

Formation and Properties of Dimethylamine Complexes of Palladium(II) Having *trans* Phosphorus Spanning Terdentate Ligands.

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Dimethylamine complexes of palladium(II) [(PCP)Pd(NHMe₂)](OTf) (PCP = 2,6-(R₂PCH₂)₂C₆H₃); R = Ph (**1**), R = Cy (**2**)), have been prepared from the reaction of (PCP)Pd(OTf) and dimethylamine. The complex **1** is stable both in solution and in the solid state, while **2** is stable only in solution in the presence of dimethylamine although the formation of **2** in solution is quantitative by NMR spectroscopy. A solution NMR spectroscopic study shows that dimethylamine favors over carbon monoxide in the coordination sphere of palladium(II) having rigid terdentate ligands. The complexes **1** and **2** in chlorinated solvents undergo a chlorine abstract reaction yielding Pd(2,6-(R₂PCH₂)₂C₆H₃)Cl in the presence of a base such as dimethylamine and DABCO (diazabicyclooctane), in which a transient dimethylamido palladium(II) species likely involves.

Introduction

Dimethylamine is a useful reagent source for a nitrogen-containing compound functionalized with dimethylamino group. Transition metal mediated conversion of dimethylamine into a nitrogen-containing molecule *via* C-N bond formation is one of important objects in catalysis.¹ Dimethylamine complexes of platinum group metals are rare, however, due to the steric congestion inhibiting the coordination of dimethylamine.² A few precedent examples of dimethylamine complexes of platinum group metals are a square planar Pt(II) complex,³ and Pt(IV) complexes in monomeric and dimeric formulas.⁴ Hartwig and co-workers have recently reported a Pd(II) dimethylamine complex Pd(P(*o*-Tol)₃)(NHMe₂)(*p*-MeC₆H₄)Br, involving a catalytic amination of arylhalide to dimethylarylamine.^{1,5} We report herein novel dimethylamine complexes of palladium(II) containing terdentate ligands of *trans* spanning phosphorus donor sets anchored to 2,6-positions on a phenyl ring.

Experimental Section

All preparations of air sensitive compounds were carried out on a standard Schlenk line or in an inert atmosphere glove box under argon. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone ketyl under nitrogen, and then stored over molecular sieve. Benzene, *n*-hexane, and *n*-pentane were distilled from sodium/benzophenone ketyl with tetraglyme (tetraethylene glycol dimethyl ether). All chlorinated solvents such as CHCl₃ and CH₂Cl₂ were dried by refluxing over lithium aluminum hydride or calcium hydride under nitrogen. Palladium chloride was supplied by Kojima Chemicals Co., Ltd., and used without purification. Anhydrous dimethylamine, diphenylphosphine, potassium diphenylphosphide, 1,5-cyclooctadiene, AgOTf, α,α' -dibromo-*m*-xylene, CDCl₃, CD₂Cl₂ and carbon monoxide were purchased from Aldrich Chemical Company, and used as supplied. Dicyclohexylphosphine was supplied by Strem Chemicals Inc. All other

reagents were from various commercial companies. The complexes of Pd(2,6-(Ph₂PCH₂)₂C₆H₃)Cl and Pd(2,6-(Cy₂PCH₂)₂C₆H₃)Br were prepared according to the literature methods.⁶

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets. ¹H (199.975 MHz) and ³¹P{¹H} (80.950 MHz) NMR spectra were measured on a Varian Gemini 200 spectrometer in CDCl₃, otherwise noted, using the deuterium signal of the solvent as an internal lock frequency. ¹H and ³¹P{¹H} chemical shifts were obtained relative to TMS and 85% H₃PO₄, respectively. Conductivity measurements were obtained with a TOA conductivity meter (CM-40S). Nitromethane was used as solvent in a cell containing platinized electrodes (cell constant = 1.014 cm⁻¹). Elemental analyses were performed at Korea Basic Science Institute in Seoul, Korea.

