

Syntheses of Amide Bonds and Activations of N-C(sp³) Bonds

Jang-Hwan Hong[†]

Abstract

In organic chemistry amide synthesis is performed through condensation of a carboxylic acid and an amine with releasing one equivalent of water via the corresponding ammonium carboxylate salt. This method is suffering from tedious processes and poor atom-economy due to the adverse thermodynamics of the equilibrium and the high activation barrier for direct coupling of a carboxylic acid and an amine. Most of the chemical approaches to amides formations have been therefore being developed, they are mainly focused on secondary amides. Direct carbonylations of tertiary amines to amides have been an exotic field unresolved, in particular direct carbonylation of trimethylamine in lack of commercial need has been attracted much interests due to the versatile product of *N,N*-dimethylacetamide in chemical industries and the activation of robust N-C(sp³) bond in tertiary amine academically. This review is focused mainly on carbonylation of trimethylamine as one of the typical tertiary amines by transition metals of cobalt, rhodium, platinum, and palladium including the role of methyl iodide as a promoter, the intermediate formation of acyl iodide, the coordination ability of trimethylamine to transition metal catalysts, and any possibility of CO insertion into the bond of Me-N in trimethylamine. In addition reactions of acyl halides as an activated form of acetic acid with amines are reviewed in brief since acyl iodide is suggested as a critical intermediate in those carbonylations of trimethylamine.

Keywords: Carbonylation; Tertiary Amine; Tertiary Amide; Trimethylamine; Dimethylacetamide; Intramolecular; Acyl iodide; Methyl iodide; Quaternary Ammonium Iodide

1. Introduction

One of the most important reaction is amide bond formation in organic chemistry, the reaction is practiced the most in industries for versatile synthetic polymers, pharmaceuticals, pesticides, and proteins^[1-4]. Traditional amide synthesis is performed through condensation of a carboxylic acid and an amine with releasing one equivalent of water via the corresponding ammonium carboxylate salt. Although the ammonium carboxylate salt can be transformed to the corresponding amide upon heating, this reaction has generally been considered to be of limited preparative value. Most of chemical approaches to amides formations are mainly focused on secondary amides^[5]. This method is suffering from tedious processes due to the adverse thermodynamics of the equilibrium and the high activation barrier for direct

coupling of a carboxylic acid and an amine^[6].

Apparently in chemical industries the most popular and reliable organic solvents are *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, and *N,N*-dimethylacetamide, the favorable properties of which are due to the amide bonds of their high polarities and stabilities. The amine functionalities of them are mainly transferred from monomethylamine and dimethylamine, both of which are manufactured with trimethylamine from condensation of methanol and ammonia by aid of solid catalyst at high temperature of about 400°C under around 20 atm^[7]. Although three methylamines are important industrial chemical intermediates with a worldwide production of approximately at 600,000 tons per year, in which the major product of trimethylamine plays only a minor role as raw [0material in the manufacture of choline chloride and tetramethylammonium hydroxide for the anisotropic etching of silicon^[7,8]. This lack of need for trimethylamine has been forcing most of methylamine production plants to circulate trimethylamine in the plant stream with keeping an equilibrium between three methylamines in spite of costly operations^[9,10].

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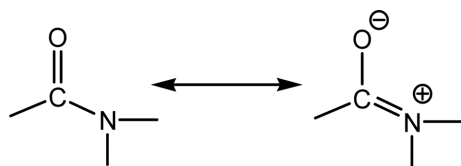


Fig. 1. Chemical structure of amide.

Among strong polar aprotic solvents, *N,N*-dimethylacetamide (DMAC) is the most widely used in syntheses of materials and fibers, in adhesive industry and electrolytic solvents, and as an excipient in drugs due to its stability and its unique physical and chemical properties of hydrogen bonds or dipole-dipole interactions between N–H or O–H bonds of substances and the solvent^[11].

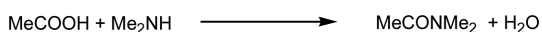
This review is focused mainly on carbonylation of trimethylamine as one of the typical tertiary amines by transition metals of cobalt, rhodium, platinum, and palladium including the role of methyl iodide as a promoter, the intermediate formation of acyl iodide, the coordination ability of trimethylamine to transition metal catalysts, and any possibility of CO insertion into the bond of Me–N in trimethylamine. Before describing the main subject reactions of acyl halides as an activated form of acetic acid with secondary and tertiary amines are reviewed in brief since acyl iodide is suggested as a critical intermediate in the carbonylations of trimethylamine.

2. Synthetic Methods of Tertiary Acetamides

2.1. Tertiary Acetamide Synthesis in Organic Chemistry

2.1.1. Tertiary Acetamide from Carboxylic Acid or Its Derivatives and Secondary Amines

In general tertiary acetamides are produced via couplings of carboxylic acid and secondary amines by forcing reaction condition at high temperature^[12–14] (Scheme 1).



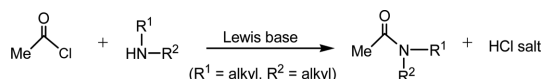
Scheme 1. Tertiary acetamide synthesis from acetic acid and secondary amine.

Also dealkylations of tertiary amines by acid anhydride have been known as reactions with poor atom-economy and limited applicability^[15,16]. Competitions of dealkylations between methyl or *n*-butyl groups and

benzylic group are reported depending on catalysts and their ligands in carbonylations of tertiary amines with acid anhydride or benzoic anhydride by using catalysts of FeCl₂, NiCl₂, ZnCl₂, CoCl₂, PdCl₂, RhCl₃, RuCl₂, and RuCl₃ at 160°C^[17].

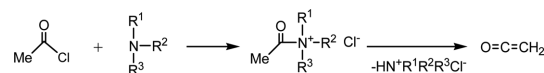
2.1.2. Tertiary Acetamide from Acyl Chloride and Secondary Amines

Acyl chloride, which is an activated form of acetic acid, reacts with secondary amines too. In the coupling reaction an additional base such as inorganic base, organic base, and even the initial amine in excess is required to trap the formed hydrogen chloride and to reserve the amine in order to react with acyl chloride to produce tertiary amide^[18] (Scheme 2).



Scheme 2. Tertiary acetamide syntheses from acyl chloride and secondary amines.

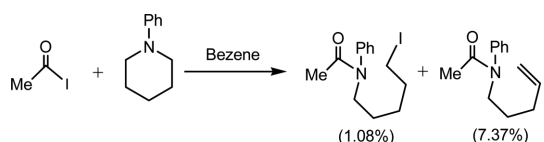
However acyl chloride usually reacts with even tertiary amines to give the corresponding quaternary acyl ammonium halides salts or ketene as a result of dehydrohalogenation from the initial acyl chloride with no formation of tertiary amide^[18] (Scheme 3).



Scheme 3. Quaternary acylammonium chloride and ketene from acyl chloride and tertiary amine.

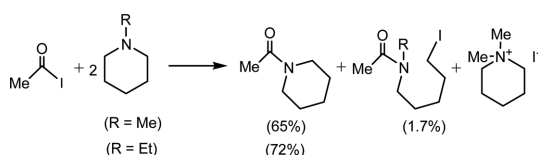
2.1.3. Tertiary Acetamide from Acyl Iodide and Secondary Amines

Acyl iodide with the carbon-iodine bond reacts with *N*-phenyl-piperidine in the molar ratio of 1:1 in benzene at 80°C produces only ring-opened products in the low yield of 9% via cleavage of the endocyclic N–C bond, 12% of which is *N*-(5-iodopentyl)-*N*-phenylacetamide (the total yield of 1.08%) and 81% of which is *N*-(pentyl-4-en-1-yl)-*N*-phenylacetamide (the total yield of 7.37%)^[19] (Scheme 4).



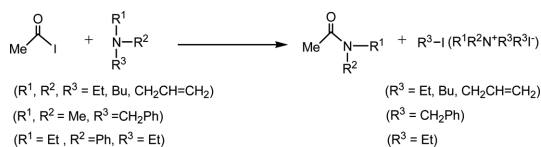
Scheme 4. Reaction of acyl iodide with *N*-phenyl piperidine.

In the case of *N*-alkyl piperidine the reaction of acyl iodide with 2 equivalent of *N*-methyl-piperidine in methylene chloride at room temperature gives *N*-acyl piperidine amide in the yield of 65% via cleavage of the exocyclic N-CH₃ bond, the ring-opened product of *N*-methyl-*N*-(5-iodo-pentyl) amide in the very small yield of 1.7% via cleavage of the endocyclic N-C bond, and *N,N*-dimethylpiperidinium, which is the cleaved methyl iodide trapped by *N*-methylpiperidine in excess. The reaction with *N*-ethyl-piperidine gives *N*-acylpiperidine in the yield of 72% via cleavage of the exocyclic N-C bond (N-CH₂CH₃) with no analogous cleavage of the endocyclic N-C bond in the piperidine ring moiety^[20] (Scheme 5).



Scheme 5. Reaction of acyl iodide with *N*-methyl-piperidine and *N*-ethyl piperidine.

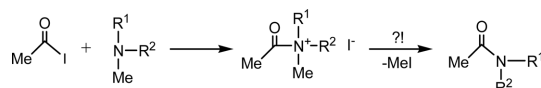
On the contrary the reaction of acyl iodide reacts with 2 equivalent of tertiary aliphatic or arylaliphatic amines at room temperature, then the corresponding amides are produced with hydrocarbon iodides (R³-I), such as ethyl iodide, butyl iodide, benzylic iodide, and allylic iodide except methyl iodide and phenyl iodide, via favorable cleavages of N-C bonds (N-R³). In the presence of the tertiary amines in excess, the cleaved hydrocarbon iodides react further with the amines to give the corresponding tetra(hydrocarbonyl)ammonium iodides. However, the yields of the acetamides are extremely lower (16-37%, the lowest for Bu₃N, the highest for triallylamine), presumably as a result of concurrent dehydroiodination of acyl iodide with the formation of ketene^[20] (Scheme 6).



