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Article

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-(R_1)-3-(R_2)imidazol-2-ylidene]$AuBr_3$ [R_1 = *i*-Pr, R_2 = CH_2Ph (**1c**); R_1 = mesityl, R_2 = CH_2Ph (**2c**); R_1 = *i*-Pr, R_2 = CH_2CO*t*-Bu (**3c**), and R_1 = *t*-Bu, R_2 = CH_2CO*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 compounds[1] 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 electrophilicity 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 tetrahedral 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 inorganic 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 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 carbenes[28] in biomedical applications[29] 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 alkynes[31] 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]$AuBr_3$ [R_1 = *i*-Pr, R_2 = CH_2Ph (**1c**); R_1 = mesityl, R_2 = CH_2Ph (**2c**); R_1 = *i*-Pr, R_2 = CH_2CO*t*-Bu (**3c**), and R_1 = *t*-Bu, R_2 = CH_2CO*t*-Bu (**4c**)] that conveniently carry

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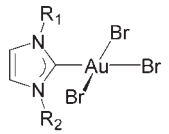


R_1 = *i*-Pr, R_2 = CH_2Ph (**1c**)

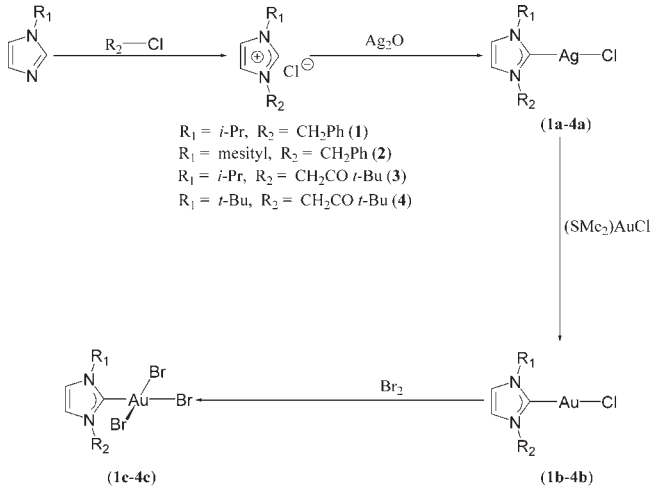
R_1 = mesityl, R_2 = CH_2Ph (**2c**)

R_1 = *i*-Pr, R_2 = CH_2CO *t*-Bu (**3c**)

R_1 = *t*-Bu, R_2 = CH_2CO *t*-Bu (**4c**)

Figure 1

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]$AuBr_3$ [R_1 = *i*-Pr, R_2 = CH_2Ph (**1c**); R_1 = mesityl, R_2 = CH_2Ph (**2c**); R_1 = *i*-Pr, R_2 = CH_2CO *t*-Bu (**3c**) and R_1 = *t*-Bu, R_2 = CH_2CO *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 Ag_2O 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)−$C_{carbene}$ resonance at 136.6−140.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum not only from the Au(I)−$C_{carbene}$ 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

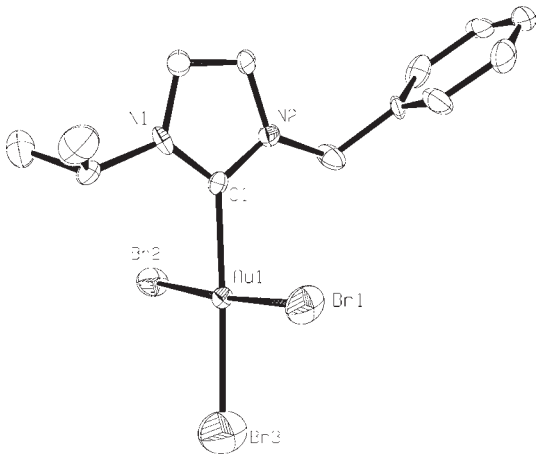


Figure 2. ORTEP of **1c** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (angstroms) and angles (degrees): N1−C1 1.33(3), N2−C1 1.345(19), Au1−C1 2.002(15), Au1−Br1 2.4154(19), Au1−Br2 2.4101(18), Au1−Br3 2.366(3), N1−C1−N2 107.5(13), C1−Au1−Br3 178.0(4).

