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Gold(III) N-Heterocyclic Carbene Complexes Mediated Synthesis of β -Enaminones From 1,3-Dicarbonyl Compounds and Aliphatic Amines

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A series of gold(III) N-heterocyclic carbene complexes [1-(R₁)-3-(R₂)imidazol-2-ylidene]AuBr₃ [R₁ = *i*-Pr, R₂ = CH₂Ph (**1c**); R₁ = mesityl, R₂ = CH₂Ph (**2c**); R₁ = *i*-Pr, R₂ = CH₂CO*t*-Bu (**3c**), and R₁ = *t*-Bu, R₂ = CH₂CO*t*-Bu (**4c**)] act as effective precatalysts in the synthesis of β -enaminones from 1,3-dicarbonyl compounds and primary amines under ambient conditions. Specifically the **1c**-**4c** complexes efficiently catalyzed the condensation of a variety of cyclic as well as acyclic 1,3-dicarbonyl compounds, namely, acetyl acetone, benzoylacetone, 2-acetylcyclopentanone, and ethyl-2-oxocyclopentanecarboxylate with primary aliphatic amines, viz., methylamine, ethylamine, *n*-propylamine, *i*-propylamine, and *n*-butylamine, yielding β -enamines at room temperature. Interestingly enough, the more electrophilic gold(III) **1c**-**4c** complexes exhibited superior activity in comparison to the gold(I) counterparts **1b**-**4b**. A comparison along a representative **4a**-**c** series further underscored the importance of gold in the reaction as both the gold(I) **4b** and gold(III) **4c** complexes were more effective than the silver analogue **4a**. The density functional theory (DFT) study revealed that the strong σ -donating nature of the N-heterocyclic carbene ligand results in a strong C_{carbene}-Au(III) interaction in the **1c**-**4c** complexes.

Introduction

 β -enaminones and β -enamino esters are important class of synthetic intermediates for a variety of biologically active compounds¹ of pharmaceutical interests particularly for their anticonvulsant,² anti-inflammatory,³ and anticancer properties.⁴ As valuable synthons, these β -functionalized enamines display interesting properties that simultaneously combine the nucleophilicity of enamine as well as the electro-

philicity of the enone functionalities. Thus, because of their strategic importance to organic synthesis, the development of convenient high yielding methods remains a key challenge in the area. A commonly used synthetic protocol employs the condensation of 1,3-dicarbonyl compounds with amines that proceeds via an addition—elimination pathway in which the addition of amine to the carbonyl moiety results in a tetra-hedral intermediate that subsequently undergoes elimination of a water molecule to give the desired product.⁵ Not surprisingly so, the azeotropic separation of water from the reaction performed in aromatic solvent has thus been routinely used over the years in the synthesis of these compounds.⁶ The other approaches led to the development of methods that use molecular sieves,⁷ dehydrating solvents,⁸ or the Lewis acids,⁹ which not only remove the water but also facilitate the

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nucleophilic attack of the amine on the 1,3-dicarbonyl substrate. Consequently, many improved catalysis with inorgan-ic salts like $Zn(ClO_4)_2 \cdot 6H_2O$,¹⁰ $CoCl_2 \cdot 6H_2O$,¹¹ $Zn(OAc)_2 \cdot 2H_2O$,¹² $ZrOCl_2 \cdot 8H_2O$,¹³ $Sc(OTf)_3$,¹⁴ etc. have been reported lately. However, despite the advent, the new methods mostly suffer from various limitations like, the need for high reaction temperatures, prolonged reaction time, requirement of special apparatuses and the involvement of tedious product separation procedures, etc. The gold, being a late-transition metal with reduced oxophilicity, provides a single and green alternative to the synthesis of β -enaminones from 1,3-dicarbonyls and amines in terms of eliminating the need for the use of corrosive acid catalysts and also by avoiding the need for cumbersome azeotropic separation procedures.¹⁵

Notably, the catalytic exploits of gold, otherwise known as an inert coinage metal, have aroused intense interest lately,¹⁶ with the simple inorganic salts or the well-defined complexes of the noble metal, in its +I or +III oxidation states, rapidly finding use in numerous catalytic transformations.¹⁷ In particular, the more electrophilic Au(III) precatalysts are increasingly becoming popular in Lewis acid mediated diverse processes like the addition of nucleophiles to alkynes,¹⁸ cycloisomerization reactions,¹⁹ phenol synthesis,²⁰ the 1,3-dipolar cycloaddition to nitrones,²¹ the addition of 2-methylfuran or electron-rich arenes to methyl vinyl ketone,²² etc. With the N-heterocyclic carbenes (NHCs) being phenomenally successful in homogeneous catalysis,²³ the catalytic potentials of

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the gold N-heterocyclic carbene complexes have thus become a topic of current interest.²⁴ However, quite surprisingly so, of the gold(I) and gold(III) N-heterocyclic carbene complexes known until date, the later has been relatively less studied despite many gold(III) compounds exhibiting catalytic properties recently. We are aware of only a handful of examples of the utility of gold(III) N-heterocyclic carbene complexes in catalytic transformations, namely, in the addition of water to alkynes,²⁵ styrene polymerization,²⁶ and in phenol synthesis.²⁷ Given the paucity of the examples of applications of gold(III) N-heterocyclic carbene complexes in catalysis and also partly because of our interest in the utility of the N-heterocyclic carbenes²⁸ in biomedical applications²⁹ and in homogeneous catalysis,³⁰ we became interested in exploring the catalytic potentials of gold(III) N-heterocyclic carbene complexes. In this regard we have recently reported the utility of gold(I) N-heterocyclic carbene complexes for the regioselective intermolecular hydroamination of alkynes³¹ and also in the synthesis of biodegradable polylactide polymer by the ring-opening polymerization (ROP) of L-lactide.³² Continuing further along the line and extending to the higher (III) oxidation state, we chose to employ the strongly Lewis acidic gold(III) N-heterocyclic carbene complexes for a convenient synthesis of β -enaminones from the 1,3-dicarbonyl compounds and the aliphatic amines rationalizing that the electrophilic gold(III) center would facilitate the condensation reaction.

