AdCAAC} \). The conversion of \( \text{(AdCAAC)}\text{AuCl} \) into \( \text{(AdCAAC)}\text{AuOH} \) by treatment with KOH is significantly accelerated by the addition of iBuOH. \( \text{(AdCAAC)}\text{AuOH} \) is a convenient starting material for the high-yield syntheses of \( \text{(AdCAAC)}\text{AuX} \) complexes by acid/base and C–H activation reactions (X = OMMe, CN, CF \(_3\), CO, OCMe \(_2\)).

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 dimethylimidazolidinylimide derivatives \( \text{[Au\{C-(\text{NMe})\}_2\text{H}_2\}]X \) (X = Cl, BF \(_3\)). \(^4\) 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 \( \Delta N \) values, i.e., CAAC ligands behave as stronger \( \sigma \) donors. \(^9\)

On the other hand, it is becoming apparent that, even with NHC ligands, the \( \pi \)-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 \( \sigma \)-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 \( \pi \)-acceptor capability is likely to play an important role. \(^11\)–\(^15\) 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 \( \text{Me}_2\text{CAAC} \) and the 2-adamantyl ligand \( \text{AdCAAC} \) (Chart I). \(^6\)

RESULTS AND DISCUSSION

Although gold(I) chloride complexes \( \text{LAuCl} \) are most commonly employed as entries into ligand exchange reactions and catalytic transformations, often in combination with silver...
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.\textsuperscript{15} We therefore decided to prepare the corresponding CAAC gold(I) alkoxides, hydroxides, and carboxylates.

**Anion Exchange Reactions.** The reaction of (AdCAAC)-AuCl (1) with sodium tert-butoxide in toluene generates the white alkoxide complex (AdCAAC)AuO\textsubscript{Bu} (2) in essentially quantitative yield (Scheme 1).\textsuperscript{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 (AdCAAC)AuOH (3). Complex 3 is characterized in its \( ^1\)H NMR spectrum by a broadened singlet of the OH ligand at \( \delta = -0.29 \) ppm (in C\(_6\)D\(_6\)).

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 \textsubscript{Bu}OH 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 \textsubscript{Bu}O\textsuperscript{−}, which catalyzes chloride substitution.\textsuperscript{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 \( \delta \) 238, slightly upfield from the chloride precursor complex (AdCAAC)AuCl (\( \delta = 239.9 \)).

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 \([\{(AdCAAC)Au\}(_3)(\mu_3-O)]^+OH^-\). This compound was identified crystallographically (see the Supporting Information, Figure S9). It is analogous to the well-known Nesmeyanov cation,\textsuperscript{18} and its formation indicates that, in spite of the steric bulk of AdCAAC, condensation of the hydroxide can still take place.\textsuperscript{19}

Both (AdCAAC)AuO\textsubscript{Bu} (2) and (AdCAAC)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 (AdCAAC)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(1)\textsuperscript{20} and Au(III)\textsuperscript{21} hydroxides and to lead cleanly to the corresponding gold organyl complexes in excellent yields.

The reaction of 3 with trifluoroacetic acid (tfaH) affords (AdCAAC)Au(tfa) (5). This product is also accessible directly from (AdCAAC)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 \( \delta (^{13}\)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 arylxides 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 \( \delta = 236.1 \) (in C\(_6\)D\(_6\)).
The reaction of the gold hydroxide 3 with HNTf₂ in toluene is a high yield route to the Gagosz-type complex (AdCAAC)AuNTf₂ (7), which is of interest for silver-free protocols in gold catalysis. 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)AuNTf₂ complexes.

C−H Activation Reactions. The basicity of (AdCAAC)-AuOH may be exploited to activate C−H bonds. Phenylacetylene and diethyl malonate give the corresponding metalation products (AdCAAC)AuC≡CPh (8) and (AdCAAC)-AuCH(CO₂Et)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 (AdCAAC)AuCl with the lithium salt of phenylacetylene. 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 pKₐ value of the gold hydroxide to be estimated. The pKₐ values of a range of fluoroarenes have been calculated with values of 29.0 and 23.1 for C₆H₅F₅ and 1,2,4,5-C₆H₂F₄, 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 (AdCAAC)AuC₆H₅−xF₄ (10, n = 5; 11, n = 4) in...
the analogous complex (NHC)AuC₆H₂F₃ (2.026(3) and 12° yield. The formation of
atures (75° and Au
basic (AdCAAC)Au(O
these multiplets corresponded to the desired complex
2.044(3) Å).25
complexes closer to that of Larossa
31.5 or less. This reactivity places the (CAAC)AuOH
the corresponding gold alkyls (AdCAAC)AuR (R = CH₂C(O) acetophenone, deoxybenzoin, and methyl phenyl sulfone gave
AuCl/NaO
AgSbF₆ and (R 3P)AuCl/NaOtBu, which also aurate 1,3,5-
reduced yield.

