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Indazolin-*s*-ylidene–N-Heterocyclic Carbene Complexes of Rhodium, Palladium, and Gold: Synthesis, Characterization, and Catalytic Hydration of Alkynes

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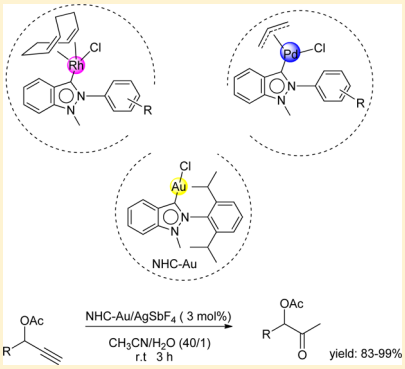
Supporting Information

ABSTRACT: A novel series of Indy-N-heterocyclic carbene ligands (Indy = indazolin-*s*-ylidene) have been developed and investigated. Via a mild Ag carbene transfer route, these new carbene ligands reacted with rhodium, palladium, and gold salts to yield the corresponding air-stable metal complexes. The product complexes were characterized by NMR spectroscopic methods and X-ray diffraction analysis. The electronic properties of these complexes were modified by the introduction of different substituents at the coordinated NHC ligands. Catalytic properties of the gold complex were evaluated in the hydration of alkynes to give the corresponding ketone products. This new type of gold N-heterocyclic carbene complex showed a high catalytic activity in the hydration of alkyne at room temperature.



INTRODUCTION

Since N-heterocyclic carbenes (NHCs) were first isolated in the free state by Arduengo and co-workers in 1991,[1] NHCs have been studied extensively as ligands in organometallic chemistry and in catalysis. Owing to their strong σ donation and the excellent stability of NHC complexes toward air and moisture,[2] N-heterocyclic carbenes often can promote higher catalytic activity than phosphane ligands.[3] In addition to the normal imidazole derivatives, Crabtree and co-workers first discovered the abnormal carbenes,[4] which have a carbenoid center adjacent to only one nitrogen atom. These abnormal carbenes have proven to be more donating than the normal carbenes.[5] Since then, various classes of NHC ligands such as py-NHCs, remote py-NHCs, have been developed[6] (Figure 1).

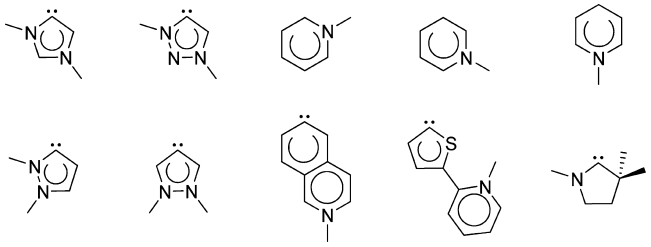


Figure 1. Some representatives for the subclasses of NHC ligands.

Huynh and co-workers pioneered the design and synthesis of indazolin-*s*-ylidene (Indy) carbenes in 2009, which showed even stronger donating capacities than the classical NHC ligands.[7] However, examples of Indy-NHC complexes and catalytic activities of these Indy-NHC complexes are still rather limited.[8,9] As the electronic properties and chemical activities of transition-metal complexes are often determined by the electronic and steric effects of their ligands,[10] we were interested in introducing an aryl group with different substituents on the central nitrogen atom of the Indy-NHCs, hoping to discover new reactive species. Herein, we report the design and synthesis of a novel series of Indy-NHC complexes which allow modifications at the coordinated Indy-N-heterocyclic carbene ligands. These complexes were isolated in good yields and were unambiguously characterized by X-ray crystallography and NMR spectroscopic methods. We have also investigated the catalytic activity of an NHC-Au complex and found that the gold Indy-NHC complex showed superior catalytic activities in the hydration of alkynes (80–99%).

