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Two Carbonylations of Methyl Iodide and Trimethylamine to Acetic acid and *N,N*-Dimethylacetamide by Rhodium(I) Complex: Stability of Rhodium(I) Complex under Anhydrous Condition

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Abstract: Rhodium(I)-complex $[Rh(CO)_2I_2^-]$ (**1**) catalyzed two carbonylations of methyl iodide and trimethylamine in NMP (1-methyl-2-pyrolidone) to acetic acid and DMAC (*N,N*-dimethylacetamide) in the presence of calcium oxide and water. The carbonylation of trimethylamine continued during the carbonylation and consumption of methyl iodide. In total, 183.8 mmol of carbonylated products was produced while consuming 24.1 mmol methyl iodide via acetic acid formation. These results clearly indicated that there were two carbonylation routes of trimethylamine and methyl iodide and the carbonylation rate of trimethylamine was faster than that of methyl iodide. Rhodium(I)-complex $[Rh(CO)_2I_2]^-$ (**1**) in the presence of trimethylamine was stable enough to be used 25 times with TON (Turnover Number) of 368 for DMAC and TON of 728 for trimethylamine. Inner-sphere reductive elimination in stepwise procedure was suggested for the formation of DMAC instead of acyl iodide intermediate under anhydrous condition.
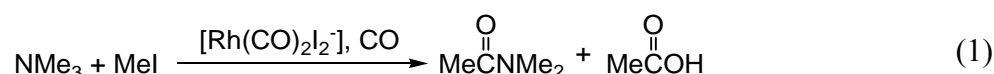
Keywords: rhodium; carbonylation; trimethylamine; dimethylacetamide; methyl iodide; acetic acid; tetramethylammonium iodide; intramolecular; inner-sphere

1. Introduction

Rhodium complexes have been intensively studied as well-known catalysts for the carbonylation of methanol to acetic acid [1,2]. In the Monsanto process, the rhodium-complex stability at low water concentrations of less than 10 wt. % have been investigated due to the high cost of product separation and the water gas shift reaction within high water concentrations of 14~15 wt. % [3–6]. Under anhydrous conditions, deactivation of catalyst occurs, giving rhodium species such as *trans*-[Rh(CO)$_2$I$_4^-$] and [Rh(CO)I$_4^-$] from iodide ligand abstraction by the active rhodium catalyst of [Rh(CO)$_2$I$_2^-$] [7,8]; therefore, substantial amount of water is required to achieve high activity and good stability of the rhodium catalyst in the carbonylations of methanol to acetic acid [9]. On the other hand, Forster reported that it took several hours to produce acyl iodide from the carbonylation of anhydrous methyl iodide at 80 °C with rhodium(I) complex [Rh(CO)$_2$I$_2^-$] [6]. To synthesize highly active and stable rhodium complexes in very low water concentration, many studies have reported about the design of suitable ligands, mainly in phosphorous containing systems [3,10,11]. Very recently, neutral rhodium(I) complexes of [Rh(CO)$_2$I(L)] (L = monodentate amines) have been synthesized and studied for their reactivity and ligand effects toward methyl iodide; reaction rates similar to those of well-known rhodium(I) anionic [Rh(CO)$_2$I$_2^-$] species is reported [12].

In this point of view, it is very interesting whether acyl iodide is formed from the carbonylation of methyl iodide by the rhodium(I) complex in trialkylamine, and whether further reaction would give the versatile amide bond [13–15].
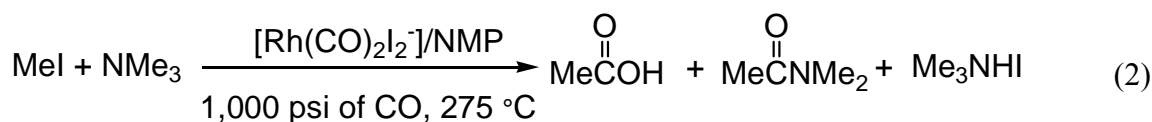
Herein, we report two novel carbonylations of methyl iodide and trimethylamine to acetic acid and DMAC (*N*,*N*-dimethylacetamide) with rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**). The stability of the rhodium(I) complex (**1**) is demonstrated by recycling it, and a plausible mechanism is suggested (Equation (1)).

$$ NMe_3 + MeI \xrightarrow{\text{[Rh(CO)}_2\text{I}_2^-\text{], CO}} MeC(=O)NMe_2 \ + \ MeC(=O)OH \tag{1} $$
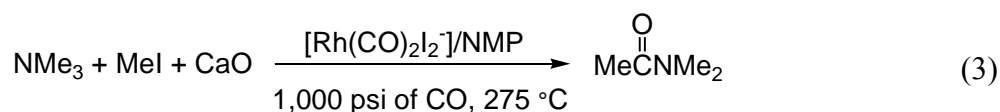
2. Results and Discussion

2.1. Two Carbonylations of Methyl Iodide and Trimethylamine to Acetic Acid and DMAC

The carbonylation of methyl iodide by rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**) in the presence of trimethylamine in NMP (1-methyl-2-pyrolidone) gave acetic acid with small amount of DMAC with formation of trimethylammonium iodide. The formation of acetic acid was expected since the rhodium (**1**) is a well-known catalyst of the Monsanto process for the carbonylation of methanol to acetic acid in the presence of water [7,8]. However, DMAC was produced as the major product with small amount of acetic acid when trimethylamine and NMP were added into the reactor through column of 4 Å molecular sieve for carbonylation. Again, acetic acid was observed as the major product from the carbonylation when small amount of water was added into reactants. If there was not enough water to react in reactants, DMAC was formed. These results indicated that Rhodium(I)-complex [Rh(CO)$_2$I$_2$]$^-$ had catalyzed two carbonylations of methyl iodide and trimethylamine to acetic acid and DMAC in the presence of limited water (Equation (2)) [16].

