558 *Bull. Korean Chem. Soc.* 1995, Vol. 16, No. 6

Notes

Synthesis, Characterization, and Reactions of Alkyl Palladium(II) and Platinum(II) Trifluoroacetate Complexes

Yong-Joo Kim* and Jae-Young Lee

Department of Chemistry,
Kangnung National University,
Kangnung 210-702, Korea

Transition metal carboxylates are extensively investigated because of versatile coordination modes such as unidentate, chelate, and symmetrical or asymmetrical bridging coordination on the carboxylate oxygen atom.[1] Late transition metal complexes having unidentate (η^1) or bridging trifluoroacetato ligands sometimes play an important role as catalysts in butadiene polymerization,[2] isocyanide polymerization,[3] and copolymerization of CO and olefins.[4] Trifluoroacetato complexes show higher solubility to organic solvents and better crystallinity than the corresponding acetate complexes. However, there have been limited number of studies about the synthesis and chemical properties of group 10 metal trifluoroacetates.[4b,5]

We have previously described preparation of group 10 metal alkoxides and have shown that the alkoxo ligands of these complexes readily react with acidic alcohols or phenol to give new alkoxo or phenoxo complexes.[6] In this work we have developed the ligand exchange reactions to preparation of trifluoroacetato palladium(II) and platinum(II) complexes by reactions of palladium(II) and platinum(II) alkoxides with trifluoroacetic acid and have characterized the complexes by spectroscopic measurements. We also examined reactions of the complexes with CO and with sodium azide.

Experimental

All manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with use of standard Schlenk technique. Solvents were distilled from Na-benzophenone. Dppm (bis(diphenyphosphino)methane), dppe (1,2-bis(diphenyphosphino)ethane), dppp (1,3-bis(diphenyphosphino)propane), PMePh$_2$, and PEt$_3$ were purchased from Aldrich Co. and used without further purification. (dppe)PdMe$_2$,[7] *trans*-PdMe$_2$(PMePh$_2$)$_2$,[7] *trans*-PdMe$_2$(PEt$_3$)$_2$,[7] (dppp)PtMe$_2$,[8] (dppm)PtMe$_2$,[8] and (dppe)PdMe(OCH(CF$_3$)$_2$)[6a] were prepared by the literature methods.

Elemental analyses were carried out by the analytical laboratory, Tokyo Institute of Technology in Japan and Korea Basic Science Center. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. NMR (¹H, ¹⁹F, and ³¹P{¹H}) spectra were obtained by JEOL-FX-100, GX-270 , and Bruker 500 spectrometers. Chemical shifts were referred to an internal Me$_4$Si, external 85% H$_3$PO$_4$ and PPh$_3$, and external CF$_3$COOH.

(dppp)PtMe(OCH(CF$_3$)$_2$) was prepared similarly to the procedure of (dppe)PdMe(OCH(CF$_3$)$_2$).[6a] ¹H NMR (CD$_2$Cl$_2$, 100 MHz, δ): 0.17 (dd, 3H, -CH$_3$, J(HP)=2.5, 7.3 Hz, J(PtH)=52 Hz), 1.5-2.6 (m, 6H, -CH$_2$-), 4.7 (sep, 1H, -CH, J(HF)=6.3 Hz), 7.2-7.8 (m, aromatic). ³¹P NMR (CD$_2$Cl$_2$, 40 MHz, δ):

1.3 (d, J(PH)=22 Hz, J(PtP)=3894 Hz), 5.9 (d, J(PH)=22 Hz, J(PtP)=1761 Hz). ¹³C NMR (CD$_2$Cl$_2$, 68.5 MHz, δ): 10.1 (d, J(CP)=7.3 Hz), 11.5 (d, J(CP)=7.4 Hz), 19.4 (d, J(CP)=2.8 Hz), 26.3, 26.7, 27.8 (d, J(CP)=6.3 Hz), 28.3 (d, J(CP)=3.7 Hz), 72.0 (sep, J(CF)=30 Hz), 128-134 (m, aromatic). Anal. Calcd. for C$_{31}$H$_{30}$F$_6$OP$_2$Pt: C, 47.2; H, 3.8. Found: C, 47.7; H, 3.5.