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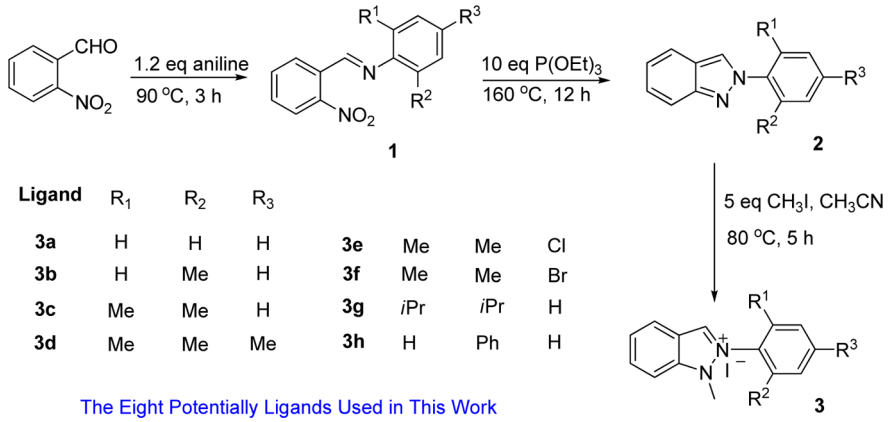
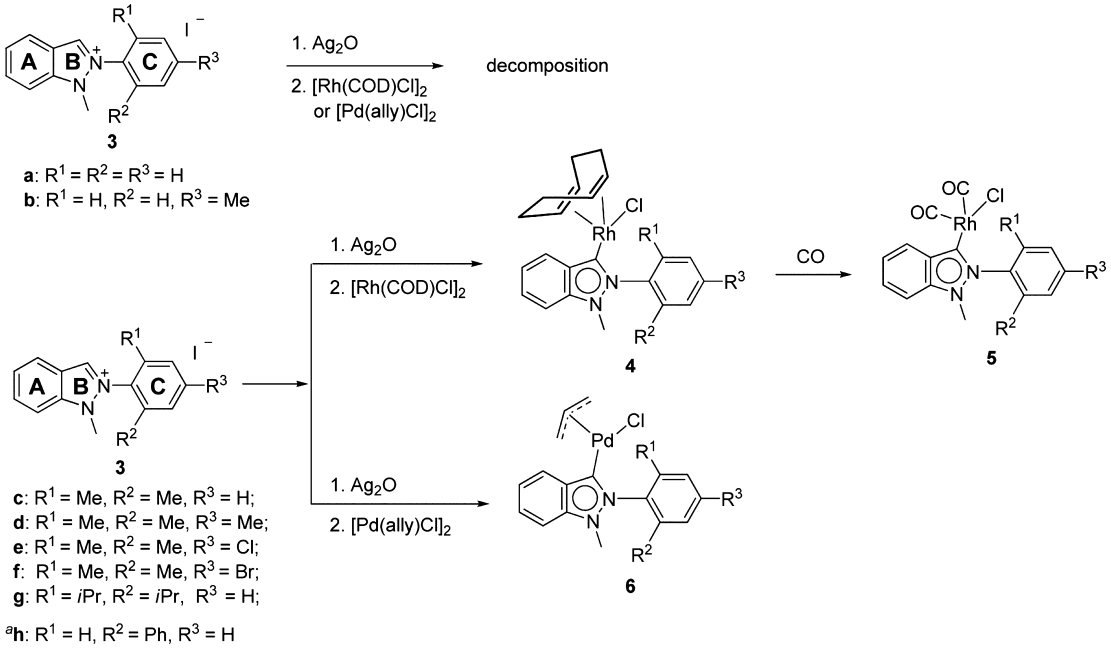
Scheme 1. Synthesis of Indazole N-Heterocyclic Carbene Ligands



Scheme 2. Synthesis of Various Metal Complexes (Rh, Pd)



RESULTS AND DISCUSSION

Synthesis of the Indy-NHC Ligands. The synthetic route of these novel Indy-NHC ligands is outlined in Scheme 1, following a previous report.[11]

Compounds **1** were prepared by a condensation reaction of 2-nitrobenzaldehyde and aniline in excellent yield (89−93%). Then, through the Cadogan reaction,[12] intramolecular cyclization was performed after adding excessive triethyl phosphate and refluxing for 12 h under an inert atmosphere to give the indazole compounds **2** in 60−68% yield. Finally, the NHC ligands **3** were conveniently synthesized in 79−90% yield by reacting indazoles with CH_3I in CH_3CN at 80 °C (Scheme 1). Synthetic details and ligand characterization data are given in the Supporting Information.

Synthesis and Structure of Rh Indy-NHC Complexes. In an initial attempt, the reactions of $[Rh(COD)Cl]_2$ with the corresponding Indy-NHC (substitution of nitrogen with phenyl (**3a**) and *o*-tolyl (**3b**)) via a silver−carbene transfer method failed to yield products. Stirring **3a**,**b** with silver oxide for 30 min in CD_2Cl_2 at room temperature in the glovebox did not form stable silver complexes, as monitored by NMR spectroscopy. We hypothesized that a change in steric bulkiness on the aryl group (C ring, Scheme 2) might stabilize the desired Rh(I) complex. After replacing the substituted group with 2,6-dimethylphenyl (**3c**), we obtained the Rh Indy-NHC complex **4c** successfully without the isolation of the presumed silver carbene intermediate. Complex **4c** was isolated and characterized by NMR spectroscopy, and the signal of the ylidene carbon atom was observed at 196.49 ppm in the ^{13}C NMR spectrum.