The auration of 1,3,5-triﬂuorobenzene by 3 and (AdCAAC)-AuCl/NaO’Bu generated in situ from (AdCAAC)-AuCl and NaO’Bu (eq 1). These mixtures proved more reactive
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 (AdCAAC)-AuCl/NaO’Bu mixtures is in contrast with the lack of reactivity of (IPr)AuOH23 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 monﬂuorobenzene. The reactivity decreases therefore in the sequence shown in Scheme 324 evidently (AdCAAC)AuOH is sufﬁciently basic to undergo reactions with C–H bonds with pKₐ values of 31.5 or less. This reactivity places the (CAAC)AuOH complexes closer to that of Larossa’s systems (Bu₃P)AuCl/ AgSbF₆ and (R,P)AuCl/NaO’Bu, which also aurate 1,3,5-triﬂuorobenzene.
The hydroxide 3 is a convenient starting material for the metalation of a series of functionalized C–H compounds. For example, the reaction of (AdCAAC)AuOH with p-methoxyacetophenone, deoxybenzoin, and methyl phenyl sulﬁone gave the corresponding gold alkyls (AdCAAC)AuR (R = CH₃C(O) C₆H₄OMe (13), CH(Ph)C(O)Ph (14) and CH₂SO₂Ph (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-diation of acetophenone en route to tamoxifen precursors.26 The reaction of 3 with acetophenone has a precedence in the formation of (Ph₃P)Au-CH₂C(O)Ph from acetophenone and Nesmeyanov’s [Au₃(μ₃-O)(PPh₃)₃]⁺ cation,27 while more recent alternative syntheses of gold α-keto alkyls have involved the use of silyl enolates with (Ph,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 ¹H NMR spectra in comparison to the signals for the free ligands. The ¹C carbene-carbon resonances for 8–15 are shifted upﬁeld relative to those for (AdCAAC)AuCl and are observed in the range 6 253.2–260.2. The Au-CHR’R” center in the C₃-symmetric complex 14 is chiral; the complex therefore shows two sets of resonances related to the AdCAAC ligand in its ¹H NMR spectrum, since the CH₃ and CMe₃ 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

Scheme 3.24

Figure 2. Crystal structure of (AdCAAC)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

Values given are calculated pKₐ values.24
spatial orientation of C(15) explains the high-field $^1$H NMR chemical shift of this methyl group, at $\delta$ 0.89, due to magnetic shielding by the aryl.

Functionalized alkyl complexes such as 13−15 should, in principle, provide access to $\alpha$-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 $\alpha$-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 BuNC gives the corresponding cationic complexes [(AdCAAC)Au(L)]$^+$ (L = CO (16); L = 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 $\nu$(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(CNtBu)][SbF$_6$] (2244 cm$^{-1}$).31

The cyano complex (AdCAAC)AuCN (18) was prepared for comparison with the CO compound, by reaction of the hydroxide (AdCAAC)AuOH with Me$_3$SiCN or of that of (AdCAAC)AuCl and KCN. Both approaches lead to almost quantitative yields of complex 18. The complex shows a $\nu$$_{CN}$
interactions of 2.99–3.090(3) Å, which falls into the range of intermolecular compounds.32 The fluorine atoms of 1,2-di-fluorobenzene, which exhibits a T-shaped C(28)–···F(8) π field of that of (AdCAAC)AuCl. The C(28)-Au distances remain approximately constant throughout this series, deviating only slightly from the value of 2.031(5) Å observed for the cyanide complex.

The crystal structures of the CO, 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 2.015(7) 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. The isonitrile complex 17 crystallized with a molecule of 1,2-difluorobenzene, which exhibits a T-shaped C−F−C−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 fluoroorganic compounds.32

In view of our earlier observation that ethylene inserts into Au(III)−trifluoroacetate bonds to give the functionalyzed alkyls Au−C3H7OAcF,33 (AdCAAC)AuOAcF was exposed to an atmosphere of ethylene for extended periods of time, either in CH2Cl2 with the addition of AgOAc as catalyst or in CH3Cl/CH3COF mixtures. However, in no instance 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(C6F5)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 precedent and proceeds smoothly in high yields with oxidants such as Br2 and PhICl2, in most cases to give products of the type (NHC)AuX3 (X = Cl, Br, I).34−41 It was therefore surprising when initial attempts at oxidizing (AdCAAC)AuX with either PhICl2 or CsBr3 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 (AdCAAC)AuCl with PhICl2 in CH2Cl2 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 [AdCAAC-Cl][AuCl4] (20a), formed by chlorination of the carbene ligand, and a larger component of yellow prisms which turned out to be the product of cocystalization of two independent molecules of [AdCAAC-Cl][AuCl4] (20b) with one molecule of (AdCAAC)AuCl, in the unit cell. The 1H 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 13C NMR resonance for the iminium carbon atom C−X is shifted upfield...
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, (McCAAC)AuCl3, partially undergoes photoinduced reductive elimination into Cl2 and the Au(I) complex (McCAAC)AuCl. The eliminated chlorine could then react with either (McCAAC)AuCl or (McCAAC)AuCl3 to give the corresponding salts [(McCAAC-Cl)[AuCl2]] and [(McCAAC-Cl)[AuCl4]], respectively. The photochemical reductive elimination of halogens from (NHC)AuBr3 and from gold(III) phosphine complexes in the presence of olefins as halogen scavengers is known to be facile. In the present case the carbene C–Au bond acts as such a halogen scavenger. Similar cleavage products 21a,b are obtained using CsBr3 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 Me2CAAC ligand and subsequently extended to AdCAAC gold compounds.

