Journal of Molecular Catalysis A: Chemical 340 (2011) 53–59

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Catalytic activities and properties of Au(III)/Schiff-base complexes in methanol oxidative carbonylation

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ARTICLE INFO

Article history:
Received 22 October 2010
Received in revised form 15 March 2011
Accepted 16 March 2011
Available online 23 March 2011

Keywords:
Homogeneous gold catalysis
Schiff base complex
Oxidative carbonylation
Methanol

ABSTRACT

Several Au(III)/Schiff-base complexes were studied and proven to be effective catalysts for oxidative carbonylation of methanol to generate dimethyl carbonate (DMC). Effects of Schiff-base ligands, promoters, and promoter mole ratio to Au(III)/Schiff-base complexes on catalytic activity were studied. When the reaction was carried out at a methanol/Au(III) molar ratio of 5060:1, an $[AuCl_2(phen)]Cl/KI$ (phen = 1,10-phenanthroline) ratio of 1:4, a CO/O_2 pressure of 2:1, and a temperature of 120 °C for 3 h, the conversion, selectivity, and TOF value of the model reaction were 10.8%, 98%, and 138.9 h^{-1}, respectively. The catalyst was characterized by FTIR, UV–vis, ^1H NMR, and cyclic voltammetry. The oxidation state of gold during the reaction and the role of KI were discussed using data on electrochemical experiments and ESI-MS. $[AuI_2(phen)]^+$ was considered an intermediate in the reaction. A plausible Au(III)/Au(I) catalytic cycle mechanism was proposed.

1. Introduction

The application of gold in catalysis has long been neglected due to the preconceived notion that gold is chemically inert. Due to the pioneering studies of Haruta and other researchers, extraordinarily good catalytic activities were observed with gold for low-temperature CO oxidation [1] and hydrochlorination of ethyne [2] in the 1980s. Since then, catalysis with gold has gained much attention [3], and many successful examples have shown that gold catalysts can indeed be applied to several fields of heterogeneous catalysis, such as oxidation reactions [4,5] water-gas shift reactions [6], and in many fields of homogeneous catalysis (i.e., e.g., carbon–carbon bond forming reactions [7], hydration of alkynes [8], hydrogenation [9], and carbonylation of olefins or aliphatic diamines [10,11]). However, despite the fact that exploration of gold in catalysis has recently surged to unprecedented levels compared with other commonly used noble metal catalysts, the generality and applicability of gold in catalysis remain relatively limited. In particular, while the effectiveness of gold in heterogeneous catalysis has been well- recognized, far less efforts has have been spent on studies regarding homogeneous gold complexes [12].

Recently, Corma reported Au-catalyzed Suzuki and Sonogashira reactions of arylhalide where the oxidation of Au(I) to Au(III) was involved [13,14]. Alternatively, external oxidants have been employed to oxidize Au(I) to Au(III), leading to dimerizations. Zhang developed the first example of C–C bond forming cross-coupling reactions, leading to the one-step synthesis of R-arylenones in combination with Au(I) oxidation. These examples not only incorporate Au(III)/Au(I) catalytic cycles into contemporaneous gold chemistry but also promise a new area of gold chemistry by merging powerful gold catalysis and oxidative metal-catalyzed cross-coupling reactions [15,16]. These promising results also demonstrate the feasibility of designing a homogeneous system with Au(III)/Au(I) catalytic cycles that facilitate reaction mechanism studies and permit systematic modification of gold catalysts to improve reaction scope and efficiency [17].

Oxidative carbonylation of methanol catalyzed by a metal complex is a typical model reaction in the field of homogeneous catalysis. Recently, some promising results have been achieved in the oxidative carbonylation of alkyl alcohol [18–20], aniline [21], and phenol [22] using Cu, Co, and Pd complexes as catalysts. We considered the Au(III) complexes to be catalytically active in the oxidative carbonylation of methanol due to the following reasons: (1) gold is located in the same group as Cu in the periodic table of elements, allowing homogeneous Au complexes to exhibit similar properties as Cu; and (2) the electronic configuration of Au(III) is very similar to that of Pd(II). In this study, we presented the successful outcome of this endeavor where Au(III)/Shiff-base complexes were used as catalysts for the oxidative carbonylation of methanol to DMC with the aid of KI (Scheme 1). Some insights into this

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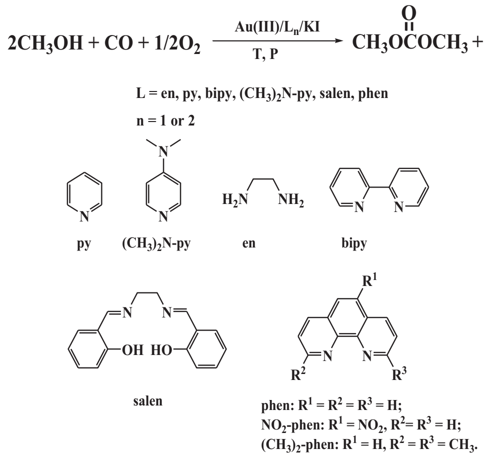
doi:10.1016/j.molcata.2011.03.008



Scheme 1. Oxidative carbonylation of methanol and gold catalysts.

catalytic reaction (i.e., shift of oxidation state of gold species during the reaction and the role of KI) were discussed. A plausible Au(III)/Au(I) catalytic cycle mechanism was also proposed.

