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Room-Temperature Hydration of Alkynes Catalyzed by Different Carbene Gold Complexes and their Precursors

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The room-temperature hydration of alkynes catalyzed by NHC-gold(I) (NHC = N-heterocyclic carbene), NAC-gold(I) (NAC = nitrogen acyclic carbene), and isocyanide gold(I) complexes was investigated carefully in the presence of different weakly coordinating anions. NHC(IPr)-AuCl/KB(C_6F_5)$_4$ (NHC(IPr) = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was found to be the most active catalyst at room temperature, and the room-temperature hydration of different alkynes could be completed in 7 h using only 0.5 mol% NHC(IPr)-AuCl/KB(C_6F_5)$_4$. It was further demonstrated that the catalyst system could be simply reused at least six times without a noticeable loss of catalytic activity.

Introduction

In recent years, gold catalysts have been paid more and more research attention because of their unique catalytic properties in many useful organic reactions.[1] Among various synthetic reactions, active gold species have a special affinity for alkyne hydration, which is an effective way to prepare ketones with 100% atom economy.[2–7] The hydration of alkynes has also been used as a benchmark to investigate the catalytic ability of gold catalysts.[4e] Although many effective catalysts have been reported for the hydration of alkynes, the implementation of this reaction at room temperature is still a challenge.[2] Researchers in this specialized field have a persistent interest in the development of alternative catalysts for the hydration of alkynes. Among the catalysts reported, gold-based compounds,[3] especially compounds of gold and N-heterocyclic carbenes (NHC-AuX, X = Cl, SbF_6, BF_4, OTf, or Br_3), have taken a prominent place.[2f,n,4–6]

Generally, these NHC-AuX catalysts are quite effective because of the special electron-donating and -withdrawing ability of the NHC.[1b,5] Although NHC-AuX catalysts modified by different functional groups on the nitrogen heterocycle[2f,4d] and coordinated with different anions (NHC-AuX, X = Cl,[2f,3e,4b,d] SbF_6,[4f,g,5,6] BF_4,[2n] OTf,[4c] or Br_3)[4a] have been used for the hydration of alkynes, most of these reactions work at high temperatures (e.g., 120 °C for NHC-AuSbF$_6$,[6a] 110 °C for NHC-AuCl,[2f] 70 °C for NHC-AuOTf[4c] and MeOH/H_2O, under reflux for NHC-AuBr$_3$[4a]). If NHC-Au-phenolate was used as a catalyst, the hydration reaction could be performed at room temperature. However, it requires 72 h to achieve 35% yield with 1 mol% catalyst.[4e]

Recently, we reported that the hydration of alkynes catalyzed by isocyanide gold compounds (NCR-Au) could be performed quite well at room temperature.[7] Usually, NCR-Au is used as the starting material for the synthesis of NHC-Au.[3c,8] NCR-Au was proven to be an effective catalyst for the hydration of alkynes at room temperature,[7] whereas NHC-Au itself served as an effective catalyst for this reaction only at high temperature.[2f,3e,4–6] Does this mean that the precursor NCR-Au is more active than NHC-Au for the hydration reaction? How can we further improve the catalytic ability of NHC-Au? Herein, we will aim to answer these two questions and try to obtain a more effective NHC-Au-based catalyst system for the room-temperature hydration of alkynes.

Results and Discussion

Six different catalysts were examined in this study: two NHC-gold(I) complexes [NHC(IPr)-AuCl (NHC(IPr) = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and NHC(IMes)-AuCl (NHC(IMes) = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)], two nitrogen acyclic carbene gold(I) complexes [NAC(Cy)-AuCl (NAC(Cy) = (cyclohexylamino)(diethylamino)methylidene) and NAC(Ph)-AuCl (NAC(Ph) = (diethylamino)(2,6-dimethylphenylamino)methylidene)], and two simple isocyanide gold(I) complexes [NC(Cy)-AuCl (NC(Cy) = cyclohexylisocyanide) and NC(Ph)-AuCl (NC(Ph) = 2,6-dimethylphenylisocyano)] (Scheme 1). These catalysts were synthesized according to known procedures.[3c,6b,7,8e,9] The hydration of phenylacetylene was selected as the probe reaction.