Here in this contribution, we report a series of gold(III) N-heterocyclic carbene complexes, namely, $[1-(R_1)-3-(R_2)$ imidazol-2-ylidene]AuBr₃ [$R_1 = i$ -Pr, $R_2 = CH_2Ph(1c)$; $R_1 =$ mesityl, $R_2 = CH_2Ph(2c)$; $R_1 = i-Pr$, $R_2 = CH_2COt-Bu(3c)$, and $R_1 = t$ -Bu, $R_2 = CH_2COt$ -Bu (4c)] that conveniently carry

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R R

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$$R_1 = i \cdot Pr, R_2 = CH_2Ph (1c)$$

$$R_1 = mesityl, R_2 = CH_2Ph (2c)$$

$$R_1 = i \cdot Pr, R_2 = CH_2CO t \cdot Bu (3c)$$

$$R_1 = t \cdot Bu, R_2 = CH_2CO t \cdot Bu (4c)$$



Scheme 1



out the condensation reaction of 1,3-dicarbonyl compounds with amines giving β -enaminones under ambient conditions (see Figure 1). Quite interestingly, the more electrophilic gold(III) N-heterocyclic carbene complexes, 1c-4c, were found to be more efficient than the gold(I) counterparts, 1b-4b.

Results and Discussion

A series of nonfunctionalized and O-functionalized sterically demanding N-heterocyclic carbene ligands were employed for stabilizing several gold(III) complexes, $[1-(R_1)-$ 3-(R_2)imidazol-2-ylidene]AuBr₃[$R_1 = i$ -Pr, $R_2 = CH_2Ph(1c)$; \mathbf{R}_1 = mesityl, \mathbf{R}_2 = CH₂Ph (**2c**); \mathbf{R}_1 = *i*-Pr, \mathbf{R}_2 = CH₂CO t-Bu (3c) and R₁=t-Bu, R₂ = CH₂CO t-Bu (4c), see Scheme 1] for studying their utility as catalyst in the synthesis of β -enaminones from 1,3-dicarbonyl compounds with aliphatic amines. Specifically, the gold(III) 1c-4c complexes were synthesized by the oxidation of the gold(I) chloro derivatives 1b-4b with molecular bromine at room temperature in 47–72% yield. The gold(I) **1b–4b** complexes were obtained from the silver analogues, 1a-4a, by treatment with Ag₂O in 52-71% yield. The formation of the gold(III) 1c-4c complexes were very much evident by appearance of the relatively upfield shifted Au(III)-Ccarbene resonance at 136.6-140.9 ppm in the ¹³C{¹H} NMR spectrum not only from the Au(I)-Ccarbene resonance in the gold(I) 1b-4b [168.9-172.1 ppm] complexes but also from the $Ag(I)-C_{carbene}$ resonance in the corresponding silver(I) [178.7-181.0] 1a-4a analogues. The Au(III)-C_{carbene} resonances in 1c-4c however appeared in the range observed for other reported



Figure 2. ORTEP of 1c with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): N1-C1 1.33(3), N2-C1 1.345(19), Au1-C1 2.002(15), Au1-Br1 2.4154(19), Au1-Br2 2.4101(18), Au1-Br3 2.366(3), N1-C1-N2 107.5(13), C1-Au1-Br3 178.0(4).

gold(III) bromo N-heterocyclic carbene complexes, namely, [1,3-bis(tert-butyl)imidazol-2-ylidene]AuBr₃ [134.2 ppm], [1,3-bis(adamantyl)imidazol-2-ylidene]AuBr₃ [132.9 ppm],²⁵ and [1,3-bis(cyclohexyl)imidazol-2-ylidene]AuBr₃[136.8 ppm].²⁵ Quite interestingly, the Au(III)–C_{carbene} resonance of a chloro derivative, namely, [4,5-dimethyl-N,N'-bis(2,6-di*i*-propylphenyl)imidazol-2-ylidene]AuCl₃ [145.7 ppm],³³ appeared slightly downfield shifted compared to the 1c-4c bromo derivatives [136.6–140.9 ppm].

The molecular structures of 1c-4c as determined by X-ray diffraction studies revealed these complexes to be discrete monomers displaying square planar geometry at the gold(III) center in agreement with the d⁸ configuration of the central metal atom while that of the corresponding gold(I) 1b, 3b, and silver(I) 2a complexes exhibited two-coordinated linear geometry at metal center in concurrence with the d¹⁰ configuration of the gold(I) and silver(I) centers. The Ccarbene-Au-(III) bond distances in 1c-4c, [2.002(15)-2.047(11) Å] were in good agreement with not only the other reported Au(III) bromo derivatives, namely, [1,3-bis(*tert*-butyl)imidazol-2-ylidene]AuBr₃ [2.015(5) Å],²⁵ [1,3-bis(adamantyl)imidazol-2-ylidene]AuBr₃ [2.052(6) Å],²⁵ and [1,3-bis(cyclohexyl)-imidazol-2-ylidene]AuBr₃ [2.04(2) Å]²⁵ but also with the gold(III) chloro derivatives, namely, [4,5-dimethyl-N,N'-bis-(2,6-di-*i*-propylphenyl)imidazol-2-ylidene]AuCl₃ [2.018 Å]³³ and [4-methyl-5-chloromethyl-*N*,*N*'-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene]AuCl₃ [2.018 Å].³³ Lastly, consistent with a shorter covalent radii of Au(I) [1.37 Å] than Ag(I) $[1.46 \text{ Å}]^{34}_{\circ}$ both the C_{carbene}-Au(I) distances [1.974(4)-1.975(4) Å] in **1b** and **3b** as well as the C_{carbene}-Au(III) bond distances [2.002(15)-2.047(11) Å] in 1c-4c, were found to be shorter than the Ccarbene-Ag(I) bond distances [2.077(2)-2.087(3) A] in **1a–3a** (see Figure 2).