Stirring a mixture of [Au(Me2CAAC)2]Cl (22) and PhICl2 in dichloromethane in the dark at 0 °C to room temperature for 6 h gave a colorless complex, [AuCl2(Me2CAAC)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 Me2CAAC 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–Cl(1) (2.064(2) Å) is slightly elongated in comparison to those of the analogous imidazolylidene complexes [AuCl2(NHC)2]+, while the Au–Cl(I) distance is closely similar.

The crystal structure and elemental analysis show the expected composition of the desired Au(III) product, [AuCl3(Me2CAAC)2]Cl. At the same time, it is a well-known fact that the 13C NMR resonance of the carbene carbon is usually shifted upfield on oxidation of Au(I) carbene complexes to Au(III). However, the 1H and 13C NMR spectra in CD2Cl2 of [AuCl2(Me2CAAC)2]Cl and its precursor [Au(Me2CAAC)2]Cl are essentially identical: δ(13C) 250.6. Therefore, we cannot exclude the possibility that in solution an equilibrium exists between [AuCl2(Me2CAAC)2]Cl and its Au(I) isomer, [Au(Me2CAAC)2]Cl, which in dichloromethane is predominantly shifted toward the Au(I) complex. It did not prove possible, however, to isolate the trichloride salt, and
numerous attempts to pick out different crystals led only to unit cell measurements corresponding to the Au(III) complex [AuCl(\(\text{Me}^2\text{CAAC}\))\(_2\)]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(\(\text{Me}^2\text{CAAC}\))\(_2\)]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\(^{\text{III}}\)]\(^+\) salts.

The oxidation of 22 with CsBr\(_2\) as selective brominating agent took a somewhat different course. Under ambient conditions [Au(\(\text{Me}^2\text{CAAC}\))\(_2\)]Cl reacts with CsBr\(_2\) to give a mixture of orange prisms of [Au(\(\text{Me}^2\text{CAAC}\))\(_2\)]Br\(_3\) (24a) and of red crystals of [Au(\(\text{Me}^2\text{CAAC}\))\(_2\)]AuBr\(_4\) (24b) (Scheme 5). In contrast, the attempted oxidation of [Au(\(\text{Me}^2\text{CAAC}\))\(_2\)]Cl with iodine gave the Au(I) diiodochloride salt [Au(\(\text{Me}^2\text{CAAC}\))\(_2\)]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 where and where oxidation with iodine has given rise to compounds of the types (NHC)AuBr\(_2\), [Au\(_2\)(NHC)]\(_2\), and (NHC)AuI\(_3\).38b,39a

A similar reactivity pattern was observed in the oxidation reactions of the more bulky monocarbenec complexes (\(^{\text{Ad}}\text{CAAC}\))AuX (X = Cl, Br, I). As was observed for the bis-carbene cation [Au(\(\text{Me}^2\text{CAAC}\))\(_2\)]\(^+\), carbene complexes of Au(III) are only obtained if ambient light is excluded. Thus, the reaction of (\(^{\text{Ad}}\text{CAAC}\))AuCl with PhICI over the temperature range from 0 °C to room temperature for 6 h in the dark led to the isolation of (\(^{\text{Ad}}\text{CAAC}\))AuCl\(_2\) (25) as a light yellow solid in almost quantitative yield (eq 3). There was no reaction at −78 °C.

The \(^{13}\)C NMR spectrum of 25 shows the carbene carbon signal at δ 218.8, substantially downfield from the carbene carbon signal of imidazolidine-type (NHC)AuCl\(_3\) complexes, which are typically observed in the range of δ 130−170.33−40 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.6b,39a There was no evidence for ligand rearrangement, e.g. to [AuCl\(_3\)(\(^{\text{Ad}}\text{CAAC}\))\(_2\)][AuCl\(_2\)], 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 carbene carbon are almost identical with those observed in numerous (NHC)AuCl\(_3\) complexes.23−30 In contrast, the reaction of (\(^{\text{Ad}}\text{CAAC}\))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 (\(^{\text{Ad}}\text{CAAC}\))AuI\(_2\) (26) were isolated (eq 4).

