J. Chosun Natural Sci.
Vol. 8, No. 4 (2015) pp. 235 – 243
http://dx.doi.org/10.13160/ricns.2015.8.4.235

# Synthesis of *N,N*-Dimethylacetamide from Carbonylation of Trimethylamine by Rhodium(I) Complex Under Anhydrous Condition

**Jang-Hwan Hong**†

## Abstract

Rhodium(I)-complex of [$Rh(CO)_2I_2^-$] catalyzed carbonylation of anhydrous-trimethylamine in the presence of methyl iodide to give DMAC (*N,N*-dimethylacetamide) in no solvent. The catalyst had been reused 20 times, the analyses and distillation of collected products showed that the yields of DMAC, MAA (*N*-methylacetamide), and DMF (*N,N*-dimethylformamide) were 82.3%, 12.6%, and 4.4%. The conversion rate of trimethylamine was 99 % and the selectivity of DMAC was 82.3% with TON (Turnover Number) of 700. Stepwise procedure of inner-sphere reductive elimination for the formation of DMAC was suggested instead of acyl iodide intermediate.

**Keywords:** Rhodium, Carbonylation, Trimethylamine, Dimethylacetamide, Tetramethylammonium Iodide, Intramolecular, Inner-sphere, Reductive-elimination

## 1. Introduction

One of the most important reactions in organic chemistry is amide bond formation[1-3]. There has been a great interests in catalyzed carbonylation of C($sp^3$)-N bond, those are mainly about aminocarbonylation of aryl halides and secondary amines [4-14]. The preparation of *N,N*-dimethylacetamide (DMAC) by the carbonylation of trimethylamine has attracted special attention due to activation of robust C($sp^3$)-N bond in trimethylamine and DMAC's versatile applications in agrochemicals, pharmaceuticals, fine chemicals, man-made fibers of polymers, and industrials coatings and films[15-17]. Several carbonylation methods of trimethylamine by transition metal complexes of Co, Rh, and Pd had been patented[18-23]. In recent Li et al. had reported for the synthesis of DMAC from the carbonylation of trimethylamine or tetramethylammonium halides by Co and Pd complexes[24-28], in which acyl iodide had been suggested as an intermediate.

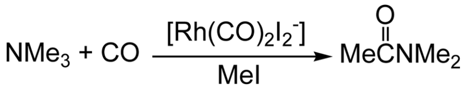
Rhodium complexes have been intensively studied as well-known catalysts for the carbonylation of methanol to acetic acid[29-30]. In Monsanto process, the rhodium-complex stability at low water concentrations of less than 10 wt.% have been investigated due to high cost of products separation and the water gas shift reaction within high water concentrations of 14~15 wt.%[31-34]. Under anhydrous conditions, deactivation of catalyst occurs, giving rhodium species such as trans-[$Rh(CO)_2I_4^-$] and [$Rh(CO)I_4^-$] from iodide ligand abstraction by the active rhodium catalyst of [$Rh(CO)_2I_2^-$][35-36]; 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 [37]. Forster reported that the rate of acyl iodide formation from the carbonylation of methyl iodide with rhodium (I) complex [$Rh(CO)_2I_2^-$] was extremely slow under anhydrous condition[34]. To synthesis of highly active and stable rhodium complexes in very low water concentration a lot of papers have been reported about the design of suitable ligands, mainly on phosphorous containing systems[31,38,39]. Very recently neutral rhodium (I) complexes of [$Rh(CO)_2I(L)$] (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 [$Rh(CO)_2I_2^-$] species were reported[40]. Unfortunately there has been no further report for the carbonylation of

---

Department of Nanopolymer Material Engineering, Pai Chai University, 155-40 Baejae-ro (Doma-Dong), Seo-Gu, Daejon 302-735, Korea

†Corresponding author : jhong@pcu.ac.kr

(Received: October 12, 2015, Revised: October 29, 2015
Accepted: November 5, 2015)



$$NMe_3 + CO \xrightarrow[MeI]{[Rh(CO)_2I_2^-]} Me\overset{O}{\overset{\|}{C}}NMe_2$$

**Scheme 1.** The carbonylation of trimethylamine under anhydrous condition.

other than methyl iodide by the rhodium (I) complexes.

Herein we report a novel synthesis of DMAC by carbonylation of trimethylamine with rhodium (I) complex stabilized with no water. For application to a large scale production repetitive using of the catalyst was also performed and a plausible mechanism is suggested (Scheme 1).

## 2. Experimental Section

### 2.1. 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. Autoclave reactor of 500 mL Sus 316 or 1000 mL Sus 316 is used for pressurized reaction with carbon monoxide. 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 ($Me_4NI$), trimethylammonium iodide ($HMe_3NI$), and rhodium (III) trichloride ($RhCl_3\cdot 3H_2O$) were purchased from a local manufacturer and Aldrich dealer, they were used without further purification unless noted. NMP and DMAC were distilled with sodium sulphate before use. NMR spectra were recorded on Bruker WP SY and Bruker AM 300 FT-NMR spectrometers. GC-MS data were obtained on HP 6890GC/5973 MSD. IR as KBr pellet on a Shimazu IR 440.