Preparation of [Pd(2,6-(Ph₂PCH₂)₂C₆H₃)(NHMe₂)]OTf (1**).** To a solution of Pd(2,6-(Ph₂PCH₂)₂C₆H₃)Cl (100 mg, 0.16 mmol) in THF (20 mL) was added a THF solution of silver triflate (42 mg, 0.16 mmol, in 2 mL THF). After filtration of AgCl formed in the reaction mixture, dimethylamine was bubbled through the filtrate. The solution volume was reduced to *ca.* 3 mL. Addition of *n*-hexane (5 mL) to the concentrated solution gave beige crystals. Column chromatography of crude products on silica gel with a THF solution of dimethylamine gave a colorless solution (Without treatment of dimethylamine to the THF eluent, partial dissociation of dimethylamine from **1** does occur to go back to the palladium triflate on column chromatography). The solution volume was reduced to *ca.* 2 mL on a rotary evaporator. Addition of *n*-hexane (5 mL) to the solution gave a white precipitate, which was isolated by vacuum filtration. The complex was dried *in vacuo* for 12 h. Yield 107 mg (85%). IR: $\nu(\text{NH})=3241\text{ cm}^{-1}$ (w, br); $\nu(\text{SO})=1262, 1153\text{ cm}^{-1}$ (vs, br). ¹H NMR (CDCl₃): δ 2.20 d (6H, CH₃); ³J(HH)=5.80 Hz, δ 3.68 br (1H, NH), δ 4.02 t (4H, CH₂); [²J(PH)+⁴J(PH)]=9.2 Hz. δ 6.9-7.8 m (23H, phenyl). ³¹P{¹H} NMR (CDCl₃): δ 41.1 s. Anal. Calcd for C₃₃H₃₄F₃-

NO_3PdS : C, 54.31; H, 4.43; N, 1.81. Found: C, 54.04; H, 4.10; N, 2.06. $\Lambda_M=93 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ (in CH_3NO_2 , $[\text{Pd}] = 0.5 \times 10^{-3} \text{ mol}$).

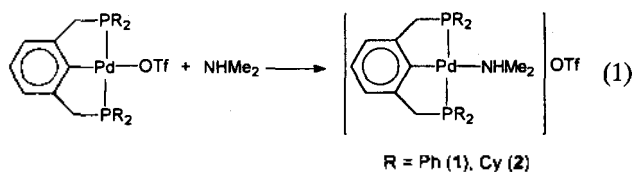
Formation of $[\text{Pd}(2,6\text{-}(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{NHMe}_2)]\text{OTf}$ (2). To a CDCl_3 solution of $\text{Pd}(2,6\text{-}(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OTf})$, which was prepared from the reaction of $\text{Pd}(2,6\text{-}(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Br}$ (15 mg, 0.022 mmol) and silver triflate (5.7 mg, 0.022 mmol) in a 5 mm NMR tube, was added gaseous NHMe_2 for a second. The complex **2** was quantitatively formed in solution as evidenced by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. ^1H NMR (CDCl_3): δ 2.71 d (6H, CH_3 ; $^3\text{J}(\text{HH})=6.00 \text{ Hz}$), δ 4.26 br (1H, NH), δ 3.27 t (4H, CH_2 ; $^2\text{J}(\text{PH})+^4\text{J}(\text{PH})=8.6 \text{ Hz}$). δ 1.1-2.3 m (44H, Cyclohexyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 51.6 s.

Reactions of **1** and **2** with carbon monoxide.

Reactions of **1** and **2** with carbon monoxide were carried out in a 5mm screw cap NMR tube equipped with PTFE septum for a needle puncture (Wilmad No 528-TR). Carbon monoxide was bubbled through CDCl_3 solutions of **1** and **2**, respectively, for ca. 5 min via a 7 inch long needle connected with a silicone tube to a CO cylinder. The reactions of **1** and **2** with carbon monoxide were monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Results and Discussion

Cationic dimethylamine complexes of palladium(II), $[(\text{PCP})\text{Pd}(\text{NHMe}_2)](\text{OTf})$ ($\text{PCP} = 2,6\text{-}(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3$; $\text{R} = \text{Ph}$ (**1**), $\text{R} = \text{Cy}$ (**2**)), have been prepared by reacting a THF solution of $(\text{PCP})\text{Pd}(\text{OTf})$ ($\text{OTf} = \text{CF}_3\text{SO}_3^-$) with gaseous dimethylamine (eq 1).⁷ The coordinated triflate ligand of Pd(II) complexes $(\text{PCP})\text{Pd}(\text{OTf})$, having anionic terdentate ligands, can be easily replaced by dimethylamine in solution. However, the relative stability of dimethylamine complexes is largely dependent on the substituent R attached to the anchored phosphorus donor ligands. For $\text{R} = \text{Ph}$, the complex **1** is stable both in solution and in the solid state. On the other hand, the complex **2** with $\text{R} = \text{Cy}$ is stable only in solution in the presence of dimethylamine. The complex **2** in the solid state could not be isolated because of decomposition going back to the Pd(II) triflate, although the formation of **2** in solution is quantitative by NMR spectroscopy.