Of particular interest is the nature of the $C_{carbene}$ -Au(III) interaction in the gold(III) 1c-4c complexes particularly for drawing a parallel with the more studied Ccarbene-Au(I) interaction in the gold(I) N-heterocyclic carbene complexes^{28c,d}

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Figure 3. Simplified orbital interaction diagram showing the major contributions of the NHC-gold bond in 1c.

as well as in other related Au(I)/(III) complexes.³⁵ In this regard, the detailed density functional theory (DFT) study was performed at the B3LYP/SDD, 6-31G(d) level of theory using atomic coordinates obtained from their respective X-ray diffraction data. Specifically, the geometry optimization followed by single point calculations were performed on the gold(I) 1b, 3b and gold(III) 1c-4c complexes (Supporting Information, Tables S2–S7). The natural bond orbital (NBO) calculations were then performed at the same level of theory for obtaining additional insights about the electronic structure of these complexes. The strong σ -donating ability of the imidazole based N-heterocyclic carbene ligand to the metal center was very much evident in the Mulliken and the natural charge analyses that showed, concomitant to the ligand binding, loss of the electron density at the carbene center of the NHC ligand fragment in gold(I) 1b and **3b** complexes as well as in the gold(III) 1c-4c complexes as opposed to the free NHC ligand (Supporting Information, Tables S8–S13). Also guite expectedly, both natural and Mulliken charge analysis showed that the metal center is more electron deficient in gold(III) 1c-4c complexes as compared to the gold(I) 1b and 3b complexes. The natural bond orbital (NBO) analysis also showed that the electron donation from the NHC ligand fragment occurred on to the 6s orbital of the metal center in the gold(I) 1b, 3b, and

gold(III) **1c–4c** complexes (Supporting Information, Tables S14 and S15).

Additional insights on the NHC-Au interaction were obtained from the charge decomposition analysis (CDA) studies that examined the extent of σ -donation from the NHC ligand to the metal center (NHC $\xrightarrow{\sigma}$ AuCl) or (NHC $\xrightarrow{\sigma}$ AuBr₃), as designated by *d*, compared to the back-donation of electrons from the metal to NHC fragment (NHC $\stackrel{\pi}{\longleftarrow}$ AuCl) or (NHC $\stackrel{\pi}{\longleftarrow}$ AuBr₃), represented by b, in the gold(I) **1b**, **3b** and gold(III) 1c-4c complexes. A high d/b ratio of 3.97-25.7in gold(III) 1c-4c complexes and of 4.72-4.78 in gold(I) 1b and **3b** complexes indicate strong σ -donating nature of the imidazole based N-heterocyclic carbene ligands (Supporting Information, Table S16). A further glimpse of the NHC-Au σ interaction could be obtained from the molecular orbital (MO) correlation diagram constructed from the contribution of the individual fragment molecular orbital (FMO) of the NHC ligand and the AuX_n (X = Cl, Br; n = 1, 3) fragments in the gold(III) 1c-4c complexes and the gold(I) 1b and 3b complexes. Quite interestingly, the molecular orbital (MO) depicting the σ interaction in the gold(III) 1c [HOMO-29], 2c [HOMO-37], 3c [HOMO-32], and 4c [HOMO-34] complexes and in the gold(I) 1b [HOMO-21] and 3b [HOMO-23] complexes were found to be deeply buried thereby indicating a stable nature of the NHC-Au interaction (Figure 3 and Supporting Information, Figures S7– S17). Indeed, the NHC-Au bond dissociation energy values as computed using the B3LYP/SDD, 6-31G(d) level of

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entry	reagent	reagent	product	Au(I)				Au(III)			
								yield ^b			
				1b	2b	3b	4b	1c	2c	3c	4c ^c
1		H ₂ N	O HN	33	32	34	31	42	40	53	56 (48)
2	<u> </u>	H ₂ N	O HN	33	23	20	27	70	64	69	51 (50)
3		H ₂ N	O HN	49	35	26	26	99	66	99	69 (68)
4	<u> </u>	H ₂ N		4	1	4	1	40	51	49	50 (37)
5	0 0	I									
5		H ₂ N		45	38	21	22	>99	>99	>99	>99 (72)
6		H ₂ N	O HN	7	1	5	4	60	49	29	37
7		HaN		15	12	16	19	20	25	22	20
	Pn ~ `		Ph	15	12	10	10	39	35	32	39
8	<u> </u>	H ₂ N	NH O	20	10	19	11	32	31	25	29
9^d	Î Î	H ₂ N		28	24	24	28	44	41	46	50
	$\langle \mathcal{Y} \rangle$										
10^{a}	<u> </u>	H ₂ N		43	32	35	40	60	54	51	50
11	0 0										
11	OEt	H ₂ N 5	OEt	14	6	9	16	36	28	28	34
12	Î Î.	H ₂ N	NH O	11	o	11	o	24	24	42	26
	() OEt		OEt	11	8	11	0	24	24	43	50
13		H ₂ N		13	13	20	20	52	49	44	37 (31)
	\Box		OEt								

^{*a*} Reaction conditions: 1.00 mmol of amine, 0.25 mmol of ketone, 5 mol % of catalyst, 15 mol % of AgBF₄, 5 mL of CH₃CN at room temperature for 6 h. ^{*b*} The yields (%) were determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard. ^{*c*} The isolated yields for a representative precatalyst **4c** are given in parentheses. ^{*d*} Only the major product is shown.

theory for the gold(III) **1c** [82.9 kcal/mol], **2c** [82.8 kcal/mol], **3c** [83.0 kcal/mol], and **4c** [81.3 kcal/mol] and the gold(I) **1b** [82.5 kcal/mol] and **3b** [83.7 kcal/mol] complexes are comparable to each other as well as to the other reported gold(I) N-heterocyclic carbene complexes, namely, [1-(benzyl)-3-(*N*-tert-butylacetamido)imidazol-2-ylidene]AuCl [82.7 kcal/mol], ^{28d} [1-(*i*-propyl)-3-{*N*-(2,6-di-*i*-propylphenylacetamido)-imidazol-2-ylidene}]_2Au_2 [81.0 kcal/mol], ^{28c} and [1-(tert-butyl)-3-{*N*-(2,6-di-*i*-propylphenylacetamido)imidazol-2-ylidene}]_2Au_2 [79.0 kcal/mol]^{28c} (Supporting Information, Table S17).