2. Experimental

2.1. Materials and characterization

The 1,10-phenanthroline monohydrate (phen·H_2O), 2,2-bipyridine, pyridine, $HAuCl_4·4H_2O$, KI, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), acetonitrile, anhydrous methanol, and anhydrous ethanol were analytically pure reagents. They were used as received.

2.2. Synthesis of Au(III)/Schiff-base complexes

In the general catalyst synthesis [23,24], an ethanol solution of phen (10 mL, 0.96 M) was added to an ethanolic solution of 1.0 g $HAuCl_4$ (10 mL) under stirring. The mixture was stirred for 4 h under reflux conditions. At the end of the reaction, a large amount of yellow or orange solid was formed. After filtration, washing with ethanol (3× 5 mL), and drying in air, $AuCl_2$(phen)]Cl was obtained with 95% yield, showing the following elemental composition: C, 29.62%; H, 1.72%; N, 5.68%; $AuCl_3C_{12}H_8N_2$ requires C, 29.79%; H, 1.67%; N, 5.79%; ^{1}H NMR (DMSO-d_6, δ, ppm): 9.70 (d, 2H), 9.34 (d, 2H), 8.52 (s, 2H), 8.44 (m, 2H); IR (KBr, cm^{-1}): 1637 (s), 1582 (s), 1513 (m), 1485 (m), 1413 (s), 1218 (m), 853 (m), 703 (s) cm^{-1}; and UV–vis: $\lambda_{max}(CH_3OH)$/nm: 230, 280, 317.

2.3. Oxidative carbonylation of methanol

All reactions were conducted in a 100 mL stainless steel autoclave equipped with a mechanical stirrer, polytetra-fluoroethylene (PTFE) liner, and an automatic temperature controller according to the procedure reported in the literature [18,19]. Typically, 0.15 mmol Au(III) complex and 30 mL anhydrous methanol (0.74 mol) were charged into the autoclave. The autoclave was then pressurized with CO/O_2 at room temperature. During the reaction, the total pressure was maintained at 3.0 MPa by the regular addition of CO. After the reaction, the liquid mixture was evaporated, and the obtained distillate was analyzed by gas chromatography (GC) with a flame ionization detector and an HP-5 capillary column.

Safety advice: Although oxidative carbonylation of methanol has been industrialized by ENI chem for 30 years [25] and no security incident has been reported up to date, high-pressure carbonylation experiments with compressed gases represent a significant safety risk and should only be conducted in conjunction with the use of suitable equipment and special care.

2.4. Catalyst characterization

FTIR spectra in KBr pellets were recorded with a Bruker Equinox 55 FTIR spectrophotometer in the range of 4000–400 cm^{-1}. The UV–vis spectra were measured with a Shimadzu UV-2550 PC UV–vis spectrophotometer in the range of 800–200 nm. The C, H, and N elemental analyses were carried out on a Vario ELIII Elemental Analyzer. ^{1}H NMR spectra were obtained using a Bruker AV 400 spectrometer in DMSO-d_6, with tetramethylsilane as the internal standard. ESI-MS spectra were recorded using Agilent 1100 LC/MSD Trap XCT.

Cyclic voltammetry measurement was performed in acetonitrile using tetrabutylammonium tetrafluoroborate (Bu_4NBF_4, 0.1 M = 0.1 mol L^{-1}) as supporting electrolyte using the Electrochemical Workstation CS300 at room temperature. A conventional three-electrode system was employed. A Pt coil served as a working electrode, and a large Pt foil was used as a counter electrode. A commercial saturated calomel electrode (SCE) was utilized as the reference electrode. Current–voltage curves were measured at 50 mV s^{-1}. All potentials were reported in volts versus SCE. The gold complex concentration was 1–3 mM. All measurements were performed in well-deaerated solutions under nitrogen atmosphere. Cyclic voltammetry on the blank solution of Bu_4NBF_4 showed no electrochemical activity between −1.5 and 1.5 V.