Preparation of (dppe)PdMe(OCOCF$_3$), (1) and (dppe)Pd(OCOCF$_3$)$_2$, (2). To a stirred toluene (6 mL) solution of (dppe)PdMe(OCH(CF$_3$)$_2$) (180 mg, 0.27 mmol) was added trifluoroacetic acid (30 mg, 0.27·mmol) at room temperature. After stirring for 2 h the resulting pale yellow solution was concentrated to half under vacuum and 5 mL of hexane was added to afford white precipitates of 1, which was filtered, washed with small amounts of toluene, and dried *in vacuo*: 150 mg, 88%. Anal. Calcd. for C$_{29}$H$_{27}$F$_3$O$_2$P$_2$Pd: C, 55.0; H, 4.3. Found: C, 55.2; H, 4.4.

A similar reaction between (dppe)PdMe(OCH(CF$_3$)$_2$) and excess amount of trifluoroacetic acid gave pale yellow crystals of (dppe)Pd(OCOCF$_3$)$_2$, (2) (160 mg, 91%). Anal. Calcd. for C$_{30}$H$_{24}$F$_6$O$_4$P$_2$Pd: C, 49.3; H, 3.3. Found: C, 49.5; H, 3.4.

Complex 2 was also obtained from the reaction of 1 with excess trifluoroacetic acid.

Complexes 1 and 2 were independently prepared from the reactions of (dppe)PdMe$_2$ with equimolar or excess trifluoroacetic acid in quantitative yield and identified by IR and NMR spectroscopy.

Preparation of (dppp)PtMe(OCOCF$_3$), (3). To a stirred ether (5 mL) solution of (dppp)PtMe(OCH(CF$_3$)$_2$) (300 mg, 0.38 mmol) was added trifluoroacetic acid (44 mg, 0.38 mmol) at room temperature. Stirring caused instant formation of white precipitates, which were filtered and washed with ether and hexane. (226 mg, 81%). Anal. Calcd. for C$_{30}$H$_{29}$F$_3$O$_2$P$_2$Pd: C, 49.0; H, 4.0. Found: C, 48.9; H, 4.1.

Preparation of (dppm)PtMe(OCOCF$_3$), (4). To a stirred benzene (4 mL) solution of (dppm)PtMe$_2$ (300 mg, 0.49 mmol) was added trifluoroacetic acid (56 mg, 0.49 mmol) at room temperature. After stirring for 1 h the solution was evaporated to half under vacuum to afford pale yellow precipitates, which were recrystallized from benzene/hexane (208 mg, 60%). Anal. Calcd. for C$_{28}$H$_{25}$F$_3$O$_2$P$_2$Pd: C, 47.5; H, 3.6. Found: C, 47.6; H, 3.7.

Preparation of *trans*-PdMe(OCOCF$_3$)L$_2$ (L=PMePh$_2$, (5) and L=PEt$_3$, (6). To a stirred ether suspension of *trans*-PdMe$_2$(PMePh$_2$)$_2$ (160 mg, 0.29 mmol) at −50 ℃ was added trifluoroacetic acid (33 mg, 0.29 mmol) diluted in ether (5 mL). When the temperature was raised to −20 ℃ the reaction mixture turned into a homogeneous colorless solution. After stirring for 5 h the solvent was removed under reduced pressure to give white solids of 5, which was recrystallized from ether (170 mg, 95%). Anal. Calcd. for C$_{29}$H$_{29}$F$_3$O$_2$P$_2$Pd: C, 54.9; H, 4.6. Found: C, 55.0; H, 4.6.

Complex 6 was prepared analogously (150 mg, 61%). Anal. Calcd. for C$_{15}$H$_{33}$F$_3$O$_2$P$_2$Pd: C, 38.3; H, 7.1. Found: C, 38.5; H, 7.3.