Scheme 6. Reaction of acyl iodide and tertiary amine with no elimination of methyl iodide.

Since the bond dissociation energy of carbon-iodine in acyl iodide is low^[21], acyl iodide easily reacts with acyclic tertiary amine to produce the corresponding quaternary acylammonium iodide salt. Then the adduct

decomposes to the corresponding acetamide with cleavage of the N-C(alkyl) and formation hydrocarbon iodide, the yield of the acetamide is low due to the dehydroiodination of acyl iodide with formation of ketene. The cleavage reactivity of N-C bond is increased in the order of N-Ph << N-C(ring) < N-CH₃ << N-CH₂CH₃, N-allyl, N-benzylic^[22] (Scheme 7).



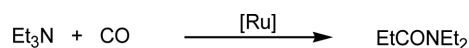
Scheme 7. Reaction of acyl iodide and tertiary amine with an elimination of methyl iodide.

It is hardly known that acyclic tertiary acyl amide is produced with methyl iodide via cleavage of N-CH₃ bond in quaternary *N*-methyl-acylammonium iodide, which is formed from acyl iodide and acyclic tertiary amine.

2.2. Carbonylation of Tertiaryamine to Tertiary Amide by Transition Metal Complexes

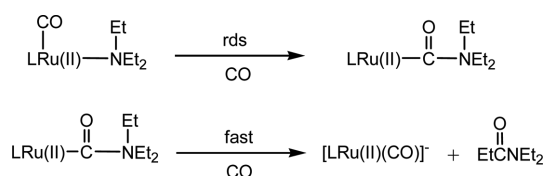
2.2.1. Carbonylation of Triethylamine by Ruthenium Complex

Carbonylation of triethylamine by the ruthenium complex of K[Ru(III)(EDTA-H)Cl]•2H₂O in aqueous medium is reported to provide *N,N*-diethylpropanamide in the yield of 100% in the temperature range of 80~100°C under CO pressure between 5 to 26 atm by M. M. Taquikhan *et al.*^[23] (Scheme 8).



Scheme 8. Carbonylation of triethylamine by ruthenium (II) complex.

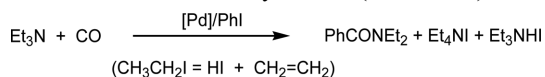
Based on the kinetic study for the carbonylation reaction the amide is produced via intra-molecular elimination of the coordinated amine and the carbonylation rate of triethylamine is about double that of diethylamine due to the higher stability of triethylamine Ru-complex as compared to that of diethylamine Ru-complex. They have observed that the carbonylation rates of amines show first order dependence with respect to catalyst, substrates, and dissolved CO concentrations. It is proposed that the rate determining step is the CO insertion into the Ru-N bond^[24]. The proposed mechanism is similar to that suggested by Sternberg *et al.* for the carbonylation of dimethylamine to *N,N*-dimethylformamide by Co₂(CO)₈ catalyst^[25] (Scheme 9).



Scheme 9. Intra-molecular elimination of *N,N*-diethylpropanamide.

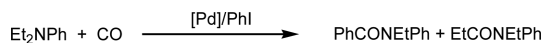
2.2.2. Carbonylation of Tertiary Amine by Palladium Complex

Tanaka and Kobayashi have reported carbonylation of tertiary amines with phenyl iodide or ethyl iodide by the palladium complex of $(\text{Ph}_3\text{P})_2\text{PdPhI}$ at 120°C under 20 atm of CO pressurized at room temperature^[26]. The carbonylation of triethylamine with phenyl iodide is described to give *N,N*-diethylbenzamide in the yield of 73.9% with two salts of tetraethylammonium iodide and triethylammonium iodide. Both salts are produced from triethylamine via its salt formations with the cleaved ethyl iodide and hydrogen iodide generated by dehydroiodination from the ethyl iodide (Scheme 10).



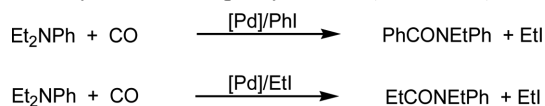
Scheme 10. Carbonylation of triethylamine with phenyl iodide by palladium complex.

In contrast carbonylation of diethylaniline with phenyl iodide gives *N*-ethyl-*N*-phenylbenzamide and an unexpected *N*-ethyl-*N*-phenylpropanamide in the yields of 41.7% and 9.2% respectively (Scheme 11).



Scheme 11. Carbonylation of diethylaniline with phenyl iodide by palladium complex.

The unexpected amide is considered to be produced from the carbonylation of diethylaniline with ethyl iodide, which is generated from the first carbonylation of diethylaniline with phenyl iodide (Scheme 12).

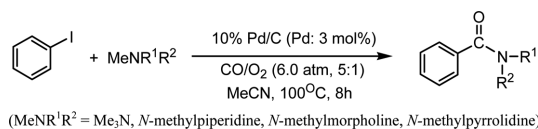


Scheme 12. Carbonylations of diethylaniline with aryl iodide and ethyl iodide by palladium complex.

Prominently Tanaka and Kobayashi have confirmed that *N,N*-ethyl,phenyl propanamide is not formed without ethyl iodide from Co-catalyzed carbonylation of

diethylaniline in German patent by BASF^[27]. Therefore they have emphasized that organic iodides are essential to the transition metal-catalyzed carbonylations of tertiary amines based on their results.

For decades palladium catalyzed carbonylation of aryl halides have attracted great interests, those are mainly focused on aminocarbonylations of aryl iodides and secondary amines^[28,29]. In recent Pd/C-catalyzed aminocarbonylation of aryl iodide with tertiary amine is reported to give tertiary amide via oxidative C-N bond activation of the tertiary amine, then aminocarbonylations of trimethylamine, *N*-methylpiperidine, *N*-methylmorpholine, and *N*-methylpyrrolidine produce the corresponding tertiary amides in the low yields of 53%, 52%, 38%, and 49% respectively^[30] (Scheme 13).



Scheme 13. Aminocarbonylation of aryl iodide and tertiary amine by palladium catalyst.

The low carbonylation yields are attributed to the difficulties in cleavage of N-CH₃ bond to form 'methyl iodide' too and alkyl iodide or aryl iodide is essential promoter for the palladium catalyzed carbonylations.

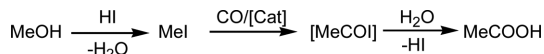
3. Carbonylation of Trimethylamine with Methyl Iodide by Transition Metal Complexes

3.1. Role of Methyl Iodide and Its Regeneration from Tetramethylammonium Iodide

3.1.1. Acyl Iodide Formation from Methyl Iodide Promoter

In the carbonylations of methanol to acetic acid by the transition metal complexes of cobalt, rhodium, iridium, palladium, and nickel, acyl iodide has been known as an intermediate for decades^[31-37], in chemical industry Monsanto process and Cativa process are the most well-known^[38,39]. In the typical catalytic cycles methyl iodide promoter is transformed to acyl iodide intermediate, reaction of which with water easily produces acetic acid and hydrogen iodide. Hydrogen iodide reacts with methanol to provide the promoter of methyl iodide with water. The easy formation of acetic acid is attributed to the low bond dissociation energy of carbon-iodine in

acyl iodide^[21] (Scheme 14).



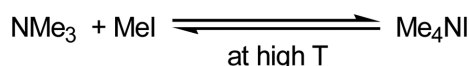
Scheme 14. Carbonylation of methanol to acetic acid with methyl iodide by transition metal catalysts.

Several carbonylation methods of trimethylamine by the transition metal complexes of Co, Rh, Ir, and Pd have been patented, nevertheless there has been no industrial application so far^[40-45]. All of those transition metal complexes catalyse not only the carbonylation of methanol to acetic acid, but also they are active and effective with only methyl iodide (Scheme 15).



Scheme 15. Carbonylation of trimethylamine with methyl iodide by catalysts.

Since the promoter of methyl iodide reacts with trimethylamine to give tetramethylammonium iodide salt quickly^[46], it is a curious whether methyl iodide is available in excess of trimethylamine during the carbonylations. In theoretical and experimental studies under atmosphere pressure, it has been demonstrated that tetramethylammonium halide salts are decomposed to an equimolar mixture of trimethylamine and an methyl halide via unimolecular process only at high temperature (about 10% decomposition of Me₄NX at about 555 K for X=Cl, at about 575 K for X=Br, I)^[47,48] (Scheme 16).



Scheme 16. Thermal decomposition of tetramethylammonium iodide at high temperature.

3.1.2. Coordination Ability of Trimethylamine to Transition Metals

Trimethylamine is a powerful N-donor ligand with no

π -bonding character, it can form transition metal complexes combining both low oxidation state and low coordination number^[49]. Decades ago platinum and palladium complexes of trimethylamine are prepared such as trans-PtCl₂(NMe₃)₂, trans-PtBr₂(NMe₃)₂, and trans-PdCl₂(NMe₃)₂, the trans-effect of nitrogen in which is suggested much less than phosphorous and nearer to that of the chloride ion by IR and NMR spectroscopies^[50]. Trimethylamine complexes of Zn (II), Fe (III), Mo (II) chlorides and Mo (V), Mo(VI), oxochlorides, Zr (IV) halides, Hf (IV) halides, and AlCl₃ are also reported^[51-55]. Especially for the trimethylamine complexes of Lewis acids, the metal centers in the structure of AlCl₃(NMe₃)₂ and FeCl₃(NMe₃)₂ are five-coordinate and both nitrogen atoms occupy the axial positions of the trigonal bipyramid with staggered arrangement of the substituents on the nitrogen atoms^[51,55].

In this point it seems reasonable that the transition metals of Co, Rh, Ir, and Pd are able to form their coordinated complexes with trimethylamine during the carbonylations of it.