$$\text{MeI} + \text{NMe}_3 \xrightarrow[\text{1,000 psi of CO, 275 °C}]{[\text{Rh(CO)}_2\text{I}_2^-]/\text{NMP}} \text{MeCOH} + \text{MeCNMe}_2 + \text{Me}_3\text{NHI} \quad (2)$$
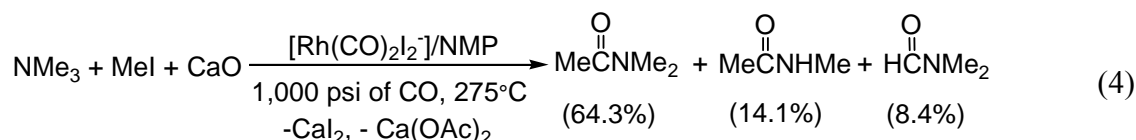
2.2. Carbonylation of Trimethylamine in the Presence of Calcium Oxide and Repetive Using Catalyst

From the above results, the amount of water in reactants seemed to be critical for the formation of DMAC; therefore, calcium oxide was added into reactants with other reagents for carbonylation. Surprisingly, the carbonylation reaction by rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**) with methyl iodide, trimethylamine, and calcium oxide gave only DMAC with no formation of acetic acid and trimethylammonium iodide, the yield of DMAC was observed as 97% based on trimethylamine (the mole ratio of trimethylamine to catalyst (**1**); 27.7 mmol to 3.78 mmol, Equation (3)).

$$\text{NMe}_3 + \text{MeI} + \text{CaO} \xrightarrow[\text{1,000 psi of CO, 275 °C}]{[\text{Rh(CO)}_2\text{I}_2^-]/\text{NMP}} \text{MeCNMe}_2 \quad (3)$$

Whether the catalyst can be used repeatedly is an interesting question; therefore, repetive using catalyst was performed. On using catalyst repetively, DMAC was obtained as the major product with no acetic acid up to the third time or fourth time using, but further using of the catalyst resulted in delay for the pressure decreasing of carbon monoxide in reactor due to its lost of catalytic activity. In this case, if additional methyl iodide was added into the reaction medium, then again DMAC was produced as the major from the carbonylation. However, upon repetive using catalyst, byproducts of MAA (*N*-methylacetamide) and DMF (Dimethylformamide) were produced and a large amount of solid was formed in the reactor. After volatiles were removed by short-path distillation from the reaction mixture, the resulted residual solid was confirmed as mixture of CaI$_2$(NMP)$_6$, CaI$_2$(DMAC)$_6$, and Ca(OAc)$_2$. For their identification, separately solvated calcium iodides were prepared from the reaction of calcium iodide hydrate with NMP and DMAC. The mole ratio of CaI$_2$ to Ca(OAc)$_2$ was confirmed as 1:1 by ^{1}H-NMR spectroscopy. When the amount of calcium oxide was reduced to one third, the activity of catalyst was lost quickly with rapid increasing of MAA and DMF byproducts. Trimethylamine of 12.5 g (211.8 mmol) and methyl iodide 3.4 g (24.1 mmol) were used totally for the carbonylation during five times recycling of catalyst. The yields of DMAC, MAA, and DMF were 11.87 g (136.2 mmol, 64.3%), 1.18 g (29.8 mmol, 14.1%), and 1.30 g (17.8 mmol, 8.4%), respectively. The conversion rate of trimethylamine was 86.8% and the selectivity of DMAC was 74.1% (Equation (4)).

$$\text{NMe}_3 + \text{MeI} + \text{CaO} \xrightarrow[\substack{\text{1,000 psi of CO, 275°C} \\ \text{-CaI}_2, \text{- Ca(OAc)}_2}]{[\text{Rh(CO)}_2\text{I}_2^-]/\text{NMP}} \underset{(64.3\%)}{\text{MeCNMe}_2} + \underset{(14.1\%)}{\text{MeCNHMe}} + \underset{(8.4\%)}{\text{HCNMe}_2} \quad (4)$$

These results showed that in the presence of calcium hydroxide rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**) had catalyzed two carbonylations of trimethylamine and methyl iodide to DMAC and acetate moiety of calcium acetate with formation of calcium iodide via acylation procedure until no methyl iodide remained in reactants during the carbonylation reaction.

From the above results, it was concluded that during two carbonylations of trimethylamine and methyl iodide, calcium hydroxide and/or calcium oxide had retarded completely the consumption of methyl iodide by removing water and/or lowering its reactivity as hydroxide while they were transformed into
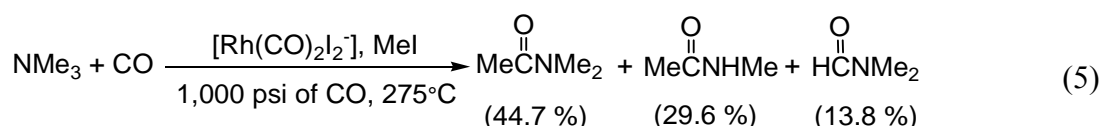
calcium iodide and calcium acetate via acylation procedure of methyl iodide and in the end the carbonylation of trimethylamine was halted due to complete consumption of methyl iodide in reaction mixture.