Reactions of 1 and 2 with NaN$_3$. To a stirred THF (10 mL) solution of (dppe)PdMe(OCOCF$_3$) (595 mg, 0.94 mmol) was added aqueous THF (6 mL) solution of NaN$_3$ (9 mg, 1.4 mmol) at room temperature. After stirring for 3 h the solvent was evaporated under reduced pressure to

Notes

Bull. Korean Chem. Soc. 1995, Vol. 16, No. 6 559

give a yellowish residue, which was redissolved in CH_2Cl_2 and filtered. Addition of n-hexane to the filterate caused formation of pale yellow precipitate of (dppe)PdMe(N₃), (7) which was filtered and dried in vacuo (316 mg, 60%). IR (KBr): 2036 cm⁻¹. ¹H NMR (CDCl₃, 100 MHz, δ): 0.68 (dd, 3H, *J*(HP)=2.4, 7.5 Hz, Pd-Me), 2.3 (m, 4H, Pd-CH₂), 7.3-7.8 (m, 20H, aromatic). ³¹P NMR (40 MHz, CDCl₃, δ): 32, 58 (d, *J*(PP)=29 Hz). Anal. Calcd. for C₂₇H₂₇N₃P₂Pd: C, 57.7; H, 4.8; N, 7.5 Found: C, 57.5; H, 4.7; N, 7.1.

A similar reaction of (dppe)Pd(OCOCF₃)₂ with three equivalents of NaN₃ gave (dppe)Pd(N₃)₂, (8) as a yellow solid in 69% yield. IR (KBr): 2040 cm⁻¹. ¹H NMR (CDCl₃, 100 MHz, δ): 2.4 (m, 4H) 7.5-7.9 (m, 20H, aromatic). ³¹P NMR (40 MHz, CDCl₃, δ): 64 (s). Complex 8 was independently prepared by the ligand exchange reaction of (tmeda)Pd(N₃)₂[9] with equimolar amount of dppe, which was identified by IR and NMR spectroscopy.

Reaction of 5 with CO. Complex 5 (170 mg, 0.27 mmol) was dissolved in toluene (5 mL) at room temperature. After evacuation of the system CO (1 atm) was introduced at the temperature. The colorless reaction mixture slowly turned to pale yellow. After stirring for 9 h the solvent was evaporated to give a white solid of *trans*-Pd(MeCO)(OCOCF₃)(PMePh₂)₂, (9) which was washed with hexane and dried *in vacuo*; 170 mg, 96%. IR(KBr): 1692, 1672 cm⁻¹. ¹H NMR (CDCl₃, 500 MHz, δ): 1.5 (s, 3H, Pd-COMe), 1.9 (t, 6H, PMePh₂, 4 Hz), 7.4-7.7 (m, 20H, aromatic). ³¹P NMR (40 MHz, CDCl₃, δ, ext. PPh₃): 2.5 (s). ¹³C NMR (CDCl₃, 125 MHz, δ): 11.9 (t, *J*(CP)=13 Hz, PdCOMe), 37.9 (t, *J*(CP)=19 Hz, PMePh₂), 116 (q, *J*(CF)=280 Hz, CF₃), 162 (q, *J*(CF)=35 Hz, OCOCF₃), 231(s, CO), 128-133 (m, aromatic). Anal. Calcd. for C₃₀H₂₉O₃F₃P₂Pd: C, 54.4; H, 4.4. Found: C, 54.6; H, 4.5.

Results and Discussion

We first examined isolation of alkylpalladium(II) acetate

complex from reaction of alkylpalladium(II) alkoxide with acetic acid but its poor crystallinity gave an impetus for us to use trifluoroacetic acid to give alkylpalladium(II) trifluoroacetate complex. Reaction of (dppe)PdMe(OCH(CF₃)₂) with an equimolar amount of trifluoroacetic acid gives (dppe) PdMe(OCOCF₃), (1) in 88% yield as shown eq. 1. However, this reaction in the presence of excess trifluoroacetic acid affords (dppe)Pd(OCOCF₃)₂, (2) as a pale yellow solid.