3.2. Carbonylation of Trimethylamine by Palladium Complexes

3.2.1. Carbonylation of Trimethylamine with Tetramethylammonium Iodide by Palladium Complex

The first carbonylation of trimethylamine by palladium and ruthenium complexes to *N,N*-dimethylacetamide is reported by G. Li group^[56]. The palladium catalyst's performance is improved by the tuning of ligands with promoters and the catalytic system is optimized in PdC/bipy (bipy=2,2'-bipyridine) with tetramethylammonium iodide promoter. Carbonylation of dried trimethylamine by the palladium catalyst system produces *N,N*-dimethylacetamide in the high selectivity of 98.1% and in the high yield of 90.8% with the high

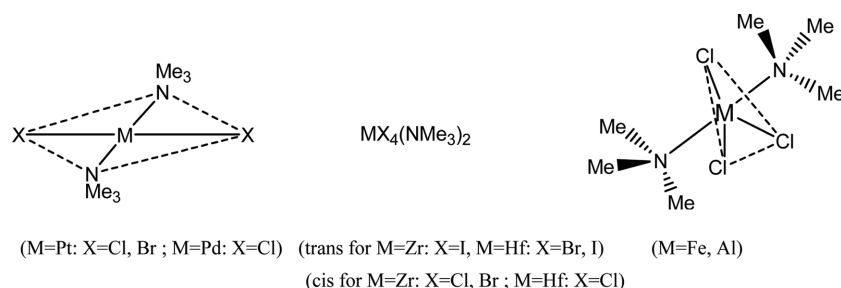
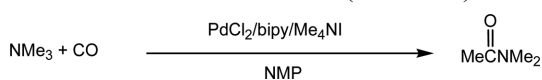


Fig. 2. Trimethylamine complexes of Pt, Pd, Zr, Hf, Fe, and Al.

turnover number (TON, 90.0 mmol, DMAC per mole of PdCl₂ as used 0.1 mol %). The high efficiency of the catalyst is attributed to tetramethylammonium iodide to prevent palladium black formation. Typically the mole ratio of 20 mmol : 0.2 mol : 4.5 mmol between Me₃N : PdCl₂ : Me₄N⁺I⁻ is used in 15 ml of NMP, the reaction mixture under 30 atm of CO at room temperature is heated at 200°C for several hours (Scheme 17).



Scheme 17. Pd-catalyzed carbonylation of trimethylamine with tetramethylammonium iodide.

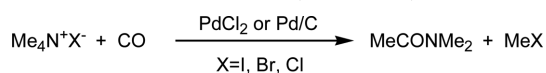
From GC-MS analysis of the reaction mixture the formation of acetic acid is confirmed, methyl iodide is suggested such as promoter in the carbonylation of methanol to acetic acid. The carbonylations with other promoter such as KI, Et₄N⁺I⁻, *n*-Bu₄N⁺I⁻, Me₄N⁺Br⁻, or Me₄N⁺Cl⁻ are investigated to produce *N,N*-dimethylacetamide in the yields of 17.8%, 17.2%, 28.2%, 82.7%, and 10.0% respectively, the low yields of which are attributed to the difficulties in generation of methyl iodide from the promoter of Me₄N⁺Cl⁻ by the authors^[56].

Nevertheless the promoters of KI, Et₄N⁺I⁻, and *n*-Bu₄N⁺I⁻ are apparently not methyl iodide sources, it is implying that there is an effect and/or role of iodide

anion itself on the formation of methyl iodide or acyl-complex for the carbonylations.

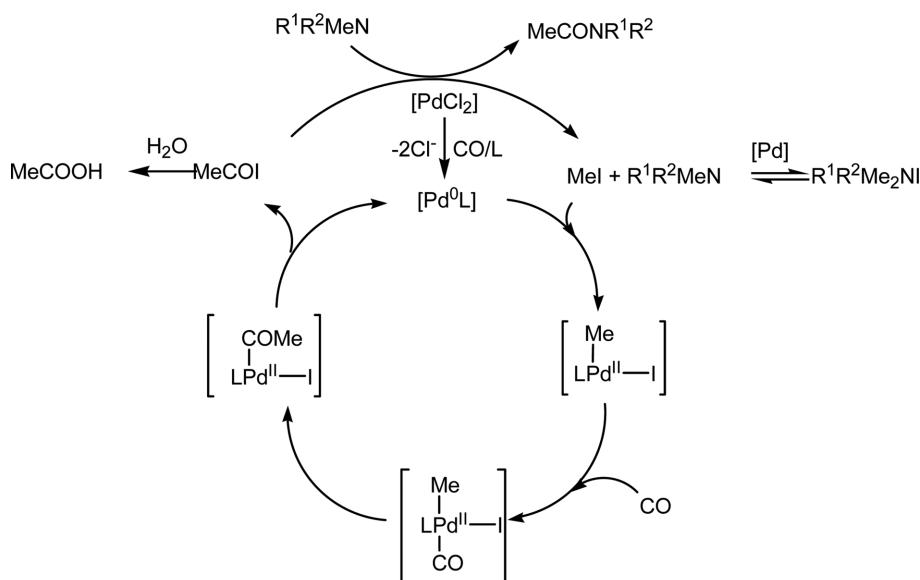
3.2.2. Carbonylation of Tetramethylammonium iodide by Palladium Complex

Carbonylation of tetramethylammonium iodide by the catalyst of PdCl₂ or Pd/C is reported to provide *N,N*-dimethylacetamide in the yield of 96.9% with the low loading catalyst of 0.05 mol % corresponding to the turnover frequency of 242 h⁻¹. Typically the mole ratio of 0.0075 mmol : 15 mmol between PdCl₂ : Me₄N⁺I⁻ is used in 50 ml of NMP^[57] (Scheme 18).



Scheme 18. Pd-catalyzed carbonylation of quaternary ammonium halides.

The higher activity of Pd/C, which has been recycled six times with a slight decrease in activity, than that of PdCl₂ is attributed to the formation of no palladium black by the stabilization of nano-sized palladium colloids and clusters by tetraalkylammonium salts^[34,58-62]. The carbonylations of other quaternary ammonium halide, such as cyclo-BuMe₃N⁺I⁻, cyclo-PentylMe₃N⁺I⁻, (EtO)₂Me₂N⁺I⁻, PhMe₃N⁺I⁻, and Me₄N⁺Br⁻, are investigated to deliver the corresponding tertiary acetamides



($\text{R}^1\text{R}^2\text{Me}_2\text{NI}$ = cyclo-BuMe₃NI, cyclo-PentylMe₃NI, (EtO)₂Me₂NI, PhMe₃NI or Me₄NBr)

Fig. 3. Proposed mechanism for Pd-catalyzed carbonylations of quaternary ammonium iodides.

in moderately good yields apparently. In contrast from the carbonylation with Me₄N⁺Cl⁻, *N,N*-dimethylacetamide is obtained in the very low yield of 5.9%, the low yield of which is attributed to the low activity and/or the less generation of methyl chloride^[57].

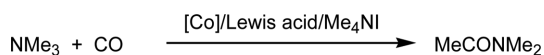
3.2.3. Suggested Mechanism for the Palladium Catalyzed Carbonylation

In the suggested mechanism the decomposition of tetramethylammonium iodide provides trimethylamine and methyl iodide, the oxidative addition of which to Pd⁰ reduced from PdCl₂ forms Pd(II)-Me complex. Coordination and migratory insertion of CO to Pd(II)-Me complex gives Pd(II)-acetyl complex, reductive elimination of which regenerates Pd⁰ and acyl iodide. Then acyl iodide intermediate reacts with trimethylamine to produce *N,N*-dimethylacetamide and methyl iodide via the decomposition of the unstable quaternary acyltrimethyl ammonium iodide salt^[52,57] (Fig. 3).

3.3. Carbonylation of Trimethylamine by Cobalt Complexes

3.3.1. Carbonylation of Trimethylamine with Tetramethylammonium Iodide and Lewis Acid by Cobalt Complexes

Lewis acid, such as AlCl₃, FeCl₃, BiCl₃, and InCl₃, is added to tetramethylammonium iodide promoter to increase the catalytic activity of Na⁺[Co(CO)₄]⁻ by the same research group of G. Li *et al.*^[63]. The catalytic system is optimized in Na[Co(CO)₄]⁻/AlCl₃/Me₄N⁺I⁻ with the mole ratio of 1 mmol : 6 mmol : 3 mmol : 34 mmol between Na[Co(CO)₄]⁻ : AlCl₃ : Me₄N⁺I⁻ : Me₃N in 50 ml of anhydrous NMP. When the water content in NMP is less than 0.1%, *N,N*-dimethylacetamide is produced in the high yield of 96.4% with the high selectivity of 98%. In the presence of water the carbonylation gives byproducts of acetic acid and *N,N*-dimethylformamide, which is considered to be produced from the carbonylation of dimethylamine. Dimethylamine is also presumed to be provided from the decomposition of trimethylammonium iodide (Scheme 19).



Scheme 19. Co-catalyzed carbonylation of Me₃N with Lewis acid and promoter of Me₄NI.

The carbonylations of other tertiary amines, such as

Me₂NEt, PhMe₂N, *N*-methylpyrrolidine, *N*-methylpiperidine, and *N*-methylmorpholine, provide the corresponding acetamides of *N*-ethyl-*N*-methylacetamide, *N*-methyl-*N*-phenylacetamide, *N*-acetylpyrrolidine, *N*-acetyl-piperidine, and *N*-acetylmorpholine in the yields of 63% to 94%^[63].