Surprisingly, the carbonylation of trimethylamine had been continued with sustaining stability of rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) during the carbonylation and consuming of methyl iodide. In total 183.8 mmol of DMAC, MAA, and DMF was produced during the consuming of 24.1 mmol methyl iodide via acetic acid formation. These results clearly indicated that there were two carbonylation routes of trimethylamine and methyl iodide and the carbonylation rate of trimethylamine was faster than that of methyl iodide in the presence of calcium oxide and/or calcium hydroxide.

2.3. Carbonylation of Trimethylamine in the Presence of Calcium Oxide under Anhydrous Condition and Repetive Using Catalyst

Whether rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) can be used repeatedly for the carbonylation of trimethylamine with no formation of calcium salt under anhydrous condition is an interesting question; therefore, to prepare anhydrous trimethylamine, it was passed through a KOH column, 4 Å molecular sieve column, and dry ice-cold trap sequentially, since commercial trimethylamine is produced with water from condensation of methanol and ammonia on alumino-silicate catalyst.

The carbonylation of anhydrous trimethylamine in NMP by rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) with methyl iodide and calcium oxide gave DMAC as the major product with no acetic acid. The catalyst was used repetively 25 times with a modified autoclave of 1000 mL sus 316, while some amount of volatile aliquot was taken out each carbonylation cycle every one hour and additional methyl iodide and trimethylamine were also added in reactants. During the last run, the pressure of the reactor was not decreased, rather it increased; therefore, the procedure of repetive using catalyst was ceased. As before, on repetive using the catalyst, the amount of MAA and DMF byproducts increased gradually. However, there was no solid formed such as solvated calcium iodide and calcium acetate in reaction mixture since there was no formation of acetic acid in the absence of water under anhydrous condition. Total amount of trimethylamine added was 132.1 g (2234.8 mmol) and total amount of methyl iodide added was 15.7 g (110.6 mmol). The mole ratio of trimethylamine to catalyst (**1**) was 2234.8 mmol to 2.73 mmol. The analysis of collected products showed that the conversion rate of trimethylamine was 88.0% and DMAC selectivity was 50.6%. Rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) showed good stability with catalyst TON of 368 for DMAC and TON of 728 for trimethylamine during the carbonylation reaction. The yields were 86.78 g DMAC (996.1 mmol, 44.7%), 48.00 g MAA (662.1 mmol, 29.6%), and 22.56 g DMF (308.6 mmol, 13.8%). However, the byproducts, MAA and DMF, were 43.1% of total products (Equation (5)).
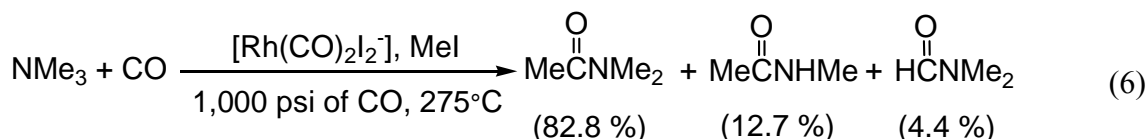
$$NMe_3 + CO \xrightarrow[\text{1,000 psi of CO, 275°C}]{[Rh(CO)_2I_2^-],\ MeI} \underset{(44.7\ \%)}{Me\overset{O}{\overset{\|}{C}}NMe_2} + \underset{(29.6\ \%)}{Me\overset{O}{\overset{\|}{C}}NHMe} + \underset{(13.8\ \%)}{H\overset{O}{\overset{\|}{C}}NMe_2} \qquad (5)$$

These results indicated that rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) was stable under an anhydrous condition and had catalyzed carbonylation of trimethylamine to DMAC with formation of MAA and DMF byproducts. However, it was not clear whether the byproducts, MAA and DMF, were produced due to calcium oxide and/or any calcium salts during the carbonylation reaction. DMAC seemed to be transformed into MAA and DMF in some way because both MAA and DMF had carbonyl moieties

and the pressure of the reactor had been rather increased by something other than carbon monoxide during the last carbonylation reaction.

2.4. Carbonylation of Trimethylamine in No Solvent under Anhydrous Condition and Repetive Using Catalyst

The carbonylation of anhydrous trimethylamine by rhodium(I) complex [$Rh(CO)_2I_2^-$] (**1**) with catalytic amount of methyl iodide in no solvent gave DMAC as the major product (Equation (6)) [16]. Furthermore, the catalyst had been used 20 times with no additional methyl iodide. On repetive using the catalyst, the amount of MAA and DMF in product was increased gradually too. On the last run, the pressure of the reactor did not decreased, rather it increased; therefore, the procedure of repetive using catalyst was ceased. The analyses of collected products showed that the conversion rate of trimethylamine was 99% and DMAC selectivity was 82.3%. The yields were 164.9 g (DMAC), 21.3 g (MAA), and 7.4 g (DMF) with mole ratio of 82.8%:12.7%:4.4%. The amount of MAA and DMF byproducts was still high: 17% of total product. The percentage of which, however, was much lower than that of the carbonylation in the presence of calcium oxide. The TON of catalyst was 700 for DMAC and TON of methyl iodide was 296 for trimethylamine.

