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A Gold(I) Complex Based on 1,8-Naphthyridine Functionalized *N*-Heterocyclic Carbene (NHC) and Its Catalytic Activity

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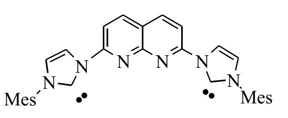
A gold complex containing 2,7-bis(mesitylimidazolylidenyl)naphthyridine (**NHC-NP**) has been synthesized. Thus, reaction of [{Ag_3(**NHC-NP**)$_2$}$(PF_6)_3$] with [Au(Me_2S)Cl] provided an unusual digold complex bridged by two **NHC-NP**, forming a 20-membered dinuclear metallacycle [{Au_2(**NHC-NP**)$_2Cl_2$}-$(PF_6)_2$] (**2**) in high yield. This complex was characterized by spectroscopic and elemental analysis. This gold complex is active for the hydrolysis of 2,2,5-trimethyl-1,3-dioxane-5-methanol and can be recycled without losing the activity.

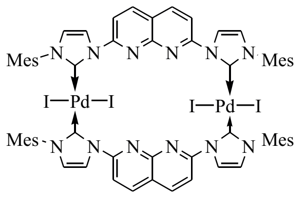
Keywords: Gold; Heterocyclic carbene; Naphthyridine; Hydrolysis; Acetal.

INTRODUCTION

Nowadays *N*-Heterocyclic carbenes (NHCs) are relatively common donors for various transition metal ions owing to its strong σ-donating ability.[1] Analogous to phosphines, design and investigation of NHC chelating molds have received much attention because they allow to prepare a variety of geometrical complexes.[1-3] As part of our ongoing research project on the coordinating capability of polydentates containing NHC donors toward transition metal ions, we have described the preparation of the palladium complex **1** containing a bis(*N*-heterocyclic carbene)-naphthyridine (**NHC-NP**) ligand and its catalytic activity on Kumada coupling reactions.[3] In this work, we would like to illustrate the coordination chemistry of **NHC-NP** toward Au(I) ions and the catalytic activity of the resulting complex.



NHC-NP



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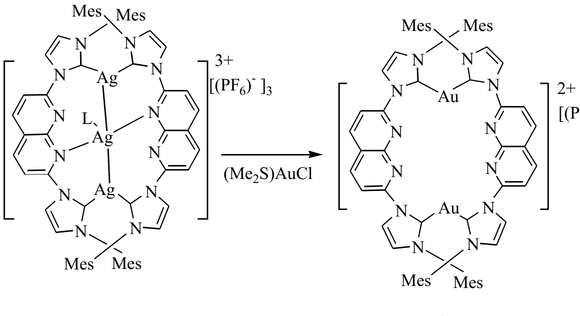
RESULTS AND DISCUSSION

Preparation of the Gold Complex 2

Silver NHC complex **3** was prepared according to the reported procedure.[4] Reaction of **3** with [(Me_2S)AuCl] in anhydrous dichloromethane generated the air-stable digold complex (Eq. 1). Complex **2** was isolated as a light yellow microcrystalline solid in 85% yield and fully characterized by NMR spectroscopies and elemental analysis. The ESI-HRMS exhibits a molecular ion signal with *m/z* = 695.2194 that is consistent with the formula of $[C_{64}H_{60}N_{12}Au_2]^{2+}$ (Calcd. 695.2197). This information clearly demonstrates the structure **2** which is in a coordination mode with two metal ions with two NHC-NP ligands. In addition, The molar conductivity of the complex in methanol ($\Lambda_M \sim 170\ cm^2\ \Omega^{-1}\ mol^{-1}$) is consistent with formation of a 2:1 electrolyte, suggesting that the complex might be dissociated into $[Au_2(bpnp)_2]^{2+}$ and $2(PF_6)^-$.



3, L= CH_3CN **2**

(1)

The ^{1}H NMR spectrum of **3** shows five sets of signals in the aromatic region (two from naphthyridine, two from imidazole and one from mesityl group), which permits us to establish the symmetrical structure in the molecule. The ^{13}C NMR spectrum of **2** also shows only one resonance for the carbene carbons at δ 186.3, which is in the normal range for Au-NHC complexes. These observations evidence the symmetrical nature of the naphthyridine-NHC liagnd in

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Dedicated to the memory of Professor Yung-Son Hon (1955–2011).

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this gold complex. In addition, comparison of the NMR shifts between **2** and the palladium analog **1** can tell the similar structural features between two compounds.[3]

Stability of the Gold Complex 2

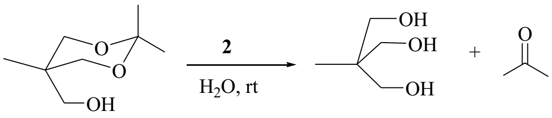
Complex **2** is stable toward air and water. In order to investigate further about the stability of Au-C$_{(carbene)}$ bonds, this digold complex was subjected to react with trifluoroacetic acid. The reaction of **2** with excess of CF_3COOH in $CDCl_3$ in a sealed NMR tube was monitored by ^1H NMR spectroscopy. Complex **2** remained retained in the solution of $CF_3COOH/CDCl_3$ over a temperature range (r.t to 50 °C) even for a longer period, indicating that Au-C$_{carbene}$ bond is stable toward acid.