### 2.2. The Preparation of Rhodium(I) Complex $[Rh(CO)_2I_2^-]$ (1)

Rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) was prepared via three different routes and IR spectral data of it in the carbonyl region were consistent with those reported in literature[41].

*Method A* : $RhCl_3\cdot 3H_2O$ (0.71 g, 2.70 mmol) in NMP or DMAC of 25 mL, MeI (1.5 mL, 3.42 g, 24.10 mmol), and $Me_3N$ (2.18 mL, 1.43 g, 24.19 mmol) were charged in a stainless steel autoclave of 500 mL. Or $Me_4NI$ (4.83 g, 24.00 mmol) was used instead of the respective MeI and $Me_3N$. 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.

*Method B* : $RhCl_3\cdot 3H_2O$ (0.71 g, 2.70 mmol), MeI (0.56 mL, 1.28 g, 9.00 mmol), and $Me_3N$ (20.0 mL, 12.5 g, 211.8 mmol) were charged in a stainless steel autoclave of 1,000 mL. 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.

*Method C* : Dichlorotetracarbonyldirhodium complex $[Rh(\mu\text{-}Cl)(CO)_2]_2$ was prepared from rhodium trichloride of $RhCl_3\cdot 3H_2O$ according to the procedure in literature[43,44]. Trimethylamine (0.60 mL, 0.39 g, 6.66 mmol) and methyl iodide (0.20 mL, 0.46 g, 3.24 mmol) were added to $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.53 g, 1.36 mmol) in NMP or DMAC of 25 mL via syringe according to the modified procedure in literature[37,44,45]. 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.

### 2.3. The Carbonylation of Methyl Iodide with Trmethylamine Containing of Water

The respective rhodium catalyst was prepared by method A, B, and C. They were used in situ and showed the same catalytic activity for two carbonylations of methyl iodide and trimethylamine to acetic acid and DMAC in the presence of CaO[46]. Typical carbonylation was performed in Sus 316 autoclave reactor of 500 mL. An orange solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.53 g, 1.36 mmol) in NMP (50 mL) was added into the reactor with MeI (0.56 mL, 1.28 g, 9.00 mmol) and $Me_3N$ (20.00 mL, 13.12 g, 222.00 mmol). It was pressurized with CO to 350 psi at room temperature. Then it was heated with stirring at 150°C for 1 h and at 275°C for 1 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. Acetic acid was observed as the major (the mole ratio of 1 : 2 for DMAC to acetic acid) when NMP and trimethylamine were used as being purchased. DMAC was observed as the major (the mole ratio of 2 : 1 for DMAC to acetic acid) when trimethylamine and NMP were added into the reactor through column of 4 Å molecular sieve. The mole ratio of 1 : 10 for DMAC to acetic acid was observed when small amount of water (0.37 g, 20.54 mmol) was added into the reactants. After all volatiles compounds were removed from the reaction mixture, brownish solid residue was obtained. From the solid residue tetramethylammonium iodide ($Me_4NI$) and trimethylammonium iodide ($HNMe_3I$) were confirmed with the authentic compounds by $^1$H-NMR spectroscopy. Yield; 93~98% (DMAC and acetic acid based on trimethylamine), $^1$H-NMR ($D_2O$, ext. ref.); $Me_4NI$, 3.09 ppm (s, 12H); $HNMe_3I$, 2.84 ppm (s, 9H), 4.65 ppm (s, 1H).

### 2.4. The Preparation of Anhydrous 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. Trimethylamine was stored with 4 Å molecular sieve under 0-5°C before use. Water concentration of trimethylamine was reduced from 4,500 ppm to 220 ppm, those of which were measured by Karl Fisher titrimetry of Metrohm.

### 2.5. The Carbonylation of Anhydrous Trimethylamine and Repetitive Using Catalyst

Autoclave of 1,000 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 respective rhodium catalyst was prepared by method A, B, and C and it was used in situ. Typical carbonylation was performed as follows; After purging of the reactor 3 to 4 times with CO, $RhCl_3·3H_2O$ (0.71 g, 2.70 mmol), $Me_3N$ (20.00 mL, 13.12 g, 222.00 mmol), and MeI (1.10 g, 7.70 mmol) were added into it. Then it was pressurized with CO to 350 psi at room temperature and it was heated at 150°C with stirring for 1 h. It was heated at 275°C with stirring for another 1 h under CO pressure. When the pressure of reactor became low to 950 psi at 275°C, it was pressurized with CO up to 1,000 psi. Then cooling medium at 120°C was circulated via cooling coil inside the autoclave reactor for 1 h and about 10 g of aliquot received in receiver below the cooling coil was taken out via outlet from the reactor by CO pressure. The circulation of cooling medium was closed and an additional trimethylamine of 10 mL was added into the reactor by high pressure liquid pump with pressure of 1,050 psi. The above carbonylation procedure was repeated a total of 20 times, it took 22 h. On the last run the pressure of reactor was not decreased, rather increased. 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: 135.8 g (2.297 mol); Total amount of methyl iodide added: 1.10 g (7.70 mmol). Yield (%, based on trimethylamine): DMAC (164.9 g, 1.892 mol, 82.3%), MAA (21.3 g, 0.291 mol, 12.6%), and DMF (7.4 g, 0.101 mol, 4.4%), Conversion rate of trimethylamine: 99%; selectivity of DMAC: 82.3%, rhodium atom's TON for DMAC : 700.