Usually, gold chloride complexes of NHC and NAC (NHC-AuCl and NAC-AuCl) are used as precursors to synthesize NHC-AuX and NAC-AuX (X = SbF_6, BF_4, OTf, PF_6).[2f,3e,4b–g,5,6] It has also been reported that NHC-AuCl itself can serve as a catalyst for the hydration of phenylacetylene at high temperature.[2f]

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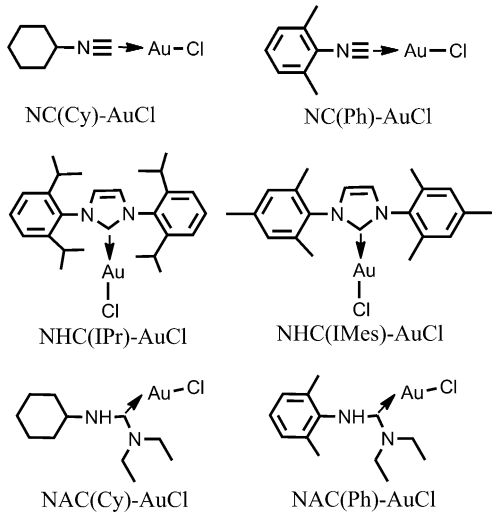


Scheme 1. Catalysts used for the hydration of alkynes.

However, if we lowered the reaction temperature to 25 °C, both the reactions catalyzed by NHC-AuCl and NAC-AuCl (Figure 1 a) proceed very poorly. Although 99% yield can be obtained in 24 h in the room-temperature hydration of phenylacetylene catalyzed by NC(Cy)-AuCl in the presence of $KB(C_6F_5)_4$,[7] this reaction almost does not work if only NC(Cy)-AuCl or NC(Ph)-AuCl was used as the catalyst (Figure 1 a).

The gold cation is thought to be the active center in the hydration of phenylacetylene.[2f,4e,7,10] Hence, the control of the equilibrium concentration of the gold cation in solution should be an effective way to influence the catalytic activity of these catalysts. For example, the addition of NaCl can inhibit the hydration of phenylacetylene catalyzed by NHC-AuCl because the increased Cl^- concentration makes the equilibrium shift from NHC-Au^+ towards NHC-AuCl.[2f] The use of weakly coordinating anions is an effective method to release gold cations.[4e,7] Although many weakly coordinating anions (such as SbF_6^-, BF_4^-, PF_6^-, and OTf^-) have been used in the hydration reaction catalyzed by NHC-AuCl, the reaction catalyzed by NHC-AuX (X = SbF_6, BF_4, PF_6, and OTf) still requires a high temperature.[2b,n,4c,f,g,6a] Herein, we have also tested the hydration of phenylacetylene using NHC-$AuBF_4$ and NHC-$AuSbF_6$ as catalysts at room temperature. To avoid the influence of the Ag ion, which is thought to be a catalyst for the hydration of phenylacetylene,[11] KBF_4 and $KSbF_6$ were used instead of $AgBF_4$ and $AgSbF_6$. NHC(IPr)-$AuSbF_6$ is known as a very active catalyst for the alkyne hydration reaction at 120 °C as only 50 ppm catalyst was required for the hydration of phenylacetylene.[6a] However, if the temperature was lowered to 25 °C, the reaction catalyzed by NHC(IPr)-$AuSbF_6$ proceeds quite slowly (conversion = 28% in 5 h using 5 mol% catalyst) and other catalytic compounds have nearly no function in the reaction (Figure 1 b and c). This suggests that BF_4^- and SbF_6^- are not good additives to release gold cations at room temperature.