Table 1
Catalytic performance of different catalysts in oxidative carbonylation.[a]

Entry	Catalysts	Promoter	Substrate/catalyst (mol)	Conversion (%)[b]	Selectivity (%)[c]	TOF (h^{-1})[d]
1	$HAuCl_4$	–	5060	–	–	–
2	$HAuCl_4$	–	2500	–	–	–
3	$AuCl_3$(py)	–	5060	0.6	93.2	7.4
4	$AuCl_3$(py)	KI	5060	1.8	95.1	23.2
5	$[Au(en)_2]Cl_3$	KI	5060	4.7	92.9	60.5
6	$[AuCl_2$(salen)]Cl	KI	5060	4.6	91.6	59.2
7	$[AuCl_2$(bipy)]Cl	KI	5060	5.5	95.9	70.8
8	$[AuCl_2$(phen)]Cl	KI	5060	10.8	98.5	138.9
9	$AuCl_3((CH_3)_2$N-py)	KI	5060	8.8	97.5	113.2
10	$[AuCl_2(NO_2$-phen)]Cl	KI	5060	Trace	–	–
11	$[AuCl_2((CH_3)_2$-phen)]Cl	KI	5060	6.3	96.4	81.1

[a] Reaction conditions: methanol, 30 ml; KI, 0.586 mmol; P_{total} = 3.0 MPa ($P_{CO}/P_{O_2} = 2$); 120 °C; 4 h; stirring speed, 850 rpm.
[b] Conversion of methanol.
[c] Selectivity to DMC.
[d] TOF (mol converted methanol/mol catal. h).

Table 2
Catalytic performance of $[AuCl_2(phen)]Cl$ with different halide promoters.[a]

Entry	Promoter (mmol)	Promoter/Au (mol ratio)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	No	No	Trace	–	–
2	KCl	4	Trace	–	–
3	KBr	4	1.8	92.3	23.2
4	CH_3I	4	4.9	94.7	63.1
5	I_2	2	5.2	96	66.9
6	KI	2	5.2	97.2	66.9
7	KI	4	10.8	98.5	138.9
8	KI	8	2.3	96.7	29.6

[a] Unless otherwise specified, all reactions were carried out under the following conditions: Au(III) complexes, 0.02 mol % of methanol; methanol, 30 mL; $P_{total} = 3.0$ MPa ($P_{CO}/P_{O_2} = 2:1$); 120 °C; 4 h; stirring speed, 850 rpm.

3. Results

3.1. Catalytic studies

Initially, different gold complexes were used as catalysts for the oxidative carbonylation of methanol. The results are summarized in Table 1. First, the gold species, $HAuCl_4$, was employed for this reaction; however, its activity was poor, and no DMC was detected (Table 1, entries 1 and 2). In this case, tiny gold particles were formed in the reaction, indicating the susceptibility of $HAuCl_4$ under these reaction conditions. Recently, Hashmi and colleagues [26] used some gold complexes to catalyze the transformation of alkynes to phenols, and they observed that pyridine gold complexes showed better results than the others. Cinellu et al. [27] reported the use of an Au(III)/bipyridine complex for performing the oxidation of cyclic alkenes. Inspired by these reports, we attempted to use Shiff-base ligands to stabilize gold ion. In the first instance, $AuCl_3(py)$ was used (Table 1, entry 3), obtaining 0.6% of methanol conversion and 93.2% selectivity to DMC. More importantly, the TOF value reached 7.4 h^{-1}, which was higher than that in our previous research on the oxidative carbolylation of methanol using Cu-based catalysts [18,19]. Au(III) is unstable and can be easily reduced to gold metal in the presence of carbon monoxide. However, in the oxidative carbonylation of methanol catalyzed by $AuCl_3(py)$, a clear solution was obtained at the end of the reaction. This result implies that no Au(0) was formed in the presence of nitrogen-containing ligands. Based on the literature survey, nitrogen-containing ligand provides a very good means of stabilizing Cu(I), and it has been used as a multi-functionalized promoter for carbonylation reactions [18].

Despite the low conversion of methanol at this stage, it is undoubtedly an important hint that gives us impetus to investigate further the performance of the gold complex in oxidative carbonylation of methanol. When KI was used as a promoter in the $AuCl_3(py)$-catalyzed reaction, a considerable improvement in terms of reaction rate and TOF value was observed under the same reaction conditions (Table 1, entry 4). In order to improve carbonylation performance, the other components involved in this system were then optimized. The screening of ligands revealed that $[AuCl_2(phen)]Cl$ is the best catalyst. Under an optimal condition, the methanol conversion and selectivity to DMC reached 10.8% and 98.5%, respectively. TOF value reached as high as 138.9 h^{-1} when the reaction was performed under a very high molar ratio of methanol to catalyst (Table 1, entry 8). This value is 19 times higher than that obtained using the initial catalyst $AuCl_3(py)$. In particular, the effects of the ligands on the gold catalysts were studied. As shown in Table 1, the promotional effect of various ligands on the activity increases in the following order: py < en ≈ salen < bipy < phen (Table 1, entries 4–8). The complex $AuCl_3((CH_3)_2N\text{-}py)$ exhibits better activity than $AuCl_3(py)$ (Table 1, entry 9). This can be ascribed to the nucleophilicity of the dimethylamino group that increases the electron density of the nitrogen atom in the pyridyl ring, consequently enhancing the coordination ability of this ligand to the Au(III) center. The significant effects of the ligand substituent can be demonstrated by the fact that only trace amounts of the product was obtained using a 1,10-phenanthroline derivative containing an electron-withdrawing group, 5-nitro-1,10-phenanthroline (Table 1, entry 10). In this case, the poor activity might be resulted from an electronic effect. Although presence of an electron-donating group is beneficial for enhancing the catalytic activity of Au(III) complexes, at the same time, steric effect has also to be considered in order to improve the catalytic performance of the catalyst. For example, in the case of 2,9-dimethyl-1,10-phenanthroline, although the methyl here is an electron-donating group, however, with this ligand, a decreased TOF value (81.1 h^{-1}) was obtained (Table 1, entry 11). In our case, steric hindrances of the two methyl groups might be responsible for the decreased activity. This is probably due to steric hindrances between the two methyl groups. In light of this discussion, at this stage, the best ligand in this system is 1,10-phenanthroline.