## 3. Results and Discussion

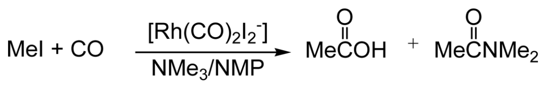
Neutral rhodium complex $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and rhodium trichloride(III) hydrate ($RhCl_3·3H_2O$) were transformed to anionic diiododicarbonylrhodium complex $[Rh(CO)_2I_2^-]$ (**1**) in the presence of tetramethylammonium iodide under the pressure of carbon monoxide during carbonylation reaction[35,47,48]. The rhodium(I) complex (**1**) is a well-known catalyst for the carbonylation of methanol to acetic acid in the presence of water[35,36] (Scheme 2).

The respective rhodium complex prepared via different routes showed the same carbonylation activity of methyl iodide and trimethylamine to acetic acid and DMAC in the presence of CaO[46]. The carbonylation of methyl iodide by rhodium(I) complex (**1**) in the pres-

$$RhCl_3{\bullet}3H_2O \xrightarrow{CO} [Rh(m\text{- }Cl)(CO)_2]_2 \xrightarrow{[I^-]} [Rh(m\text{- }I)(CO)_2]_2 \xrightarrow{[I^-]} [Rh(CO)_2I_2^-]$$

$$RhCl_3{\bullet}3H_2O \xrightarrow{CO,\ Me_3N,\ MeI} [Rh(CO)_2I_2^-]$$

**Scheme 2.** Synthesis of rhodium(I) catalyst $[Rh(CO)_2I_2^-]$ (**1**) via different routes.



$$\mathrm{MeI + CO \xrightarrow[NMe_3/NMP]{[Rh(CO)_2I_2^-]} MeC(=O)OH + MeC(=O)NMe_2}$$

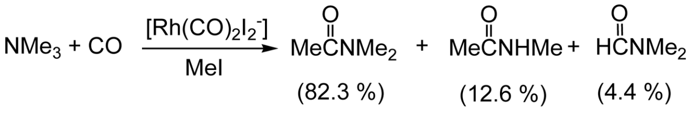
**Scheme 3.** The carbonylation of methyl iodide.

ence of trimethylamine in NMP gave acetic acid with small amount of DMAC with formation of trimethylammonium iodide ($Me_3NHI$). The unusual formation of DMAC, which was carbonylation product of trimethylamine, had encouraged us to perform another carbonylation reaction. When trimethylamine and NMP were added into reactor through column of 4 Å molecular sieve, DMAC was produced as the major with an small amount of acetic acid (Scheme 3).

The formation of acetic acid was seemed to be due to the presence of water in reaction medium. Therefore to prepare anhydrous trimethylamine, it had been passed through KOH column, 4 Å molecular sieves column, and dryice-cold trap sequentially since commercial trimethylamine was produced with water from condensation of methanol and ammonia on alumino-silicate catalyst. The carbonylation of anhydrous trimethylamine by rhodium(I) complex $[Rh(CO)_2I_2^-]$ (**1**) in the presence of methyl iodide without solvent gave DMAC as the major product with no acetic acid. Furthermore the catalyst had been used repetitively 20 times with no additional methyl iodide. On repetitive using catalyst the amount of MAA and DMF byproducts increased gradually. At the last run the pressure of reactor was not decreased and rather increased, therefore the procedure of reusing catalyst was ceased. It seemed to be that some of DMAC produced was transformed into MAA and DMF with increasing pressure of reactor by other than carbon monoxide. The analyses of collected products showed that the conversion rate of trimethylamine was 99% and DMAC selectivity was 82.3%. The yields of DMAC, MAA, and DMF were 82.3 %, 12.6%, and 4.4% with the catalyst's TON of 700 for DMAC. (Scheme 4.)

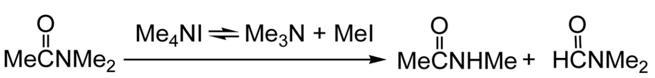
Without any rhodium catalyst separately DMAC was heated in the presence of trimethylamine, methyl iodide or tetramethylammonium iodide in autoclave under the same reaction conditions as those of trimethylamine carbonylation (under CO pressure of 1,000 psi at temperature of 275°C), DMAC was remained in the presence of trimethylamine for 20 h. However, in the presence of tetramethylammonium iodide large amount of DMAC was gradually transformed into MAA, DMF, and very small amount of intractable tar. Especially in the presence of methyl iodide, DMAC was transformed into intractable tar with increasing pressure of reactor over a short time. These results indicated clearly that under the carbonylation condition, tetramethylammonium iodide was decomposed into trimethylamine and methyl iodide[49], in the presence of which some of DMAC produced was transformed into MAA and DMF during the reaction (Scheme 5)[46].