Significantly all of the gold(III) 1c-4c complexes carried out efficient synthesis of β -enaminones from the reaction of 1, 3-dicarbonyl compounds with primary aliphatic amines in good to excellent yields (24 to >99%) (eq 1; Table 1). Specifically, when the 1,3-dicarbonyls, namely, acetyl acetone, benzoylacetone, 2-acetylcyclopentanone, and ethyl-2-oxocyclopentanecarboxylate, were treated with a variety of primary aliphatic amines, namely, methylamine, ethylamine, *n*-propylamine, *i*-propylamine, and *n*-butylamine, at 5 mol % of the 1c-4c precatalyst loading in the presence of 3 equiv of AgBF₄, the formation of the corresponding β -enaminones were observed at room temperature after 6 h. Quite interestingly, the gold(III) 1c-4c complexes were found to be more active (24 to >99%) than the corresponding Au(I) 1b-4b counterparts that displayed subdued conversions (1-49%)under analogous conditions (Table 1), thereby underscoring the importance of the electrophilicity of a gold(III) center in the catalysis. Further support in favor of the greater electrophilicity of the metal center in gold(III) 1c-4c complexes than the gold(I) 1b and 3b complexes also came from the density functional theory (DFT) studies based on the natural and Mulliken charge analysis (Supporting Information, Tables S8-S13). More interestingly so, the importance of gold as a metal in the catalysis is conspicuous in the fact that for a representative 4a-c series, both the gold(III) 4c (29 to >99%) and the gold(I) **4b** (1-40\%) precatalysts showed higher conversions that its silver(I) analogue 4a (3-26%)(Table 1 and Supporting Information, Table S18). The presence of considerable ligand influence in the catalysis runs of 1c-4c become very much evident when compared to the blank runs, performed in the absence of both AgBF₄ and the gold catalyst that showed a significantly subdued conversion 1-22%, thus highlighting the important difference made by the N-heterocyclic carbene ligands in the catalysis (Table 1 and Supporting Information, Table S18). Similarly, a comparison with the control runs performed with only AgBF₄ (1-39%) showed significant amplification in the case of the gold(III) 1c-4c precatalysts (24 to >99%) (Table 1 and Supporting Information, Table S18). Lastly, with the intent of checking the possibility of free N-heterocyclic carbene ligand, obtained from the decomposition of 1c-4cprecatalysts, being responsible for the observed catalysis, experiments were performed with the in situ generated carbene, prepared from the treatment of a representative imidazolium chloride salt (4) with KO^tBu, which showed subdued conversion (13-36%) for three substrates as compared to 4c (37 to >99%) under identical reaction conditions (Table 1 and Supporting Information, Table S19). The homogeneous nature of the catalysis reaction was tested by performing the classical mercury drop experiments that showed no reduction in gold(III) 1c-4c activities in the presence (22 to >99%) and absence of mercury (24 to >99%).



 $R_1 = Me, Et, n-Pr, i-Pr, n-Bu$ $R_2 = Me, Ph$ $R_3 = Me, OEt$

In order to study the chemoselectivity of amination reaction for the unsymmetrical 1,3-dicarbonyl compounds, namely, benzoylacetone, 2-acetylcyclopentanone, and ethyl-2-oxocyclopentanecarboxylate, subsequent characterization employing ¹H NMR, ¹³C $\{^{1}H\}$ NMR, and IR studies of the product, formed for a representative precatalyst 4c, for these unsymmetrical substrates were undertaken. In the case of the benzoylacetone substrate (Table 1, entries 6 and 7), only one product was observed consistent with the imination occurring at the acetyl position.³⁶ For the cyclic substrate, 2-acetylcyclopentanone (Table 1, entry 8), the imination occurred exclusively at the ring carbonyl moiety for the reaction with ethyl amine³⁷ whereas a mixture of isomers, consisting of the ring carbonyl imination being the major product (41-60%) for the 1c-4c precatalysts along with the presence of a minor product arising from the imination of the acetyl moiety (11-17%) were observed for the reactions with the *n*-propyl and *n*-butyl amines (Table 1, entries 9 and 10). Lastly, for a representative cyclic β -ketoester substrate, namely, ethyl-2-oxocyclopentanecarboxvlate (Table 1, entries 11-13), the imination occurred solely on the ketone carbonyl moiety yielding cyclic β -aminoester.^{10,38}

Important is the comparison of the performances of gold-(III) **1c**–**4c** precatalysts with other reported initiators for the synthesis of β -enaminones from 1,3-dicarbonyl compounds and primary aliphatic amines. Though several d-^{10,11,14} and f-block^{9b,39} metals have been reported, we are aware of only one prior report of the use of a gold(III) initiator, namely, NaAuCl₄,¹⁵ for the reaction of 1,3-dicarbonyl compounds with primary and secondary amine substrates yielding β -enaminones in good to excellent yields at a relatively low catalyst loading of 2.5 mol % at room temperature in 7 h. Hence against this backdrop, the well-defined **1c**–**4c** precatalysts for the condensation of 1,3-dicarbonyls with amines under ambient conditions is relevant as it represent yet another new application of N-heterocyclic carbenes in gold catalysis.

Conclusions

In summary, the gold(III) **1c**–**4c** complexes carry out the condensation of 1,3-dicarbonyl compounds with primary amines under ambient conditions. The gold(III) **1c**–**4c** complexes were found to be more superior to the gold(I) **1b**–**4b** complexes, thereby highlighting the greater electrophilicity of the gold(III) center is better for catalysis. More significantly,

the 1c-4c complexes represent another new application of N-heterocyclic carbene based gold(III) precatalysts for the synthesis of β -enaminones from the reaction of 1,3-dicarbonyls and primary aliphatic amines.