It is documented that reaction of diamino-substituted carbenes with sulfur yields the corresponding thiourea.[5] We have found that some NHC copper complexes react with sulfur to yield the corresponding thiourea. Reactivity of **2** with sulfur was investigated to probe the stability of Au-C$_{carbene}$ bond. Treatment of **2** with excess of sulfur in refluxing acetone did not cause any decomposition of **2** with recovery of **2**.

The coordination ability of phosphine toward Au(I) ions is fairly strong. However, the NHC moiety on the gold center cannot be replaced by phosphines. Under refluxing conditions, complex **2** did not undergo ligand substitution with excess of triphenylphosphine even for a prolong heating. From these observations, the NHC moiety is stable toward oxidation with sulfur or aerial oxygen, acidic cleavage, and ligand substitution with phosphines. In all instances, the NHC moiety remains intact, again demonstrating the good strength of Au-C$_{NHC}$ bond.

Catalysis

According to the coordination behavior presented above, it would be interesting to test the catalytic activity of **2**. Quite a number of reports have demonstrated that NHC-Au are good catalysts for C-H activation, alkyne hydration and polymerization.[6] Among this context, the catalytic active NHC-Au species responsible for these catalysis are limited to those with the formula of [(NHC)AuL], i.e. the mono NHC substituted complexes. We have screened the catalytic activity of **2** toward alkyne hydration and polymerization, but complex **2** shows no activity at all. This is presumably due to the shortage of the coordination site for catalysis. However, we found that the complex **2** is active for the hydrolysis of 2,2,5-trimethyl-1,3-dioxane-5-methanol (**4**) in aqueous medium (Eq. 2).



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(2)

In a typical experiment for the reaction, acetal **4** (0.1 mmol) and complex **2** (0.005 mmol) in water (1 mL) were placed in the flask with stirring at room temperature for 6 h. The complex **2** was separated by extraction with dichloromethane and then analyzed by ^1H NMR spectroscopy. The spectral data of the extracted product are essentially identical to those of complex **2**, showing that this complex is stable under the catalytic reaction. Furthermore, it can be reused as the catalyst for the hydrolysis of **4**. We have learned that complex **2** remains the same activity after five cycles.

To the best of our knowledge, there is no precedent report concerning $[(NHC)_2Au]^+$ species as catalysts on the hydrolysis of acetals. NHCs are known to be strong donating ligands and do not dissociate from the metal centers. Thus the species of $[(NHC)_2Au]^+$ species acts as a Lewis acid for catalyzing the hydrolysis of acetals. Certainly, the hydrophobic effect of the catalyst in aqueous solution might also play a role in this hydrolysis particularly for the homogeneity of this reaction medium.[7] Due to the strong bonding strength in Au-C bonds, complex **2** is stable under catalytic conditions.

In summary, we have successfully prepared and characterized a new dinuclear gold(I) complex containing a bis(*N*-heterocyclic carbene)naphthyridine ligand. This dinuclear bis-NHC complex **2** appears fairly stable toward oxidants and acids. Moreover, complex **2** shows an excellent reactivity on the hydrolysis of 2,2,5-trimethyl-1,3-dioxane-5-methanol.

EXPERIMENTAL

General information

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on either a Bruker AM-300 or a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR. All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassed process. Silver carbene complex **3** were prepared accordingly to the method reported previously.[4]

Complex 2

A mixture of **3** (196 mg, 0.13 mmol) and [(Me_2S)AuCl] (80 mg, 0.27 mmol) in a flask capped with a septum was evacuated and flashed with nitrogen. Anhydrous CH_2Cl_2 (5 mL) was syringed into the above flask and the resulting mixture was stirred at room temperature for 6 h. The reaction mixture was then filtered through Celite to remove silver salts. The filtrate was concentrated and the residue was chromatographed on silica gel with elution of CH_2Cl_2. Upon concentration, the desried complex was obtained as light-yellow solids (187 mg, 85 %): ^{1}H NMR (400 MHz, d_6-acetone) δ 2.00 (s, $C_6H_2(CH_3)_3$, 24H), 2.41 (s, $C_6H_2(CH_3)_3$, 12H), 7.10 (s, $C_6H_2(CH_3)_3$, 8H), 7.70 (d, J = 2.0 Hz, NCHCHN, 4H), 8.24 (d, J = 8.7 Hz, naphthyridine, 4H), 8.30 (d, J = 2.0 Hz, NCHCHN, 4H), 8.39 (d, J = 8.7 Hz, naphthyridine, 4H); ^{13}C NMR (100 MHz, d_6-acetone) δ 17.9, 21.3, 117.9, 121.8, 122.9, 125.2, 130.3, 135.7, 136.2, 140.5, 141.4, 152.6, 153.7, 186.3 ($C_{carbene}$); $^{31}P\{^1H\}$ (161.9 MHz, d_6-acetone) δ -144.2 (sept, $J_{P\text{-}F}$ = 705.8 Hz); ESI-HRMS calcd. for $[C_{64}H_{60}N_{12}Au_2]^{2+}$: m/z = 695.2197; found m/z = 695.2194; Anal. Calcd for $C_{64}H_{60}Au_2F_{12}N_{12}P_2$: C, 45.73; H, 3.60; N, 10.00. Found: C, 45.33; H, 3.36; N, 9.83.

ACKNOWLEDGEMENTS

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