Acyl iodide has been known as an intermediate in the carbonylation of methanol to acetic acid and/or acetic anhydride[35,50-52] and bond dissociation energy of C-I in acyl iodide is very low[53]. In the case of Co and Pd complexes, acyltrimethylammonium iodide has been suggested as an intermediate, from which DMAC and methyl iodide have been produced in some way[25-28]. 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 unstrained C($sp^3$)-N bond[54-56]. Long ago, Forster reported that the rate of acyl iodide formation from the carbonylation of anhydrous methyl iodide with rhodium (I) complex $[Rh(CO)_2I_2^-]$ was



$$\mathrm{NMe_3 + CO \xrightarrow[MeI]{[Rh(CO)_2I_2^-]} \underset{(82.3\ \%)}{MeC(=O)NMe_2} + \underset{(12.6\ \%)}{MeC(=O)NHMe} + \underset{(4.4\ \%)}{HC(=O)NMe_2}}$$

**Scheme 4.** The carbonylation of anhydrous trimethylamine without solvent.



$$\mathrm{MeC(=O)NMe_2 \xrightarrow{Me_4NI \rightleftharpoons Me_3N + MeI} MeC(=O)NHMe + HC(=O)NMe_2}$$

**Scheme 5.** Transformation of DMAC in the presence of tetramethylammonium iodide.

extremely slow[35].

In this work rhodium trichloride(III) hydrate ($RhCl_3 \cdot 3H_2O$) was heated with methyl iodide in excess of trimethylamine under the pressure of carbon monoxide, anionic diiododicarbonylrhodium complex [$Rh(CO)_2I_2^-$] (**1**) was formed. No evidence of acyltrimethylammonium iodide formation was found from rhodium complex (**1**) catalyzed carbonylations of trimethylamine under anhydrous condition. 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 (**1**) under anhydrous condition.

During the carbonylation of trimethylamine formation of neutral rhodium complex [$Rh(CO)_2I(NMe_3)$] (**2**) was suggested from iodide substitutions of anionic rhodium species (**1**) by trimethylamine ligand in abundance. Neutral dimer rhodium complex [{$Rh(CO)_2Cl$}$_2$] was also transformed to anionic complex (**1**) in the presence of tetramethylammonium iodide during the carbonylation of trimethylamine. Then the iodide substitution of (**1**) by trimethylamine in abundance was suggested to give neutral complex [$Rh(CO)_2I(NMe_3)$] (**2**), which had catalytic carbonylation activity of trimethylamine to DMAC under anhydrous condition[46]. Although the isolation of rhodium complex (**2**) was not successful in some reason[40], rhodium(III) halides are known to react with carbon monoxide in hydroxylic media with excess halide to give anionic rhodium(I) species [$Rh(CO)_2X_2^-$][35,48,49] and halides substitutions of the anionic rhodium(I) species by neutral ligands had been reported to give neutral complexes of [$Rh(CO)_2LX$] (L = amines, X = Cl, Br, I)[40]. Oxidative addition of methyl iodide, which is provided from the unimolecular decomposition of tetramethylammonium iodide at higher temperature of 275°C than those of the other carbonylations[31-34,36], to **2** results in the formation of σ-bond ($Rh\text{-}CH_3$) in [$RhMe(CO)_2(NMe_3)I_2$] (**3**), the unstable species of which isomerizes to acetyl intermediate [$Rh(COMe)(CO)I_2(NMe_3)$] (**4**) via methyl-migratory insertion to rhodium-carbonyl bond. Further addition of carbon monoxide to the vacant site of **4** provides pseudo-octahedral complex [$Rh(COMe)(CO)_2I_2(NMe_3)$] (**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[40]. Therefore *trans*-iodo ligand is more labile than *cis*-iodo ligand[57], thus the former easily can attack at the carbon atom of coordinated trimethylamine ligand having more electrophilicity than those of tertiary amine or quarternary 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 of **5** is proceeded to inner-sphere reductive elimination of DMAC and methyl iodide concurrently providing of dimer [{$Rh(\mu\text{-}I)((CO)_2$}$_2$] and/or the original neutral rhodium catalyst of **2** in abundance of trimethylamine. These procedures are able to be cycled if promoter 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 (**1**) produces acetic acid with trimethylammonium iodide ($Me_3NHI$) 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 (**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. In this reason, it is suggested that substitution of iodo ligand on the complex (**5**) by hydroxide anion gives another pseudo-octahedral complex [$Rh(COMe)(CO)_2I(NMe_3)(OH)$] (**6**). Then, from the complex (**6**) inner-sphere reductive elimination of acyl moiety and hydroxide moiety gives acetic acid simultaneously providing dimer [{$Rh(\mu\text{-}I)((CO)_2$}$_2$] and/or the original neutral rhodium catalyst (**2**) in abundance of trimethylamine (Fig. 1).