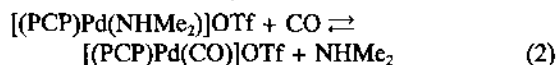


A crude product of **1** isolated from a THF/*n*-hexane solution can be purified by column chromatography on silica gel with an eluent of a THF solution of dimethylamine to give an analytically pure compound as white-off crystals (see experimental section). The isolated yield of **1** after column chromatography is 85%. The complex **1** has been fully characterized by various spectroscopic methods. The IR spectrum of **1** shows a characteristic $\nu(\text{NH})$ absorption band at 3241 cm^{-1} (w, br). The absorption bands for the counter ion CF_3SO_3^- have been observed at ca. 1262 and 1153 cm^{-1} with strong intensities. In the ^1H NMR spectrum,

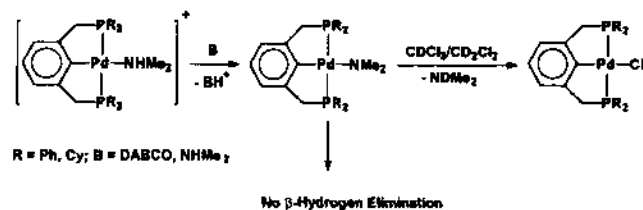
the methyl protons have been observed at δ 2.20 as a doublet resonance ($^3\text{J}(\text{HH}) = 5.80 \text{ Hz}$) due to the coupling with the NH proton which has been observed at δ 3.68 as a broad signal. This NH resonance could be verified by the observation of its disappearance on addition of D_2O into the CDCl_3 solution, resulting in the methyl resonance converging to a single peak. The resonance for methylene protons (PCH_2) has been observed at δ 4.02. The *trans* geometry of **1** in a monomeric formula has been verified by the observation of the pseudo-triplet resonance for the methylene protons due to the "virtual coupling" of *trans* phosphorus.⁸ The observed value of $^2\text{J}(\text{PH})+^4\text{J}(\text{PH})$ for **1** is 9.2 Hz.^{9,10} The dimethylamine moiety of $\text{Pd}(\text{NH}(\text{CH}_3)_2)$ in the complex has been verified not only by the doublet resonances for the methyl protons due to the coupling with the NH proton but by the relative peak intensities of the methyl, methylene, and phenyl protons in the ^1H NMR spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 shows a single resonance at δ 41.1. The observed downfield shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance for **1** is due to a chelating ring system of the PCP ligand.¹¹ The molar conductivity measurement for **1** shows that the complex is a 1:1 electrolyte ($\Lambda_M = 93 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ (CH_3NO_2), $[\text{1}] = 0.5 \times 10^{-3} \text{ mol}$).¹²

On the contrary to the isolation of **1**, the complex **2** is only stable in solution. The formation of **2** can be verified not only by the methyl resonances as doublet at δ 2.71 ($^3\text{J}(\text{HH}) = 6.00 \text{ Hz}$) due to the coupling with NH proton but by the relative peak intensities of the methyl, phenyl, methylene, and cyclohexyl protons in the ^1H NMR spectrum. The signal for the NH has been observed at δ 4.26, and verified by the D_2O experiment. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 shows a single resonance at δ 51.6, indicating only a single compound in solution. Although the complex **2** could not be isolated, the quantitative formation of **2** in solution has been confirmed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data which are closely consistent with those assigned to the complex **1**. The stability difference observed for the complex **2**, particularly having a rigid chelate ligand system, can be mainly explained by a steric congestion of bulky cyclohexyl substituents.

No reaction of **1** with carbon monoxide has been observed. On the other hand, **2** reacts with CO to give the carbonyl complex $[\text{Pd}(2,6\text{-}(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{CO})]\text{OTf}$ (**3**),¹⁰ although predominant species in solution under atmospheric pressure of CO is the dimethylamine complex (the ratio of $2/3 = \text{ca. } 7$ by the NMR spectroscopy). However, the addition of dimethylamine to the solution of the carbonyl complex $[\text{Pd}(2,6\text{-}(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{CO})]\text{OTf}$,^{10,13} independently synthesized from the reaction of $\text{Pd}(2,6\text{-}(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OTf})$ with CO, leads to the formation of complexes **1** and **2**, respectively; no side-product, neither a carbamoyl derivative nor dimethylformamide by the nucleophilic attack of NHMe_2 to the coordinated CO, has been observed. A solution NMR spectroscopic study shows that dimethylamine favors over carbon monoxide in the coordination sphere of palladium(II) having rigid terdentate ligands.