Tetrakis(pentafluorophenyl)borate [$B(C_6F_5)_4^-$], known as a noncoordinating anion, has been used as an excellent chloride scavenger.[12,13] Recently, $B(C_6F_5)_4^-$ has been used successfully as a counterion in the gold-catalyzed room-temperature

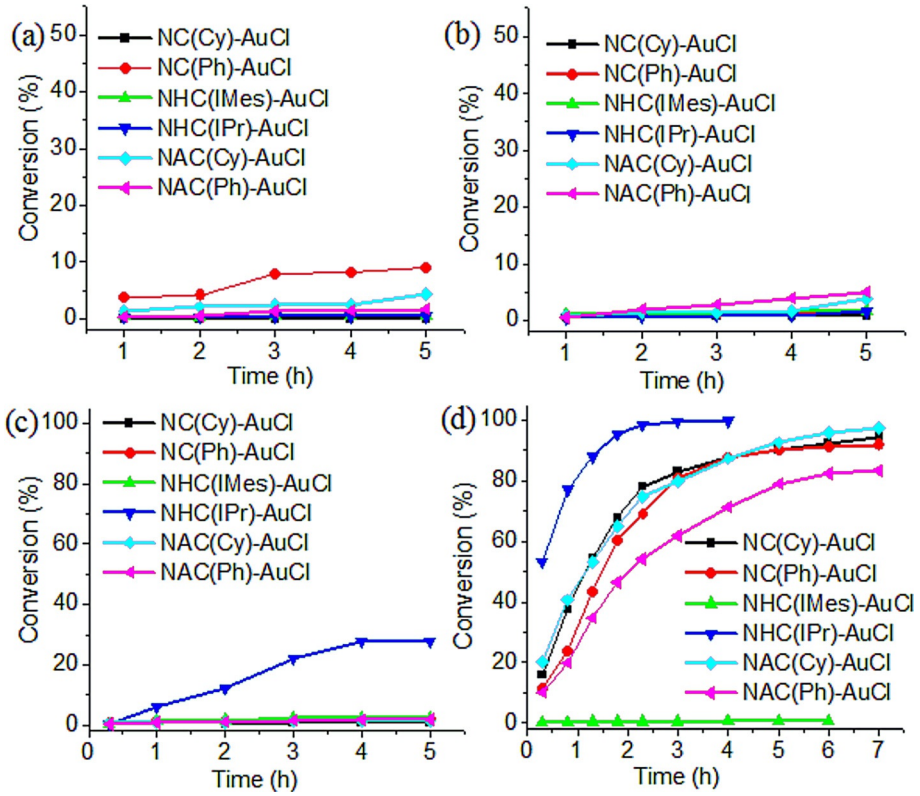
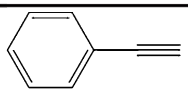
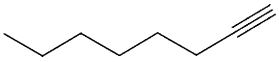
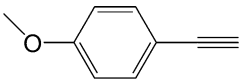
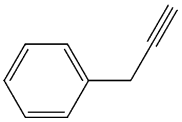
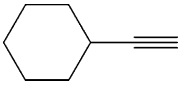


Figure 1. Hydration of phenylacetylene using 5 mol% catalyst in the presence of a) no additive, b) KBF_4, c) $KSbF_6$, and d) $KB(C_6F_5)_4$ at 25 °C.