A similar stepwise procedures to the above reductive

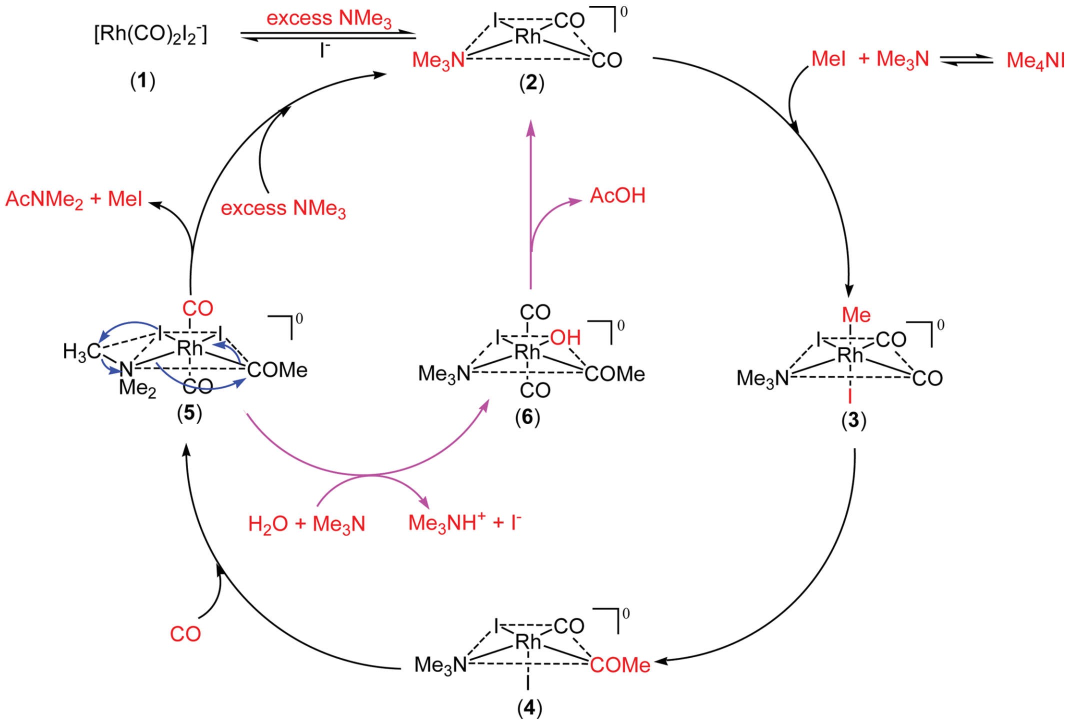


**Fig. 1.** Mechanism of rhodium(I)-catalyzed carbonylation of trimethylamine.

eliminations has been reported to afford acid anhydride or acetic acid via rhodium(III) complex $[Rh(COMe)(CO)_2I_2L]$ (L = water, $AcO^-$), which was formed from the pseudo-octahedral complex $[Rh(COMe)(CO)_2I_3^-]$ by substitution of an iodide ligand with acetate anion or water[57] due to the high energy of acyl idodide in theory[58]. 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 $[\{Rh(\mu\text{-}I)(COMe)(CO)I_2\}^-]_2$ and $[Rh(CO)_2I_2^-]$ with *N,N*-diethylacetamide via acylation and decoordination of the monodentating diethylamine ligand in abundance of methyl iodide[40]. 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[59].

## 4. Conclusions

Rhodium(I)-complex $[Rh(CO)_2I_2^-]$ (**1**) catalyzed carbonylation of trimethylamine in the presence of methyl iodide to give DMAC (*N,N*-dimethylacetamide) under anhydrous condition. Stepwise procedure of an intramolecular reductive elimination was suggested for the formation of DMAC and acetic acid in the carbonylation of trimethylamine and methyl iodide. 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

The author thanks Prof. Sung-Jun Cho, Prof. Young Baek Kim, and Prof. Sungsoo Kim (Pai Chai University, Daejon S. Korea), and Won-Il Jung and Hong-Lae Kim (Neomega Co., Ltd, Daejon S. Korea) for great supporting with fund, facilities, and assistant.

## References

[1] V. R. Pattabiraman and J. W. Bode, “Rethinking amide bond synthesis”, Nature, Vol. 480, pp. 471-479, 2011.

[2] C. L. Allen and J. M. J. Williams, “Metal-catalyzed approaches to amide bond formation”, Chem. Soc.

Rev., Vol. 40, pp. 3405-3415, 2011.

[3] Sud. Roy, Suj. Roy, and G. W. Gribble, "Metal-catalyzed amidation", Tetrahedron, Vol. 68, pp. 9867-9923, 2012.

[4] T. Kobayashi and M. Tanaka, "Cleavage of C-N bonds of tertiary amines and carbonylation of organic halides with palladium complexes as catalysts leading to formation of tertiary amides", J. Organomet. Chem., Vol. 231, pp. C12-14, 1982.