The complex **1** is stable in chlorinated solvents such as



Scheme 1.

CDCl_3 and CD_2Cl_2 in the absence of bases, while a solution of **1** with a base such as dimethylamine and DABCO (diazabicyclooctane) slowly yields the chloro complex $\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Cl}$ which is verified by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.^{6a} The complex **2** in CDCl_3 also undergoes a chlorine abstract reaction giving $\text{Pd}(2,6-(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Cl}$ in the presence of a base.^{6b} The formation of $\text{Pd}(2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Cl}$ ($\text{R} = \text{Ph}, \text{Cy}$) observed from the reactions of **1** and **2** with a base can be explained by a sequence of reactions involving deprotonation of the coordinated dimethylamine leading to a dimethylamido derivative, which then reacts with the chlorinated solvent giving the chloro palladium(II) complex. Although this explanation is rather speculative, a rare precedent of a dimethylamido palladium(II) complex prepared from deprotonation of the coordinated dimethylamine with a base, which is only stable at low temperature, has been recently reported.^{1c} A pathway involving a free chlorine radical or a chloride ion can not be ruled out. A palladium(II) hydride likely resulting from β -hydrogen elimination of dimethylamido species has not been observed in this reaction. A suggested reaction pathway is shown in Scheme 1.

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References

- (a) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (b) Brynza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (c) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (d) Baiker, A.; Richarz, W. *Tetrahedron Lett.* **1977**, 1937. (e) Ganguly, S.; Roundhill, D. M. *Polyhedron*, **1990**, *9*, 2517. (f) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794.
- (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, **1987**. (b) Watt, G. W.; Upchurch, D. G. *Adv. Chem. Ser.* **1966**, *62*, 253.
- Anderson, J. S.; Carmichael, J. W.; Cordes, A. W. *Inorg. Chem.* **1970**, *9*, 143.
- Abel, E. W.; Goldsworthy, D. H.; Heard, P. J.; Kite, K. *Polyhedron* **1995**, *14*, 515.
- Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030.
- (a) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6. (b) Cross, R. J.; Kennedy, A. R.; Muir, K. W. *J. Organomet. Chem.* **1995**, *487*, 227.
- A solution of $\text{Pd}(2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OTf})$ has been prepared from $\text{Pd}(2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)\text{Br}$ and silver triflate. For $\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OTf})$: ^1H NMR (CDCl_3): δ 3.88 t (4H, CH_2 ; $|^2\text{J}(\text{PH})+^4\text{J}(\text{PH})|=9.0$ Hz). δ 7.0-7.8 m (23H, phenyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 36.8 s. For $\text{Pd}(2,6-(\text{Cy}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{OTf})$: ^1H NMR (CDCl_3): δ 3.14 t (4H, CH_2 ; $|^2\text{J}(\text{PH})+^4\text{J}(\text{PH})|=8.6$ Hz). δ 1.2-2.4 m (44H, Cy). δ 6.9-7.0 m (3H, phenyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 55.0 s.
- Verkade, J. G. *Chem. Rev.* **1972**, *9*, 1.
- The observed value of $|^2\text{J}(\text{PH})+^4\text{J}(\text{PH})|$ for a series of (PCP)MX complexes has been reported in the range of 8-9 Hz; see Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 207. Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 195.
- Yun, J. G.; Seul, J. M.; Lee, K. D.; Kim, S.; Park, S. *Bull. Korean Chem. Soc.* **1996**, *17*, 311.
- Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
- The molar conductance (Λ_m) for the complexes of 1:1 electrolyte type at concentration $ca. 10^{-3}$ has been suggested in the range of 75-95 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$; see Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
- For $[\text{Pd}(2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)(\text{CO})]^+$; see Steffey, B. D.; Miedaner, A.; Maciejewski-Farmer, M. L.; Bernatis, P. R.; Herring, A. M.; Allured, V. S.; Carperos, V.; DuBois, D. L. *Organometallics* **1994**, *13*, 4844.