3.3.2. The effects of the Promoters and the Role of Lewis Acid in the Carbonylations

Various candidates for the promoter are investigated such as KI, I₂, MeI, Et₄NI, AlCl₃, AlCl₃ with Me₄NI *et al.* The effects of promoters such as KI and I₂ are not significant, it results in the low yields of less than 3.6% for *N,N*-dimethylacetamide. In particular the carbonylation of trimethylamine in the presence of only aluminum trichloride is reported to give *N,N*-dimethylacetamide in the low yield of 14.3% to 23.1% depending on the amount of AlCl₃. The carbonylation with methyl iodide or tetramethylammonium iodide instead of aluminum trichloride results in the higher yields of over 33.5% for the amide than that of aluminum trichloride. Furthermore, the effect of only tetramethylammonium iodide is enhanced by adding Lewis acid of AlCl₃, FeCl₃, BiCl₃, or InCl₃, which results in the high yields of 69.7% to 94.0% for *N,N*-dimethylacetamide. The enhanced catalytic effect is ascribed to both of Me₄NI promoter and AlCl₃, which is suggested to react with trimethylamine providing more active species of Cl₂Al-NMe₂ than that of trimethylamine by the authors^[63].

First of all it is characteristic that the Co-catalyzed carbonylations with only AlCl₃ without methyl iodide source is still providing *N,N*-dimethylacetamide in even low yield of 23.1%.

3.3.3. Suggested Mechanism for Cobalt-Catalyzed Carbonylation with Lewis Acid

In the proposed mechanism in Fig. 4, the nucleophilic attack of the species **A** either on the activated C-N bond in AlCl₃ adduct of tertiary amine or on the generated methyl iodide leads to 18e tetracarbonyl intermediate **B**. Subsequent insertion of CO into Co-CH₃ bond affords intermediate **C**. Then, the active species **C** is able to react readily with tertiary amine to form Co-complex **D** with unstable quaternary acylammonium salt. Immediately, the desired product is formed with releasing of methyl iodide by the decomposition of unstable species **D**. In addition the final product of the acetamide is also

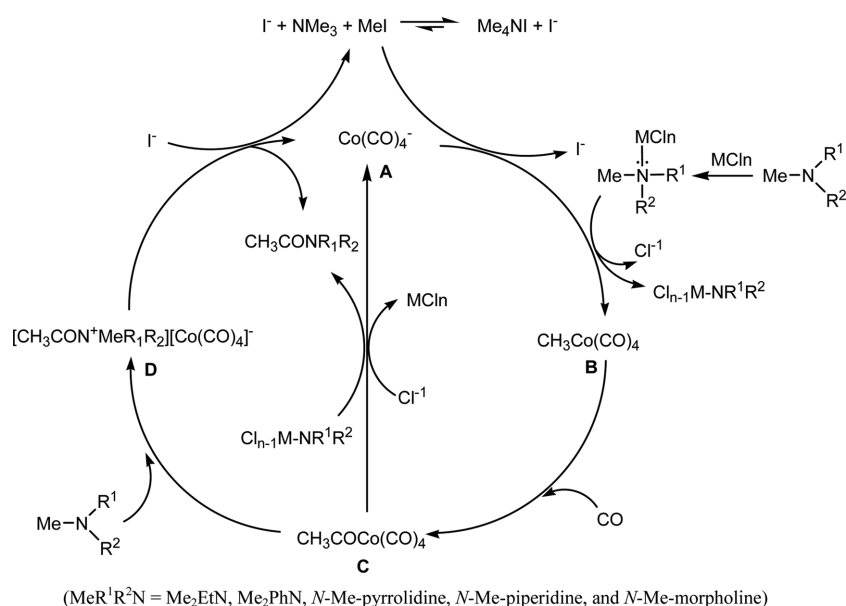


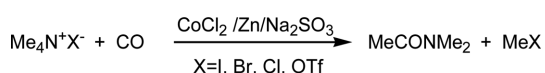
Fig. 4. Proposed mechanism for the carbonylation of tertiary amine with Lewis acid and tetraalkylammonium iodide by $[\text{Co}(\text{CO})_4]^-$ complex.

able to be produced by the reaction of $\text{AlCl}_2\text{-NR}^1\text{R}^2$ and species **C**. Two intermediates of $\text{Cl}_2\text{Al-NMe}_2$ and $[\text{MeCONMe}_3]^+$ are suggested to be related to the formation of *N,N*-dimethylacetamide.

3.4. Carbonylation of Quaternary Ammonium Salts by Cobalt Complex

3.4.1. Carbonylation of Tetramethylammonium Salts by Cobalt Complex

By using the catalyst of $\text{NaCo}(\text{CO})_4$ or prepared from CoCl_2 , Zn, and Na_2SO_3 , the carbonylation of Me_4NX in NMP under anhydrous condition is investigated to give *N,N*-dimethylacetamide in the yield of 13.3% to 98.2% depending on the anion of X. Typically the mole ratio of 0.075 mmol : 15 mmol between $\text{NaCo}(\text{CO})_4$: Me_4NI in 50 ml of NMP is applied and the highest TON of 334 is obtained for *N,N*-dimethylacetamide. The anion of tetramethylammonium salt has been suggested to have a great effect on the activity of the salt, the activity of which is increased in the order $\text{Cl} < \text{OTf} < \text{Br} < \text{I}$ due to the easy recovery of $\text{CH}_3\text{-X}^{[64]}$ (Scheme 20).



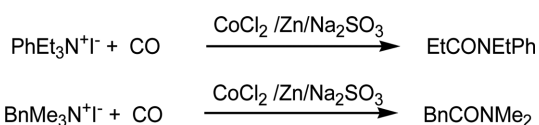
Scheme 20. Co-catalyzed carbonylation of tetramethyl ammonium halides.

It is described that increasing the amount of water in the mixture lowers both of the catalytic activity and the selectivity for *N,N*-dimethylacetamide with rapidly increasing the yield of acetic acid and *N,N*-dimethylformamide, in which the respective hydroxyl group and the hydrogen atom are thought to be come from the water in NMP solvent.

3.4.2. Carbonylation of Other Quaternary Ammonium Iodides by Cobalt Complex

By the same cobalt catalyst without promoter the carbonylations of only quaternary ammonium salts, such as $\text{EtMe}_3\text{N}^+\text{I}^-$, $\text{PhMe}_3\text{N}^+\text{I}^-$, $\text{cyclo-BuMe}_2\text{N}^+\text{I}^-$, $\text{cyclo-PentylMe}_2\text{N}^+\text{I}^-$, *N,N*-dimethylpyrrolidinium iodide, *N,N*-dimethylpiperidinium iodide, and *N,N*-dimethylmorpholinium iodide, are investigated to provide the corresponding acetamides in the yields of more than 70%^[64]. Each formation of the acetamide is suggested due to the generation and regeneration of methyl iodide during the carbonylation via acyl iodide intermediate.

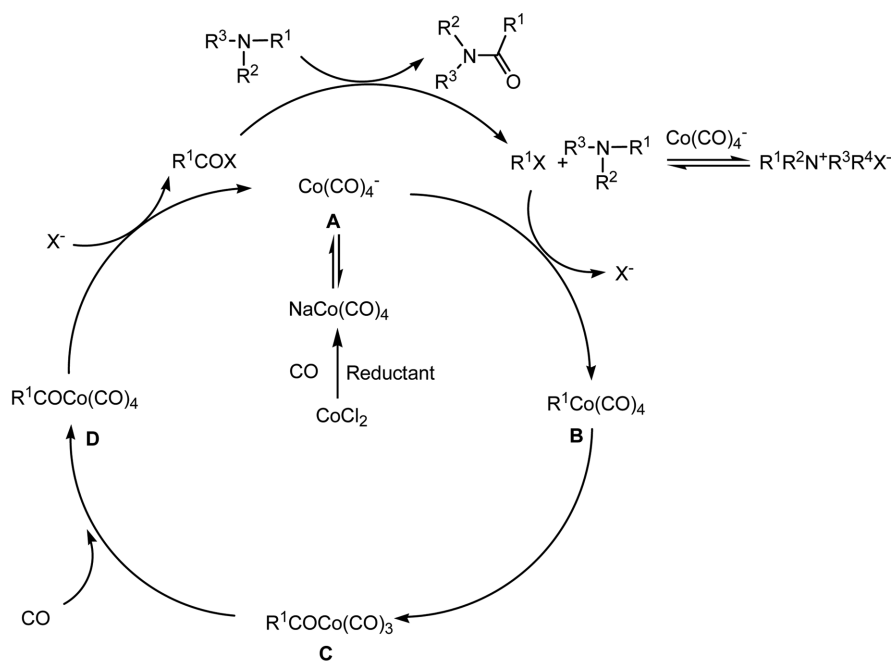
The carbonylations of triethylphenylammonium iodide and trimethylbenzylammonium iodide produce *N*-ethyl, *N*-phenyl-propanamide and *N,N*-dimethylbenzylamide in the yield of 49.7% and 41.7% respectively^[64] (Scheme 21).

**Scheme 21.** Carbonylations of Et₃PhN⁺I⁻ and Me₃BnN⁺I⁻.

The results are showing the generations of ethyl iodide and benzyl iodide via intermediates of propionyl iodide and 2-phenyl acetyl iodide in the carbonylations.

3.4.3. Suggested Mechanism for Cobalt-Catalyzed Carbonylation of Quaternary Ammonium Salts

In the proposed mechanism acyl iodide is suggested as a key intermediate based on the formation of acetic acid and *N,N*-dimethylacetamide. The generation of methyl iodide from quaternary ammonium iodide is reacted with the catalyst of [Co(CO)₄]⁻, the nucleophilic attack of which on methyl iodide leads to CH₃Co(CO)₄. The addition and insertion of carbon monoxide to the CH₃-Co bond in CH₃Co(CO)₄ provides CH₃COC(CO)₄, the reaction of which with iodide anion gives acyl iodide and the catalyst of [Co(CO)₄]⁻ in the first step of the cycle^[64] (Fig. 5).