[5] M. M. Taqui Khan, S. B. Halligudi, S. Shukla, and S. H. R. Abdi, "Kinetic study of carbonylation of N-butylamine using homogeneous water soluble $Ru^{II}$-EDTA-CO catalyst", Journal of Molecular Catalysis, Vol. 51, pp. 129-135, 1989.

[6] I. Ryu, K. Nagahara, N. Kambe, N. Sonoda, S. Kreimerman, and M. Komatsu, "Metal catalyst-free by design. The synthesis of amides from alkyl iodides, carbon monoxide and amines by a hybrid radical/ionic reaction", Chem. Commun., Vol. 18, pp. 1953-1954, 1998.

[7] J. R. Martinelli, T. P. Clark, D. A.Watson, R. H. Munday, and S. L. Buchwald, "Palladium-catalyzed aminocarbonylation of aryl chlorides at atmospheric pressure: The dual role of sodium phenoxide", Angew. Chem. Int. Ed., Vol. 46, pp. 8460-8463, 2007.

[8] A. Mansour, T. Kehat, and M. Portnoy, "Dendritic effects in catalysis by Pd complexes of bidentate phosphines on a dendronized support: Heck vs. carbonylation reactions", Org. Biomol. Chem., Vol. 6, pp. 3382-3387, 2008.

[9] Y. Zhu, L. Chuanzhao, A. O. Biying, M. Sudarmadji, A. Chen, D. T. Tuan, and A. M. Seayad, "Stabilized well-dispersed Pd(0) nanoparticles for aminocarbonylation of aryl halides", Dalton T., Vol. 40, pp. 9320-9325, 2011.

[10] T. T. Dang, Y. Zhu, S. C. Ghosh, A. Chen, C.L.L. Chai, and A.M. Seayad, "Atmospheric pressure aminocarbonylation of aryl iodides using palladium nanoparticles supported on MOF-5", Chem. Commun., Vol. 48, pp. 1805-1807, 2012.

[11] F. Tinnis, O. Verho, K. P. J. Gustafson, C.-W. Tai, J.-E. Bäckvall, and H. Adolfsson, "Efficient palladium-catalyzed aminocarbonylation of aryl iodides using palladium nanoparticles dispersed on siliceous mesocellular foam", Chem-Eur. J., Vol. 20, pp. 5885-5889, 2014.

[12] T. Fang, X.-H. Gao, R.-Y. Tang, X.-G. Zhang, and C.-L. Deng, "A novel Pd-catalyzed N-dealkylative carbonylation of tertiary amines for the preparation of amides", Chem. Commun., Vol. 50, pp. 14775-14777, 2014.

[13] B. Dutta, S. Omar, S. Natour, and R. Abu-Reziq, "Palladium nanoparticles immobilized on magnetic nanoparticles: An efficient semi-heterogeneous catalyst for carbonylation of aryl bromides", Catal. Commun., Vol. 61, pp. 31-36, 2015.

[14] B. Urbán, M. Papp, D. Srankó, and R. Skoda-Földes, "Phosphine-free atmospheric carbonylation of aryl iodides with aniline derivatives in the presence of a reusable silica-supported palladium", J. Mol. Catal. A-Chem., Vol. 397, pp. 150-157, 2015.

[15] C. L. Berre, P. Serp, P. Kalck, and G. P. Torrence, "Acetic acid", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH Verlag GmbH, pp. 1-34, 2014.

[16] D. Stoye, "Solvents in Ullmann's Encyclopedia of Industrial Chemistry", Weinheim: Wiley-VCH Verlag GmbH, 2000.

[17] OECD SIDS Initial Assessment Report for 13th SIAM, Bern, Switzerland, 6-9 November 2001.

[18] H. Friederich and K. Sepp, "A process for the preparation of carboxamides", DE Patent 948056, 1956.

[19] K. Nozaki, "Dimethylacetamide production", US Patent 3407231, 1968.

[20] H. E. Bellis, "Dimethylacetamide from carbonylation of trimethylamine", EP Patent 0185823, 1984.

[21] T. Kazuo, "Dimethylacetamide production", JP Patent 3275656, 1991.

[22] J. R. Zhan, J. B. Guo, and X. L. Jiang, "Method for preparing N,N-dimethylacetamide", CN Patent 101003491, 2007.

[23] P. Roose, "Process for preparing secondary amides by carbonylation of a corresponding tertiary amine", WO Patent 2010057874 A1, 2010.

[24] H. Mei, W. Han, J. Hu, S. Xiao, Y. Lei, R. Zhang, W. Mo, and G. Li, "Palladium-catalyzed unstrained $C(sp^3)$-N bond activation: The synthesis of N,N-dimethylacetamide by carbonylation of trimethylamine", Appl. Organomet. Chem., Vol. 27, pp. 177-183, 2013.

[25] Y. Lei, R. Zhang, W. Han, H. Mei, Y. Gu, B. Xiao, and G. Li, "Promotion effects of Lewis acid/ $(CH_3)_4NI$ on $[Co(CO)_4]^-$ -catalyzed C-N bond activation in the carbonylation of trimethylamine", Catal. Commun., Vol. 38, pp. 45-49, 2013.