This is in contrast to the oxidative addition of iodine observed with other types of NHC complexes, which form gold(III) iodides.39b,45 The formation of triiodides and iodine adducts has previously been observed for phosphine and isonitrile Au(I) complexes.35a,44 Indications for the redox equilibrium LAu\(^{\text{III}}\)(I\(_2\)) ⇌ LAu\(^{\text{II}}\)(I\(_3\)) were not detected.

The structure of 26 is shown in Figure 7. According to the Cambridge Structural Database the only closely analogous
compound with a triiodide moiety is \( \left[ \text{[BuNC]}_{\text{2}}\text{Au} \right] \text{[AuI]}_{\text{2}} \), reported by Schmidbaur.\(^\text{43}\) The Au–I(1) and I(2)–I(3) bond lengths for the complex (\( \text{[AdCAAC]}\text{AuI}_{\text{2}} \) (2.5684(4) and 2.7626(5) Å) are almost identical with those for \( \left[ \text{[BuNC]}_{\text{2}}\text{Au} \right] \text{[AuI]}_{\text{2}} \) (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 polyniobide complexes.\(^\text{46}\) Analysis of intermolecular contacts shows neither aurophilic interactions (the shortest distance between gold atoms is 7.521 Å) nor polyniobide chain formation.

**CONCLUSION**

The \( \text{AdCAAC} \) ligand produces a gold(I) hydroxide with slightly increased basicity in comparison to the imidazoylidene-type complex (NHC)\text{AuI}. 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 THF. The oxidation reactions of CAAC-supported gold(1) complexes by halogens, on the other hand, did not conform to the expectations for electron-rich complexes, and only stronger oxidants, such as PhI\text{ClO}, 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–carbon 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 carbones provide therefore an interesting contrast to those of more strongly \( \pi \)-accepting imidazole-based NHC carbones.

**EXPERIMENTAL SECTION**

### General Considerations.

Unless stated otherwise, all reactions were carried out in air. Solvents were distilled and dried as required. Pentfluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3,5-trifluorobenzene, sodium tert-butoxide, diethyl malonate, trimethylhydrazide, triethylxylamine, trifluoroacetyl chloride, tert-butyl alcohol, \( \text{BuNC}, \text{KCN}, \text{and C}_{6} \text{H}_{5} \text{Br} \) were purchased from Sigma-Aldrich and used as received.

### Synthesis of (\( \text{AdCAAC} \))\text{AuO} (3).

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

**Method B.** An excess of distilled water \((5 \text{ mL})\) was added to the stirred solution of (\( \text{AdCAAC} \))\text{Au} \((194 \text{ mg}, 0.30 \text{ mmol})\) 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 \((5 \text{ mL})\) and dried under vacuum for 1 day. Yield: 171 mg \((0.29 \text{ mmol, 97%})\).

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

**Synthesis of (\( \text{AdCAAC} \))\text{Au(OH)} (3).**

**Method A.** Under an argon atmosphere, an oven-dried 25 mL Schlenk flask was charged with (\( \text{AdCAAC} \))\text{Au(OH)} \((79 \text{ mg}, 0.14 \text{ mmol})\), and 10 mL of THF. The stirred suspension was added tert-butyl alcohol \( \left(0.02 \text{ mL, 0.2 mmol} \right) \), and stirring was continued for 36 h at room temperature. The dark suspension was filtered through a Celite pad \((3 \times 5 \text{ mL})\) and washed with additional THF \((2 \times 5 \text{ mL})\). Water \( \left(4 \text{ mL} \right) \) was added to the THF solution, after which it was concentrated to ca. 7 mL. Water \( \left(10 \text{ mL} \right) \) was added to the cloudy suspension. All volatiles were removed under vacuum \((30 \text{ °C, 20 mbar})\). If any coloration of the solid remained, it could be redissolved in THF/\text{H}_{2} \text{O} \((4:1)\) and passed through Celite. The white residue was washed with hexanes \((5 \text{ mL})\) and dried under vacuum for 1 day. Yield: 171 mg \((0.29 \text{ mmol, 97%})\).

**Synthesis of (\( \text{AdCAAC} \))\text{Au(c-C}_{6} \text{H}_{5} \text{F)} (4).**

**Method A.** Under an argon atmosphere, an oven-dried 25 mL Schlenk flask was charged with a stirring bar, (\( \text{AdCAAC} \))\text{Au(OH)} \((97 \text{ mg}, 0.15 \text{ mmol})\), and 10 mL of THF. The stirred suspension was stirred for 15 min, and the volatiles were removed under vacuum. The white residue was washed with hexanes \((5 \text{ mL})\) and dried under vacuum for 1 day. Yield: 92 mg \((0.14 \text{ mmol, 92%})\).