hydrohydrazinations of alkynes.[14] A high concentration of free gold cations should be generated upon the addition of $B(C_6F_5)_4^-$. The chloride abstraction can be monitored by NMR spectroscopy. A 1:1 mixture of NHC(IPr)-AuCl and $KB(C_6F_5)_4$ was stirred in THF for 1 h. After the removal of KCl and THF, a ^{13}C NMR spectrum shows that the δ value of the carbene carbon atom shifts from 175.51 to 173.68 ppm (the NMR spectra of NHC(IPr)-AuCl and NHC(IPr)-Au[$B(C_6F_5)_4$] are presented in the Supporting Information). As expected, the hydration reaction catalyzed by NHC(IPr)-AuCl in the presence of $KB(C_6F_5)_4$ works perfectly at room temperature (conversion = 99% in 2 h; Figure 1 d). This result is far better than our previous finding that 99% conversion could be obtained in 24 h for the same reaction catalyzed by NC(Cy)-AuCl and $KB(C_6F_5)_4$.[7] Notably, there are almost no examples of alkyne hydration catalyzed by NHC(IPr)-AuCl under such mild conditions.[2f,4–6,15] Previous research has shown that NHC(IMes)-AuCl is not active for the hydration reaction.[6a] Herein, it is further demonstrated that even if $KB(C_6F_5)_4$ is used, NHC(IMes)-AuCl is still a very poor catalyst for this reaction. However, in the presence of $KB(C_6F_5)_4$, the NAC-AuCl catalytic system becomes more effective than that shown previously, and the reaction time was shortened to 7 h rather than 5 days.[3c] Notably, NC(Cy)-AuCl showed a similar catalytic ability to NAC-AuCl in the presence of $KB(C_6F_5)_4$ although NC(Cy)-AuCl was the precursor for the synthesis of NAC-AuCl.[3c,8]

The excellent catalytic ability of NHC(IPr)-AuCl/$KB(C_6F_5)_4$ urged us to explore the hydration of various alkynes. If 5 mol% NHC(IPr)-AuCl/$KB(C_6F_5)_4$ was used, the hydration of 1-octyne, cyclohexylacetylene, 2-propynylbenzene, and 4-methoxyphenylacetylene can be finished in 20 min with a good yield of ketone (Table 1). Even though the catalyst loading was reduced to 0.5 mol%, 99% conversion of alkynes also can also be obtained in 7 h for all the substrates investigated here. If the catalyst loading was further reduced to 0.05 mol%, although the reaction also works at room temperature, only 23.0% acetophenone was obtained in 24 h.

Table 1. Hydration of various alkynes under standard conditions[a].

Entry	Reactant	Catalyst [mol%][b]	Time	Yield [%][c]
1		5	3 h	>99.9 (91)
		0.5	7 h	99.4
		0.05	24 h	23.0
2		5	20 min	>99.9 (98)
		0.5	2.3 h	98.7
3		5	20 min	>99.9 (93)
		0.5	4 h	98.9
4		5	20 min	>99.9 (95)
		0.5	4 h	99.8
5		5	20 min	>99.9 (99)
		0.5	2.3 h	98.5

[a] Reaction conditions: substrate (1 mmol), catalyst, methanol (1 mL), H_2O (1 mL), 25 °C. [b] Loading of NHC(IPr)-AuCl/$KB(C_6F_5)_4$. [c] GC yield with biphenyl as the internal standard (isolated yield presented in parentheses).

Previously, we reported a rare example of the room-temperature hydration of alkynes catalyzed by NC(Cy)-AuCl.[7] Herein, it is found that for the hydration of various alkynes, the reactions catalyzed by 0.5 mol% NHC(IPr)-AuCl/$KB(C_6F_5)_4$ are always faster than those catalyzed by 0.5 mol% NC(Cy)-AuCl/$KB(C_6F_5)_4$ (Figure 2).

Usually, the hydration of internal alkynes is more difficult because of the low reactivity of these compounds.[15] Herein, we also tested the catalytic ability of NHC(IPr)-AuCl/$KB(C_6F_5)_4$ for the hydration of some internal alkynes (1-phenylpropyne and 1,2-diphenylacetylene) at room temperature (Figures S1 and S2). Satisfactorily, these reactions proceed quite well at room temperature. The hydration of phenylacetylene can be completed in 3 h, and two products were obtained with a preference to phenylacetone.