Experimental Section

General Procedures. All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Ag₂O was purchased from S. D. Fine Chemicals (India) and used without any further purification. 1-tert-Butylimidazole,40 [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl (1a),^{32a} 1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazolium chloride (2).⁴¹ [1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]AgCl (2a),⁴² and [1-(*i*-propyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2ylidene]AgCl $(3a)^{28e}$ were synthesized according to modified literature procedures. ¹H and ¹³C {¹H} MMR spectra were recorded on a Varian and Bruker 400 MHz NMR spectrometer. ¹H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-TOF spectrometer. Elemental analysis was carried out on Thermo Quest FLASH 1112 series (CHNS) elemental analyzer. GC spectra were obtained on a PerkinElmer Clarus 600 equipped with a flame ionization detector (FID). Gas chromatography-mass spectrometry (GC-MS) spectra were obtained on a PerkinElmer Clarus 600 T equipped with an electron impact (EI) source. X-ray diffraction data for compounds 1b, 2a, 3b, 1c-2c, and 4c were collected on an Oxford Diffraction XCALI-BUR-S diffractometer, and the data for compound 3c were collected with a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data collection and refinement parameters are summarized in Table S1 in the Supporting Information. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 6.10).⁴³

Synthesis of [1-(*i***-Propyl)-3-(benzyl)imidazol-2-ylidene]AuCl (1b).** A mixture of [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]-AgCl (1a) (0.556 g, 1.62 mmol) and (SMe₂)AuCl (0.476 g, 1.62 mmol) in dichloromethane (~50 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered, and the solvent was dried under vacuum to give the product 1b as a white solid (0.497 g, 71%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.33 (br, 5H, C₆H₅), 7.09 (s, 1H, NCHCHN), 7.00 (s, 1H, NCHCHN), 5.33 (s, 2H, CH₂), 4.99 (sept, 1H, ³J_{HH} = 6 Hz, CH(CH₃)₂), 1.46 (d, 6H, ³J_{HH} = 6 Hz, CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 168.9 (Au–NCN), 135.1 (*ipso*-C₆H₅), 128.8 (*m*-C₆H₅), 128.4 (*p*-C₆H₅), 128.0 (*o*-C₆H₅), 120.8 (NCHCHN), 117.4 (NCHCHN), 54.9 (CH₂), 53.5 (CH(CH₃)₂), 23.2 (CH(CH₃)₂). IR data (KBr pellet) cm⁻¹: 3145 (m), 3109 (s), 2971 (s), 1588 (m), 1449 (s), 1427 (s), 1233 (s), 1189 (m), 747 (s), 719 (s), 461 (w). Anal. Calcd for C₁₃H₁₆AuClN₂: C, 36.08; H, 3.73; N, 6.47. Found: C, 36.21; H, 3.59; N, 6.34.

Synthesis of [1-(*i*-Propyl)-3-(benzyl)imidazol-2-ylidene]AuBr₃ (1c). A mixture of [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]-AuCl (1b) (0.386 g, 0.891 mmol) and liquid Br₂ (0.427 g, 2.67 mmol) in dichloromethane (~10 mL) was stirred for 1 h at room temperature. The reaction mixture was dried under vacuum to give the product 1c as a brown solid (0.409 g, 72%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.42 (br, 5H, C₆H₅), 7.21 (s, 1H,

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NCHCHN), 7.00 (s, 1H, NCHCHN), 5.35 (s, 2H, CH₂), 5.03 (sept, 1H, ${}^{3}J_{HH} = 6$ Hz, CH(CH₃)₂), 1.57 (d, 6H, ${}^{3}J_{HH} = 6$ Hz, CH(CH₃)₂), 1.³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 139.0 (Au-NCN), 132.7 (*ipso*-C₆H₅), 129.7 (*m*-C₆H₅), 129.6 (*p*-C₆H₅), 129.5 (*o*-C₆H₅), 123.7 (NCHCHN), 119.5 (NCHCHN), 55.0 (CH₂), 54.2 (CH(CH₃)₂), 22.9 (CH(CH₃)₂). IR data (KBr pellet) cm⁻¹: 3130 (m), 2979 (s), 1468 (s), 1440 (s), 1427 (s), 1233 (s), 1188 (s), 1073 (w), 1028 (w), 726 (s). Anal. Calcd for C₁₃H₁₆AuBr₃N₂: C, 24.51; H, 2.53; N, 4.40. Found: C, 24.84; H, 3.12; N, 4.54.

Synthesis of 1-(Benzyl)-3-(2,4,6-trimethylphenyl)imidazolium Chloride (2). 2,4,6-Trimethylphenylimidazole (0.436 g, 2.34 mmol) and benzyl chloride (0.296 g, 2.34 mmol) were taken in toluene (~10 mL) and heated at 120 °C for 12 h during which a white precipitate was formed. The precipitate was collected by filtration and was washed with hot hexane ($\sim 15 \text{ mL}$) and dried under vacuum to give the product 2 as white crystalline solid (0.517 g, 71%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 10.84 (s, 1H, NCHN), 8.13 (s, 1H, NCHCHN), 7.73 (br, 2H, C₆H₅), 7.31 (br, 3H, C₆H₅), 7.07 (s, 1H, NCHCHN), 6.92 (s, 2H, m-C₆H₂-{2,4,6-Me₃}), 5.98 (s, 2H, CH₂), 2.31 (s, 3H, *p*-C₆H₂{2,4,6-Me₃}), 2.02 (s, 6H, $o-C_6H_2\{2,4,6-Me_3\}$). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C), δ 140.7 (ipso-C₆H₅), 138.1 (NCHN), 134.0 (ipso- $\underline{C}_{6}H_{2}$ {2,4,6-Me₃}), 133.9 (*o*- $\underline{C}_{6}H_{2}$ {2,4,6-Me₃}), 130.7 (*p*- $\underline{C}_{6}H_{2}$ - $\{2,4,6-Me_3\}$, 129.5 (*m*-C₆H₂ $\{2,4,6-Me_3\}$), 128.9 (*o*-C₆H₅), 128.8 (p-C₆H₅), 128.7 (m-C₆H₅), 127.9 (NCHCHN), 123.3 (NCH-CHN), 52.9 (CH₂), $\overline{20.6}$ (*p*-C₆H₂{2, $\overline{4}$,6-*Me*₃}), 17.1 (*o*-C₆H₂- $\{2,4,6-\underline{Me}_3\}$). IR data (KBr pellet) cm⁻¹: 3155 (m), 3065 (m), 2975 (s), 1542 (m), 1457 (m), 1376 (w), 1197 (m), 1161 (m), 877 (w), 767 (m), 719 (s). HRMS (ES): m/z 277.1704 [NHC + H]⁺, calcd 277.1705. Anal. Calcd for C₁₉H₂₁N₂Cl: C, 72.95; H, 6.77; N, 8.95. Found: C, 72.57; H, 7.22; N, 8.26.