We further explored the effect of different substituents on the phenyl ring on the coordination process. When the *para* position of ring C was substituted with a methyl group (**3d**), the reaction rate and yield remained the same as for **3c**. When the *para* position of ring C was substituted with halogens (**3e**,**f**), the silver carbene intermediates were inclined to precipitate. Thus, to obtain high yields of rhodium complexes **4e**,**f**, addition of $[Rh(COD)Cl]_2$ needed to be executed in 20 min after mixing Ag_2O and ligands **3e**,**f**. When ring C had two sterically bulky *i*Pr substituents at the 2,6-positions, the silver carbene intermediate was stable, and the corresponding metal complex **4g** was obtained in almost quantitative yield (93%).

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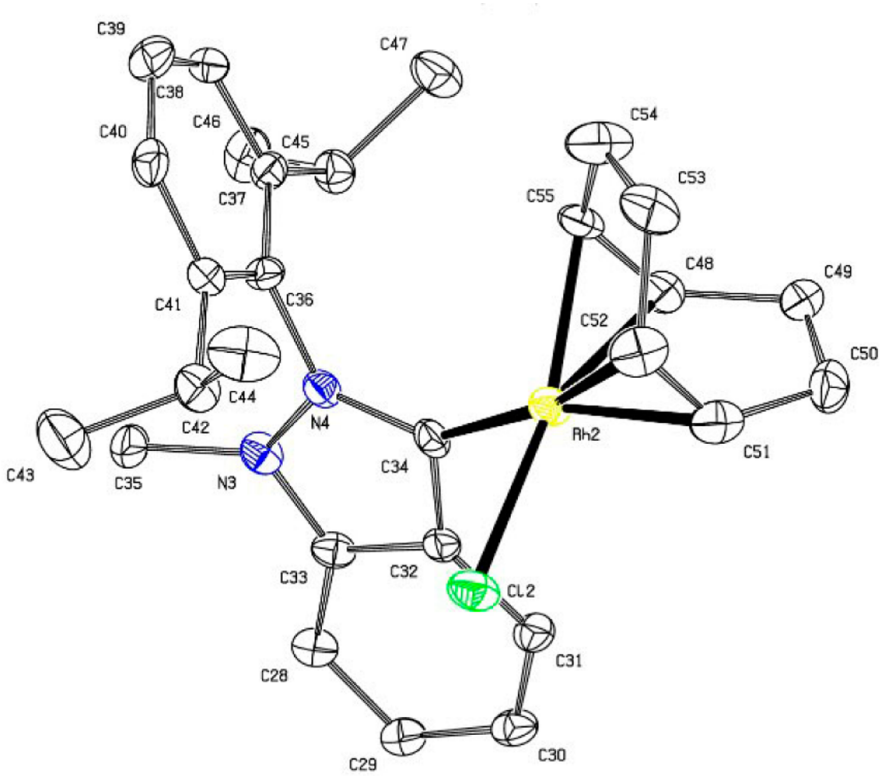
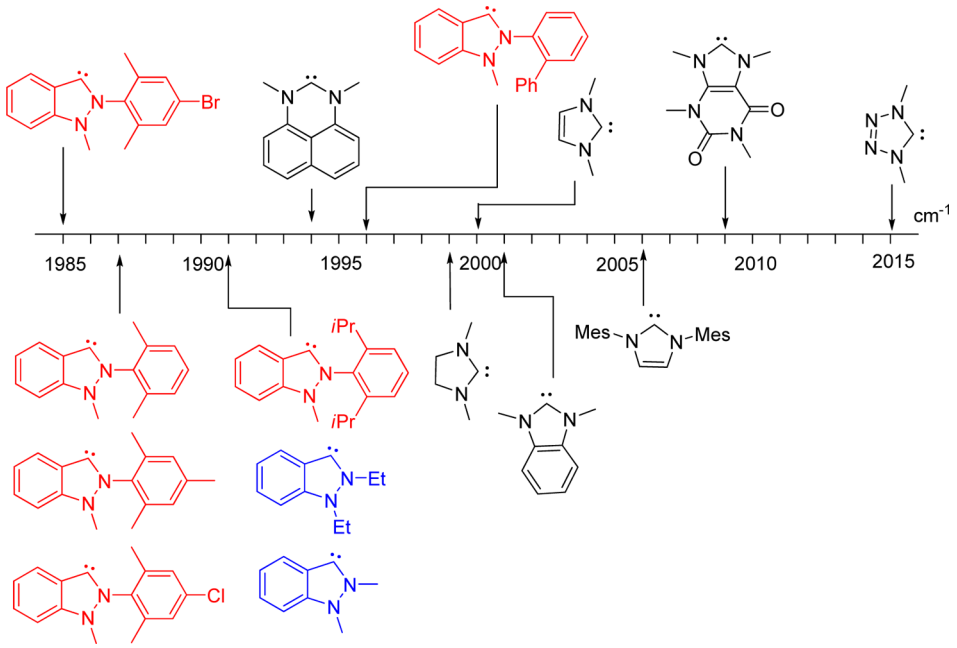


Figure 2. Molecular structure of complex **4g**. Hydrogen atoms are omitted for clarity.