As NHC-AuX compounds are expensive, the recycling of NHC-AuX catalysts is of great significance and has attracted wide attention.[10] However, the poor stability of NHC-AuCl compounds makes recycling a big challenge at high temperature. NHC(IPr)-AuCl benefits from the mild hydration conditions reported here and is quite stable during the whole reaction process. It makes the reuse of the catalyst system quite simple. When the reaction finishes, there are two phases in the reaction system. After phase separation, the water phase that contains the catalyst was reused directly without any treatment. The catalyst was recycled and reused six times without a noticeable loss of catalytic activity (Figure 3). This is quite meaningful because no example of catalyst recycling has been reported to date for the high-temperature hydration of alkynes catalyzed by other NHC-gold compounds.[2f,4–6] The results obtained here suggest that the NHC(IPr)-AuCl/$KB(C_6F_5)_4$ system is robust and recyclable under mild conditions.

Conclusions

To investigate the catalytic ability of gold(I) for the hydration of alkynes, three ligand types (N-heterocyclic carbene (NHC), nitrogen acyclic carbene, and isocyanide) and four different counterions (Cl^-, BF_4^-, SbF_6^-, and $B(C_6F_5)_4^-$) were used to form complexes with gold(I). Both the ligand and counterion play vital roles in the catalysis for the following reasons: (1) NHC(IMes)-AuX (NHC(IMes) = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) is not active no matter what counterion was used; (2) Ligand-AuCl is not active no matter what the ligand is; (3) The addition of $KB(C_6F_5)_4$ can improve the catalytic ability of these gold(I) compounds. As far as we know, although many NHC-Au catalysts have been investigated for the hydration of alkynes,[2f,n,4–6] NHC(IPr)-AuCl/$KB(C_6F_5)_4$ (NHC(IPr) = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is the most effective at room temperature. Carbene gold(I) compounds have been used widely as catalysts in many reactions.[1a,b,16] The addition of $KB(C_6F_5)_4$ to increase the concentration of free gold

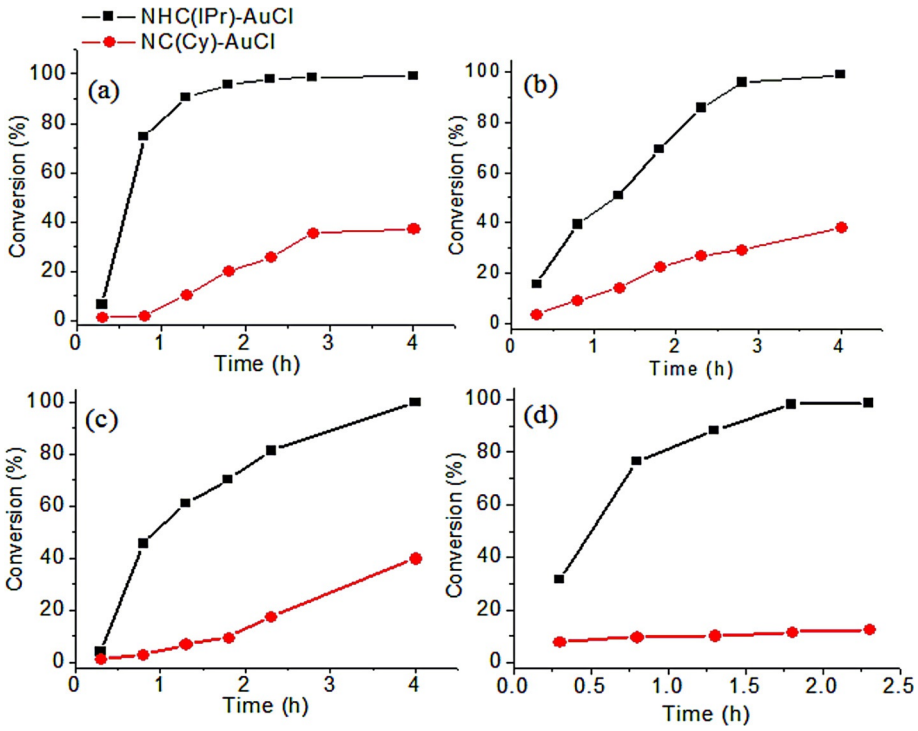


Figure 2. Hydration of a) cyclohexylacetylene, b) 4-methoxyphenylacetylene, c) 2-propynylbenzene, and d) 1-octyne catalyzed by 0.5 mol% NHC(IPr)-AuCl/$KB(C_6F_5)_4$ or NC(Cy)-AuCl/$KB(C_6F_5)_4$ at 25 °C.