gold(III) bromo N-heterocyclic carbene complexes, namely, [1,3-bis(*tert*-butyl)imidazol-2-ylidene]$AuBr_3$ [134.2 ppm],[25] [1,3-bis(adamantyl)imidazol-2-ylidene]$AuBr_3$ [132.9 ppm],[25] and [1,3-bis(cyclohexyl)imidazol-2-ylidene]$AuBr_3$ [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]$AuCl_3$ [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 d^8 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 d^{10} configuration of the gold(I) and silver(I) centers. The $C_{carbene}$−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]$AuBr_3$ [2.015(5) Å],[25] [1,3-bis(adamantyl)imidazol-2-ylidene]$AuBr_3$ [2.052(6) Å],[25] and [1,3-bis(cyclohexyl)-imidazol-2-ylidene]$AuBr_3$ [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]$AuCl_3$ [2.018 Å][33] and [4-methyl-5-chloromethyl-*N*,*N*′-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene]$AuCl_3$ [2.018 Å].[33] Lastly, consistent with a shorter covalent radii of Au(I) [1.37 Å] than Ag(I) [1.46 Å],[34] 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 $C_{carbene}$−Ag(I) bond distances [2.077(2)−2.087(3) Å] 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 $C_{carbene}$−Au(I) interaction in the gold(I) N-heterocyclic carbene complexes[28c,d]

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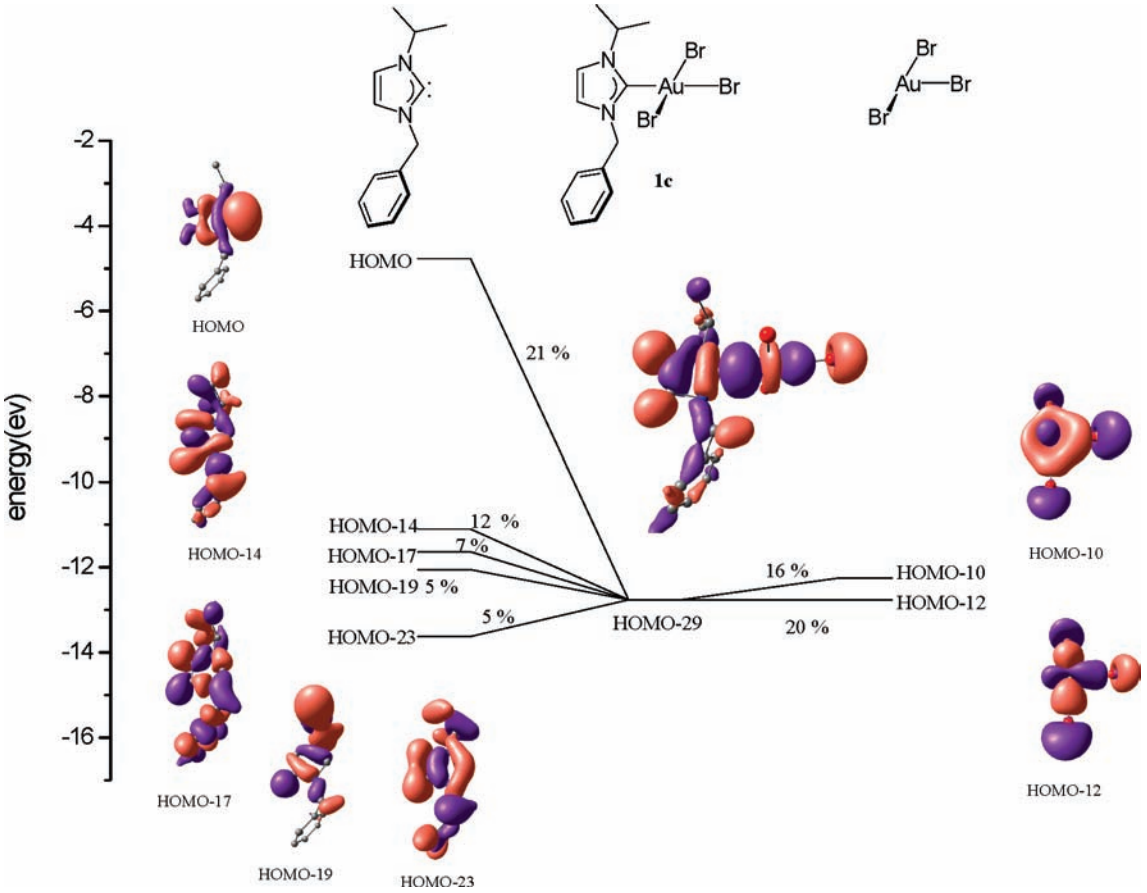

Figure 3. Simplified orbital interaction diagram showing the major contributions of the NHC−gold bond in **1c**.