Scheme 3. Comparison of Donating Abilities of Different NHC Ligands on the IR Scale



Interestingly, when the NHC precursor **3h** with iodine ion reacted with Ag_2O and then $[Rh(COD)Cl]_2$, a mixture of two complexes was observed with similar NMR resonance patterns. This phenomenon has been noted previously by Crabtree et al. and was assigned to a mixture of a chloride complex and an iodide complex.[13] An exchange of the iodide ion in compound **3h** with chloride ion by stirring compound **3h** with DOWEX 21K exchange resin for 12 h circumvented this problem. Subsequently Rh complex **4h** was obtained in pure form in 89% yield.

As depicted in Figure 2, the molecular structure of complex **4g** was confirmed by single-crystal X-ray analysis. Selected geometrical parameters of complex **4g** are as follows: Rh(2)–C(34) = 1.981(11) Å, Rh(2)–C(55) = 2.073(12) Å, Rh(2)–C(52) = 2.185(15) Å, Rh(2)–C(51) = 2.181(14) Å, Rh(2)–C(48) = 2.049(13) Å, and Rh(2)–Cl(2) = 2.374(4) Å. Bond lengths were in the expected range.[8]

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Synthesis of Rh−CO Indy-NHC Complexes and Comparison of Donating Abilities of Different Indy-NHC Ligands. Complexes **5** were easily prepared by treating complexes **4** with CO in CH_2Cl_2 at room temperature for 10 min, resulting in a quick substitution of the COD ligand by a CO ligand (Scheme 2).

The IR stretching frequencies of CO groups in the dicarbonyl rhodium complex $RhCl(CO)_2L$ are commonly used to assess the electronic properties of a given ligand L.[10,14,15] Normally a more donating ligand would result in a lower CO stretching frequency. Some reports used average values, while others compared the stretching frequencies of the *trans*-CO (ν_{asym}). To evaluate the donating abilities of these novel Indy-NHC ligands, complexes **4c−h** were converted to the corresponding carbonyl complexes **5c−h**. The stretching frequencies of these *trans*-CO ligands (1985−1996 cm^{-1}) were lower than those for most previously reported NHCs.[15] This observation indicated that this series of new ligands might have stronger donating abilities (Scheme 3). However, metal−CO stretching frequencies are not always accurate in measuring the donating capacity of the ligands. The $^{13}C_{carbene}$ signals of the complexes $RhCl(CO)_2L$ appeared at 183.00−183.35 ppm, which also showed that most of these ligands have stronger donating abilities than other NHCs.[8,15b]

Synthesis of the Pd Indy-NHC Complexes. The versatility of the Indy-NHC ligands was further demonstrated through transmetalation with $[Pd(allyl)Cl]_2$ to yield Pd^I complexes. However, the reaction of the NHC precursor of **3h** with both iodide ion and chloride counterion failed to give a stable Pd^I Indy-NHC complex by using the same route. Steric hindrance plays an important role in chelating with transition metals, and in our hands, more than one methyl group of R^1 or R^2 was needed to promote the formation of the desired complex.

As depicted in Figure 3, the molecular structure of complex **6g** was also unambiguously confirmed by single-crystal X-ray analysis. Selected geometrical parameters of complex **6g** are as follows: Pd(1)−C(6) = 2.035(3) Å, Pd(1)−Cl(8) = 2.353(9) Å, Pd(1)−C(30) = 2.094(3) Å, Pd(1)−C(20) = 2.111(5) Å, Pd(1)−C(21) = 2.181(6) Å, Cl(8)−Pd(1)−C(6) = 92.94(8)°. Bond lengths were in the expected range.[16]

Synthesis of an Au Indy-NHC Complex and Its Catalytic Application. The Indy-NHC ligands failed to react with $[AuCl(SMe_2)]$ by a silver carbene transfer method to give Au^I Indy-NHC complexes. One exception is for the ligand with *i*Pr (**3g**), which gave complex **7** in 94% yield (Scheme 4). The combination of steric bulkiness and strong electron donating ability of ligand **3g** might contribute to the successful formation of complex **7**.