**Method B.** A scintillation vial was charged in air with a stirring bar, (\( \text{AdCAAC} \))\text{Au(OH)} \((60 \text{ mg}, 0.10 \text{ mmol})\), and 10 mL of THF. The stirred suspension was stirred for 15 min, and the volatiles were removed under vacuum. The white residue was washed with hexanes \((2 \times 4 \text{ mL})\) and dried under vacuum. Yield: 92 mg \((0.14 \text{ mmol, 92%})\).
Synthesis of \((\text{AdCAAC})\text{Au(OAcF)}\) (5). A Schlenk flask was charged with \((\text{AdCAAC})\text{AuCl}\) (59 mg, 0.10 mmol) and diethyl malonate (16 mg, 0.10 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%).

\[ \text{AdCAACAu(OAcF)} \to \text{AdCAACAu(OAc)} + \text{malonate} \]

Synthesis of \((\text{AdCAAC})\text{Au(OCH)}(\text{CO}_{2}\text{Et})\) (8). A scintillation vial was charged with a stirring bar, \((\text{AdCAAC})\text{AuOH}\) (59 mg, 0.10 mmol), and ethyl acetate (23 mg, 0.2 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%).

\[ \text{AdCAACAuOH} + \text{ethyl acetate} \to \text{AdCAACAu(OCH)}(\text{CO}_{2}\text{Et}) \]

Synthesis of \((\text{AdCAAC})\text{Au(3,5-di-} \text{F}-\text{C}_{6}\text{H}_{4})\text{F} \) (10). A Schlenk flask was charged with \((\text{AdCAAC})\text{AuCl}(118 \text{ mg, 0.2 mmol})\) and a pentfluorobenzaldehyde solution (42 μL, 0.4 mmol) in toluene (2 mL). The reaction 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 × 2 mL) and dried under vacuum to give an off-white solid. Yield: 140 mg (0.19 mmol, 95%).

\[ \text{AdCAACAuCl} + \text{pentafluorobenzaldehyde} \to \text{AdCAACAu(3,5-di-} \text{F}-\text{C}_{6}\text{H}_{4})\text{F} \]

Synthesis of \((\text{AdCAAC})\text{AuPNF}_{2}\) (9). A Schlenk vial was charged with a stirring bar, \((\text{AdCAAC})\text{AuOH}\) (59 mg, 0.10 mmol), and hexamethylphosphoramide (23 mg, 0.2 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: 86 mg (0.091 mmol, 91%).

\[ \text{AdCAACAuOH} + \text{hexamethylphosphoramide} \to \text{AdCAACAuPNF}_{2} \]
Synthesis of \((\text{AdCAAC})\text{Au}(\text{p}-\text{methoxyphenyl})\) (13). A scintillation vial was charged with \((\text{AdCAAC})\text{AuOH}\) (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%).

Synthesis of \((\text{AdCAAC})\text{Au}(\text{deoxybenzoinyl})\) (14). A scintillation vial was charged with \((\text{AdCAAC})\text{AuOH}\) (76 mg, 0.128 mmol) and \(p\)-deoxybenzoin (15 μL, 0.20 mmol) in toluene (2 mL). The mixture was heated to 70 °C for 18 h. The yellow solution with some black precipitate was cooled to the room temperature. The yellow solution was decanted from the gray suspension. The product was extracted with CH2Cl2 and filtered through a Celite pad (1 cm) which was washed with an additional 6 mL of CH2Cl2. 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%).

Synthesis of \((\text{AdCAAC})\text{Au}(\text{CH}2\text{C(O)-O-C6H4})\) (15). A scintillation vial was charged with \((\text{AdCAAC})\text{AuOH}\) (94 mg, 0.15 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 residue was washed with hexanes (2 × 4 mL) and dried under vacuum to give a white solid. Yield: 55 mg (0.076 mmol, 81%).
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**Synthesis of ($^{19}$CAAC)AuCl(NO) (16).** A Schlenk flask was charged with ($^{19}$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 with bubbling with CO for 1 min followed by stirring at room temperature for 2 h. Precipitation 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.

**1H 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$_{(CH}_2$)), 2.47−1.85 (m, 14H, adamantyl CH and CH$_2$), 1.44 (s, 6H, 2CH$_3$), 1.35 (d, $J = 12.7$ Hz, 6H, 6CH$_{(CH}_2$)), 1.33 (d, $J = 6.7$ Hz, 6H, CH$_{(CH}_3$)) ppm. 13C ($^3$)NMR (75 MHz, CD$_2$Cl$_2$): δ 241.1 (C carbene), 182.4 (s, CO), 144.7 (o-C), 134.2 (C$_p$), 131.2 (p-C), 125.7 (m-C), 80.8 (C$_q$), 65.4 (C$_{ipso}$), 67.9 (CH$_3$), 38.4 (CH$_3$), 36.9, 36.8, 33.8 (CH$_3$), 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. Calc'd for C$_{34}$H$_{46}$AuNSO$_2$: C, 43.13; H, 5.49; N, 3.19.