$$NMe_3 + CO \xrightarrow[\text{1,000 psi of CO, 275°C}]{[Rh(CO)_2I_2^-], MeI} \underset{(82.8\%)}{MeC(O)NMe_2} + \underset{(12.7\%)}{MeC(O)NHMe} + \underset{(4.4\%)}{HC(O)NMe_2} \quad (6)$$
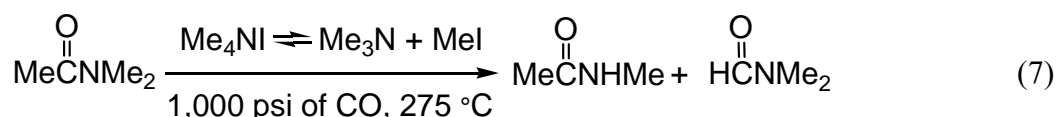
These results showed that rhodium(I) complex (**1**) was stable in the presence of trimethylamine without either solvent or water and methyl iodide was regenerated during the reaction. It was remarkable that rhodium(I) complex [$Rh(CO)_2I_2^-$] (**1**) was stable in the absence of water because substantial amount of water was required to achieve high activity and good stability of rhodium catalyst in the carbonylation of methanol to acetic acid [9].

However, it was not clear whether the byproducts of MAA and DMF were produced from the carbonylation itself or from the transformation of DMAC, and how methyl iodide was regenerated during the carbonylation of trimethylamine to DMAC.

2.5. Transformation of DMAC into MAA and DMF in the Presence of Tetramthylammonium Iodide

To find out whether the byproducts, MAA and DMF, were formed from the carbonylation of trimethylamine, some experiments were carried out. Without any rhodium compound, separately DMAC was heated in the presence of trimethylamine, methyl iodide and trimethylamine, and tetramethylammonium iodide under the same reaction conditions as those of trimethylamine carbonylation (under CO pressure of 1000 psi at temperature of 275 °C). DMAC remained in the presence of trimethylamine for 20 h. However, in the presence of tetramethylammonium iodide, large amount of DMAC was gradually transformed into MAA and DMF, and very small amount of intractable tar. Especially in the presence of methyl iodide, DMAC was transformed into intractable tar with increasing pressure in the reactor over a short time. These results indicated clearly that under the carbonylation condition, tetramethylammonium iodide was decomposed into trimethylamine and methyl iodide. The same unimolecular decomposition of tetramethylammonium iodide was reported experimentally and
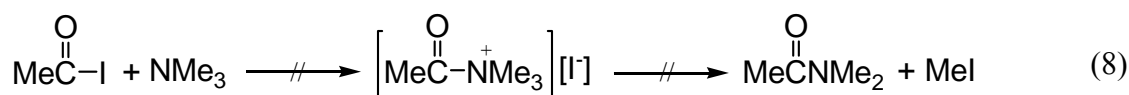
theoretically [17]. Therefore, it was concluded that some of DMAC produced from the carbonylation of trimethylamine was transformed into MAA and DMF with increasing pressure of reactor due to the presence of methyl iodide, which was provided from the unimolecular decomposition of tetramethylammonium iodide in reaction medium during the carbonylation reaction (Equation (7)). From the carbonylation results of trimethylamine, it was observed that a smaller amount of DMAC (17%) was transformed into MAA and DMF in the absence of calcium hydroxide and solvent than that of DMAC (49%) in the presence of calcium hydroxide (calcium oxide).

$$\underset{MeCNMe_2}{\overset{O}{\|}} \xrightarrow[\text{1,000 psi of CO, 275 °C}]{Me_4NI \rightleftharpoons Me_3N + MeI} \underset{MeCNHMe}{\overset{O}{\|}} + \underset{HCNMe_2}{\overset{O}{\|}} \qquad (7)$$

2.6. DMAC Formation from Other Intermediate than Acyl Iodide in the Carbonylation of Trimethylamine

Acyl iodide has been known as an intermediate in the carbonylation of methanol to acetic acid and/or acetic anhydride [7,12,18–20] and bond dissociation energy of carbon-iodine in acyl iodide is very low [21]. In the case of Co and Pd complexes, acyltrimethylammonium halides have been suggested as an intermediate, from which DMAC and methyl iodide had been produced in some way [22–25]. However, organic reactions of acyl iodide and tertiary amines with mole ratio of 1:2 have been reported to involve the cleavage of C–N bond to give alkyl iodide, this was limited to benzyl, allyl, ethyl, or butyl iodide due to the robustness of the unstrained $C(sp^3)$–N bond [26–28]. Prolonged reaction of acyl iodide with *N*-methylpiperidine had resulted in reluctant cleavages of the exocyclic C–N to give *N*-acetylpiperidine (16%) and *N,N*-dimethylpiperidinium iodide to an insignificant extent [28]. Long ago, Forster reported that the rate of acyl iodide formation from the carbonylation of anhydrous methyl iodide with rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**) was extremely slow [6]. In these two carbonylations of trimethylamine and methyl iodide, no evidence of acyltrimethylammonium iodide formation was found. First of all, it was observed that there were two carbonylation routes of trimethylamine and methyl iodide and the carbonylation rate of trimethylamine was faster than that of methyl iodide. It is concluded that increasing electron density at the rhodium center by different ligands consequently enhances the overall rate of acetic acid formation by facilitating the oxidative addition of methyl iodide [29–33] and electron density at the rhodium center was increased by monodentate amine ligands [12].