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 quite 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 $\xrightarrow{\sigma}$ $AuBr_3$), as designated by d, compared to the back-donation of electrons from the metal to NHC fragment (NHC $\xleftarrow{\pi}$ AuCl) or (NHC $\xleftarrow{\pi}$ $AuBr_3$), represented by b, in the gold(I) **1b**, **3b** and gold(III) **1c**−**4c** complexes. A high d/b ratio of 3.97−25.7 in 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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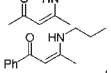
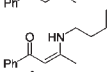
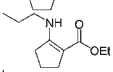
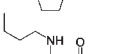
Table 1. Selected Results Synthesis of β-Enaminones Catalyzed by **1b**−**4b** and **1c**−**4c**[a]

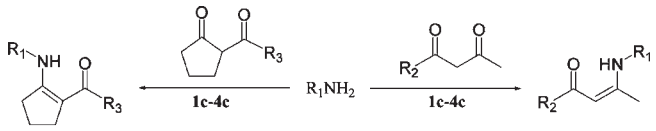
entry	reagent	reagent	product	Au(I) yield[b]				Au(III) yield[b]			
				1b	**2b**	**3b**	**4b**	**1c**	**2c**	**3c**	**4c**[c]
1		H_2N—		33	32	34	31	42	40	53	56 (48)
2		H_2N		33	23	20	27	70	64	69	51 (50)
3		H_2N		49	35	26	26	99	66	99	69 (68)
4		H_2N		4	1	4	1	40	51	49	50 (37)
5		H_2N		45	38	21	22	>99	>99	>99	>99 (72)
6		H_2N		7	1	5	4	60	49	29	37
7		H_2N		15	12	16	18	39	35	32	39
8		H_2N		20	10	19	11	32	31	25	29
9[d]		H_2N		28	24	24	28	44	41	46	50
10[d]		H_2N		43	32	35	40	60	54	51	50
11		H_2N		14	6	9	16	36	28	28	34
12		H_2N		11	8	11	8	24	24	43	36
13		H_2N		13	13	20	20	52	49	44	37 (31)

[a] Reaction conditions: 1.00 mmol of amine, 0.25 mmol of ketone, 5 mol % of catalyst, 15 mol % of $AgBF_4$, 5 mL of CH_3CN 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 $AgBF_4$, 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 $AgBF_4$ 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 $AgBF_4$ (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**−**4c** precatalysts, 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^{t}Bu, 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 ^{1}H NMR, ^{13}C{^{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 amine[37] 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-oxocyclopentanecarboxylate (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, $NaAuCl_4$,[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. Ag_2O 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-2-ylidene]AgCl (**3a**)[28e] were synthesized according to modified literature procedures. ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a Varian and Bruker 400 MHz NMR spectrometer. ^{1}H 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 XCALIBUR-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 (SMe_2)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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.33 (br, 5H, $C_6\underline{H}_5$), 7.09 (s, 1H, NC$\underline{H}$CHN), 7.00 (s, 1H, NCHC$\underline{H}$N), 5.33 (s, 2H, C$\underline{H}_2$), 4.99 (sept, 1H, $^3J_{HH}$ = 6 Hz, C$\underline{H}$(CH_3)$_2$), 1.46 (d, 6H, $^3J_{HH}$ = 6 Hz, CH(C$\underline{H}_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 168.9 (Au−N$\underline{C}$N), 135.1 (*ipso*-$\underline{C}_6H_5$), 128.8 (*m*-$\underline{C}_6H_5$), 128.4 (*p*-$\underline{C}_6H_5$), 128.0 (*o*-$\underline{C}_6H_5$), 120.8 (N$\underline{C}$HCHN), 117.4 (NCH$\underline{C}$HN), 54.9 ($\underline{C}H_2$), 53.5 ($\underline{C}$H(CH_3)$_2$), 23.2 (CH($\underline{C}H_3$)$_2$). 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 $C_{13}H_{16}AuClN_2$: 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]AuBr$_3$ (1c). A mixture of [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]-AuCl (**1b**) (0.386 g, 0.891 mmol) and liquid Br_2 (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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.42 (br, 5H, $C_6\underline{H}_5$), 7.21 (s, 1H,