**Synthesis of [(^6)CAAC]Au(pBu) (17).** A Schlenk flask was charged with [(^6)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. 2 mL, and an excess of pBuNC (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%).

**1H 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$_{(CH}_2$)), 2.40−1.83 (m, 14H, adamantyl CH and CH$_2$), 1.48 (s, 9H, C(CH$_3$)), 1.39 (s, 6H, 2CH$_3$), 1.35 (d, $J = 6.7$ Hz, 6H, CH$_{(CH}_3$)) ppm. 13C ($^3$)NMR (75 MHz, CD$_2$Cl$_2$): δ 242.6 (C carbene), 144.8 (o-C), 142.4 (br s, CN'Bu) 134.5 (C$_p$), 130.4 (p-C), 125.3 (m-C), 79.5 (C$_q$), 65.1 (C$_{ipso}$), 58.6 (br s, C(NCMe$_3$)), 48.0 (CH$_3$), 38.5 (CH$_3$), 36.9, 36.1, 34.0 (CH$_3$), 29.5 (CNC(CH$_3$)), 29.0 (CH), 28.9, 27.8, 26.8, 26.6, 22.7 (CH$_3$) ppm. IR (ATR, cm$^{-1}$): 2973, 2899, 2241 (CN'Bu), 1338, 1450, 1373, 1194, 1147, 1097, 803, 776, 654, 523. Anal. Calc'd for C$_{34}$H$_{46}$AuSbN$_3$: C, 34.43; H, 5.41; N, 3.14. Found: C, 43.13; H, 5.49; N, 3.19.

**Synthesis of [(^6)CAAC]AuCN (18).** Method A. Trimethylsilyl cyanide (20 μL, 0.150 mmol) was added to the solution of [(^6)CAAC]AuCl (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 (2 × 4 mL) and dried under vacuum to give an off-white solid. Yield: 98 mg (0.134 mmol, 85%).

**Method B.** [(^6)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 (0.070 mmol, 92%).

**1H 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$_{(CH}_3$)), 2.32−1.79 (m, 14H, adamantyl CH and CH$_2$), 1.37 (d, $J = 6.7$ Hz, 6H, CH$_{(CH}_3$)), 1.34 (s, 6H, 2CH$_3$), 1.30 (d, $J = 6.7$ Hz, 6H, CH$_{(CH}_3$)) ppm. 13C ($^3$)NMR (75 MHz, CD$_2$Cl$_2$): δ 253.1 (C carbene), 149.5 (CN), 144.9 (o-C), 134.8 (C$_p$), 129.8 (p-C), 124.9 (m-C), 78.0 (C$_q$), 64.9 (C$_{ipso}$), 48.3 (CH$_3$), 38.8 (CH$_3$), 37.0, 35.6, 34.2 (CH$_3$), 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, 1427, 1370, 1097, 934, 808, 727. Anal. Calc'd for C$_{34}$H$_{46}$AuSbF$_6$: C, 56.00; H, 6.54; N, 4.66. Found: C, 56.16; H, 6.61; N, 4.72.

**Synthesis of [(^6)CAAC]Au(pnorbornene) (19).** A Schlenk flask was charged with [(^6)CAAC]AuOAc (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 withdrawn under vacuum to afford a white powder which was additionally dried under vacuum overnight. Yield: 96 mg (0.074 mmol, 85%).
Addition of EtO (10 mL) gave a yellow precipitate, which was washed with EtO (2 × 5 mL) and dried under vacuum: yield 63 mg. Crystallization by layering a CH2Cl2 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 dichloro[1]catenil] ate ([AuCl2](2)Br) (19b) while the major component of yellow prisms turned out to be the cocrystallization product [2[AdCAAC-AuCl](CH2Cl2)]: 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 [AdCAAC-AuCl]2.CH2Cl2 and CH2Cl2. The 1H and 13C NMR spectra of the two salts [AdCAAC-AuCl]2 and [AdCAAC-AuCl]2·CH2Cl2 are essentially identical. Elemental analysis was not carried out due to formation of a product mixture.

**Synthesis of [AdCAAC-AuCl]2·CH2Cl2 (20b).** A solution of (AdCAAC)AuCl (61 mg, 0.11 mmol) and PhCl (58 mg, 0.23 mmol) in 5 mL of CH2Cl2 was stirred for 3 h at room temperature. A yellow solution resulted, which was concentrated to ca. 0.3 mL. The addition of EtO (10 mL) gave a yellow precipitate, which was washed with EtO (2 × 5 mL) and dried under vacuum. Yield: 74 mg, 0.089 mmol, 98%.