Figure 4 shows the molecular structure of gold complex **7**. The Au(1)−C(7) (2.015(10) Å) and Au(1)−Cl(1) (2.285(3) Å) bond lengths were within the expected ranges.[9]

There have been several reports on cationic gold-catalyzed hydration of alkynes. The product α-hydroxyl methyl ketone skeleton has proven to be a useful building block in organic synthesis and natural products. It widely exists in biologically relevant molecules, such as cytochalasin, sesquiterpene, and secokotomolide.[17] The catalytic hydration of alkynes is an environmentally friendly and cost-effective synthetic method. However, most of the reported procedures required mineral acid as promoters or high temperature.[18] A simple, efficient, and stable catalyst is highly desired from a practical viewpoint. Herein we applied our air-stable gold Indy-NHC complex to

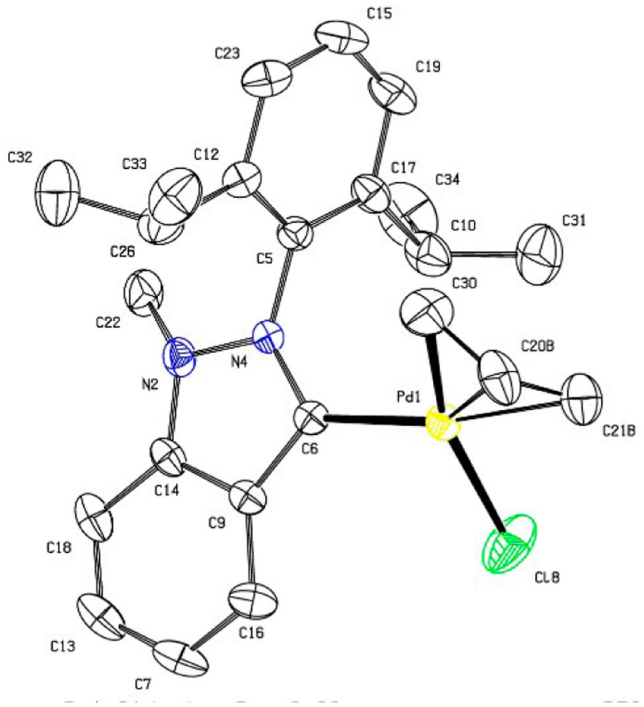
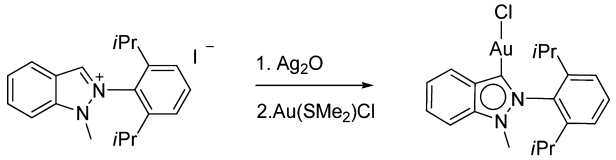


Figure 3. Molecular structure of complex **6g**. Hydrogen atoms are omitted for clarity.

Scheme 4. Synthesis of Au Complex 7



3g **7**

achieve an efficient catalytic hydration of alkynes. The reaction occurred at room temperature in air, affording products in high yields after a short reaction time.

We initiated our investigation on the model reaction of hydration of 1-phenylpropargyl ester using the gold Indy-NHC complex **7** as a catalyst. To optimize the reaction parameters, solvents and catalyst loadings were screened (Table 1). The CH_3CN/H_2O solvent mixture (40/1) provided the best results, giving the desired α-acetoxy ketone in nearly quantitative yield (96% isolated yield) (entry 9).

Interestingly, the amount of water had no obvious effect on the product yield (entries 8, 10, 7, and 11). As for the catalyst loadings, 3 mol % of NHC-Au complex/$AgSbF_6$ provided an excellent yield (95% isolated yield) (entry 12). However, the yield decreased to 70% when the catalyst loading was reduced to 1 mol % (entry 14). Taken together, we used the combination of 3 mol % of AuI Indy-NHC complex/$AgSbF_6$ and CH_3CN/H_2O (40/1) at room temperature as the optimized reaction conditions for this transformation.

With the optimized reaction conditions in hand, we next evaluated the scope of substrates. The results are summarized in Table 2. A series of substrates with different functional groups were examined; the products were isolated in moderate to excellent yield (83−99%, **9a−l**). The Au^I Indy-NHC complex catalyst was shown to be highly effective for this transformation. As shown, electron-withdrawing groups includ-

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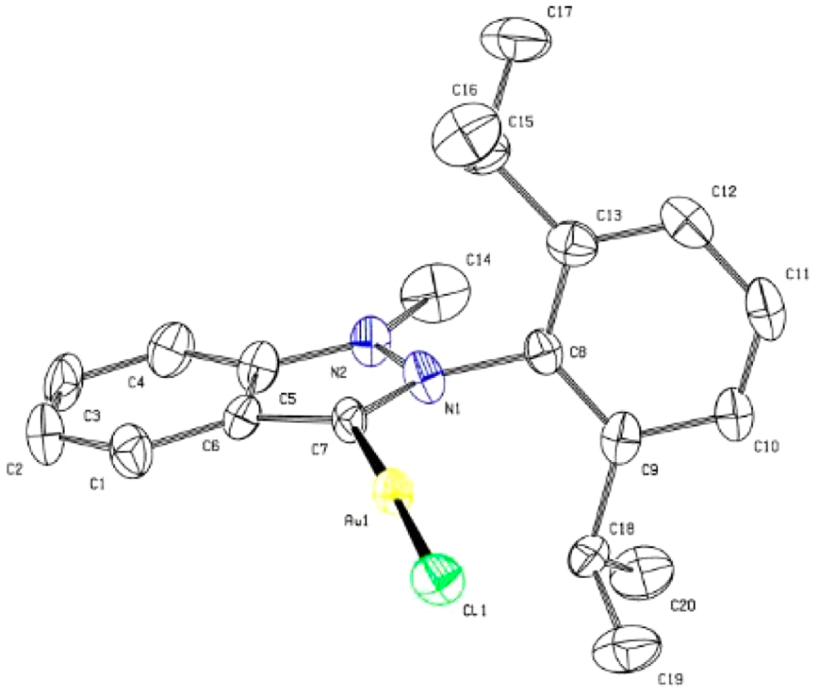
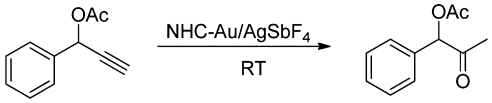