(1)
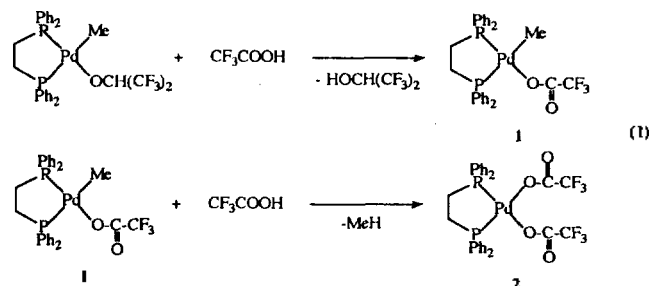
Complexes 1 and 2 are characterized by IR, NMR (¹H, ¹⁹F, and ³¹P[¹H]), and elemental analyses. IR spectra of 1 and 2 show very strong bands due to $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ at *ca.* 1690 and *ca.* 1410 cm⁻¹, respectively (See Table 1). The values are similar to those reported for other trifluoroacetate complexes.[5] Also, the separation between the two carbon-oxygen frequencies (Δv) is 280 cm⁻¹ suggesting a unidentate (η¹) coordination to transition metal.[4b,10] A single peak in the ¹⁹F NMR spectra of trifluoroacetato complexes indicates the presence of the trifluoroacetato group. The ³¹P[¹H] NMR spectrum of 1 shows two doublets in agreement with the *cis* configuration having nonequivalent phosphine ligands, while the spectrum of 2 shows a singlet due to two equivalent phosphine ligands.

In the previous report we have shown that reactions of (dppe)PdMe(OCH(CF₃)₂) and *cis*-PtMe(OCH(CF₃)₂)(PMe₃)₂ with excess phenol give palladium(II) phenoxide, (dppe)

Table 1. Spectral Data of Complexes 1-6[a]

| Complex	IR (cm⁻¹)[b]			¹H		¹⁹F[d]	³¹P[¹H][e]
	v_{asym} (CO₂)	v_{sym} (CO₂)	Δv	M-CH₃	M-*Phosphine* or others		
1	1690	1410	280	1.2 (dd)	1.2-1.4 (m)	5.3 (s)	40 (d), 64 (d)
				J(HP)=8, 2 Hz	6.8-7.9 (m)		*J*(PP)=25 Hz
2	1696	1416	280		2.4-2.5 (m)	2.3 (s)	64 (s)
3	1690	1420	270	0.4 (dd)	1.9 (m), 2.5 (m)	2.0 (s)	0.7 (d), 9.8 (d)
				J(HP)=7, 3 Hz	7.3-7.6 (m)		*J*(PP)=22 Hz
				J(PtH)=43 Hz			*J*(PtP)=4341, 1169 Hz
4	1698	1406	292	0.9 (dd)	4.2 (dd)	2.0 (s)	−17 (d), −35 (d)
				J(HP)=7, 2 Hz	*J*(HP)=8, 11 Hz		*J*(PP)=37 Hz
				J(PtH)=46 Hz			*J*(PtP)=1263, 4071 Hz
5[b]	1680	1410	270	−0.1 (t)	1.8 (m)	2.1 (s)	20 (s)
				J(HP)=6 Hz	7.1-7.8 (m)		
6[b]	1680	1405	275	0.1 (t)	1.0-1.7 (m)	2.1 (s)	25 (s)
				J(HP)=6 Hz			

[a]Abbreviations: s, singlet; d, doublet; t, triplet, dd, doublet of doublets; m, multiplet; bm, broad multiplet; q, quartet; sep, septet. NMR spectra were recorded in CDCl₃, unless otherwise noted. [b]In CD₂Cl₂. [c]KBr disk. Δv≥200 cm⁻¹ is generally found in the complexes where structural studies show unidentate acetate coordination. See ref. 10. [d]94 MHz in each solvents. Ppm downfield from external CF₃COOH. [e]40 MHz in each solvents. Ppm downfield from external PPh₃.