Synthesis of [1-(Benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2ylidene]AgCl (2a). A mixture of 1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazolium chloride (2) (0.569 g, 1.82 mmol) and Ag₂O (0.211 g, 0.911 mmol) in dichloromethane (~40 mL) were stirred at room temperature for 4 h. The reaction mixture was filtered and the solvent was removed under vacuum to give the product 2a as a dark brown solid (0.317 g, 41%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.32 (br, 5H, C₆H₅), 7.00 (s, 1H, NCHCHN), 6.89 (s, 2H, *m*-C₆H₂{2,4,6-Me₃}), 6.78 (s, 1H, NCHCHN), 5.44 (s, 2H, C<u>H</u>₂), 2.28 (s, 3H, p-C₆H₂{2,4,6-<u>Me</u>₃}), 1.98 (s, 6H, o-C₆H₂{2,4,6-<u>Me</u>₃}). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 181.0 (Ag-NCN), 139.4 (ipso-C₆H₅), 135.7 (ipso-C₆H₂{2,4,6-Me₃}), 135.3 ($\overline{o-C_6H_2}$ {2,4,6-Me₃}), 134.6 ($\overline{p-C_6H_2}$ {2,4,6-Me₃}), 129.3 $(m-C_6H_2\{\overline{2},4,6-Me_3\})$, 129.1 $(o-C_6H_5)$, 128.6 $(p-C_6H_5)$, 127.5 ($m-\overline{C}_6H_5$), 123.2 (NCHCHN), 121.4 (NCHCHN), 55.4 (\underline{CH}_2) , $20.\overline{8}$ (p-C₆H₂{2,4,6- $\overline{M}e_3$ }), 17.4 (o-C₆H₂{2,4, $\overline{6}$ - Me_3 }). IR data (KBr pellet) cm⁻¹: 3166 (m), 3130 (m), 3030 (w), $\overline{2917}$ (m), 1496 (s), 1445 (m), 1445 (s), 1411 (m), 1031 (m), 857 (s), 586 (w). Anal. Calcd for C19H20AgClN2: C, 54.37; H, 4.80; N, 6.67. Found: C, 55.23; H, 4.57; N, 6.62.

Synthesis of [1-(Benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2ylidene]AuCl (2b). A mixture of [1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]AgCl (2a) (0.218 g, 0.519 mmol) and (SMe₂)AuCl (0.153 g, 0.519 mmol) in dichloromethane (~50 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered, and the solvent was dried under vacuum to give the product **2b** as a white solid (0.159 g, 60%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.37 (br, 5H, C₆<u>H</u>₅), 7.06 (s, 1H, NCHCHN), 6.94 (s, 2H, m-C₆ H_2 {2,4,6-Me₃}), 6.83 (s, 1H, NCHC*H*N), 5.50 (s, 2H, C*H*₂), 2.34 (s, 3H, *p*-C₆H₂{2,4,6-*Me*₃}), 2.04 (s, 6H, *o*-C₆H₂{2,4,6-*Me*₃}). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 172.1 (Au-NCN), 139.6 (ipso-C₆H₅), 135.3 $(ipso-C_6H_1\{2,4,6-Me_3\}), 134.7 (o-C_6H_2\{2,4,6-Me_3\}), 129.4 (p-1)$ $C_{6}H_{2}\{2,4,6-Me_{3}\}), 129.1 (m-C_{6}H_{2}\{2,4,6-Me_{3}\}), 129.0 (o-C_{6}H_{5}),$ 128.7 (p-C₆H₅), 127.8 (m-C₆H₅), 122.8 (NCHCHN), 120.7 (NCHCHN), 55.0 (CH₂), $\overline{21.1}$ (*p*-C₆H₂{2,4, $\overline{6}$ -Me₃}), 17.8 (*o*- $C_6H_2{\overline{2},4,6-\underline{Me_3}}$). IR data (KBr pellet) cm⁻¹: 3126 (m), 2919 (m), 1487 (s), 1449 (s), 1418 (m), 1242 (s), 1031 (m), 855 (m), 725

(s). Anal. Calcd for C₁₉H₂₀AuClN₂: C, 44.85; H, 3.96; N, 5.51. Found: C, 45.21; H, 3.81; N, 5.06.

Synthesis of [1-(Benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2ylidene]AuBr₃ (2c). A mixture of [1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]AuCl (2b) (0.206 g, 0.404 mmol) and liquid Br₂ (0.194 g, 1.21 mmol) in dichloromethane (\sim 5 mL) was stirred for 1 h at room temperature. The reaction mixture was dried under vacuum to give the product 2c as a brown solid (0.198 g, 69%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.47 (br, 5H, C₆H₅), 7.11 (s, 1H, NCHCHN), 7.06 (s, 1H, NCHCHN), 6.98 (s, 2H, m-C₆ H_2 {2,4,6-Me₃}), 5.56 (s, 2H, C H_2), 2.35 (s, 3H, $p-C_6H_2\{2,4,6-\underline{Me_3}\}), 2.22 (s, 6H, o-C_6H_2\{2,4,6-\overline{Me_3}\}).$ ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 140.9 (Au-NCN), 135.2 (ipso- $C_{6}H_{5}$), 132.9 (*ipso-C*₆H₂{2,4,6-Me₃}), 130.1 (*o-C*₆H₂{2,4,6-Me₃}), 129.8 $(p-C_6H_2\{2,4,6-Me_3\})$, 129.7 $(m-C_6H_2\{2,4,6-Me_3\})$, 129.4 $(o-C_6H_2\{2,4,6-Me_3\})$ C_6H_5), 126.3 (*p*- C_6H_5), 126.0 (*m*- C_6H_5), 123.2 (NCHCHN), 123.0 (NCHCHN), 55.6 (CH₂), 21.3 (p-C₆H₂{2,4,6-<u>Me₃</u>}), 19.6 (o- $C_6H_2\{\overline{2},4,6-\underline{Me}_3\}$). IR data (KBr pellet) cm⁻¹: 3159 (m), 2920 (m), 1482 (s), 1456 (s), 1432 (s), 1229 (s), 1032 (m), 720 (s), 683 (m). Anal. Calcd for C₁₉H₂₀AuBr₃N₂: C, 32.00; H, 2.83; N, 3.93. Found: C, 32.47; H, 2.91; N, 4.18.