Figure 4. Molecular structure of complex **7**. Hydrogen atoms are omitted for clarity.

Table 1. Survey of Reaction Conditions



entry	solvent	amt of catalyst (mol %)	yield (%)
1	acetone/H_2O (20/1)	4	34[a]
2	dioxane/H_2O (20/1)	4	60[a]
3	DCM/H_2O (20/1)	4	trace[a]
4	THF/H_2O (20/1)	4	80[a]
5	MeOH/H_2O (20/1)	4	85[a]
6	DMF/H_2O (20/1)	4	51[a]
7	CH_3CN/H_2O (20/1)	4	90[a]
8	CH_3CN/H_2O (50/1)	4	83[a]
9	CH_3CN/H_2O (40/1)	4	99;[a] 96[b]
10	CH_3CN/H_2O (30/1)	4	92[a]
11	CH_3CN/H_2O (10/1)	4	62[a]
12	CH_3CN/H_2O (40/1)	3	95[b]
13	CH_3CN/H_2O (40/1)	2	80[b]
14	CH_3CN/H_2O (40/1)	1	70[b]

[a]GC yield. [b]Isolated yield.

ing halogen groups at the 4- or 3-positions on the aromatic ring gave the desired products in excellent yield (**9b**–**f**). Hydration of the terminal triple bond with an electron-poor *ortho* substituent on the aromatic ring of propargyl acetates also produced the corresponding ketones (**9g**–**j**) in excellent yields. Importantly, 1-(naphthalen-1-yl)prop-2-ynyl acetate substrate and an aliphatic ring derived ester were also examined and afforded the expected product in good yields (83% yield of **9k**, 86% yield of **9l**, respectively).

CONCLUSION

In summary, we have reported the synthesis of a serial of new Indy-N-heterocyclic carbene ligands with strong donating ability. Utilizing these ligands, we synthesized a novel series of rhodium/palladium/gold Indy-NHC complexes. All complexes have been fully characterized and molecular structures of representative examples were determined by X-ray diffraction analysis. Among them, the isopropyl-substituted ligand (**3g**) not only coordinated with rhodium and palladium but also reacted with the gold salt to form an air-stable Au^I Indy-NHC complex in high yield. Finally, the gold *i*Pr-NHC complex showed high activity in catalyzing the hydration of alkynes (83–99%). Further studies on tuning the properties of these types of N-heterocyclic ligands and other transition-metal carbene complexes are in progress.

EXPERIMENTAL SECTION

All solvents were distilled under N_2 before use and were stored in a drybox. All chemicals were purchased and used without any further purification unless otherwise specified. Column chromatography was performed on 200–300 mesh silica gel (Qingdao Haiyang Chemical). Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Melting points (mp) were determined on a DR-2 MP apparatus (New Skylight Corp., Tianjin, People's Republic of China). ^1H NMR and ^{13}C NMR data were obtained on a Bruker 400 MHz nuclear resonance spectrometer unless otherwise specified. The chemical shifts are given as dimensionless δ values and are referenced relative to TMS. Gas chromatographs were recorded on a Shimadzu GC-2014 spectrometer. HRMS spectra were obtained in ESI mode and performed by The Analytical Instrumentation Center at Peking University Shenzhen Graduate School.