$AuCl(PPh_3)$, an Au(I) complex proven to be an active catalyst for the carbonylation of amines by Deng et al. [28], was also examined in this model reaction. Unfortunately, under identical conditions, only a small amount of DMC was obtained at a TOF value of 5.1 h^{-1}. A well-known homogeneous Pd catalyst system, $PdCl_2(phen)$/KI, was also examined. However, in this case, only about 1% methanol conversion and 11.6 h^{-1} TOF were obtained. GC/MS analysis revealed that the main by-product of the reaction is methyl acetate.

3.2. Effect of promoter on oxidative carbonylation

The effect of promoter on this catalytic system was also investigated. Promoters are very important for enhancing the performance of catalysts and understanding the reaction mechanisms [29–31]. As shown in Table 2, the best catalytic performance was achieved by the combination of $[AuCl_2(phen)]Cl$ and KI (Table 2, entry 7). When KBr was used as a promoter, only 1.8% methanol conversion and 92.3% selectivity to DMC were obtained (Table 2, entry 3). No reaction occurred when KCl was used alone (Table 2, entry 2). In the absence of a promoter, $[AuCl_2(phen)]Cl$ produced only trace amounts of DMC (Table 2, entry 1). These results indicate that the use of iodide as a promoter is very important for the progress of the model reaction. As such, other iodine-containing reagents, such as I_2 and CH_3I, were applied in combination with $[AuCl_2(phen)]Cl$. Similar results (i.e., 5% methanol conversion and >94% selectivity to DMC) were obtained in both cases (Table 2, entries 4 and 5). According to previously published results, the significant promoting effect of KI on the $[AuCl_2(phen)]Cl$ catalyzed oxidative carbonylation of methanol can be ascribed mainly to an easy dissociation of the iodide anion in the reaction [32].

The effect of KI dosage on the catalytic performance of $[AuCl_2(phen)]Cl$ in the oxidative carbonylation of methanol was

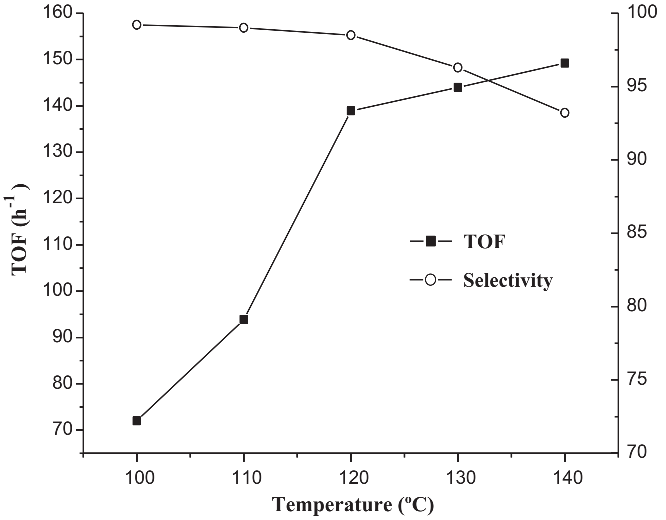


Fig. 1. Effect of reaction temperature on the oxidative carbonylation. Reaction conditions: Au(III) complexes, 0.02 mol % of methanol; methanol, 30 ml; KI, 0.586 mmol; P_{total} = 3.0 MPa ($P_{CO}/P_{O_2} = 2$); 4 h;stirring speed, 850 rpm.

also considered. The best results were obtained when an 4 mol equivalent of KI was used. When large excess amounts of KI was used, the catalytic activity of [AuCl$_2$(phen)]Cl decreased significantly (Table 2, entry 8). This could have resulted from a preferential coordination of the iodide anion, compared with methanol, to Au(III) species, restricting the interaction between the substrate and active centers [33].

