

(1995).

## References

- (a) Kralicek, J.; Kubanek, V.; Kondelikova, J. *German Patent* 1973, 2,301,784; (b) Kralicek, J.; Kubanek, V.; Kondelikova, J.; Casensky, B.; Machacek, J. *German Patent* 1976, 2,445,647; (c) Bukac, Z.; Sebenda, J. *U.S. Patent* 1976, 3, 962,239.
- (a) Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B. *J. L. J. Organomet. Chem.* 1989, 369, 147. (b) Becker, B.; Corriu, R.; Guérin, C.; Henner, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1987, 28(1),409. (c) Corriu, R. J. P. *J. Organomet. Chem.* 1990, 400, 81.
- Riviere, P.; Satge, J.; Soula, D. *J. Organomet. Chem.* 1974, 72, 329.
- Speier, J. L.; Zimmerman, R. E. *J. Am. Chem. Soc.* 1955, 77, 6395.
- Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Yeon, S. H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* 1995, 16(11), 1109.
- Woo, H.-G.; Song, S.-J.; Cho, E. J.; Jung, I. N. Unpublished results.
- 2-Phenyl-1,3-disilapropane (1): GC/MS (m/e (relative intensity)): 152 (40) (M<sup>+</sup>), 121 (53), 120 (100), 119 (38), 105 (33), 93 (19), 91 (15), 53 (12).  
Benzylsilane: GC/MS (m/e (relative intensity)): 122 (30) (M<sup>+</sup>), 121 (45), 119 (10), 105 (100), 93 (50), 91 (20), 53 (10).  
1-Phenyl-3,5-disilapentane (2): GC/MS (m/e (relative intensity)): 180 (20) (M<sup>+</sup>), 163 (1), 152 (19), 149 (31), 135 (41), 119 (2), 102 (100), 91 (45), 77 (20), 74 (80), 71 (20), 53 (81), 51 (10).  
1-Phenyl-4-silyl-3,5-disilapentane (3): GC/MS (m/e (relative intensity)): 210 (20) (M<sup>+</sup>), 179 (35), 154 (10), 147 (12), 130 (80), 105 (100), 91 (50), 77 (25), 73 (60), 71 (50), 65 (20), 51 (12).  
Phenethylsilane: GC/MS (m/e (relative intensity)): 136 (62) (M<sup>+</sup>), 133 (18), 119 (1), 108 (80), 105 (75), 91 (100), 77 (30), 65 (20), 58 (21), 51 (20).
- Seyferth, D.; Lang, H. *Organometallics* 1991, 10, 551.
- Armitage, A. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, Ch. 1.

## Synthesis and Characterization of Dicationic Diammine Complex of Palladium(II) Chelating with DPPE

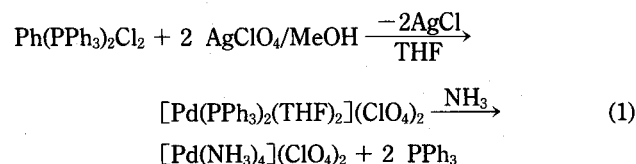
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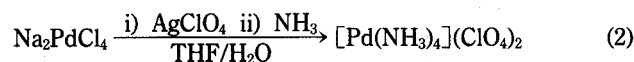
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Although ammine complexes of transition metals have been known since the early history in the classical coordination chemistry, such complexes containing tertiary phosphines or organic moieties are relatively rare.<sup>1</sup> Recently there has been an increasing interest in the amido complexes of transition metals because of their potential applications for catalysis.<sup>2</sup> One class in this category is such complexes of late transition metals having unsubstituted amide ligand NH<sub>2</sub>.<sup>3</sup> Ammine complexes having tertiary phosphines are useful synthetic precursors for unsubstituted amido complexes in which the coordinated tertiary phosphines can stabilize electronically and sterically with a variety of substituents.<sup>4</sup> Ammonia is a very weak acid (*pK<sub>a</sub>*=33) and the N-H bond dissociation energy in ammonia is very high (107 kcal/mol).<sup>5</sup> Ammonia upon coordination to cationic metal center, however, becomes considerably acidic to be deprotonated by appropriate base.