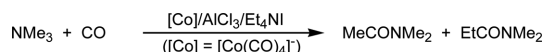
(R¹ = MeI, EtI, BnI, R¹R²R³R⁴N⁺I⁻ = Me₄N⁺I⁻, EtMe₃N⁺I⁻, PhMe₃N⁺I⁻, cyclo-BuMe₂N⁺I⁻, cyclo-PentylMe₂N⁺I⁻, *N,N*-dimethylpyrrolidinium iodide, *N,N*-dimethylpiperidinium iodide, *N,N*-dimethylmorpholinium iodide)

Fig. 5. Proposed mechanism for Co-catalyzed carbonylation of quaternary ammonium halides.

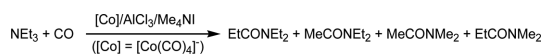
3.5. Competitive Transference of Amino Moiety from Quaternary Ammonium Iodide to the Final Amide

3.5.1. Carbonylations of Tertiary Amine and Quaternary Ammonium Iodide by Cobalt Complex

Co-catalyzed carbonylation of trimethylamine (34 mmol) in the presence of tetraethylammonium iodide (3 mmol) and aluminum trichloride is reported to produce *N,N*-dimethylacetamide in the low yield of 21.7% with the byproduct of *N,N*-dimethylpropanamide^[63] (Scheme 22).

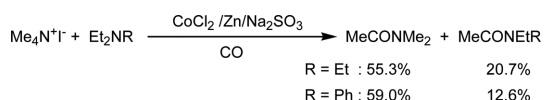
**Scheme 22.** Co-catalyzed carbonylation of Me₃N with Lewis acid and Et₄NI.

On the other hand the carbonylation of triethylamine (34 mmol) in the presence of tetramethylammonium iodide (3 mmol) and aluminum trichloride is investigated to give four different amides such as *N,N*-diethylpropanamide, *N,N*-diethylacetamide, *N,N*-dimethylacetamide, and *N,N*-dimethylpropanamide in the yields of 21.3%, 12.8%, 1.2%, and 0.7% respectively^[63] (Scheme 23).



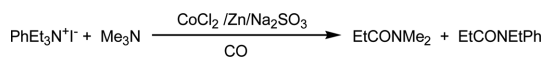
Scheme 23. Co-catalyzed carbonylation of Et₃N with Lewis acid and Me₄NI.

The carbonylation of tetramethylammonium iodide and triethylamine or diethylaniline in the ratio of 1:1 is reported to provide *N,N*-dimethylacetamide with another acetamide^[64] (Scheme 24).



Scheme 24. Co-catalyzed carbonylation of Me₄NI and Et₃N or Et₂NPh.

The carbonylation of triethylphenylammonium iodide and trimethylamine in the ratio of 1:1 is reported to give two propanamides of *N,N*-dimethyl-propanamide and *N,N*-ethylphenyl-propanamide in the yield of 32.1% and 10.6% respectively^[64] (Scheme 25).

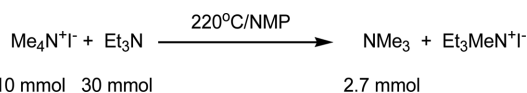


Scheme 25. Co-catalyzed carbonylation of PhEt₃NI and Me₃N.

It is characteristic that two tertiary amides are obtained from the coupling of acyl and propionyl moieties with two amino moieties (favorably with dimethyl amino moiety).

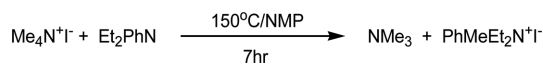
3.5.2. Thermal Equilibrium of Methyl Iodide from Tetramethylammonium Iodide and Triethylamine

Thermal generation of methyl iodide from triethylamine and tetramethylammonium iodide at 220°C in NMP is reported^[64] (Scheme 26).



Scheme 26. Generation of methyl iodide from Me₄NI to form Et₃NMeI in NMP.

Generation of trimethylamine is measured in the yield of 27.3% at 200°C, 6.4% at 180°C, and 0% at 150°C from the mixture of tetramethylammonium iodide and diethylaniline with no catalyst^[63] (Scheme 27).



Scheme 27. Thermal reaction between Me₄NI and Et₂NPh in NMP.

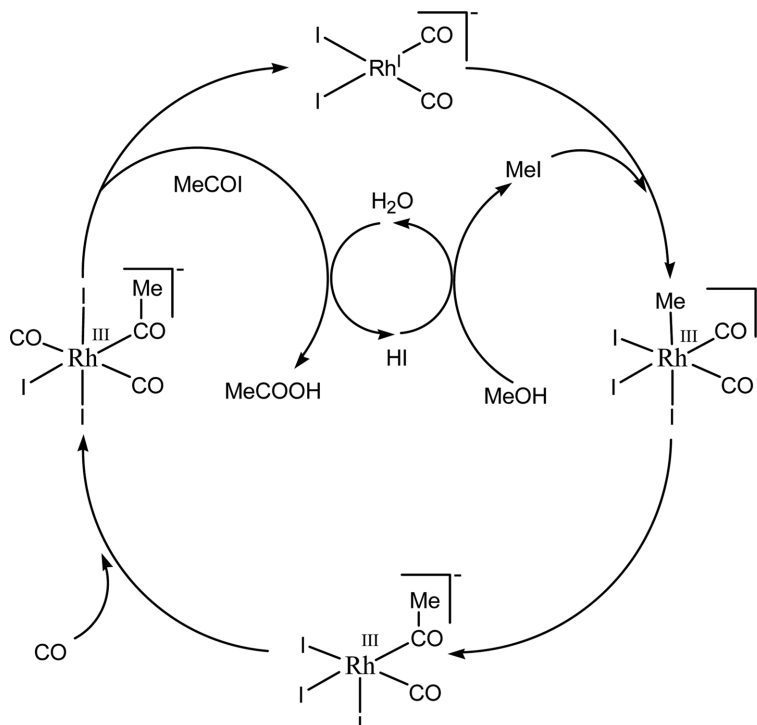


Fig. 6. Rhodium-catalyzed carbonylation of methanol to acetic acid in Monsanto process.

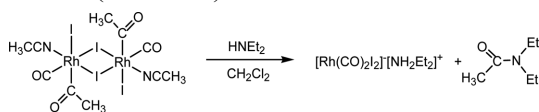
In this point the formation of *N,N*-dimethylacetamide in the yield of 7.1% at 140°C is solely attributed to the catalytic carbonylation effect of tetramethylammonium iodide by the catalyst of [Co(CO)₄]⁻ [63]. Presumably the formation of the amide is indicating the formation of CH₃Co(CO)₄ (**B**) by the nucleophilic attack of [Co(CO)₄]⁻ at methyl group.

3.6. Carbonylation of Trimethylamin by Rhodium Complex

3.6.1. Acylation of Diethylamine with Methyl Iodide by Rhodium Complex

When the water content is higher than 8 wt% in Monsanto process, the rate determining step is the oxidative addition of methyl iodide to rhodium center^[39]. The rate of acyl iodide formation in the carbonylation of anhydrous methyl iodide by rhodium (I) complex of [Rh(CO)₂I₂]⁻ is reported extremely slow by D. Forster^[65-68]. However increasing electron density at the rhodium center by ligands such as amines and phosphines consequently enhances the overall rate of acetic acid formation by facilitating the oxidative addition of methyl iodide to the rhodium center^[32, 69-73] (Fig. 6).

In this point it is plausible assumption that trimethylamine is able to accelerate the oxidative addition of methyl iodide promoter to the rhodium complex if there is any methyl iodide in the reaction medium during the carbonylation of trimethylamine. Surprisingly the transference of acyl group to diethylamine is observed by P. Kalck *et al.*, the addition of 2 equivalent diethylamine to rhodium complex [RhI(μ-I)(COMe)(CO)NCCH₃]₂ provides the rhodium complex of [Rh(CO)₂I₂]⁻[H₂N⁺Et₂]⁺ and *N,N*-diethylacetamide with no formation of acyl iodide^[32] (Scheme 28).



Scheme 28. Synthesis of *N,N*-diethylacetamide from Et₂NH by [RhI(μ-I)(COMe)(CO)NCCH₃]₂.

The acyl coordinated rhodium complex is synthesized in acetonitrile from the oxidative addition of methyl iodide to the dimer complex of [RhI(μ-I)(CO)₂]₂, which is the same catalyst used in Monsanto process. It has been reported that a stepwise procedure of an intramolecular reductive elimination affords acetic acid or acid anhydride via rhodium (III) complex [Rh(COMe)(CO)₂I₂L]

(L=water, AcO⁻), which is formed from the pseudo-octahedral complex [Rh(COMe)(CO)₂I₂]⁻ by the substitution of an iodide ligand with water or acetate anion^[74]. Acyl iodide intermediate is excluded due to the high formation energy of it, which has been calculated in theory^[75]. Based on these results *N,N*-diethylacetamide seems to be synthesized by an intramolecular reductive elimination of acyl moiety and diethylamino moiety via a rhodium complex with both ligand of diethylamine and acyl moiety coordinated to the rhodium metal center.

3.6.2. Carbonylation of Trimethylamine with Methyl iodide by Rhodium Complex

Rhodium complex of [Rh(μ-I)(CO)₂]₂ or [Rh(CO)₂I₂]⁻ is applied to the carbonylation of trimethylamine with methyl iodide without solvent under anhydrous condition by J.-H. Hong^[76]. *N,N*-dimethylacetamide is produced in 99% of the conversion rate for trimethylamine and in 82% of the selectivity for the acetamide with TON of 700 when the carbonylation is performed at 275°C for 2 hr under CO pressure of 24 atm at room temperature. Products of *N,N*-dimethylacetamide, *N*-methylacetamide, and *N,N*-dimethylformamide are obtained in the yields of 82.3%, 12.6%, and 4.4% respectively (Scheme 29).



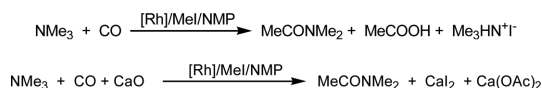
Scheme 29. Rh-catalyzed carbonylation of trimethylamine with methyl iodide.