Therefore, herein, intermediates other than acyl iodide and/or acyltrimethylammonium iodide are suggested for the formation of DMAC from the carbonylation of trimethylamine by rhodium(I) catalyst system of [Rh(CO)$_2$I$_2^{-1}$].

$$\underset{MeC-I}{\overset{O}{\|}} + NMe_3 \xrightarrow{\quad\quad} \left[\underset{MeC-NMe_3}{\overset{O}{\|}}\right][I^-] \xrightarrow{\quad\quad} \underset{MeCNMe_2}{\overset{O}{\|}} + MeI \qquad (8)$$

2.7. A Plausible Mechanism for the Formation of DMAC in the Carbonylation of Trimethylamine

The rhodium(I) complex [Rh(CO)$_2$I$_2^{-1}$] (**1**) is subsequently transformed into [Rh(CO)$_2$I(NMe$_3$)] (**2**) by substitution of iodide ligand with trimethylamine in abundance under pressure of carbon monoxide. Oxidative addition of methyl iodide, which is provided from the unimolecular decomposition of tetramethylammonium iodide at a higher temperature of 275 °C than those of the other

carbonylations [3,6–8], to **2**) results in the formation of σ-bond (Rh-CH$_3$) in [RhMe(CO)$_2$(NMe$_3$)I$_2$] (**3**), the unstable species of which isomerizes to acetyl intermediate of [Rh(COMe)(CO)I$_2$(NMe$_3$)] (**4**) via methyl-migratory insertion to rhodium-carbonyl bond. Further addition of carbon monoxide to the vacant site of **4** provides pseudo-octahedral complex [Rh(COMe)(CO)$_2$I$_2$(NMe$_3$)] (**5**). The bond between rhodium and nitrogen in **5**) is mainly σ-dative bond from nitrogen atom to rhodium atom. The rhodium (III) complex (**5**) in high oxidation state has two carbonyl groups to reduce electron density of rhodium atom via dπ-pπ* back-bonding; this makes the coordinated nitrogen more electrophilic than that of free tertiary amine. Acetyl group of rhodium complex has a large *trans* influence to *trans*-iodo ligand each other, and it is reported that the bond length of *trans* Rh-I to acetyl group is significantly longer than that of *cis* Rh-I to acetyl group [12]. Therefore *trans*-iodo ligand is more labile than *cis*-iodo ligand [34], thus the former easily can attack at the carbon atom of coordinated trimethylamine ligand having more electrophilicity than those of tertiary amine or quaternary amine. Furthermore, the trimethylamine ligand is in *cis*-position to both of iodo and acetyl ligands forming quasi-four-membered ring of iodine atom, rhodium atom, nitrogen atom, and carbon atom of a methyl group attached to nitrogen atom of the coordinated trimethylamine ligand. Once triggering of a labile iodo ligand in rhodium complex [Rh(COMe)(CO)$_2$I$_2$(NMe$_3$)] (**5**) is proceeded to inner-sphere reductive elimination of DMAC and methyl iodide concurrently providing of dimer [{Rh(μ-I)((CO)$_2$}$_2$] and/or the original neutral rhodium catalyst of [Rh(CO)$_2$I(NMe$_3$)] (**2**) in abundance of trimethylamine. These procedures are able to be recycled if co-catalyst of methyl iodide is not consumed in the reaction. By the way, as there is some amount of water in reactants, it is obvious that the carbonylation of methyl iodide by rhodium(I) complex [Rh(CO)$_2$I$_2$$^{-1}$] (**1**) produces acetic acid with trimethylammonium iodide of Me$_3$NHI in the presence of trimethylamine. This is the scavenger's pathway to consume promoter of methyl iodide providing trimethylammonium iodide, since unimolecular decomposition of it gives no methyl iodide but hydrogen iodide and trimethylamine. Nevertheless, it seems to be unlikely that rhodium(I) complex [Rh(CO)$_2$I$_2$$^{-1}$] (**1**) has remained as it is with no substitution of iodo ligand by trimethylamine ligand despite its strong electron-donating ability and its abundance in reaction medium. Therefore, it is suggested that substitution of iodo ligand on the complex [Rh(COMe)(CO)$_2$I$_2$(NMe$_3$)] (**4**) by hydroxide anion gives another pseudo-octahedral complex [Rh(COMe)(CO)$_2$I(NMe$_3$)(OH)] (**6**). Then, from the complex (**6**) inner-sphere reductive elimination of acyl moiety and hydroxide moiety gives acetic acid simultaneously providing dimer [{Rh(μ-I)((CO)$_2$}$_2$] and/or the original neutral rhodium catalyst [Rh(CO)$_2$(NMe$_3$)I] (**2**) in abundance of trimethylamine. As Forster reported that the rate of acyl iodide formation from the carbonylation of anhydrous methyl iodide with rhodium(I) complex [Rh(CO)$_2$I$_2$$^-$] (**1**) was extremely slow [6], it was observed that the carbonylation rate of trimethylamine was faster than that of methyl iodide in the reaction since increasing electron density at the rhodium center by trimethylamine ligand enhanced the oxidative addition rate of methyl iodide [29–33]. Therefore, from the carbonylation of trimethylamine in the presence of hydroxide anion or limited water, DMAC was obtained as the major product (Figure 1).
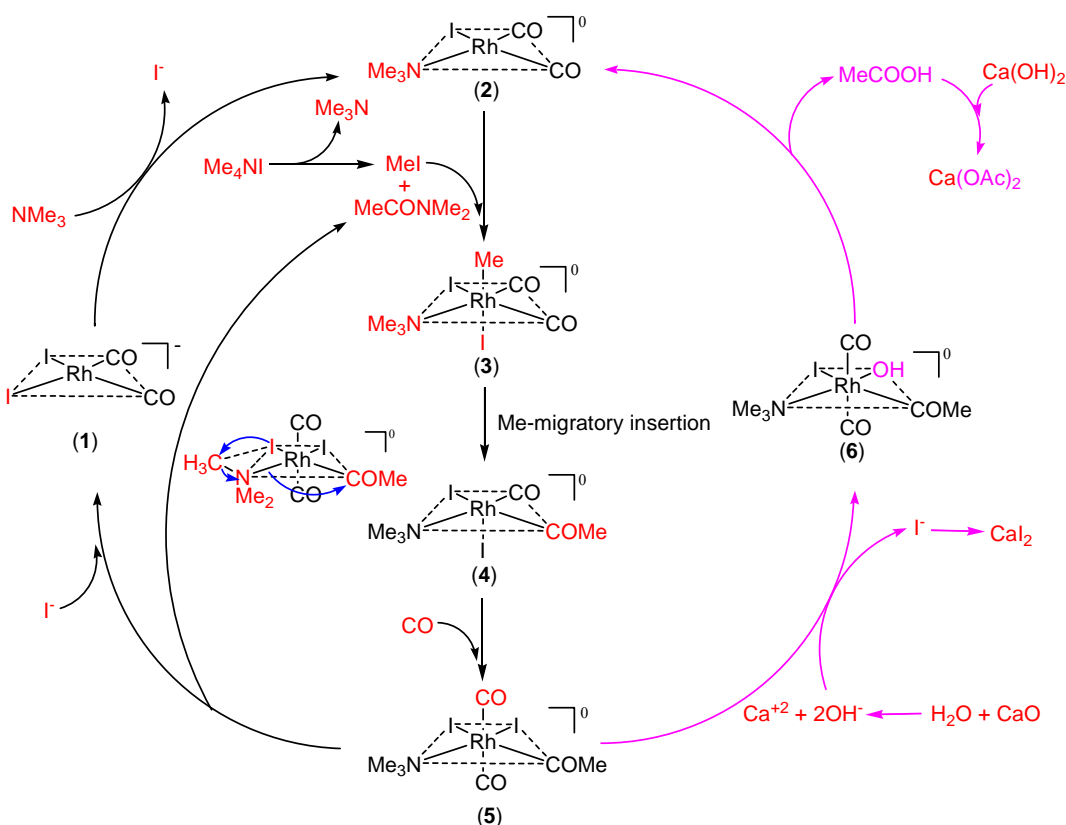
Figure 1. Mechanism of rhodium-catalyzed carbonylation of trimethylamine.