Synthesis and Characterization of 1g. A mixture of 2-nitrobenzaldehyde (2.30 g, 15.2 mmol) and 2,6-diisopropylaniline (1.2 equiv.) was stirred at 90 °C for 3 h and then cooled to room temperature. Ethanol (10 mL) was added to the reaction mixture, and the solution was placed in a refrigerator overnight for recrystallization. The resulting precipitate was filtered and washed with 3 × 4 mL of cold ethanol to give a yellow solid. Yield: 93%. Mp: 67–68 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.34 (dd, J = 7.8, 1.4 Hz, 1H), 8.13 (dd, J = 8.2, 1.1 Hz, 1H), 7.80 (m, 1H), 7.68 (m, 1H), 7.17 (m, 3H), 3.03 (m, 2H), 1.22 (d, J = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.22, 149.34, 148.31, 137.52, 133.77, 131.35,

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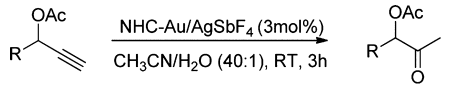
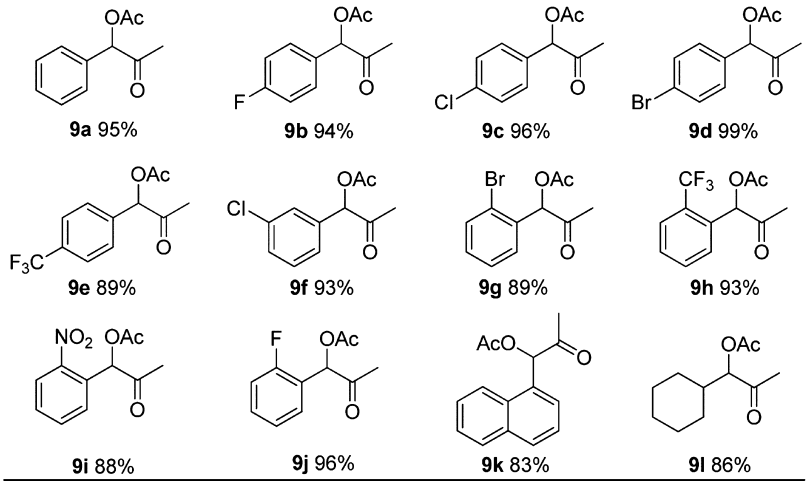
Table 2. Au^{I} Indy-NHC Complex Catalyzed Hydration of Alkynes[a]





[a]Reaction conditions: 3% catalyst, 0.5 M substrate in CH_3CN/H_2O (40/1) at room tempertaure for 3 h. Isolated yields are given.

131.04, 129.70, 124.77, 124.59, 123.14, 27.95, 23.50. HRMS (ESI^+): 311.1755; calcd mass for $[C_{19}H_{23}N_2O_2]^+$ 311.1760.

Synthesis and Characterization of 2g. Compound **1g** (10 mmol) and triethyl phosphate (10 equiv) were loaded into a 100 mL sealed tube and stirred at 160 °C for 12 h. The solvent was then removed under reduced pressure. The residue obtained was purified by silica gel chromatography to give **2g** as a white solid. Yield: 68%. Mp: 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.38 (dd, J = 11.6, 3.8 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.19 (m, 1H), 2.18 (m, 2H), 1.16 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.88, 146.15, 137.13, 130.17, 126.12, 125.67, 123.51, 122.09, 121.64, 120.38, 118.21, 28.20, 24.65, 24.02. HRMS (ESI^+): 279.1837; calcd mass for $[C_{19}H_{23}N_2]^+$ 279.1861.

Synthesis and Characterization of 3g. An excess of CH_3I (5 equiv) was added to a solution of compound **2** (1 mmol) in CH_3CN, and the reaction mixture was stirred at 80 °C for 5 h. The solvent was then removed under reduced pressure. The residue was subsequently washed with diethyl ether (3 × 2 mL) to give **3g** as a yellow solid. Yield: 90%. Mp: 195−197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 8.50 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.94 (m, 1H), 7.71 (t, J = 7.9 Hz, 1H), 7.56 (m, 1H), 7.43 (d, J = 7.9 Hz, 2H), 4.11 (s, 3H), 1.92 (dd, J = 13.6, 6.8 Hz, 2H), 1.18 (dd, J = 6.6, 5.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.00, 140.76, 135.66, 135.27, 134.16, 127.55, 126.45, 125.55, 124.62, 119.88, 112.13, 35.32, 29.09, 25.33, 23.04. HRMS (ESI^+): 293.2025; calcd mass for $[C_{20}H_{25}N_2]^+$ 293.2012.