3.3. Effect of temperature on oxidative carbonylation

Fig. 1 shows the effect of reaction temperature on [AuCl$_2$(phen)]Cl/KI-catalyzed synthesis of DMC at 3.0 MPa and a CO/O$_2$ molar ratio of 2. Only a small amount of DMC was obtained below 100 °C. With the increase of reaction temperature from 100 °C to 120 °C, methanol conversion increased significantly; as a result, the TOF value also increased rapidly. However, the selectivity to DMC decreased from 99.2% to 93.2% as the reaction temperature elevated from 100 °C to 140 °C. Performing the reaction >120 °C, the by-product DME was detected. Subsequently, the reaction was performed at 120 °C.

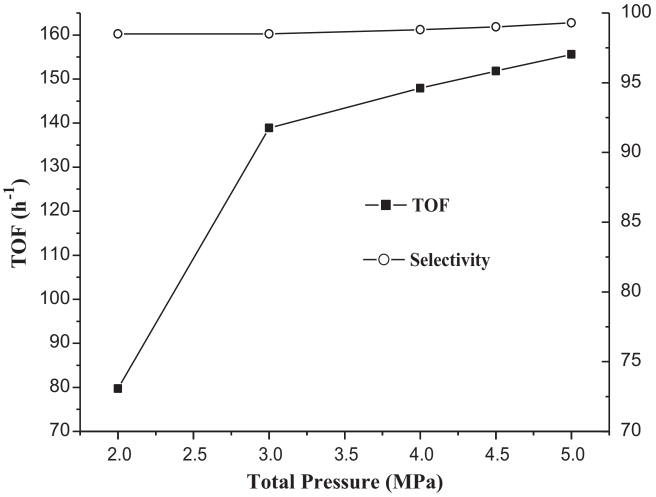


Fig. 2. Effect of reaction total pressure on the oxidative carbonylation. Reaction conditions: Au(III) complexes, 0.02 mol % of methanol; methanol, 30 ml; KI, 0.586 mmol; 120 °C; 4 h;stirring speed, 850 rpm.

3.4. Effect of pressure on the oxidative carbonylation

The influence of total O$_2$ and CO pressure on the oxidative carbonylation was also examined, the results of which are presented in Fig. 2. The selectivity to DMC seemed to be insusceptible to the increase in the total pressure from 2.0 MPa to 5.0 MPa. However, TOF of the catalyst was sensitive, increasing from 79.7 h^{-1} to 155.6 h^{-1} with the increase in total pressure. Despite the fact that high pressure favors the generation of DMC, our model reaction was performed at 3.0 MPa considering the safety factor.

4. Discussion

4.1. Electrochemical properties of [AuCl$_2$(phen)]Cl

The electrochemical behavior of [AuCl$_2$(phen)]Cl was studied in acetonitrile solution by cyclic voltammetry. The obtained result was compared with that of a reference Au(III) inorganic compound (HAuCl$_4$·4H$_2$O) (Fig. 3). Both complexes showed a very similar electrochemical behavior, and two well-defined cathodic peaks were observed in both the voltammograms (I and II). Particularly, the height of the first peak in the voltammograms was approximately

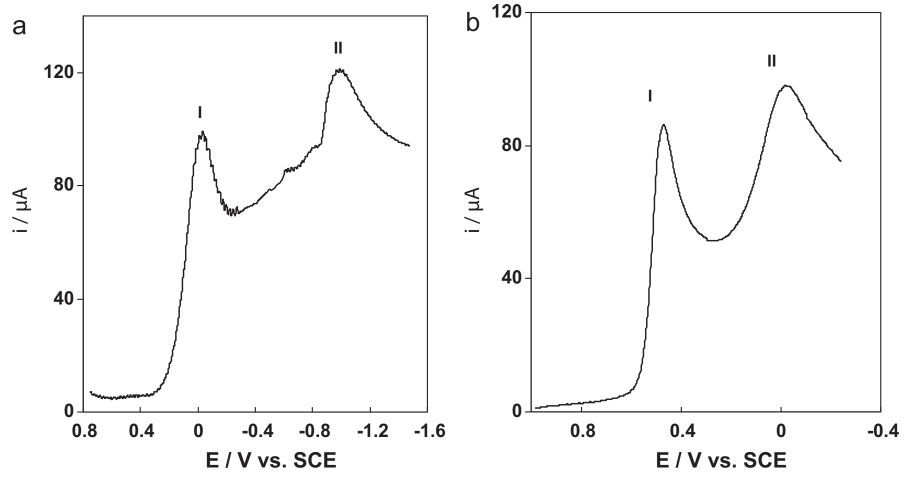


Fig. 3. Cyclic voltammograms: (a) 2 mM HAuCl$_4$·4H$_2$O and (b) 2 mM [AuCl$_2$(phen)]Cl in 0.1 M. Bu$_4$NBF$_4$/CH$_3$CN solutions, scan rate 50 mV s^{-1}.