[26] Y. Lei, R. Zhang, and G. Li, "Cobalt-catalyzed unstrained C-N bond activation: the synthesis of tertiary amides by carbonylation of tertiary amines",

International Journal of Chemical, Environmental & Biological Sciences, Vol. 1, pp. 762-764, 2013.

[27] Y. Lei, R. Zhang, Q. Wu, H. Mei, B. Xio, and G. Li, “Carbonylation of quaternary ammonium salts to tertiary amide using $NaCo(CO)_4$ catalyst”, J. Mol. Catal. A-Chem., Vol. 381, pp. 120-125, 2014.

[28] Y. Lei, R. Zhang, L. Wu, Q. Wu, H. Mei, and G. Li, “Palladium-catalyzed carbonylation of quaternary ammonium halides to tertiary amides”, Appl. Organomet. Chem., Vol. 28, pp. 310-314, 2014.

[29] A. Fulford, C. E. Hickey, and P. M. Maitlis, “Factors influencing the oxidative addition of iodomethane to $[Rh(CO)_2I_2]^-$, the key step in methanol and methylacetate carbonylation”,Factors influencing the oxidative addition of iodomethane to $[Rh(CO)_2I_2]^-$, the key step in methanol and methyl acetate carbonylation”, J. Organomet. Chem., Vol. 398, pp. 311-323, 1990.

[30] A. Fulford, N. A. Bailey, H. Adams, and P. M. Maitlis, “The synthesis, properties, and crystal structure of $^nBu_4N$ $[Rh(CO)_2(OAc)_2]$, and the exchange of acetate, chloride, and iodide in $^nBu_4N[Rh(CO)_2(X)_2]$”, J. Organomet. Chem., Vol. 417, pp. 139-147, 1991.

[31] M. Christophe and G. Süss-Fink, “Ligand effects in the rhodium-catalyzed carbonylation of methanol”, Coordin. Chem. Rev., Vol. 243, pp. 125-142, 2003.

[32] N. Yoneda, S. Kusano, M. Yasui, P. Pujado, and S. Wilcher, “Recent advances in processes and catalysts for the production of acetic acid”, Appl. Catal. A-Gen., Vol. 221, pp. 253-265, 2001.

[33] B. L. Smith, G. P. Torrence, M. A. Murphy, and A. Aguiló, “The rhodium-catalyzed methanol carbonylation to acetic acid at low water concentrations: The effect of iodide and acetate on catalyst activity and stability”, Journal of Molecular Catalysis, Vol. 39, pp. 115-136, 1987.

[34] D. Forster, “Mechanistic pathways in the catalytic carbonylation of methanol by rhodium and iridium complexes”, Adv. Organomet. Chem., Vol. 17, pp. 255-267, 1979.

[35] D. Forster, “On the mechanism of a rhodium-complex-catalyzed carbonylation of methanol to acetic acid”, J. Am. Chem. Soc., Vol. 98, pp. 846-848, 1976.

[36] G. W. Adamson, J. J. Daly, and D. Forster, “Reaction of iodocarbonylrhodium ions with methyl iodide. Structure of the rhodium acetyl complex: $[Me_3PhN^+]_2[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$”, J. Organomet. Chem., Vol. 71, pp. C17-C19, 1974.

[37] A. Haynes, B. E. Mann, G. E. Morris, and P. M. Maitlis, “Mechanistic studies on rhodium-catalyzed carbonylation reactions: spectroscopic detection and reactivity of a key intermediate, $[MeRh(CO)_2I_3]^-$”, J. Am. Chem. Soc., Vol. 115, pp. 4093-4100, 1993.

[38] C. M. Frech, and D. J. Milstein, “Direct observation of reductive elimination of methyl iodide from a rhodium(III) pincer complex: the importance of sterics”, J. Am. Chem. Soc., Vol. 128, pp. 12434-12435, 2006.

[39] L. Gonsalvi, J. A. Gaunt, H. Adams, A. Castro, G. J. Sunley, and A. Haynes, “Quantifying steric effects of a-diimine ligands. Oxidative addition of MeI to rhodium(I) and migratory insertion in rhodium(III) complexes”, Organometallics, Vol. 22, pp. 1047-1054, 2003.

[40] R. J. Adcock, D. H. Nguyen, S. Ladeira, C. L. Berre, P. Serp, and P. Kalck, “Reactivity of rhodium(I) complexes bearing nitrogen-containing ligands toward $CH_3I$: synthesis and full characterization of neutral cis-$[RhX(CO)_2(L)]$ and acetyl $[RhI(\mu\text{-}I)(COMe)(CO)(L)]_2$ complexes”, Inorg. Chem., Vol. 51, pp. 8670-8685, 2012.

[41] A. Haynes, P. M. Maitlis, R. Quyoum, C. Pulling, H. Adams, S. E. Spey, and R. W. Strange, “Structure and reactivity of polymer-supported carbonylation catalyts”, Journal of the chemical Society, Dalton Transactions, Vol. 12, pp. 2565-2572, 2002.