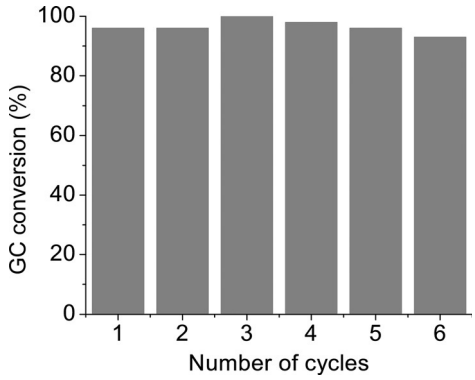


Figure 3. Recycling of the NHC(IPr)-AuCl/$KB(C_6F_5)_4$ system in the hydration of phenylacetylene.

cations should be a useful method to improve the catalytic ability of carbene gold(I) compounds in these reactions.

Experimental Section

Materials and methods

All solvents and chemicals were commercially available and used without further purification unless otherwise stated. NMR spectra were determined by using a Bruker DPX 300 MHz spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard. Elemental analysis was performed by using an Elementarvario EL II. The purity of the raw materials and the reaction solution was analyzed by using a GC5890C gas chromatograph fitted with a SE-30 column (50 m, 0.25 μm) and a hydrogen flame detector. The structure and concentration of the product and byproducts were further identified by using an HP6890 GC–MS spectrometer by comparing retention times and fragmentation patterns with authentic samples.

Synthesis of isocyanide gold(I) complexes

Preparation of (tht)AuCl: $HAuCl_4{\cdot}4H_2O$ (1 g) was dissolved in H_2O/C_2H_5OH (20 mL, 4:1) and excess tetrahydrothiophene was added slowly dropwise under stirring. The yellow solution became turbid, and a white solid appeared. (tht)AuCl was collected by filtration and dried in a thermostatic vacuum drier. (tht)AuCl was obtained as a colorless powder (Yield: 65%).

Preparation of NC(Cy)-AuCl and NC(Ph)-AuCl: (tht)AuCl (0.5 g) was dissolved in THF (20 mL), and a solution of cyclohexylisonitrile (0.2 g) or 2,6-dimethyphenyl isocyanide (0.2 g) in THF was added. The reaction mixture was stirred for 12 h at RT. The solvent was removed, and the resulting precipitate was recrystallized from THF/light petroleum (1:10) (Yield: 55%, 67%).

NC(Cy)-AuCl: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.94–3.88 (m, 1H), 2.06–1.98 (m, 2H), 1.87–1.72 (m, 4H), 1.57–1.41 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 54.97, 31.54, 24.52, 22.62 ppm; elemental analysis calcd for $C_7H_{11}AuClN$ (calculated mass = 341.02): C 24.61, H 3.25, N 4.10; found C 24.99, H 3.41, N 4.10.

NC(Ph)-AuCl: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.39–7.33 (t, 1H), 7.20–7.17 (d, 2H), 2.46 ppm (s, 6H); ^{13}C NMR (CDCl3, 300 MHz): δ = 144.90, 136.25, 131.08, 128.51, 18.44 ppm; elemental analysis calcd for C_9H_9AuClN (calculated mass = 363.01): C 29.73, H 2.49, N 3.85; found C 29.84, H 2.71, N 3.74.