A similar stepwise procedure to the above reductive eliminations has been reported to afford acetic acid or acid anhydride via rhodium (III) complex [Rh(COMe)(CO)$_2$I$_2$L] (L = water, AcO$^-$), which was formed from the pseudo-octahedral complex [Rh(COMe)(CO)$_2$I$_3$$^-$] by substitution of an iodide ligand with water or acetate anion [34] due to the high energy of acyl idodide in theory [35]. The comparable five-coordinated rhodium (III) complex [Rh(COMe)(CO)I$_2$(HNEt$_2$)] to the rhodium (III) complex [Rh(COMe)(CO)I$_2$(NMe$_3$)] (**4**) has been reported to give anionic species of [{Rh(μ-I)(COMe)(CO)I$_2$}$^-$]$_2$ and [Rh(CO)$_2$I$_2$$^-$] with *N,N*-diethylacetamide via acylation and decoordination of the monodentating diethylamine ligand in abundance of methyl iodide [12]. In the case of triethylamine, its carbonylation by water soluble ruthenium (III) complex has been reported to produce only *N,N*-diethylpropionamide via intra-molecular elimination [36].

2.8. For Industrial Application in Future

The rhodium(I) complex [Rh(CO)$_2$I$_2$$^{-1}$] (**1**) was stable in the presence of trimethylamine. It is remarkable since substantial amount of water is required to achieve high activity and good stability of the rhodium catalyst in the carbonylations of methanol to acetic acid [9]. In this work, the rhodium(I) complex [Rh(CO)$_2$I$_2$$^{-1}$] (**1**) was used repectively more than 20 times with catalytic amount of methyl iodide under anhydrous condition. In the near future, we hope that this report will be helpful for commercialization of DMAC production with no corrosive reagents and for coping with the challenge of reducing water content and reducing the cost of products separation in methanol carbonylation plants.