**Synthesis of (AdCAAC)AuCl** (61 mg, 0.11 mmol) and LiBr (88 mg, 1 mmol) in 10 mL of acetone was warmed to room temperature with stirring for 1 h. The suspension was filtered through Celite (1 cm). All volatiles were removed under vacuum to give a white solid with one solvate molecule of CH2Cl2. Yield: 72.5 mg (0.098 mmol, 98%).

**Reaction of [Au(Me2CAAC)2]Cl with CsBr3 at –78°C.** A mixture of [Au(Me2CAAC)2]Cl (89 mg, 0.10 mmol) and CsBr3 (38 mg, 0.10 mmol) in 5 mL of CH2Cl2 was stirred for 20 min at –78°C and warmed to room temperature. The colorless solution was concentrated to ca. 0.3 mL. Addition of EtO (10 mL) gave an off-white precipitate, which was washed with EtO (2 × 5 mL) and dried under vacuum. Yield: 91 mg (0.94 mmol, 94%). Crystallization by layering a CH2Cl2 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 [Au(Me2CAAC)2]Cl·CH2Cl2 and yellow prisms as [Au(Me2CAAC)2]Cl.

**Synthesis of [AdCAAC-AuCl]2·Cl (23).** A mixture of [Au(Me2CAAC)2]Cl (80 mg, 0.10 mmol) and PhCl (28 mg, 0.10 mmol) in 5 mL of CH2Cl2 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 EtO (10 mL) gave an off-white solid with one solvate molecule of CH2Cl2. Yield: 102.5 mg (0.097 mmol, 96%).

**Synthesis of (AdCAAC)AuBr.** A suspension of (AdCAAC)AuCl (61 mg, 0.11 mmol) and LiBr (88 mg, 1 mmol) in 10 mL of acetone was 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 CH2Cl2 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 [AdCAAC-AuBr]2 ([AuBr2](2)·Cl) (21a) and a small amount of red prisms of [AdCAAC-AuBr]2 ([AuBr2](2)·Cl) (21b). Both give identical 1H and 13C NMR spectra.

**Synthesis of (AdCAAC)AuBr with CsBr.** A suspension of (AdCAAC)Au-Br·CH2Cl2 (74 mg, 0.10 mmol) in 5 mL of CH2Cl2 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 CH2Cl2 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 [AdCAAC-AuBr]2·Cl ([AuBr2](2)·Cl) (21a) and a small amount of red prisms of [AdCAAC-AuBr]2·Cl ([AuBr2](2)·Cl) (21b). Both give identical 1H and 13C NMR spectra.

**Synthesis of [AdCAAC-AuCl]2·Br (24a) and red prisms of [AdCAAC-AuCl]2·AuBr (24b).** Both give identical 1H NMR spectra.

**Synthesis of [AdCAAC-AuCl]2·Br (24c).** A solution of [AdCAAC-AuCl]2·Br (80 mg, 0.10 mmol) and I2 (26 mg, 0.10 mmol) in 3 mL of CH2Cl2 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 oil product, which was concentrated and washed with 5 mL of EtO and dried under vacuum: yield: 102.5 mg (0.097 mmol, 97%).
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82.4 (Cq), 54.6 (Cq), 49.4 (CH2), 28.9 (Cipso), 129.8 (C carbene), 144.9 (Cq), 133.5 (Cq), 130.1 (p-C), 125.1 (m-C), 82.4 (Cipso), 45.6 (Cipso), 49.4 (CH2), 28.9 (CH2), 28.8, 25.7, 22.6 (CH aromatic) ppm. Anal. Calcd for C27H39AuCl3N: C, 45.37; H, 5.83; N, 2.59. Found: C, 45.37; H, 5.83; N, 2.59.

Synthesis of (AdCAAC)AuI (25). All operations have to be carried out with minimum exposure to light. A scintillation vial was charged with (AdCAAC)AuCl (61 mg, 0.10 mmol) and PhICl2 (29 mg, 0.105 mmol) and wrapped in aluminum foil. Chilled CH2Cl2 (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 Et2O (15 mL) gave a pale yellow precipitate which was washed with Et2O (2 × 5 mL) and dried under vacuum. Yield: 64 mg (0.095 mmol, 95%).