two times higher than that of the second one. These peaks could be ascribed to transformation of gold species in the following sequence: (i) a two-electron reduction of Au(III) species to Au(I) at approximately 0 V versus SCE (for $HAuCl_4 \cdot 4H_2O$ [34]) or 0.5 V versus SCE (for $[AuCl_2(phen)]Cl$); and (ii) the subsequent reduction of Au(I) to Au(0) at more negative potentials (approximately −1.0 V in the case of $HAuCl_4$ versus SCE [35] and 0.1 V versus SCE in the case of $[AuCl_2(phen)]Cl$). These results clearly verify the (i) existence of a 3^+ oxidation state of gold in the complex $[AuCl_2(phen)]Cl$; and (ii) in the presence of the 1,10-phenanthroline ligand, Au(III) species seemed more potent for resisting reduction than without the ligand. This tendency can be also confirmed by a previous observation. Although a shining golden metal particle was formed after a reaction with the $HAuCl_4$ catalyst, $[AuCl_2(phen)]Cl$-catalyzed reaction yielded a very clear solution, and no Au(0) was observed in the presence of this nitrogen-containing ligand under the same reaction conditions. Therefore, both electrochemistry investigation and catalytic test using $HAuCl_4$ and $[AuCl_2(phen)]Cl$ demonstrate undoubtedly that the enhancing effect of the nitrogen-containing ligand 1,10-phenanthroline on the stability of Au(III) is the key to render Au(III) species efficient for the model catalytic reaction.

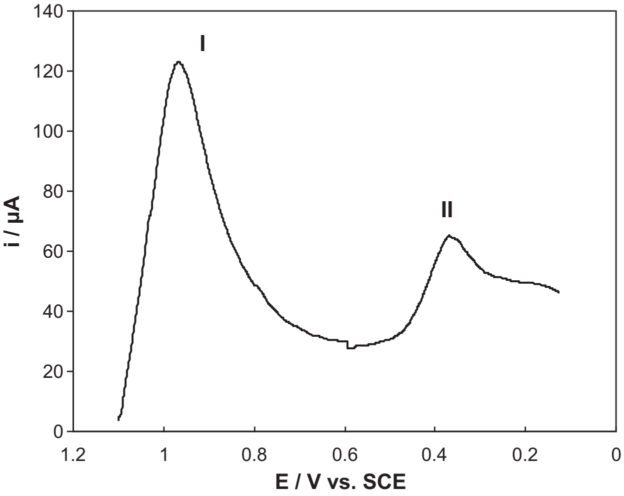


Fig. 4. Cyclic voltammograms: 1 mM $[AuCl_2(phen)]Cl/KI$ (1:4 mol/mol) in 0.1 M Bu_4NBF_4/. CH_3CN solutions, scan rate 50 mV s^{-1}.

4.2. Role of KI

Cyclic voltammetry was also utilized to shed light on the role of KI in Au-catalyzed methanol oxidative carbonylation. The cyclic voltammetric profiles of $[AuCl_2(phen)]Cl$ and $[AuCl_2(phen)]Cl/KI$ (1:4 mol/mol) in acetonitrile solutions are shown in Figs. 3b and 4, respectively.

The electrochemical behavior of $[AuCl_2(phen)]Cl$ and the cyclic voltammetric response of $[AuCl_2(phen)]Cl/KI$ also showed a two-step reduction sequence in view of the fact that two peaks were observed at 0.96 V vs SCE (peak I) and 0.40 V vs SCE (peak II), respectively (Fig. 4). However, compared with $[AuCl_2(phen)]Cl$, the reduction of Au species in $[AuCl_2(phen)]Cl/KI$ system occurred in a relatively positive potential range under the same conditions (Fig. 3b): 0.50 V vs SCE (peak I) and 0.10 V vs SCE (peak II). Similar results were also obtained in two Pd systems including $PdX_2(phen)$ (X = Cl, I) [36] and $PdX_2(PPh_3)_2$ (X = Cl, I) [37]. These results could be partially responsible for the high activity obtained using $[AuCl_2(phen)]Cl/KI$ as a catalyst. In addition, when KI was added to a methanol solution of $[AuCl_2(phen)]Cl$,