3. Experimental Section

3.1. Reagents and Instruments

Air sensitive reactions were performed under nitrogen atmosphere using standard Schlenk techniques and air sensitive reagents were transferred in nitrogen-filled glove box. 1-Methyl-2-pyrolidone (NMP), trimethylamine, *N,N*-dimethylacetamide (DMAC), *N*-methylacetamide (MAA), *N,N*-dimethylformamide (DMF), methyl iodide, carbon monoxide (purity of 99.99%), tetramethylammonium iodide (Me$_4$NI), trimethylammonium iodide (HMe$_3$NI), calcium oxide (CaO), calcium iodide hydrate (CaI$_2$), and rhodium(III) trichloride (RhCl$_3$·3H$_2$O) were purchased from a local manufacturer (SF Chemical Co. Ltd., Daejon, S. Korea) and Aldrich dealer (Daejon, S. Korea); they were used without further purification unless noted. Dichlorotetracarbonyldirhodium complex of [Rh(μ-Cl)(CO)$_2$]$_2$ was prepared from rhodium trichloride of RhCl$_3$·3H$_2$O according to the procedure in the literature [37]. NMP and DMAC were distilled with sodium sulfate before use. NMR spectra were recorded on Bruker WP SY and Bruker AM 300 FT-NMR spectrometers. GC-MS data were obtained on HP 6890 5973 GC-MS system equipped with a methyl silicon capillary column. IR as KBR pellet on a Shimazu IR 440 and melting points were measured on a Wagner & Meunz Co., München, Germany, capillary type. Autoclave reactor of 500 mL sus 316 or 1000 mL sus 316 is used for pressurized reaction with carbon monoxide. The inside and upper part of autoclave of 1000 mL sus 316 was designed with cooling coil above and doughnut type of receiver below, then some amount of volatile product could be taken out via outlet during the reaction.

3.2. The preparation of Rhodium(I) Complex (1)

Method A: Rhodium(I) complex [Rh(CO)$_2$I$_2^{-1}$] (**1**) was prepared according to the procedure in the literature [8,38,39]. Me$_4$NI (4.83 g, 24.00 mmol) was added to [Rh(μ-Cl)(CO)$_2$]$_2$ (0.52 g, 1.34 mmol) in NMP of 50 mL in a Sus 316 atuoclave of 500 mL under CO at room temperature. Then the reaction mixture was stirred overnight under CO. The respective MeI and Me$_3$N were also used instead of Me$_4$NI. It was used *in situ* for the carbonylation of trimethylamine.

Method B: Rhodium(I) complex [Rh(CO)$_2$I$_2^{-1}$]] (**1**) was prepared according to the procedure the in literature [6,40–42]. RhCl$_3$·3H$_2$O (0.72 g, 2.73 mmol) in NMP of 100 g, MeI (1.5 mL, 3.42 g, 24.1 mmol), and Me$_3$N (5.0 mL, 3.28 g, 55.5 mmol) were charged in a Sus 316 autoclave of 1000 mL. Me$_4$NI was also used instead of the respective MeI and Me$_3$N. After purging 3 to 4 times with CO, the autoclave was pressurized with CO to 350 psi at room temperature. It was heated at 150 °C for 1 h. It was used *in situ* for the carbonylation of trimethylamine.

3.3. The Carbonylation of Trimethylamine with Calcium Oxide

The respective rhodium catalysts prepared by Method A and B were used *in situ* for the carbonylations of trimethylamine and there was no different in results. A 500 mL Stainless steel autoclave reactor was used with NMP or DMAC solvent of 50 mL, there was no significant solvent effect observed. In the typical reaction, trimethylamine (2.16 mL, 1.42 g, 24.0 mmol), methyl iodide (1.50 mL, 3.41 g, 24.0 mmol), calcium oxide (1.0 g, 17.8 mmol), and the catalyst of [Rh(μ-Cl)(CO)$_2$]$_2$ (0.73 g, 1.89 mmol)

in 50 mL NMP were added to the reactor, it was pressurized with CO to 350 psi at room temperature. It was heated at 150 °C with stirring for 1 h, and then it was heated at 275 °C with stirring for 2 h. When the pressure of the reactor lowered to 950 psi, it was pressurized with CO up to 1000 psi. The reactor was cooled to room temperature and depressurized, and the total amount of reaction mixture was weighed. Workup and short-pass distillation of reaction mixture with dry-ice cold-trap gave volatile compounds, to which was added hexamethyldisiloxane (20 μL, 15.28 mg) as an internal standard. It was analyzed by GC-MS and NMR spectroscopy. The yield of DMAC (2.03 g, 23.3 mmol) was observed as 97% based on trimethylamine (1.42 g, 24.0 mmol).

In the typical reaction, trimethylamine (2.50 mL, 1.64 g, 27.7 mmol), methyl iodide (1.50 mL, 3.40 g, 24.1 mmol), calcium oxide (1.0 g, 17.8 mmol), and dicarbonylchlorodirhodium of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.73 g, 1.89 mmol) in 50 mL NMP were added to the reactor. The same carbonylation procedure was performed as described above. Aliquot part was decanted from reaction mixture and it was collected. An additional 4 mL of trimethylamine was added to the residue in the reactor and the same carbonylation was carried out with it. The carbonylation procedure was repeated until the catalyst had been used five times. Workup and distillation of the collected aliquots and reaction mixture in reactor gave liquid mixture and it was analyzed with internal standard of *n*-octanol by GC-MS and ^{1}H-NMR spectroscopy. From the solid residue, calcium salts of $Ca(OAc)_2$, $CaI_2(NMP)_6$, and $CaI_2(DMAC)_6$ were confirmed with the authentic compounds by ^{1}H-NMR spectroscopy. The mole ratio of CaI_2 to $Ca(OAc)_2$ was observed as 1:1. Separately, the respective solvated calcium iodide was prepared from the solvation reaction of calcium iodide hydrate (0.5 g) in 5 mL of NMP and in 5 mL of DMAC, they were crystalized in a refrigerator. Trimethylamine of 12.5 g (211.8 mmol) and methyl iodide 3.4 g (24.1 mmol) were used totally for the carbonylation during recycling catalyst five times. Yields: DMAC (11.87 g, 136.2 mmol, 64.3%), MAA (1.18 g, 29.8 mmol, 14.1%), DMF (1.30 g, 17.8 mmol, 8.4%), The conversion rate of trimethylamine ; 86.8%. the selectivity of DMAC; 74.1%, CaI_2 $(NMP)_6$; mp 120–122 °C (*cf.* CaI_2 mp. 780 °C), ^{1}H-NMR (D_2O, ext. ref.); 1.95 (quint, 2H), 2.33 (t, 2H), 2.74 (s, 3H), 3.39 (t, 2H), $Ca(OAc)_2$; ^{1}H-NMR (D_2O, ext. ref.); 1.79 (s, 3H), $CaI_2(DMAC)_6$; white colorless crystal, ^{1}H-NMR (D_2O, ext. ref.); 1.99 (s, 3H), 2.81 (s, 3H), 2.97 (s, 3H).