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NC*H*CHN), 7.00 (s, 1H, NCHC*H*N), 5.35 (s, 2H, C*H*$_2$), 5.03 (sept, 1H, $^3J_{HH}$ = 6 Hz, C*H*(CH$_3$)$_2$), 1.57 (d, 6H, $^3J_{HH}$ = 6 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 139.0 (Au−N*C*N), 132.7 (*ipso*-*C*$_6$H$_5$), 129.7 (*m*-*C*$_6$H$_5$), 129.6 (*p*-*C*$_6$H$_5$), 129.5 (*o*-*C*$_6$H$_5$), 123.7 (N*C*HCHN), 119.5 (NCH*C*HN), 55.0 (*C*H$_2$), 54.2 (*C*H(CH$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$). 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 $C_{13}H_{16}AuBr_3N_2$: 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 (~15 mL) and dried under vacuum to give the product **2** as white crystalline solid (0.517 g, 71%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 10.84 (s, 1H, NC*H*N), 8.13 (s, 1H, NC*H*CHN), 7.73 (br, 2H, C$_6$*H*$_5$), 7.31 (br, 3H, C$_6$*H*$_5$), 7.07 (s, 1H, NCHC*H*N), 6.92 (s, 2H, *m*-C$_6$*H*$_2${2,4,6-Me$_3$}), 5.98 (s, 2H, C*H*$_2$), 2.31 (s, 3H, *p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 2.02 (s, 6H, *o*-C$_6$H$_2${2,4,6-*Me*$_3$}). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C), δ 140.7 (*ipso*-*C*$_6$H$_5$), 138.1 (N*C*HN), 134.0 (*ipso*-*C*$_6$H$_2${2,4,6-Me$_3$}), 133.9 (*o*-*C*$_6$H$_2${2,4,6-Me$_3$}), 130.7 (*p*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.5 (*m*-*C*$_6$H$_2${2,4,6-Me$_3$}), 128.9 (*o*-*C*$_6$H$_5$), 128.8 (*p*-*C*$_6$H$_5$), 128.7 (*m*-*C*$_6$H$_5$), 127.9 (N*C*HCHN), 123.3 (NCH*C*HN), 52.9 (*C*H$_2$), 20.6 (*p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 17.1 (*o*-C$_6$H$_2${2,4,6-*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 $C_{19}H_{21}N_2Cl$: 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-2-ylidene]AgCl (2a). A mixture of 1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazolium chloride (**2**) (0.569 g, 1.82 mmol) and Ag_2O (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%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.32 (br, 5H, C$_6$*H*$_5$), 7.00 (s, 1H, NC*H*CHN), 6.89 (s, 2H, *m*-C$_6$*H*$_2${2,4,6-Me$_3$}), 6.78 (s, 1H, NCHC*H*N), 5.44 (s, 2H, C*H*$_2$), 2.28 (s, 3H, *p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 1.98 (s, 6H, *o*-C$_6$H$_2${2,4,6-*Me*$_3$}). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 181.0 (Ag−N*C*N), 139.4 (*ipso*-*C*$_6$H$_5$), 135.7 (*ipso*-*C*$_6$H$_2${2,4,6-Me$_3$}), 135.3 (*o*-*C*$_6$H$_2${2,4,6-Me$_3$}), 134.6 (*p*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.3 (*m*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.1 (*o*-*C*$_6$H$_5$), 128.6 (*p*-*C*$_6$H$_5$), 127.5 (*m*-*C*$_6$H$_5$), 123.2 (N*C*HCHN), 121.4 (NCH*C*HN), 55.4 (*C*H$_2$), 20.8 (*p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 17.4 (*o*-C$_6$H$_2${2,4,6-*Me*$_3$}). IR data (KBr pellet) cm^{-1}: 3166 (m), 3130 (m), 3030 (w), 2917 (m), 1496 (s), 1445 (m), 1445 (s), 1411 (m), 1031 (m), 857 (s), 586 (w). Anal. Calcd for $C_{19}H_{20}AgClN_2$: 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-2-ylidene]AuCl (2b). A mixture of [1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]AgCl (**2a**) (0.218 g, 0.519 mmol) and (SMe$_2$)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%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.37 (br, 5H, C$_6$*H*$_5$), 7.06 (s, 1H, NC*H*CHN), 6.94 (s, 2H, *m*-C$_6$*H*$_2${2,4,6-Me$_3$}), 6.83 (s, 1H, NCHC*H*N), 5.50 (s, 2H, C*H*$_2$), 2.34 (s, 3H, *p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 2.04 (s, 6H, *o*-C$_6$H$_2${2,4,6-*Me*$_3$}). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 172.1 (Au−N*C*N), 139.6 (*ipso*-*C*$_6$H$_5$), 135.3 (*ipso*-*C*$_6$H$_1${2,4,6-Me$_3$}), 134.7 (*o*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.4 (*p*-*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*-*C*$_6$H$_5$), 127.8 (*m*-*C*$_6$H$_5$), 122.8 (N*C*HCHN), 120.7 (NCH*C*HN), 55.0 (*C*H$_2$), 21.1 (*p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 17.8 (*o*-C$_6$H$_2${2,4,6-*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 $C_{19}H_{20}AuClN_2$: 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-2-ylidene]AuBr$_3$ (2c). A mixture of [1-(benzyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]AuCl (**2b**) (0.206 g, 0.404 mmol) and liquid Br$_2$ (0.194 g, 1.21 mmol) in dichloromethane (~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%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.47 (br, 5H, C$_6$*H*$_5$), 7.11 (s, 1H, NC*H*CHN), 7.06 (s, 1H, NCHC*H*N), 6.98 (s, 2H, *m*-C$_6$*H*$_2${2,4,6-Me$_3$}), 5.56 (s, 2H, C*H*$_2$), 2.35 (s, 3H, *p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 2.22 (s, 6H, *o*-C$_6$H$_2${2,4,6-*Me*$_3$}). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 140.9 (Au−N*C*N), 135.2 (*ipso*-*C*$_6$H$_5$), 132.9 (*ipso*-*C*$_6$H$_2${2,4,6-Me$_3$}), 130.1 (*o*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.8 (*p*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.7 (*m*-*C*$_6$H$_2${2,4,6-Me$_3$}), 129.4 (*o*-*C*$_6$H$_5$), 126.3 (*p*-*C*$_6$H$_5$), 126.0 (*m*-*C*$_6$H$_5$), 123.2 (N*C*HCHN), 123.0 (NCH*C*HN), 55.6 (*C*H$_2$), 21.3 (*p*-C$_6$H$_2${2,4,6-*Me*$_3$}), 19.6 (*o*-C$_6$H$_2${2,4,6-*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 $C_{19}H_{20}AuBr_3N_2$: 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-2-oxobutyl)imidazol-2-ylidene]AgCl (**3a**) (0.517 g, 1.47 mmol) and (SMe$_2$)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%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.02 (s, 1H, NC*H*CHN), 6.97 (s, 1H, NCHC*H*N), 5.20 (s, 2H, C*H*$_2$), 5.05 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 1.51 (d, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.30 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 207.5 (*C*O), 170.8 (Au−N*C*N), 122.7 (N*C*HCHN), 116.7 (NCH*C*HN), 55.2 (*C*H$_2$), 53.7 (*C*H(CH$_3$)$_2$), 43.7 (*C*(CH$_3$)$_3$), 26.3 (C(*C*H$_3$)$_3$), 23.4 (CH(*C*H$_3$)$_2$). IR data (KBr pellet) cm^{-1}: 1721 (s) ($\nu_{C=O}$). Anal. Calcd for $C_{12}H_{20}AuClN_2O$: 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]AuBr$_3$ (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 Br$_2$ (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%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.33 (s, 1H, NC*H*CHN), 7.29 (s, 1H, NCHC*H*N), 5.24 (s, 2H, C*H*$_2$), 5.03 (sept, 1H, $^3J_{HH}$ = 6 Hz, C*H*(CH$_3$)$_2$), 1.57 (d, $^3J_{HH}$ = 6 Hz, CH(C*H*$_3$)$_2$), 1.32 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 205.3 (*C*O), 136.6 (Au−N*C*N), 126.3 (N*C*HCHN), 119.1 (NCH*C*HN), 54.2 (*C*H$_2$), 54.1 (*C*H(CH$_3$)$_2$), 44.0 (*C*(CH$_3$)$_3$), 26.5 (C(*C*H$_3$)$_3$), 22.9 (CH(*C*H$_3$)$_2$). IR data (KBr pellet) cm^{-1}: 1724 (s) ($\nu_{C=O}$). Anal. Calcd for $C_{12}H_{20}AuBr_3N_2O$: 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%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 10.67 (s, 1H, NC*H*N), 7.32 (s, 2H, NCHC*H*N), 5.97 (s, 2H, C*H*$_2$), 1.72 (s, 9H, C(C*H*$_3$)$_3$), 1.32 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ 207.0 (*C*O), 136.0 (N*C*HN), 124.2 (N*C*HCHN), 118.6 (NCH*C*HN), 59.7 (*C*H$_2$), 54.0 (*C*(CH$_3$)$_3$), 43.0 (*C*(CH$_3$)$_3$), 29.5 (C(*C*H$_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$). IR data (KBr pellet) cm^{-1}: 1716 (s) ($\nu_{C=O}$). 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-2-oxobutyl) imidazolium chloride (**4**) (2.18 g, 8.41 mmol) and Ag_2O