Reported here is the synthesis and characterization of a novel dicationic palladium(II) diammine complex containing 1,2-bis(diphenylphosphino)ethane as a supporting ligand. Our initial attempt to synthesize dicationic diammine complex having monodentate bis-triphenylphosphine has been proven not successful. When gaseous ammonia was added to a THF solution of [Pd(PPh<sub>3</sub>)<sub>2</sub>(THF)](ClO<sub>4</sub>)<sub>2</sub> prepared *in situ* by the reaction of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 2 equivalents of AgClO<sub>4</sub>, dicationic tetraammine complex [Pd(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (1) was obtained (eq. 1). The formation of 1 can be explained by a sequence of reactions involving the initial formation of [Pd(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, and then further substitution of coordinated triphenylphosphines with excess ammonia. We can not observe the intermediate complex [Pd(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. The formulation of 1 has been confirmed by its independent synthesis from the reaction of aqueous THF solution of [PdCl<sub>4</sub>]<sup>2-</sup>, 4 equivalents of AgClO<sub>4</sub> and ammonia (eq. 2).<sup>6</sup>



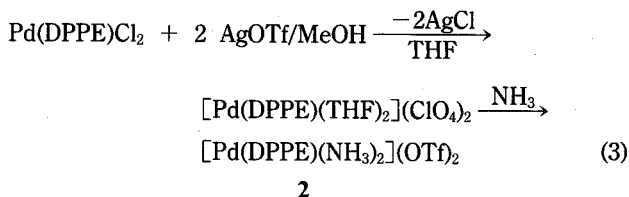
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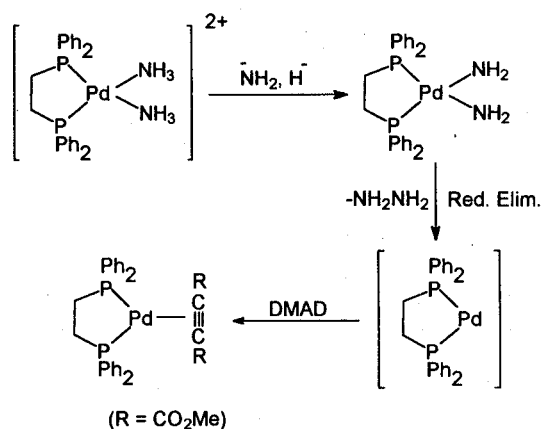
Targeting diammine complex of bis-phosphine palladium (II) has been successfully prepared by employing 1,2-bis(diphenylphosphino)ethane as chelating ligand in the displace-

ment of monodentating triphenylphosphines, in which the chelating DPPE can not be liberated by excess ammonia. The complex  $[\text{Pd}(\text{DPPE})(\text{NH}_3)_2](\text{OTf})_2$  (DPPE =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ,  $\text{OTf} = \text{CF}_3\text{SO}_3$ ), (**2**) was synthesized by the abstraction of chloride from the compound  $\text{Pd}(\text{DPPE})\text{Cl}_2$  using 2 equivalents of silver triflate in the presence of excess ammonia as shown in eq. 3. The compound **2** is hygroscopic, and can be isolated as beige crystals from THF/*n*-hexane under argon atmosphere. Although the isolated compound was pure by the evidence of  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, the compound containing a half molecule of ether  $[\text{Pd}(\text{DPPE})(\text{NH}_3)_2](\text{OTf})_2 \cdot 1/2(\text{OC}_4\text{H}_{10})$  was isolated for microanalysis by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{ether}$  under argon atmosphere.<sup>7</sup>