It is characteristic that the rhodium catalysts is stable in trimethylamine without any solvent under anhydrous condition.

3.6.3. Carbonylation of Trimethylamine with Methyl iodide in Presence of Water

The rhodium catalyzed carbonylation of trimethylamine in the presence of water is reported to provide *N,N*-dimethylacetamide, acetic acid, trimethylammonium iodide simultaneously until complete consumption of methyl iodide in the reaction mixture. The iodine atom of methyl iodide promoter is transformed into trimethylammonium iodide, which is the trapped hydrogen iodide by trimethylamine, and acetic acid as in the carbonylation process of methanol. The acetic acid formation is suggested as the scavenger of methyl iodide promoter since there is no methanol to regenerate

methyl iodide in the reaction mixture. The carbonylation of trimethylamine in the presence of calcium oxide is reported to give *N,N*-dimethylacetamide too until complete consumption of methyl iodide into both of calcium acetate and calcium iodide, both salt of which in the ratio of 1:1 are confirmed as NMP solvated form by NMR spectroscopy and analytical methods^[77] (Scheme 30).



Scheme 30. Rh-catalyzed carbonylation of trimethylamine with methyl iodide and water.

The rhodium complex is observed as stable and durable species, usually the catalyst shows the instability and extremely low oxidative-addition rate of the methyl iodide under anhydrous condition^[38,39], for the carbonylation of trimethylamine under anhydrous conditions due to the σ -coordination of trimethylamine as a ligand to the rhodium metal center.

3.6.4. Suggested Mechanism for Carbonylation of Trimethylamine by Rhodium Complex

In the suggested mechanism the formation of acyl

iodide intermediate is excluded since once acyl iodide is formed, then it reacts faster with water or hydroxide than trimethylamine, then producing only acetic acid. Instead of acyl iodide intermediate a stepwise procedure of an intramolecular reductive elimination is suggested for the formation of *N,N*-dimethylacetamide and acetic acid depending on elimination of the ligated moieties (the trimethylamine and hydroxide) and acyl moiety coordinated to the rhodium center. The increasing electron density at the rhodium center by the coordinated trimethylamine^[32] is consequently enhancing the overall rate of the oxidative addition of methyl iodide^[34,37,65,78,79]. The formation of acetic acid is attributed to the step of the scavenging methyl iodide to turn into wasting iodide salts of trimethylammonium iodide. If the catalytic activity of the reaction mixture becomes inactive, its catalytic activity is regenerated by adding more methyl iodide into the reaction mixture (Fig. 7).

4. Discussion

4.1. Generation of Methyl Iodide and Its Acylation

Methyl iodide is essential to the carbonylation of trimethylamine as well as for the carbonylation of meth-

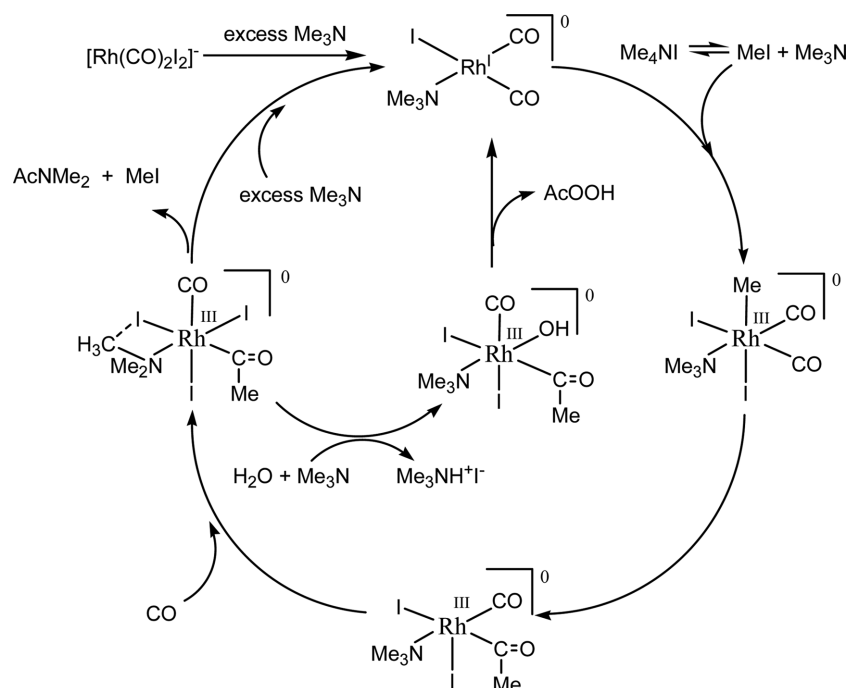


Fig. 7. Proposed mechanism of Rh-catalyzed carbonylation of trimethylamine.

anol to acetic acid. Merely methyl iodide can be supplied in the form of quaternary ammonium iodide salts even if the thermal decomposition of tetramethylammonium iodide is demonstrated at only high temperature via unimolecular process^[47]. It is characteristic and surprising that the high yield for the carbonylation of trimethylamine is obtained in the presence of catalytic amount of iodide anion or almost no methyl iodide due to the formation of tetramethylammonium iodide in plenty of trimethylamine. On the contrary the carbonylation of trimethylamine in the absence of methyl iodide sources leaves us the similar question of how methyl iodide, CH₃-Co-complex, or CH₃-Pd-complex is generated even in the small amount of only iodide sources such as KI, I₂, Et₄NI, and *n*-Bu₄NI. In this point it is plausible that there is an effect of the catalysts on the formation of methyl iodide or CH₃-M_T-complex can be formed via the coordinated trimethylamine to the metal center of the catalysts by an aid of iodide anion itself.

4.2. Generation of Alkyl Iodide and Its Carbonylation

Carbonylations of tertiary amines with methyl iodide promoter are observed to provide various tertiary acyl derivatives. Carbonylations of alkyl iodides other than methyl iodide are also demonstrated regardless of alkyl iodide sources such as combinations of quaternary ammonium iodide salts and tertiary amines, these reactions are surely useful for the preparations of various acyclic and cyclic tertiary amides. Further researches are expected in detail in near future.

4.3. Generation of Methyl Iodide and Its Hydrolysis

In common the high yields for all carbonylations of trimethylamine are observed under anhydrous conditions and the formations of acetic acid and trimethylammonium iodide are due to the presence of water in solvent and trimethylamine. Therefore the formation of acetic acid is the scavenging step to waste the methyl iodide promoter such as iodide salts of trimethylammonium iodide or calcium iodide. Moreover it is interesting that *N,N*-dimethylacetamide is produced with acetic acid in the presence of water since the hydrolysis rate of acyl moiety with water is slower than that of the coupling with dimethylamino moiety.

4.4. Generation of Acyl Iodide, Its Hydrolysis, and Its Amide Formation

Usually acyl iodide is suggested and accepted as the

intermediate in the carbonylation of methanol, acyltrimethylammonium iodide is suggested as an intermediate in the carbonylation of trimethylamine to *N,N*-dimethylacetamide in most reports except the rhodium catalyzed carbonylation. In this point it is the subject to be studied further in detail about the formation of acyl iodide or acyltrimethylammonium iodide as an intermediate with the role of iodide anion itself.

4.5. Coordination of Trimethylamine to Transition Metals and Lewis Acid

In the molecule of trichloro bis(trimethylamine) aluminum, AlCl₃(NMe₃)₂, the metal center is five-coordinate and the two N atoms occupy the axial positions of the trigonal bipyramid and the arrangement of the substituents bonded to aluminum and nitrogen atoms is staggered^[55]. The structure of AlCl₃(NMe₃)₂ is very similar to that of FeCl₃(NMe₃)₂^[51], in which there is no π -component to the Fe-N bonds and the significant longer Fe-N bond distance than the Fe-N bond distances in FeCl₃(4-cyanopyridine) as a result of the steric crowding induced by tetrahedral, axial nitrogen centers. Dimethylaminodichloroalane of Cl₂AlNMe₂ in gas phase and in benzene is known as dimers with bridging of dimethylamine between two aluminum atoms^[80]. In this point it is expected that Lewis acid of aluminum trichloride, iron trichloride, or even the catalysts of transition metals would form its complex with trimethylamine. The bonding situation of the complex is expected to be similar to the forming sp³ hybridization on nitrogen center in the TBP structures of aluminum and iron, which is able to make the methyl groups nucleophilic. Then probably a nucleophilic attack of halide anion or anionic Co-complex at the methyl groups of the coordinated trimethylamine might be led to form methyl halide or CH₃-Co-complex via cleavage of the N-CH₃ bond, or to accomplish the carbonylation of the N-CH₃ bond via migration of CO to the N-Metal bonds.

4.6. The Formation of *N,N*-dimethylformamide and *N*-methylacetamide

Most of the carbonylations are reported to produce *N,N*-dimethylacetamide with byproducts of *N,N*-dimethylformamide and *N*-methylacetamide. It is reported that *N,N*-dimethylacetamide is decomposed into *N,N*-dimethylformamide and *N*-methylacetamide in the presence of methyl iodide without any catalysts probably

due to the formation of ketene with trimethylammonium iodide via *N,N,N*-trimethylacyl ammonium iodide^[76]. Also the carbonylations in the presence of water gives byproducts of *N,N*-dimethylformamide and *N*-methylacetamide with acetic acid, it is ascribed to the generation of hydrogen iodide or its salt of trimethylammonium iodide^[56,64].

4.7. Competitive Transference of Amino Moiety to the Final Amide Product during Carbonylation

From the carbonylation of quaternary ammonium iodide and tertiaryamine four different amides are observed, they are combinations of two amides and two amino moieties. The results are explained that acyl iodide and propionyl iodide are coupled with two kind of tertiary amine, which are added or produced, to form four different amides^[63,64]. However, there is a possibility to form a favorable amide via the coordination of tertiary amines to the metal center of the catalyst complex such as trimethylamine complexes of Pt, Pd, Fe, Al, and others. It has been reported that palladium catalyzes amine exchange reaction of tertiary amines^[81].