(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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.21 (s, 1H, NC*H*CHN), 6.92 (s, 1H, NCHC*H*N), 5.21 (s, 2H, CH_2), 1.74 (s, 9H, C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 208.0 (*C*O), 178.7 (Ag−N*C*N), 121.3 (N*C*HCHN), 118.7 (NCH*C*HN), 57.6 (*C*H$_2$), 56.7 (*C*(CH$_3$)$_3$), 43.2 (*C*(CH$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 26.1 (C(*C*H$_3$)$_3$). IR data (KBr pellet) cm^{-1}: 1718 (s) ($\nu_{C=O}$). Anal. Calcd for $C_{13}H_{22}AgClN_2O$: 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-2-oxobutyl)imidazol-2-ylidene]AgCl (**4a**) (0.509 g, 1.39 mmol) and (SMe_2)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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.13 (s, 1H, NC*H*CHN), 6.92 (s, 1H, NCHC*H*N), 5.32 (s, 2H, CH_2), 1.86 (s, 9H, C(CH_3)$_3$), 1.31 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 207.6 (*C*O), 170.9 (Au−N*C*N), 120.6 (N*C*HCHN), 118.5 (NCH*C*HN), 59.2 (*C*H$_2$), 56.5 (*C*(CH$_3$)$_3$), 43.7 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 26.4 (C(*C*H$_3$)$_3$). IR data (KBr pellet) cm^{-1}: 1720 (s) ($\nu_{C=O}$). Anal. Calcd for $C_{13}H_{22}AuClN_2O$: 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]AuBr$_3$ (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 Br_2 (0.227 g, 1.42 mmol) in dichloromethane (~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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.40 (s, 1H, NC*H*CHN), 7.23 (s, 1H, NCHC*H*N), 5.34 (s, 2H, CH_2), 1.89 (s, 9H, C(CH_3)$_3$), 1.32 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 205.2 (*C*O), 138.3 (Au−N*C*N), 125.6 (N*C*HCHN), 122.2 (NCH*C*HN), 61.9 (*C*H$_2$), 55.1 (*C*(CH$_3$)$_3$), 40.4 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 26.6 (C(*C*H$_3$)$_3$). IR data (KBr pellet) cm^{-1}: 1724 (s) ($\nu_{C=O}$). Anal. Calcd for $C_{13}H_{22}AuBr_3N_2O$: 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)AuBr$_3$ 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) analysis[49] 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).[50] 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)AuBr$_3$ type species, **1c**−**4c**, can be divided into three parts: (i) σ-donation from the [NHC → AuCl] in gold(I) and [NHC → AuBr$_3$] in the gold(III) fragment; (ii) π-back-donation from the [NHC ← AuCl] in gold(I) and [NHC ← AuBr$_3$] 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), $AgBF_4$ (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 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 $AgBF_4$ (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 diethyleneglycol-di-*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), $AgBF_4$ (15 mol %, 0.039 mmol), excess Hg(0) (~100 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 diethyleneglycol-di-*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; ^{1}H and $^{13}C\{^{1}H\}$ 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.