Synthesis of [1-(*i*-Propyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AuCl (3b). A mixture of [1-(*i*-propyl)-3-(3,3-dimethyl-2oxobutyl)imidazol-2-ylidene]AgCl (3a) (0.517 g, 1.47 mmol) and (SMe₂)AuCl (0.433 g, 1.47 mmol) in dichloromethane (~40 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered, and the solvent was dried under vacuum to give the product 3b as a white solid (0.339 g, 52%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.02 (s, 1H, NCHCHN), 6.97 (s, 1H, NCHC-HN), 5.20 (s, 2H, CH₂), 5.05 (sept, 1H, ³J_{HH} = 7 Hz, CH(CH₃)₂), 1.51 (d, ³J_{HH} = 7 Hz, CH(CH₃)₂), 1.30 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 207.5 (CO), 170.8 (Au–NCN), 122.7 (NCHCHN), 116.7 (NCHCHN), 55.2 (CH₂), 53.7 (CH-(CH₃)₂), 43.7 (C(CH₃)₃), 26.3 (C(CH₃)₃), 23.4 (CH(CH₃)₂). IR data (KBr pellet) cm⁻¹: 1721 (s) ($\nu_{C=0}$). Anal. Calcd for C₁₂-H₂₀AuClN₂O: C, 32.70; H, 4.57; N, 6.36. Found: C, 33.60; H, 4.69; N, 5.83.

Synthesis of [1-(*i*-Propyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AuBr₃ (3c). A mixture of [1-(*i*-propyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AuCl (3b) (0.102 g, 0.232 mmol) and liquid Br₂ (0.111 g, 0.696 mmol) in dichloromethane (~10 mL) was stirred for 1 h at room temperature. The reaction mixture was dried under vacuum to give the product **3c** as a brown solid (0.071 g, 47%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.33 (s, 1H, NCHCHN), 7.29 (s, 1H, NCHCHN), 5.24 (s, 2H, CH₂), 5.03 (sept, 1H, ³J_{HH} = 6 Hz, CH(CH₃)₂), 1.57 (d, ³J_{HH} = 6 Hz, CH-(CH₃)₂), 1.32 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 205.3 (CO), 136.6 (Au–NCN), 126.3 (NCHCHN), 119.1 (NCHCHN), 54.2 (CH₂), 54.1 (CH(CH₃)₂), 44.0 (C(CH₃)₃), 26.5 (C(CH₃)₃), 22.9 (CH(CH₃)₂). IR data (KBr pellet) cm⁻¹: 1724 (s) ($\nu_{C=O}$). Anal. Calcd for C₁₂H₂₀AuBr₃N₂O: C, 22.35; H, 3.13; N, 4.34. Found: C, 22.01; H, 2.94; N, 4.57%.

Synthesis of 1-(*tert*-Butyl)-3-(3,3-dimethyl-2-oxobutyl) Imidazolium Chloride (4). A mixture of 1-*tert*-butylimidazole (1.88 g, 15.2 mmol) and chloropinacolone (2.05 g, 15.2 mmol) was put in toluene (~15 mL) and refluxed for 24 h during which a white solid precipitated was formed. The precipitate was collected by decanting off the toluene and was washed with hot hexane (~15 mL) and dried under vacuum to give the product **4** as a white solid (2.24 g, 57%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 10.67 (s, 1H, NC*H*N), 7.32 (s, 2H, NCH*CH*N), 5.97 (s, 2H, *CH*₂), 1.72 (s, 9H, C(*CH*₃)₃), 1.32 (s, 9H, C(*CH*₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 207.0 (*C*O), 136.0 (*NC*HN), 124.2 (*NC*HCHN), 118.6 (*NC*H*C*HN), 59.7 (*C*H₂), 54.0 (*C*(*C*H₃)₃), 43.0 (*C*(*C*H₃)₃), 29.5 (*C*(*C*H₃)₃), 25.9 (*C*(*C*H₃)₃). IR data (KBr pellet) cm⁻¹: 1716 (s) ($\nu_{C=0}$). HRMS (ES): *m*/*z* 223.1813 [NHC + H]⁺, calcd 223.1810.

Synthesis of [1-(*tert*-Butyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AgCl (4a). A mixture of 1-(*tert*-butyl)-3-(3,3-dimethyl-2oxobutyl) imidazolium chloride (4) (2.18 g, 8.41 mmol) and Ag₂O

(0.977 g, 4.21 mmol) in dichloromethane (~50 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered, and the solvent was dried under vacuum to give the product 4a as a dark brown solid (1.39 g, 45%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.21 (s, 1H, NCHCHN), 6.92 (s, 1H, NCHCHN), 5.21 (s, 2H, $C\underline{H}_2$), 1.74 (s, 9 \overline{H} , $C(C\underline{H}_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$). ¹³ $C\{^1H\}$ NMR (CDCl₃, 100 MHz, 25 °C): δ 208.0 (CO), 178.7 (Ag–NCN), 121.3 (NCHCHN), 118.7 (NCHCHN), 57.6 (CH2), 56.7 $(\underline{C}(CH_3)_3)$, 43.2 ($\underline{C}(CH_3)_3$), 31.6 ($C(\overline{C}H_3)_3$), 26.1 ($C(\overline{C}H_3)_3$). IR data (KBr pellet) cm⁻¹: 1718 (s) ($\nu_{C=O}$). Anal. Calcd for C₁₃H₂₂AgClN₂O: C, 42.70; H, 6.06; N, 7.66. Found: C, 42.73; H, 6.00; N, 7.98.

Synthesis of [1-(tert-Butyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AuCl(4b). A mixture of [1-(tert-butyl)-3-(3,3-dimethyl-2oxobutyl)imidazol-2-ylidene]AgCl (4a) (0.509 g, 1.39 mmol) and (SMe₂)AuCl (0.411 g, 1.39 mmol) in dichloromethane (~40 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered, and the solvent was dried under vacuum to give the product 4b as a white solid (0.383 g, 61%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.13 (s, 1H, NCHCHN), 6.92 (s, 1H, NCHCHN), 5.32 (s, 2H, CH2), 1.86 (s, 9H, C(CH3)3), 1.31 (s, 9H, C(*CH*₃)₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 25 °C): δ 207.6 (CO), 170.9 (Au-NCN), 120.6 (NCHCHN), 118.5 (NCHCHN), 59.2 (CH₂), 56.5 (C(CH₃)₃), 43.7 (C(CH₃)₃), 31.8 (C(CH₃)₃), 26.4 $(C(CH_3)_3)$. IR data (KBr pellet) cm⁻¹: 1720 (s) ($\nu_{C=0}$). Anal. Calcd for C13H22AuClN2O: C, 34.34; H, 4.88; N, 6.16. Found: C, 35.17; H, 5.10; N, 6.12.