1H NMR (300 MHz, CD2Cl2): δ 7.52 (t, J = 7.7 Hz, 2H, CH(aromatic)), 7.38 (d, J = 7.5 Hz, 2H, CH(aromatic)), 7.30 (d, J = 7.7 Hz, 3H, CH(aryl)), 7.09 (t, J = 7.2 Hz, 2H, Cipso), 6.87 (d, J = 7.9 Hz, 2H, Cipso), 6.81 (d, J = 7.5 Hz, 2H, Cipso), 6.71 (d, J = 7.9 Hz, 2H, Cipso), 6.69 (d, J = 7.7 Hz, 2H, Cipso), 6.67 (d, J = 7.7 Hz, 2H, Cipso), 6.60 (d, J = 7.9 Hz, 2H, Cipso), 6.57 (dd, J = 7.9, 7.7 Hz, 1H, CH-aromatic), 3.96 (br d, J = 12.6 Hz, 2H, CH2(Carrier)), 1.36 (s, 6H, 2CH3), 1.30 (d, J = 7.6 Hz, 6H, CH(CH3)2), 1.27 (d, J = 7.6 Hz, 6H, CH(CH3)2), 1.25 (d, J = 6.7 Hz, 6H, CH(CH3)2), 1.21 (s, 6H, 2CH3), 1.02 (br d, J = 6.7 Hz, 6H, CH(CH3)2) ppm.

31P{1H} NMR (121 MHz, CD2Cl2): δ 13.9 (C carrier), 13.7, 13.5, 13.3 (C carrier), 13.2 (C carrier), 13.1 (C carrier), 12.9 (C carrier), 12.8 (C carrier), 12.7 (C carrier), 12.6 (C carrier), 12.5 (C carrier), 12.4 (C carrier), 12.3 (C carrier), 12.2 (C carrier), 12.1 (C carrier), 12.0 (C carrier), 11.9 (C carrier), 11.8 (C carrier), 11.7 (C carrier), 11.6 (C carrier), 11.5 (C carrier), 11.4 (C carrier), 11.3 (C carrier), 11.2 (C carrier), 11.1 (C carrier), 11.0 (C carrier), 10.9 (C carrier), 10.8 (C carrier), 10.7 (C carrier), 10.6 (C carrier), 10.5 (C carrier), 10.4 (C carrier), 10.3 (C carrier), 10.2 (C carrier), 10.1 (C carrier), 10.0 (C carrier), 9.9 (C carrier), 9.8 (C carrier), 9.7 (C carrier), 9.6 (C carrier), 9.5 (C carrier), 9.4 (C carrier), 9.3 (C carrier), 9.2 (C carrier), 9.1 (C carrier), 9.0 (C carrier), 8.9 (C carrier), 8.8 (C carrier), 8.7 (C carrier), 8.6 (C carrier), 8.5 (C carrier), 8.4 (C carrier), 8.3 (C carrier), 8.2 (C carrier), 8.1 (C carrier), 8.0 (C carrier), 7.9 (C carrier), 7.8 (C carrier), 7.7 (C carrier), 7.6 (C carrier), 7.5 (C carrier), 7.4 (C carrier), 7.3 (C carrier), 7.2 (C carrier), 7.1 (C carrier), 7.0 (C carrier), 6.9 (C carrier), 6.8 (C carrier), 6.7 (C carrier), 6.6 (C carrier), 6.5 (C carrier), 6.4 (C carrier), 6.3 (C carrier), 6.2 (C carrier), 6.1 (C carrier), 6.0 (C carrier), 5.9 (C carrier), 5.8 (C carrier), 5.7 (C carrier), 5.6 (C carrier), 5.5 (C carrier), 5.4 (C carrier), 5.3 (C carrier), 5.2 (C carrier), 5.1 (C carrier), 5.0 (C carrier), 4.9 (C carrier), 4.8 (C carrier), 4.7 (C carrier), 4.6 (C carrier), 4.5 (C carrier), 4.4 (C carrier), 4.3 (C carrier), 4.2 (C carrier), 4.1 (C carrier), 4.0 (C carrier), 3.9 (C carrier), 3.8 (C carrier), 3.7 (C carrier), 3.6 (C carrier), 3.5 (C carrier), 3.4 (C carrier), 3.3 (C carrier), 3.2 (C carrier), 3.1 (C carrier), 3.0 (C carrier), 2.9 (C carrier), 2.8 (C carrier), 2.7 (C carrier), 2.6 (C carrier), 2.5 (C carrier), 2.4 (C carrier), 2.3 (C carrier), 2.2 (C carrier), 2.1 (C carrier), 2.0 (C carrier), 1.9 (C carrier), 1.8 (C carrier), 1.7 (C carrier), 1.6 (C carrier), 1.5 (C carrier), 1.4 (C carrier), 1.3 (C carrier), 1.2 (C carrier), 1.1 (C carrier), 1.0 (C carrier), 0.9 (C carrier), 0.8 (C carrier), 0.7 (C carrier), 0.6 (C carrier), 0.5 (C carrier), 0.4 (C carrier), 0.3 (C carrier), 0.2 (C carrier), 0.1 (C carrier), 0.0 (C carrier).
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