560 *Bull. Korean Chem. Soc.* **1995**, Vol. 16, No. 6

Notes

PdMe(OPh)[6b] and platinum(II) phenoxide. *cis*-PtMe(OPh) (PMe₃)₂ or hydrogen-bonded complex, *cis*-PtMe(OR)(HOR) (PMe₃)₂ (R = Ph),[6c] respectively. In the above reaction (eq. 1) trifluoroacetic acid, being more acidic than fluorinated alcohol or phenol, readily reacts with methylpalladium(II) alkoxide to give methylpalladium(II) trifluoroacetate complex and further reacts with remaining methyl ligand in the palladium complex to give bistrifluoroacetato palladium(II) complex. The result is in contrast with the previous observation that methyl ligand of palladium(II) or platinum(II) alkoxide complexes does not react with excess fluorinated alcohol or phenol at all. Methanol does not react with these complexes due to lower acidity.

Reaction of (dppp)PtMe(OCH(CF₃)₂) with equimolar amount of trifluoroacetic acid also proceeds to give (dppp) PtMe(OCOCF₃), 3 as a white solid which has been characterized by IR and NMR spectra as well as elemental analysis.
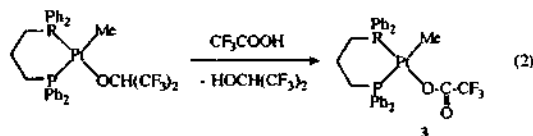
$${}^{31}P\{{}^{1}H\}$$ NMR spectrum of 3 shows two doublets with Pt satellites in agreement with the *cis* structures of the complexes having two nonequivalent phosphines. Complexes 1-3 are also obtained from the protonolysis of (dppe)PdMe₂ and (dppp)PtMe₂ using equimolar or excess trifluoroacetic acid in quantitative yield. In relation to the above reactions we have extended to the following reactions of (dppm)PtMe₂ and *trans*-PdMe₂L₂ (L = PMePh₂, PEt₃) with equimolar trifluoroacetic acid as shown in eq. 3.
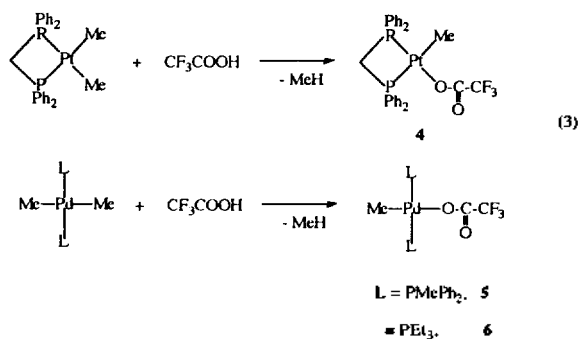
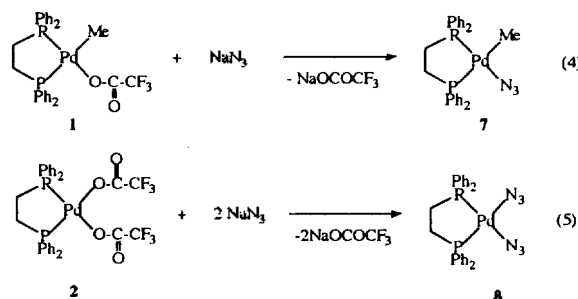

Complexes 4-6 are characterized by IR, NMR (¹H, ¹⁹F, and ³¹P{¹H}) spectroscopy, and elemental analyses. IR spectra also show strong bands due to $v_{asym}(CO_2)$ and $v_{sym}(CO_2)$ at 16 80-1698 cm⁻¹ and *ca.* 1410 cm⁻¹, which reflect the characteric of unidentate (η¹) coordination to the central metal.

Reaction of 1 and 2 with NaN₃. Recently, Murahasi and his coworkers[11] reported that in the presence of palladium catalyst the reactions of allyl acetates with azide anion afforded the corresponding allyl azides and showed their efficient conversion into the primary allyl amines. Also, they assumed that the acetate palladium(II) complex formed by oxidative addition of allyl acetate to Pd(0) species undergoes nucleophilic attack of azide anion to give allyl azides during the reaction. It is noteworthy that organic acetates are readily turned into the organic azides by transition metal cata-

lyst. The facts stimulate us to explore reaction of the acetate complexes with azide anion to give transition metal azide complexes.