[42] J. A. McCleverty, G. Wilkinson, L. G. Lipson, M. L. Maddox, and H. D. Kaesz, “Dichlorotetracarbonyldirhodium (rhodium carbonyl chloride)”, Inorganic Synthesis, Vol. 8, pp. 211-214, 1966.

[43] F. Malbosc, V. Chauby, C. Serra-Le Berre, M. Etienne, J.-C. Daran, and P. Kalck, “Solid-state and solution structures of a series of $[(HBPz_3\ Me_2)Rh(CO)(PR_3)]$ and $[(HBPz_3\ Me_2,4Cl)Rh(CO)(PR_3)]$ complexes”, Eur. J. Inorg. Chem., pp. 2689-2697, 2001.

[44] L. M. Vallarino, “Preparation and properties of a series of halocarbonylrhodates”, Inorg. Chem., Vol. 4, pp. 161-165, 1965.

[45] C. E. Hickey and P. M. Maitlis, “Oxidative addition of methyl iodide to dicarbonylrhodium(I) complexes”, Journal of the Chemical Society, Chemical Commnications, pp. 1609-1611, 1984.

[46] J.-H. Hong, “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”, Catalysts, Vol. 5, pp. 1969-1982, 2015.

[47] B. R. James and G. L. Rempel, “Direct

carbonylation of solutions containing rhodium salts", Chem. Commun., pp. 158-158, 1967.

[48] D. Forster, "Halocarbonyl derivatives of rhodium", Inorg. Chem., Vol. 8, pp. 2556-2558, 1969.

[49] M. Sawicka, P. Storoniak, P. Skurski, J. Blaxejowski, and J. Rak, "TG-FTIR, DSC and quantum chemical studies of the thermal decomposition of quarternary methylammonium halides", Chem. Phys., Vol. 324, pp. 425-437, 2006.

[50] H. Adams, N. A. Bailey, B. E. Mann, C. P. Mannel, C. M. Spencer, and A.G. Kent, "The solution behaviour of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, its reactions with CO, pyridine, and methanol, and the X-ray structure of $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$", J. Chem. Soc., Dalton Transations, pp. 489-496, 1988.

[51] L. A. Howe and E. E. Bunel, "Oxidative addition of RCOI to $[AsPh_4^+][Rh(CO)_2I_2^-]$. Synthesis of $[AsPh_4^+][RCORh(CO)_2I_3^-]$ (R = Me, Et, n-Pr, i-Pr)", Polyhedron, Vol. 14, pp. 167-173, 1995.

[52] A. Haynes, "Catalytic methanol carbonylation", Adv. Catal., Vol. 53, pp. 1-45, 2010.

[53] J. S. Roberts and H. A. Skinner, "Dissociation energies of carbon bonds, and resonance energies in hydrocarbon radicals", Transactions of the Faraday Society, Vol. 45, pp. 339-357, 1949.

[54] M. G. Voronkov, I. P. Tsyrendorzhieva, and V. I. Rakhlin, "Acyl iodide in organic synthesis: XI unusual N-C bond cleavage in tertiary amines", Russ. J. Org. Chem.+, Vol. 44, pp. 481-484, 2008.

[55] M. G. Voronkov, N. N. Vlasova, O. Y. Grigor'eva, L. I. Belousova, and A.V. Vlasov, "Acyl iodides in organic synthesis. Reactions of acetyl iodide with urea, thiourea, and their *N,N'*-disubstituted derivatives", Russ. J. Org. Chem., Vol. 45, pp. 486–490, 2009.

[56] M. G. Voronkov, I. P. Tsyrendorzhieva, and V. I. Rakhlin, "Acyl iodide in organic synthesis: Reactions with morphoine, piperidine, and N-hydrocarbylpiperidines", Russ. J. Org. Chem.+, Vol. 46, pp. 794-797, 2010.

[57] D. H. Nguyen, N. Lassauque, L. Vendier, S. Mallet-Ladeira, C. Le Berre, P. Serp, and P. Kalck, "Reductive elimination of anhydrides from anionic iodo acetyl carboxylato rhodium complexes", Eur. J. Inorg. Chem., Vol. 2014, pp. 326-336, 2014.

[58] N. Lassauque, T. Davin, D. H. Nguyen, R. J. Adcock, Y. Coppel, C. L. Berre, P. Serp, L. Maron, and P. Kalck, "Direct involvement of the acetate ligand in the reductive elimination step of rhodium-catalyzed methanol carbonylation", Inorg. Chem., Vol. 51, pp. 4-6, 2012.

[59] M. M. Taqui Khan, S. B. Halligudi, and S. H. R. Abdi, "Kinetic study of the carbonylation of diethylamine and triethylamine catalyzed by the water-soluble $K[Ru(III)(EDTA\text{-}H)Cl]\cdot 2H_2O$ complex in aqueous medium", Journal of Molecular Catalysis, Vol. 48, pp. 325-333, 1988.