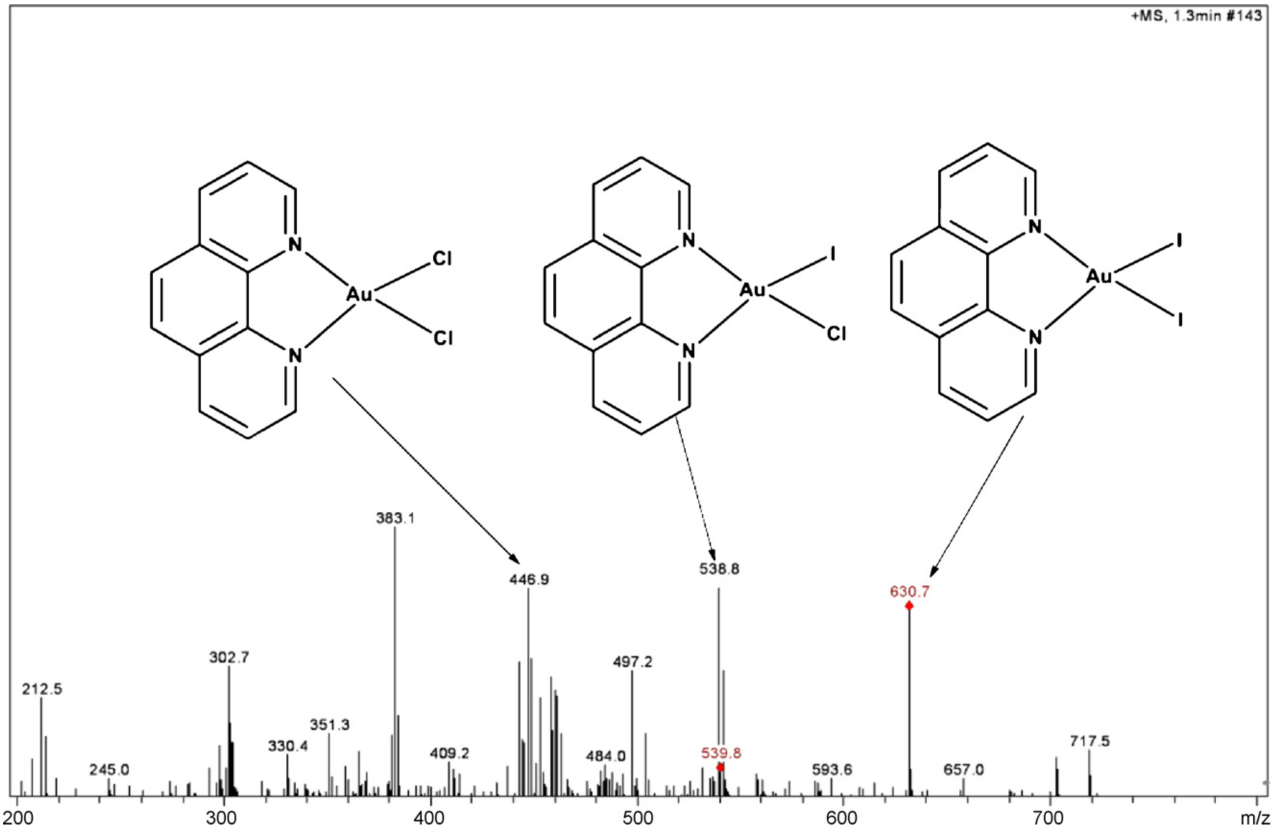


Fig. 5. ESI-MS analyses of $[AuCl_2(phen)]Cl/KI$.

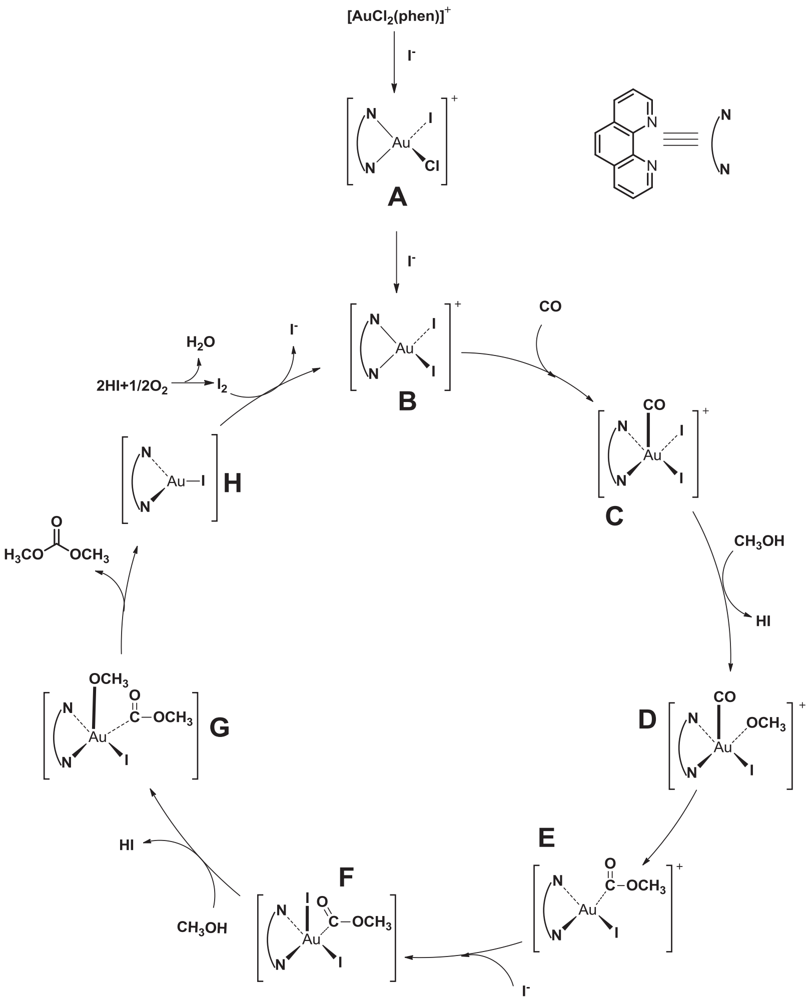


Fig. 6. A proposed mechanism of homogeneous gold-catalyzed oxidative carbonylation.