Reaction of complex 1 with NaN₃ at room temperature proceeds to give (dppe)PdMe(N₃), 7 in 60% yield. Complex 2 also reacts with two equivalents of NaN₃ to give (dppe)Pd (N₃)₂, 8 as a yellow solid.

Complexes 7 and 8 are characterized by IR, NMR spectroscopy, and elemental analyses. The infrared spectra of 7 and 8 show a characteristic strong band at 2036 and 2040 cm⁻¹ which can be assigned to the azide asymmetric stretching. Recently, we have prepared palladium(II) and platinum(II) azide complexes having chelated phosphine or amine ligands by an alternative route involving metathesis reactions of chloro complexes of these group 10 metals.[9] The above reactions (eqs. 4 and 5) provide a new synthetic method for transition metal azide complexes.

Reaction of 5 with CO. Reaction of 5 with CO (1 atm) at room temperature gives acylpalladium(II) trifluorocarboxylate, Pd(MeCO)(OCOCF₃)(PMePh₂)₂, 9 in 96% yield which has been characterized by IR, NMR (¹H, ³¹P{¹H}, and ¹³C{¹H}) spectroscopy, and elemental analysis.
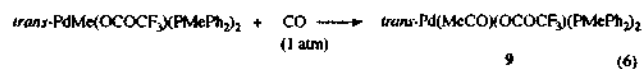
IR spectrum of 9 shows a strong absorption band at 1670 cm⁻¹ assignable to v(C=O) of the palladium-acyl group. ¹H NMR shows no signal of Pd-Me, but a singlet at 1.5 ppm assigned to Pd-COMe hydrogens. ¹³C{¹H} NMR spectrum also shows clearly the signals at 11.9, 37.9, 116, 162, and 231 ppm due to Pd-CO<u>Me</u>, PMePh₂, CF₃, OCO, and CO carbons, respectively. Previously similar reaction of CO with PdMe(OCOMe)(PEt₃)₂ was reported to give MeCOOCOMe through Pd(COMe)(OCOMe)(PEt₃)₂ which was proceeded by C-O bond formation between the acyl and carboxylato ligand of the complex promoted by the coordination of CO to Pd.[12] Under same conditions the above reaction (eq. 6) does not give any organic products. These results suggest that trifluoroacetato ligand, having stronger Pd-O bond than acetato ligand, does not undergo coupling reaction with acetyl ligand in mild conditions, but increase of the CO pressure and elevated temperature may be required in order to cause a C-O bond formation.

In summary we have prepared alkyl palladium(II) and platinum(II) trifluoroacetato complexes from the ligand exchange reactions of corresponding palladium- and platinum(II) alkoxides with trifluoroacetic acid and have succeeded in their conversion into alkyl palladium(II) and platinum(II) azide

Notes

Bull. Korean Chem. Soc. **1995**, Vol. 16, No. 6 561

complexes as well as into an acetyl palladium(II) trifluoroacetato complex.

Acknowledgment. This work was supported in part by NON-DIRECTED RESEARCH FUND(KRF), 1993. We thank Prof. Kohtaro Osakada of Tokyo Institute of Technology in Japan for helpful discussion and Prof. Soon W. Lee of Sung Kyun Kwan University for the use of CO gas.