Synthesis and Characterization of Rhodium Complex 4g. A mixture of Ag_2O (0.06 mmol, 14 mg) and compound **3g** (50 mg, 0.12 mmol) in anhydrous CH_2Cl_2 was stirred at room temperature in the dark under an argon atmosphere for 90 min. $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was then added to the mixture, which was then stirred for another 3 h to give the yellow solid complex **4g**. Yield: 93%. Mp: 198−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, J = 8.1 Hz, 1H), 7.62 (m, 2H), 7.51 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.24 (m, 3H), 5.15 (s, 1H, COD_{vinyl}), 4.90 (s, 1H, COD_{vinyl}), 3.59 (s, 1H, COD_{vinyl}), 3.41 (s, 3H), 2.86 (s, 1H, COD_{vinyl}), 2.39 (d, J = 37.2 Hz, 2H), 2.08 (s, 2H), 1.72 (m, 6H), 1.14 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.64 (d, J(Rh−C) = 45 Hz, $C_{carbene}$),148.68, 146.88, 141.38, 132.83, 132.00, 131.89, 131.10, 125.45, 123.80, 122.29, 109.23, 98.29 (CH of COD), 97.05 (CH of COD), 67.71 (CH of COD), 34.49 (NCH_3), 33.79 (CH of COD), 32.06 (CH of COD), 29.05 (CH_2 of COD), 28.321 ($C(CH_3)_2$), 28.21 (CH_2 of COD),26.34 (CH_2 of COD), 25.18 (CH_3), 24.64 (CH_3), 23.60 (CH_2 of COD).

Synthesis and Characterization of Rh−CO Complex 5g. Carbon monoxide was bubbled in a suspension of complex **4g** (20 mg) in CH_2Cl_2 (2 mL) for 10 min at room temperature. The solvent was subsequently removed under reduced pressure. The resulting residue was washed with hexane or ether to give complex **5g** as a yellow solid. Yield: 89%. Mp: 197−198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 7.8 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.38 (m, 3H), 3.58 (s, 3H), 2.48 (m, 2H), 1.36 (d, J = 6.3 Hz, 6H), 1.11 (d, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.51(d, J(Rh, C_{co}) = 39 Hz, CO), 185.64(d, J(Rh−C_{CO}) = 52 Hz, CO), 183.35(d, J(Rh−C) = 75 Hz, $C_{carbene}$), 147.41, 140.83, 132.83, 132.65, 131.95, 131.63, 131.20, 125.05, 122.79, 109.04, 34.44, 28.41, 24.85, 24.50. FT-IR (CH_2Cl_2): $\nu(CO_{sym})$ 2066 cm^{-1} (s) and $\nu(CO_{asym})$ 1991 cm^{-1} (s).

Synthesis and Characterization of Palladium Complex 6g. A mixture of Ag_2O (0.06 mmol, 14 mg) and complex **3g** (50 mg, 0.12 mmol) in anhydrous CH_2Cl_2 was stirred at room temperature in the dark under an argon atmosphere for 90 min. $[Pd(allyl)Cl]_2$ (0.06 mmol, 22 mg) was then added to the mixture, which was then stirred for another 3 h to give complex **6g** as a yellow solid. Yield: 94%. Mp: 205−207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 8.2 Hz, 1H), 7.67 (m, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.34 (m, 4H), 5.08 (m, 1H), 4.22 (dd, J = 7.6, 1.4 Hz, 1H), 3.56 (s, 3H), 3.18 (d, J = 13.7 Hz, 1H), 2.85 (d, J = 6.5 Hz, 1H), 2.69 (m, 1H), 2.39 (m, 1H), 1.74 (d, J = 11.8 Hz, 1H), 1.38 (d, J = 6.7 Hz, 3H), 1.29 (d, J = 6.7 Hz, 3H), 1.12 (dd, J = 11.4, 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.85, 147.43, 140.95, 133.83, 132.12, 131.46, 131.42, 124.68, 122.12, 114.77, 109.00, 73.52, 48.53, 34.40, 28.25, 24.73, 24.42, 24.10.

Synthesis and Characterization of Gold Complex 7. Ag_2O (0.06 mmol, 14 mg) and complex **3g** (50 mg, 0.12 mmol) were dissolved in anhydrous CH_2Cl_2, and the mixture was stirred at room temperature in the dark under an argon atmosphere for 90 min. $[AuCl(SMe_2)]$ (0.12 mmol, 36 mg) was then added to the mixture, which was then stirred for another 3 h to give complex **7** as a yellow solid. Yield: 94%. Mp: 289−291 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.37 (dd, J = 14.7, 7.8 Hz, 3H), 3.65 (s, 3H), 2.13 (m, 2H), 1.31 (d, J = 6.7 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.72, 146.72, 139.65, 133.05, 132.32, 132.06, 129.93, 128.87, 124.93, 123.00, 109.18, 33.36, 28.67, 24.96, 23.20.

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X-ray Diffraction Studies. All measurements were made on a Rigaku Saturn70 CCD diffractometer using graphite-monochromated Cu Kα radiation. Data were collected and processed using CrystalClear (Rigaku). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods[19] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[20] crystallographic software package, except for refinement, which was performed using SHELXL-97.[19]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving crystallographic data for complexes **4g** (CCDC 929101), **6g** (CCDC 929102), and **7** (CCDC 929103), ^{1}H and ^{13}C NMR and high-resolution mass spectral data and spectra of compounds **1**−**3** and **9** and complexes **4**−**7**, and experimental details, including experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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