Synthesis of NHC-gold(I) complexes

A 50 mL Schlenk flask was charged with *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (186 mg) and THF (30 mL), and then (tht)AuCl (153 mg) was added. The resulting dark green solution was protected from light and stirred at RT for at least 24 h. The remaining steps were then performed in air. THF (5 mL) was removed under reduced pressure, and light petroleum (20 mL) was added, which resulted in immediate precipitation. After it was collected by filtration, the precipitate was recrystallized from dichloromethane/pentane (1:5) (Yield: 75%).

NHC(IPr)-AuCl: ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.53–7.48 (t, 2H), 7.31 (br, 4H), 7.18 (s, 2H), 2.61–2.54 (septet, 4H), 1.36–1.43 (d, 12H), 1.24–1.21 ppm (d, 12H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 175.51, 145.59, 134.56, 131.61, 124.70, 123.11, 29.37, 24.49, 24.04 ppm; elemental analysis calcd for $C_{27}H_{36}AuClN_2$ (calculated mass = 620.22): C 52.22, H 5.84, N 4.51; found C 51.88, H 5.86, N 4.46.

NHC(IMes)-AuCl was prepared by a similar method (Yield = 80%).

NHC(IMes)-AuCl: ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.11 (s, 2H), 6.89 (s, 4H), 2.44 (s, 6H), 1.70 ppm (s, 12H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 185.14, 139.42, 134.48, 134.01, 128.81, 122.96, 21.28, 17.16 ppm; elemental analysis calcd for $C_{21}H_{24}AuClN_2$ (calculated mass = 536.13): C 46.98, H 4.51, N 5.22; found C 46.74, H 4.56, N 5.11.

Synthesis of NAC-gold(I) complexes

Diethylamine (3 equiv.) was added to a solution of an isocyanide gold(I) complex (NC(Cy)-AuCl or NC(Ph)-AuCl) (100 mg) in dichloromethane (10 mL). The mixture was stirred at RT and protected from light for 3 days. The addition of saturated NH_4Cl solution, extraction with dichloromethane, and filtration furnished NAC(Cy)-AuCl or NAC(Ph)-AuCl as a colorless solid.

NAC(Cy)-AuCl: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.47–5.44 (br, 1H), 4.27–4.18 (m, 1H), 3.96–3.89 (q, 2H), 3.31–3.24 (q, 2H), 2.10–2.06 (m, 1H), 1.76–1.70 (m, 2H), 1.63–1.58 (m, 2H), 1.44–1.33 (m, 4H), 1.30–1.26 (t, 3H), 1.23–1.18 ppm (t, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 188.40, 59.22, 53.71, 41.04, 34.28, 25.10, 24.76, 14.71, 11.97 ppm; elemental analysis calcd for $C_{11}H_{23}AuClN_2$ (calculated mass = 414.11): C 31.78, H 5.58, N 6.74; found C 31.86, H 5.39, N 6.65.

NAC(Ph)-AuCl: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.21–7.16 (m, 1H), 7.11–7.09 (d, 2H), 6.86 (br, 1H), 4.05–3.98 (q, 2H), 3.55–3.48 (q, 2H), 2.24 (S, 6H), 1.38–1.33 (t, 3H), 1.37–1.32 ppm (t, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 192.18, 136.30, 128.59, 53.64, 43.36, 18.97, 14.81, 12.42 ppm; elemental analysis calcd for $C_{13}H_{21}AuClN_2$ (calculated mass = 436.10): C 35.67, H 4.84, N 6.40; found C 35.21, H 4.83, N 6.26.

General procedure for hydration reactions

Alkynes (1 mmol), methanol (1 mL), H_2O (1 mL), catalyst (0.05 mmol), and $KB(C_6F_5)_4$ (0.05 mmol) were added to a 10 mL screw-cap vial. The reaction mixture was stirred at 25 °C. The organic layer was separated from the water layer. Conversion was determined by GC with biphenyl as the internal standard. The product was isolated by extraction into ether followed by the removal of solvent under reduced pressure at RT.

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