References

1. (a) Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: 1987; Vol. 2, p 435. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: 1988; p 466. (c) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; New York, 1982.
2. (a) Julémont, M.; Walckiers, E.; Warin, R.; Teyssié, P. *Makromol. Chem.* **1974**, *175*, 1673. (b) Dewans, F.; Teyssié, P. *Polym. Lett.* **1969**, *7*, 111. (c) Dewans, F.; Marechal, J. C.; Teyssié, P. *J. Organomet. Chem.* **1970**, *21*, 259. (d) Durand, J. P.; Dewans, F.; Teyssié, P. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 979. (e) Hadjiandreou, P.; Julémont, M.; Teyssié, P. *Macromolecules* **1984**, *17*, 2455. (f) Warin, R.; Julémont, M.; Teyssié, P. *J. Organomet. Chem.* **1980**, *185*, 413. (g) Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10507.
3. (a) Deming, T. J.; Novak, B. M. *Polym. Prepr.* **1991**, *32*, 455. (b) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 6043. (c) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101.
4. (a) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (b) Milani, B.; Alessio, E.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc. Dalton Trans.* **1994**, 1903.
5. Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. (A)* **1971**, 2667 and references to earlier work therein.
6. (a) Kim, Y.-J.; Osakada, K.; Sugita, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (b) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (c) Osakada, K.; Kim, Y.-J.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *382*, 303.
7. Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319.
8. Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.
9. Kim, Y.-J.; Choi, J.-C.; Park, K.-H. *Bull. Korean Chem. Soc.* **1994**, *15*, 690.
10. (a) Deacon, G. B.; Phillips, R. *J. Coord. Chem. Rev.* **1980**, *33*, 227. (b) Garner, C. D.; Hughes, B. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 1.
11. (a) Murahashi, S.-I.; Imada, Y.; Taniguchi, Y. *Tetrahedron Lett.* **1986**, *27*, 227. (b) Murahashi, S.-I.; Taniguchi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292.
12. Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1981**, 193.

Systematic Study on Bis(dialkylamino) aluminum Hydride : Reexamination of the Reagents for Reduction of Carboxylic Acids to Aldehydes

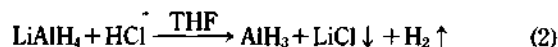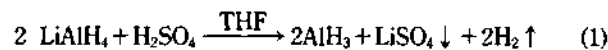Jin Soon Cha*, Keung Dong Lee, Oh Oun Kwon, Jong Mi Kim, and Hung Soo Lee[†]

Department of Chemistry, Yeungnam University, Kyongsan 712-749, Korea
[†]Department of Chemistry Education, Taegu Hyosung Catholic University, Kyongsan 713-900, Korea

Some twenty years ago, Muraki and Mukaiyama first prepared various bis(dialkylamino)aluminum hydride and applied them for the reduction of carboxylic acid derivatives to aldehydes.[1] Among the series of reagents, bis(N-methylpiperazinyl)aluminum hydride (BMPA) was shown to be the most effective for such conversions. Again, Wiemer and his co-workers confirmed that BMPA is a convenient reagent for the direct reduction of carboxylic acids to aldehydes.[2]

The procedure for the synthesis of the reagents essentially involved the preparation of aluminum hydride solution in THF. The aluminum hydride solution was prepared by treatment of a standardized solution of lithium aluminum hydride in THF with a theoretical quantity of 100% sulfuric acid[1] (eq. 1) or hydrogen chlorde[2] (eq. 2). Even though these procedures provide a pure aluminum hydride solution in THF,

$$2 \text{ LiAlH}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{THF}} 2\text{AlH}_3 + \text{LiSO}_4 \downarrow + 2\text{H}_2 \uparrow \quad (1)$$

$$\text{LiAlH}_4 + \text{HCl} \xrightarrow{\text{THF}} \text{AlH}_3 + \text{LiCl} \downarrow + \text{H}_2 \uparrow \quad (2)$$

there have been faced problems : some resistance to use of 100% sulfuric acid with lithium aluminum hydride and the solubility of lithium chloride in THF. Lithium chloride dissolves easily in THF to give solution of ~1 M.[3] In addition to that, the characterization of aminoaluminum hydrides thus prepared has not been carried out : no systematic study on the preparation of the reagent has been reported.[1,2]

Consequently, there has been a need for development of a general procedure for the preparation of pure bis(dialkylamino)aluminum hydride reagents with various dialkylamines of different steric environments. In this study, we carried out the systematic study on the preparation of pure solution of bis(dialkylamino)aluminum hydride in THF and re-examined some representative reagents for the reduction of carboxylic acids to aldehydes.

We used sodium aluminum hydride instead of lithium aluminum hydride in the synthesis of a solution of aluminum hydride in THF. The reaction of sodium aluminum hydride in THF and hydrogen chloride in diethyl ether gives an aluminum hydride solution in diethyl ether and THF with a fine solid of sodium chloride[3] (eq. 3). The solid slowly settles upon standing.