5. Conclusions

Since the first carbonylation of trimethylamine is reported by G. Li group, much progress is proceeded. From the published papers the carbonylation of trimethylamine by Pd, Pt, and Rh complexes are showing the critical role of methyl iodide as the formation of acyl iodide or $\text{CH}_3\text{-M}_1\text{-complexes}$ in the carbonylation mechanism regardless of its sources as it is added or decomposed from quaternary ammonium iodides even if the thermal decomposition of tetramethylammonium iodide is demonstrated at only high temperature via unimolecular process. Nevertheless it is surprising that the promoter of methyl iodide is active for the carbonylations even in presence of trimethylamine in excess. The presence of the water in the reaction medium does not lower the activity of the catalysts as well as carbonylation of methanol to acetic acid, but does consume the promoter of methyl iodide as trimethylammonium iodide to stop the cycles. It is an interesting field to be resolved how the carbonylations of tertiaryamines without methyl iodide sources give the corresponding amides and how acyl moiety couple with amine moieties favorably via the coordinations of tertiaryamines to

transition metals complexes.

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References

- [1] V. R. Pattabiraman and J. W. Bode, "Rethinking amide bond synthesis", *Nature*, Vol. 480, pp. 471-479, 2011.
- [2] C. Montalbetti and V. Falque, "Amide bond formation and peptide coupling", *Tetrahedron*, Vol. 61, pp. 10827-10852, 2005.
- [3] C. L. Allen and J. M. J. Williams, "Metal-catalyzed approaches to amide bond formation", *Chem. Soc. Rev.*, Vol. 40, pp. 3405-3415, 2011.
- [4] S. Roy, S. Roy, and G. W. Gribble, "Metal-catalyzed amidation", *Tetrahedron*, Vol. 68, pp. 9867-9923, 2012.
- [5] H. Lundberg, F. Tinnis, N. Selander, and H. Adolfs-son, "Catalytic amide formation from non-activated carboxylic acids and amines", *Chem. Soc. Rev.*, Vol. 43, pp. 2714-2742, 2014.
- [6] M. B. Smith and J. March, "March's advanced organic chemistry: reactions, mechanisms, and structure", Hoboken: John Wiley & Sons, Ltd., 5th, pp. 508-510, 2000.
- [7] D. R. Corbin, S. Schwarz, and G. C. Sonnichsen, "Methylamines synthesis: A review", *Catal. today*, Vol. 37, pp. 71-102, 1997.
- [8] J. T. L. Thong, W. K. Choi, and C. W. Chong, "TMAH etching of silicon and the interaction of etching parameters", *Sens. Actuators A Phys.*, Vol. 63, pp. 243-249, 1997.
- [9] C. L. Berre, P. Serp, P. Kalck, and G. P. Torrence, "Acetic acid. Ullmann's Encyclopedia of Industrial Chemistry", Weinheim: Wiley-VCH, pp. 1-34, 2013.
- [10] D. Stoye, "Solvents in Ullmann's Encyclopedia of Industrial Chemistry", Weinheim: Wiley-VCH, 2000.
- [11] F. Liu, W. Tian, X. Yang, and G. Jia, "Hydrogen-bonding and dielectric response of *N,N*-dimethylacetamide aqueous solutions under E/M fields using molecular dynamics", *J. Mol. Liq.*, Vol. 197, pp. 100-105, 2014.
- [12] E. Valeur and M. Bradley, "Amide bond formation:

- beyond the myth of coupling reagents”, *Chem. Soc. Rev.*, Vol. 38, pp. 606-631, 2009.
- [13] A. El-Faham and F. Albericio, “Peptide coupling reagents, more than a letter soup”, *Chem. Rev.*, Vol. 111, pp. 6557-6602, 2011.
- [14] H. Lundberg, F. Tinnis, N. Selander, and H. Adolfs-son, “Catalytic amide formation from non-activated carboxylic acids and amines”, *Chem. Soc. Rev.*, Vol. 43, pp. 2714-2742, 2014.
- [15] R. P. Marriella and K. H. Brown, “A novel SN1 displacement: The reaction of tertiary amines with acetic anhydride”, *Can. J. Chem.*, Vol. 49, pp. 3348-3351, 1971.
- [16] G. Drefahl, H. Lückert, and W. Kohler, “Untersuchungen über stilbene. XXXVI. notiz zur spaltung der C- N-bindung tertiärer amine durch säureanhydride und-chloride”, *Adv. Synth. Catal.*, Vol. 11, pp. 341-344, 1960.
- [17] B. T. Khai and A. Arcelli, “Homogeneous transition-metal catalysis. Cleavage of the C-N bond of tertiary amines by acid anhydrides in the presence of transition metal ions”, *J. Organomet. Chem.*, Vol. 252, pp. c9-c13, 1983.
- [18] N. O. V. Sonntag, “The reactions of aliphatic acid chlorides”, *Chem. Rev.*, Vol. 52, pp. 237-416, 1953.
- [19] M. G. Voronkov, I. P. Tsyrendorzhieva, and V. I. Rakhlin, “Acyl iodides in organic synthesis. reactions with morpholine, piperidine, and N-hydrocarbylpiperidines”, *Russian Journal of Organic Chemistry*, Vol. 46, pp. 794-797, 2010.
- [20] M. G. Voronkov, I. P. Tsyrendorzhieva, V. I. Rakhlin, “Acyl iodides in organic synthesis: XI unusual N-C bond cleavage in tertiary amines”, *Russian Journal of Organic Chemistry*, Vol. 44, pp. 481-484, 2008.
- [21] 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, 1945.
- [22] M. G. Voronkov, N. N. Vlasova, and A. V. Vlasov, “Acyl iodides in organic and organoelement chemistry”, *Russian Chemical Bulletin*, Vol. 62, pp. 1945-1961, 2013.
- [23] M. M. Taquikhan, S. B. Halligudi, S. Shukla, and S. H. R. Abdi, “Kinetic study of the carbonylation of diethylamine and trimethylamine catalyzed by the water-soluble $K[Ru(III)(EDTA-H)Cl] \cdot 2H_2O$ complexes in aqueous medium”, *J. Mol. Cat.*, Vol. 48, pp. 325-333, 1988.
- [24] M. M. Khan, S. B. Halligudi, S. Shukla, and S. H. R. Abdi, “Kinetic study of the carbonylation of n-butylamine using homogeneous water-soluble Ru(II)-EDTA-CO catalyst”, *J. Mol. Cat.*, Vol. 51, pp. 129-135, 1989.
- [25] H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, “The chemistry of metal carbonyls. III. The reaction between dicobalt octacarbonyl and dimethylamine”, *J. Am. Chem. Soc.*, Vol. 75, pp. 3148-3152, 1953.
- [26] 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-C14, 1982.
- [27] W. Reppe, “Carbonylierung I: Über die umsetzung von acetylen mit kohlenoxyd und verbindungen mit reaktionsfähigen wasserstoffatomen Synthesen α,β -ungesättigter carbonsäuren und ihrer derivate”, *European J. Org. Chem.*, Vol. 582, pp. 1-37, 1953
- [28] A. Brennfürer, H. Neumann, and M. Beller, “Palladium-catalyzed carbonylation reactions of aryl halides and related compounds”, *Angew. Chem. Int. Ed.*, Vol. 48, pp. 4114-4133, 2009.
- [29] C. F. J. Barnard, “Palladium-catalyzed carbonylation—a reaction come of age”, *Organometallics*, Vol. 27, pp. 5402-5422, 2008.
- [30] R. S. Mane and B. M. Bhanage. “Pd/C-catalyzed aminocarbonylation of aryl iodides via oxidative C–N bond activation of tertiary amines to tertiary amides”, *J. Org. Chem.*, Vol. 81, pp. 1223-1228, 2016.
- [31] 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.
- [32] 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 [Rh(μ -I)(COMe)(CO)(L)]₂ complexes”, *Inorg. Chem.*, Vol. 51, pp. 8670-8685, 2012.
- [33] A. Haynes, “Catalytic methanol carbonylation”, *Advances in Catalysis*, Vol. 53, pp. 1-45, 2010.
- [34] C. M. Thomas and G. Süß-Fink, “Ligand effects in the rhodium-catalyzed carbonylation of methanol”, *Coord. Chem. Rev.*, Vol. 243, pp. 125-142, 2003.
- [35] S. S. Tonde, A. A. Kelkar, M. M. Bhadbhade, and R. V. Chaudhari, “Isolation and characterization of an iodide bridged dimeric palladium complex in carbonylation of methanol”, *J. Organomet. Chem.*, Vol. 690, pp. 1677-1681, 2005.
- [36] N. Rizkalla, “Acetic acid production via low-pres-