the color of the solution immediately changed to brown from the original orange; a few minutes later, a deep brown solid precipitated from the solution. Following the ESI-MS analysis (Fig. 5) of the collected solid, some molecular fragment peaks (*m/z*) were detected in 630.7 ($[AuI_2(phen)]^+$), 539.8 ($[AuClI(phen)]^+$), 504.0 ($[AuI(phen)]^+$), and 412.0 ($[AuCl(phen)]^+$), indicating the fact that Cl^- in $[AuCl_2(phen)]Cl$ was exchanged with I^- after adding KI into the solution.

Iodide is one of the "softest" ligands [38]. Due to the unique properties of iodide including low oxidation state, polarizable, and electron rich compared with other halides, iodide can interact with soft metals, such as latter transition metals, more preferably and strongly [39,40]. Consequently, in a catalytic cycle that involve these species, especially metals in low oxidation states, I^- was considered an appropriate reagent that enables metal species to keep from being precipitated, resulting in the removal of metal from the cycle and consequently in an inevitable deactivation of the catalyst. This unique ability also makes iodide distinguishable from most other ligands [39,40]. Duckworth et al. [41] reported strong interactions between the gold and iodine atoms in $[AuI_2(diars)_2]I$. Indeed, Au(I) is one of the "soft" acids, and I^- is an appropriate ligand to stabilize the Au(I) species. This finding is also consistent with the results obtained from electrochemical experiments. Iodide can also be a good nucleophile and can be easily and reversibly oxidized to I_2 [42–44]. These properties of iodide are highly different with those of chloride and bromide and allow a facile proceeding of oxidative carbonylation reactions (Table 2, entries 2 and 3).

4.3. Mechanistic considerations

Xu et al. [10] synthesized $[Au(CO)_n]^+$ ($n = 1, 2$) using a facile method from commercial Au(III) oxide Au_2O_3 in concentrated H_2SO_4 that exhibits high catalytic activity for carbonylation of olefins under atmospheric pressure and room temperature to produce *tert*-carboxylic acids in high yields. The properties and reactions of some simple gold carbonyls such as AuCl(CO) have been described; however, the application of these gold carbonyl complexes in catalysis are rarely investigated [45,46]. Based on the results from both electrochemical experiments and data of the ESI-MS analysis, a plausible mechanism of homogeneous Au-catalyzed oxidative carbonylation of methanol was proposed (Fig. 6). In the beginning of the catalytic cycle, the formation of an intermediate species B occurred through a halide anion exchange of $[AuCl_2(phen)]^+$ with I^-. CO was subsequently activated by the coordination with the Au(III) center ion in the iodide complex to form gold carbonyl species C. The nucleophile methanol was bonded with Au(III) center ions to form Au(III)-OCH_3 species D through a nucleophilic displacement by eliminating HI. After the insertion of CO to Au(III)-OCH_3 bond and the subsequent nucleophilic displacement of the next methanol molecule, a new Au species G was formed. This Au species G further underwent an elimination of DMC to generate Au(I) complex H. In the presence of oxygen, HI could be oxidized to I_2. Thus, the generated H could be further reoxidized to B, where an oxidative addition of I_2 to H was involved.

5. Conclusions

Au(III)/Schiff-base complexes with the aid of KI were proven to be effective catalysts for the carbonylation of methanol to generate dimethyl carbonate. Relatively high activities were achieved by very low concentration of $[AuCl_2(phen)]Cl/KI$ catalyst. Both ligand and promoter played crucial roles in improving the catalytic activity of Au complexes. In the presence of CO in the reaction, Au(0) was not formed from Au(III) as both the nitrogen-containing ligand and KI promoter could stabilize the gold ion in the reaction conditions. These studies not only provided strong evidence for elucidating the existence of Au(I)/Au(III) catalytic cycles but also disclosed some inside information on homogeneous carbonylation using gold complex catalysts, where the active intermediate could be oxidatively transformed in the presence of N-containing ligands and KI. Electrochemical experiments and ESI-MS analysis revealed that $[AuI_2(phen)]^+$ might be a key intermediate for activating both CO and methanol molecules. Based on these results, a plausible Au(III)/Au(I) catalytic cycle mechanism was postulated.

Acknowledgements

The authors thank the Research Foundation of Science, Huazhong University of Science and Technology for the financial support. We also thank the Analytical and Testing Center, Huazhong University of Science and Technology for the spectroscopic analysis of the catalysts.

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