Synthesis of [1-(tert-Butyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AuBr₃ (4c). A mixture of [1-(*tert*-butyl)-3-(3,3-dimethyl-2-oxobutyl)imidazol-2-ylidene]AuCl (4b) (0.215 g, 0.472 mmol) and liquid Br₂ (0.227 g, 1.42 mmol) in dichloromethane (\sim 10 mL) was stirred for 1 h at room temperature. The reaction mixture was dried under vacuum to give the product 4c as a brown solid (0.197 g, 63%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 7.40 (s, 1H, NC*H*CHN), 7.23 (s, 1H, NCHC*H*N), 5.34 (s, 2H, C*H*₂), 1.89 (s, 9H, $\overline{C(CH_3)_3}$), 1.32 (s, 9H, $C(CH_{\overline{3}})_3$). ¹³C{¹H} NMR ($\overline{CDCl_3}$, 100 MHz, 25 °C): δ 205.2 (CO), 138.3 (Au-NCN), 125.6 (NC-HCHN), 122.2 (NCHCHN), 61.9 (CH₂), 55.1 (C(CH₃)₃), 40.4 $(\underline{C}(CH_3)_3)$, 31.7 $(C(\underline{CH_3})_3)$, 26.6 $(C(\overline{CH_3})_3)$. IR data (KBr pellet) cm⁻¹: 1724 (s) ($\nu_{C=0}$). Anal. Calcd for C₁₃H₂₂AuBr₃N₂O: C, 23.69; H, 3.36; N, 4.25. Found: C, 23.27; H, 3.39; N, 4.46.

Computational Methods. The density functional theory calculations were performed on the following gold(I) (NHC)AuCl type species, **1b** and **3b**, and gold(III) (NHC)AuBr₃ type species, **1c**-4c using the Gaussian 03^{44} suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with the Lee-Yang-Parr correlation functional (B3LYP) has been employed in this study.^{45,46} The Stuttgart-Dresden effective core potential (ECP) along with the valence basis set SDD is used for gold,⁴⁷ and all other atoms are treated with the 6-31G(d) basis set.⁴⁸ All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. Tight SCF convergence (10^{-8} au) was used for all calculations. Natural bond orbital (NBO) analysis⁴⁹ was performed using the NBO 3.1 program implemented in the Gaussian 03 package.

Inspection of the metal-ligand donor-acceptor interactions was carried out using charge decomposition analysis (CDA).³

CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.⁵¹ The orbital contributions in the geometry optimized gold(I) (NHC)AuCl type species, 1b and 3b, and gold(III) (NHC)AuBr₃ type species, 1c-4c, can be divided into three parts: (i) σ -donation from the [NHC \rightarrow AuCl] in gold(I) and $[NHC \rightarrow AuBr_3]$ in the gold(III) fragment; (ii) π -back-donation from the [NHC \leftarrow AuCl] in gold(I) and [NHC ← AuBr₃] in the gold(III) fragment; (iii) repulsive polarization (r).

The CDA calculations are performed using the program AOMix,⁵² using the B3LYP/SDD, 6-31G(d) wave function for 1b, 3b, and 1c-4c. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix program. The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, and the charge decomposition analysis were performed using the AOMix-CDA.53

General Procedure for the Synthesis of β -Enaminones. In a typical run, a 25 mL vial was charged with a mixture of complexes 1b or 2b or 3b or 4b or 1c or 2c or 3c or 4c (5 mol %, 0.013 mmol), AgBF₄ (15 mol %, 0.039 mmol), and acetonitrile (~ 5 mL), and to this was added the mixture of 1,3dicarbonyl compounds, primary aliphatic amines, and diethyleneglycol-di-n-butyl ether (internal standard) in a molar ratio of 1:4:1 (Table 1). The reaction mixture was stirred at room temperature for 6 h, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di*n*-butyl ether as an internal standard

General Procedure of Control Experiments for the Synthesis of β -Enaminones. In a typical run, a 25 mL vial was charged with a mixture of AgBF₄ (15 mol %, 0.039 mmol) and acetonitrile (~5 mL) and to this was added the mixture of 1,3-dicarbonyl compounds, primary aliphatic amines, and diethyleneglycoldi-n-butyl ether (internal standard) in a molar ratio of 1:4:1 (see Supporting Information, Table S18). The reaction mixture was stirred at room temperature for 6 h, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-*n*-butyl ether as an internal standard.

General Procedure for the Hg(0) Drop Test. In a typical run, a 25 mL vial was charged with a mixture of complex 4c (5 mol %, 0.013 mmol), AgBF₄ (15 mol %, 0.039 mmol), excess Hg(0) $(\sim 100 \text{ times with respect to the catalyst loading})$, and acetonitrile (~5 mL) and to this was added the mixture of 1,3-dicarbonyl compounds, primary aliphatic amines, and diethyleneglycoldi-n-butyl ether (internal standard) in a molar ratio of 1:4:1 (see the Supporting Information, Table S18). The reaction mixture was stirred at room temperature for 6 h, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-n-butyl ether as an internal standard.

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Supporting Information Available: Complete ref 44; the catalysis data of control, blank, and Hg(0) drop test results; ¹H and ¹³C{¹H} NMR of silver(I), gold(I), and gold(III) complexes; X-ray metrical data comparison table; ORTEP plots of **1b**, **2a**, **2c**,

3b, **3c**, and **4c**; the B3LYP coordinates of the optimized geometries for **1b**, **3b**, and **1c**-**4c**; NBO tables and CDA table along with orbital interaction diagrams of **1b**, **3b**, and **1c**-**4c**. This material is available free of charge via the Internet at http://pubs.acs.org.