- sure, nickel-catalyzed methanol carbonylation”, ACS Symp. Ser., Vol. 328, pp. 61-76, 1987.
- [37] N. Yoneda, S. Kusano, M. Yasui, P. Pujado, and S. Wilcher, “Recent advances in processes and catalysts for the production of acetic acid”, Appl. Cat. A Gen., Vol. 221, pp. 253-265, 2001.
- [38] A. Haynes, “Acetic acid synthesis by catalytic carbonylation of methanol”, Catalytic Carbonylation Reactions, Berlin: Springer, Vol. 18, pp. 179-205, 2006.
- [39] J. H. Jones, “The cativa™ process for the manufacture of acetic acid”, Platin. Met. Rev., Vol. 44, pp. 94-105, 2000.
- [40] H. Friederich, K. Sepp, “A process for the preparation of carboxamides”, DE Patent 948056, 1956.
- [41] K. Nozaki, E. Cerrito, “Dimethylacetamide production”, US Patent 3407231, 1968.
- [42] H. E. Bellis, “Dimethylacetamide from carbonylation of trimethylamine”, EP Patent 0185823, 1984.
- [43] T. Kazuo, “Dimethylacetamide production”, JP Patent 3275656, 1991.
- [44] J. R. Zhan, J. B. Guo, X.L. Jiang, “Method for preparing N,N-dimethylacetamide”, CN Patent 101003491, 2007.
- [45] P. Roose, “Process for preparing secondary amides by carbonylation of a corresponding tertiary amine”, WO Patent 2010057874 A1, 2010.
- [46] R. B. Fahim and E. A. Moelwyn-Hughes, “Kinetics of the reaction between methyl iodide and trimethylamine in carbon tetrachloride solution”, J. Chem. Soc. (Resumed), pp. 1035-1041, 1956.
- [47] M. Sawicka, P. Storoniak, P. Skurski, J. Błażejowski, and J. Rak, “TG-FTIR, DSC and quantum chemical studies of the thermal decomposition of quaternary methylammonium halides”, Chem. Phys., Vol. 324, pp. 425-437, 2006.
- [48] M. Sawicka, P. Storoniak, J. Błażejowski, and J. Rak, “TG-FTIR, DSC, and quantum-chemical studies on the thermal decomposition of quaternary ethylammonium halides”, J. Phys. Chem. A, Vol. 110, pp. 5066-5074, 2006.
- [49] Wood, J. S., “Stereochemical electronic structural aspects of five-coordination”, In Progress in inorganic chemistry, New York: John Wiley & Sons, pp. 227-451, 1972.
- [50] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, “Trimethylamine complexes of platinum (II) and palladium (II) and their vibrational and proton nuclear magnetic resonance spectra”, Journal of the Chemical Society, Dalton Transactions, Vol. 12, pp. 1298-1303, 1972.
- [51] K. R. Millington, S. R. Wade, G. R. Willey, and M. G. Drew, “Zinc (II), iron (III), molybdenum (II) chloride and molybdenum (V), molybdenum (VI) oxochloride complexes of trimethylamine: synthesis, spectra and X-ray crystal structure characterization”, Inorganica Chim. Acta, Vol. 89, pp. 185-191, 1984.
- [52] J. Hughes and G. R. Willey, “Trimethylamine complexes of zirconium (IV) halides”, Inorganica Chim. Acta, Vol. 20, pp. 137-140, 1976.
- [53] G. R. Willey, “Cis-tetrachlorobis (trimethylamine) hafnium (IV): synthesis and characterization”, Inorganica Chim. Acta, Vol. 21, p. L12, 1977.
- [54] S. R. Wade and G. R. Willey, “Coordination studies of hafnium (IV): reactions of HfX₄ (X=Br, I) and (π -C₅H₅)₂MCl₂ (M=Ti, Zr, Hf) with trimethylamine”, Journal of the Less Common Metals, Vol. 68, pp. 105-106, 1979.
- [55] T. Gelbrich, U. Dümichen, and J. Sieler, “Bis-adduct of trimethylamine with aluminium trichloride”, Acta Crystallogr. Struct. Chem., Vol. 55, pp. 1797-1798, 1999.
- [56] H. Mei, W. Han, J. Hu, S. Xiao, Y. Lei, R. Zhang, W. Mo, and G. Li, “Palladium-catalyzed unstrained C(sp³)-N bond activation: the synthesis of N,N-dimethylacetamide by carbonylation of trimethylamine”, Appl. Organomet. Chem., Vol. 27, pp. 177-183, 2013.
- [57] 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.
- [58] A. M. Trzeciak, W. Wojtków, J. J. Ziókowski, J. Wrzyszczyk, and M. Zawadzki, “The role of Pd colloids as catalysts in the phosphane-free methoxy-carbonylation of iodobenzene”, New J. Chem., Vol. 28, pp. 859-863, 2004.
- [59] Y.-S. Lin and A. Yamamoto, “Studies relevant to palladium-catalyzed carbonylation processes. Mechanisms of formation of esters and amides from benzylpalladium and (phenylacetyl)palladium complexes on reactions with alcohols and amines”, Organometallics, Vol. 17, pp. 3466-3478, 1998.
- [60] J. Yang, A. Hanes, and P. M. Maitlis, “The carbonylation of methyl iodide and methanol to methyl acetate catalysed by palladium and platinum iodides”, Chem. Commun., Vol. 2, pp. 179-180, 1999.
- [61] J. Kiwi and M. Grätzel, “Projection, size factors, and reaction dynamics of colloidal redox catalysts mediating light induced hydrogen evolution from water”, J. Am. Chem. Soc., Vol. 101, pp. 7214-

- 7217, 1979.
- [62] M. T. Reetz, W. Helbig, S. A. Quaiser, U. Stimming, N. Breuer, and R. Vogel, "Visualization of surfactants on nanostructured palladium clusters by a combination of STM and high-resolution TEM", *Science*, Vol. 267, pp. 367-369, 1995.
- [63] Y. Lei, R. Zhang, W. Han, H. Mei, Y. Gu, B. Xiao, and G. Li, "Promotion effect of lewis acid/(CH₃)₄Ni on [Co(CO)₄]⁻-catalyzed C-N bond activation in the carbonylation of trimethylamine", *Catal. Commun.*, Vol. 38, pp. 45-49, 2013.
- [64] Y. Lei, R. Zhang, Q. Wu, H. Mei, B. Xiao, and G. Li, "Carbonylation of quaternary ammonium salts to tertiary amides using NaCo(CO)₄ catalyst", *J. Mol. Catal. A Chem.*, Vol. 381, pp. 120-125, 2014.
- [65] D. Forster, "Mechanistic pathways in the catalytic carbonylation of methanol by rhodium and iridium complexes", *Advances in Organometallic Chemistry*, Vol. 17, pp. 255-267, 1979.
- [66] D. Forster, "Kinetic and spectroscopic studies of the carbonylation of methanol with an iodide-promoted iridium catalyst", *Journal of the Chemical Society, Dalton Transactions*, pp. 1639-1645, 1979.
- [67] P. M. Maitlis, A. Haynes, G. J. Sunley, and M. J. Howard, "Methanol carbonylation revisited: thirty years on", *Journal of the Chemical Society, Dalton Transactions*, Vol. 11, pp. 2187-2196, 1996.
- [68] A. Haynes, B. E. Mann, D. J. Gulliver, G. E. Morris, and P. M. Maitlis, "Direct observation of MeRh(CO)2I⁻, the key intermediate in rhodium-catalyzed methanol carbonylation", *J. Am. Chem. Soc.*, Vol. 113, pp. 8567-8569, 1991.
- [69] C. M. Thomas, R. Mafua, B. Therrien, R. Rusanov, H. Stoeckli-Evans, and G. Süss-Fink, "New diphosphine ligands containing ethyleneglycol and aminoalcohol spacers for the rhodium-catalyzed carbonylation of methanol", *Chemistry A European Journal*, Vol. 8, pp. 3343-3352, 2002.
- [70] D. K. Dutta, J. D. Woollins, A. M. Z. Slawin, D. Konwar, P. Das, M. Sharma, P. Bhattacharyya, and S. M. Aucott, "An alternative strategy to an electron rich phosphine based carbonylation catalyst", *Dalton Trans.*, pp. 2674-2679, 2003.
- [71] D. K. Dutta, J. D. Woollins, A. M. Z. Slawin, D. Konwar, M. Sharma, P. Bhattacharyya, and S. M. Aucott, "Rhodium(I) carbonyl complexes of mono selenium functionalized bis(diphenylphosphino) methane and bis(diphenylphosphino)amine chelating ligands and their catalytic carbonylation activity", *J. Organomet. Chem.*, Vol. 691, pp. 1229-1234, 2006.
- [72] G. W. Lamb, M. Clark, A. M. Z. Slawin, B. Williams, and L. Key, "Evaluation of C4 diphosphine ligands in rhodium catalyzed methanol carbonylation under a syngas atmosphere: Synthesis, structure, stability and reactivity of rhodium(I) carbonyl and rhodium(III) acetyl intermediates", *Dalton Trans.*, Vol. 47, pp. 5582-5589, 2007.
- [73] D. K. Dutta, J. D. Woollins, A. M. Z. Slawin, A. L. Fuller, B. Deb, P. P. Sarmah, M. G. Pathak, and D. Konwar, "Rhodium(I) carbonyl complexes of chalcogen functionalized tripodal phosphines, [CH₃C(CH₂P(X)Ph-2)(3)] {X=O, S, Se} and their reactivity", *J. Mol. Catal. A Chem.*, Vol. 313, pp. 100-106, 2009.
- [74] D. H. Nguyen, N. Lassauque, L. Vendier, S. Mallet-Ladeira, C. L. 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.
- [75] 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.
- [76] J.-H. Hong, "Synthesis of N,N-Dimethylacetamide from carbonylation of trimethylamine by rhodium(I) complex under anhydrous condition", *J. Chosun Natural Sci.*, Vol. 8, pp. 235-243, 2015.
- [77] 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.
- [78] A. Fulford, N. A. Bailey, H. Adams, and P. M. Maitlis, "The synthesis, properties, and crystal structure of nBu₄N[Rh(CO)₂(OAc)₂], and the exchange of acetate, chloride, and iodide in nBu₄N[Rh(CO)₂(X)₂]", *J. Organomet. Chem.*, Vol. 417, pp. 139-147, 1991.
- [79] B. L. Smith, G. P. Torrence, M. A. Murphy, and A. Aguilo, "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.
- [80] T. C. Bartke, A. Haaland, and D. P. Novak, "The molecular structure of dimethylaminodichloroalane dimer determined by gas phase electron diffraction", *Acta Chem. Scand. A*, Vol. 29, pp. 273-276, 1975.
- [81] S. Murahashi, H. Tsumoru, and Y. Tsuneo, "Palladium catalyzed amine exchange reaction of tertiary amines. Insertion of palladium(0) into carbon-hydrogen bonds", *J. Am. Chem. Soc.*, Vol. 100, pp. 348-350, 1978.