3.4. The Drying of Trimethylamine

Gaseous trimethylamine was passed through the first column of KOH, second column of 4 Å molecular sieve, and cold-trap of *iso*-propanol/dryice. The dried trimethylamine was stored with 4 Å molecular sieve under 0–5 °C before use. Water concentration of trimethylamine was reduced from 4500 ppm to 220 ppm, those of which were measured by Karl Fisher titrimetry of Metrohm.

3.5. The Carbonylation of Trimethylamine with CaO under Anhydrous Condition and Repetive using Catalyst

Autoclave of 1000 mL sus 316 was used and the inside and upper part of it was designed with cooling coil above and doughnut type receiver below. The rhodium catalysts prepared by Method B was used. The same carbonylation procedure was performed as above. After each carbonylation was performed, and the heating of the reactor was stopped, the cooling medium at 120 °C was circulated via cooling coil inside the autoclave for 1 h. When the reactor was cooled to room temperature, about 10 g of aliquot

received in receiver below the cooling coil was taken out via outlet from the reactor under depressurized condition. An additional 8 mL trimethylamine and 0.5 mL methyl iodide were added into the reactor, and the circulation of the cooling medium was closed. The carbonylation procedure was repeated a total of 25 times, workup and distillation of the collected products and reaction mixture of reactor gave liquid products. They were analyzed by GC-MS and ^{1}H-NMR spectroscopy. Total amount of trimethylamine added: 132.10 g (2234.8 mmol); Total amount of methyl iodide added: 15.70 g (110.6 mmol). Yield: DMAC (86.78 g, 996.1 mol, 44.7%), MAA (48.40 g, 662.1 mmol, 29.6%), and DMF (22.56 g, 308.6 mol, 13.8%), conversion rate of trimethylamine: 88.2%; selectivity of DMAC: 50.6%; TON of DMAC: 369.

3.6. Thermal Reaction of DMAC in the Presence of Methyl Iodide, Trimethylamine, Methyl Iodide and Trimethylamine, or Tetramethylammonium Iodide at 275 °C under CO (1000 psi)

Reactions were performed with no catalyst under the same reaction condition as the carbonylation of trimethylamine. DMAC under pressure of CO was heated in the presence of trimethylamine, methyl iodide, tetramethylammonium iodide, or trimethylamine and methyl iodide at 275 °C. Then the solution of mixture was analyzed by GC every 5 h during the reaction. Typically, 35 g DMAC and 3.0 g trimethylamine were charged in autoclave reactor, into which CO was pressurized up to 350 psi at room temperature. It was heated at 275 °C for 20 h and analysis of the mixture by GC showed no change. In the presence of methyl iodide (3.0 g), all reactants became tar after less than 5 h.

For the reaction of DMAC (35 g) in the presence of tetramethylammonium iodide (5.0 g), GC analysis of reaction mixture showed as follows: 5 h, DMAC:MAA:DMF with unknown tar = 98.5%:1.63%:trace; 10 h, 95.6%:4.4%:trace and 20 h, 76.0%:14.0%:trace, For the reaction of DMAC (35 g) in the presence of trimethylamine (3.0 g) and methyl idodide (4.0 g) (mole ratio of trimethylamine to methyl iodide was 3.2:1.0), GC analysis of reaction mixture showed as follows: 5 h, 97.0%:2.1%:trace; 10 h, 95.1%:4.8%:trace; and 20 h, 83.8%:12.0%:trace.

4. Conclusions

The carbonylation of trimethylamine has been continued with sustaining stability of rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**) during the carbonylation of methyl iodide consuming methyl iodide. The carbonylation rate of trimethylamine was faster than that of methyl iodide during the carbonylation reaction. Under an anhydrous condition, rhodium(I) complex [Rh(CO)$_2$I$_2^-$] (**1**) only catalyzed carbonylation of trimethylamine with catalytic amount of methyl iodide to give only DMAC (*N,N*-dimethylacetamide) and a smaller amount of DMAC (17%) was transformed into MAA and DMF in the absence of calcium hydroxide and solvent than that of DMAC (49%) in the presence of calcium hydroxide (calcium oxide). Inner-sphere reductive elimination in stepwise procedure was suggested for the formation of DMAC instead of acyl iodide intermediate under an anhydrous condition. This is expected to be a small contribution to the new design of other metal-catalyzed carbonylations for the synthesis of other acyl-heteroatom bonds.

Acknowledgments

Conflicts of Interest

The authors declare no conflict of interest.

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