The IR spectrum of **2** shows characteristic three  $\nu(\text{NH})$  absorption bands at 3180, 3250 and 3330  $\text{cm}^{-1}$  (w, br). The absorption bands of the counter ion  $\text{CF}_3\text{SO}_3^-$  have been observed ca. 1260 and 1160  $\text{cm}^{-1}$  with strong intensities as symmetric and antisymmetric  $\nu(\text{S}=\text{O})$ , respectively. The  $^1\text{H}$  NMR resonance for the coordinated  $\text{NH}_3$  protons is observed at  $\delta$  3.02.<sup>8</sup> The relative peak intensities of the coordinated ammonia, ethylene, and phenyl protons in the  $^1\text{H}$  NMR spectrum confirms the presence of the diammine moiety  $\text{Pd}(\text{NH}_3)_2$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$  shows a single resonance at  $\delta$  64.83. Molar conductivity measurement for **2** in acetonitrile shows that the complex **2** is 2 : 1 electrolyte. The calculated value of  $\Lambda_M$  was 250  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  ( $[\text{2}] = 0.5 \times 10^{-3} \text{ mol}$ ).

No reaction of **2** with water has been observed for 2 days in  $\text{CDCl}_3$  by the evidence of  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, which indicates that the coordinated ammonia to dicationic palladium(II) center can not be easily replaced by water molecule particularly having DPPE ligand.<sup>9</sup> The complex **2** has been alternatively prepared by the reaction of  $\text{Pd}(\text{DPPE})\text{Cl}_2$ ,  $\text{AgOTf}$ , and  $\text{NaOH}$  in the presence of excess ammonia. The reaction was nearly quantitative as judged by the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy; neither the dicationic hydroxy bridged dimer  $[\text{Pd}(\text{DPPE})(\mu\text{-OH})_2]^{2+}$  known as tetrafluoroborate salt<sup>10</sup> nor a deprotonated amido complex has been obtained. When **2** is treated with sodium amide or sodium hydride in THF solution at ambient temperature, the pale-yellow solution darkens slowly to give a deep red solution within an hour. Addition of *n*-hexane to the benzene extract from the residue obtained by the removal of solvent gave a dark red solid. The IR spectrum of this solid showed no absorption bands due to  $\nu(\text{SO})$  and  $\nu(\text{NH})$ . The  $^1\text{H}$  NMR spectrum of the solid in  $d_6$ -benzene showed broad signals for the coordinated DPPE. When the reaction was performed in the presence of excess dimethylacetylenedicarboxylate (DMAD), the putative complex  $\text{Pd}(\text{DPPE})$  could be trapped with DMAD to generate  $\text{Pd}(\text{DPPE})(\text{DMAD})$ .<sup>11</sup> These results implicate that a monomeric diamido palladium(II) complex formed from the reaction is unstable in solution and undergoes reductive elimination reaction to give palladium(0) com-



Scheme 1.

pound and hydrazine (Scheme I). An alternative reaction pathway involving electron transfer from amide or hydride ion can not be ruled out.

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## References

- (a) Kauffman, G. B. *Classics in Coordination Chemistry*; Dover Pub. Inc.; New York, U.S.A., 1968. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5<sup>th</sup> Ed.; Wiley: New York, U.S.A., 1988. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, 1987. (d) Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: New York, U.S.A., 1974. (e) Gavrilova, I. V.; Gel'fman, M. I.; Ivannikova, N. V.; Razumovskii, V. V. *Russ. J. Inorg. Chem.* **1971**, *16*(4), 596.
- (a) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (b) Brynza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.
- (a) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercau, J. E. *Organometallics* **1988**, *7*, 1309. (b) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 973. (c) Curtis, N. J.; Hagen, K. S.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 1571. (d) Martin, G. C.; Palenik, G. J.; Boncella, J. M. *Inorg. Chem.* **1990**, *29*, 2027. (e) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Inorg. Chem.* **1987**, *26*, 3972. (f) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1991**, *10*, 615.
- Tolman, C. A. *Chem. Rev.* **1977**, *6*, 650.
- (a) Wade, L. G. *Organic Chemistry*, 3rd Ed.; Prentice Hall: New Jersey, U.S.A., 1995; p 26. (b) McMillen, D. P.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
- The formation of **1** from the reaction of  $[\text{PdCl}_4]^{2-}$  and aqueous ammonia in the presence of  $\text{HClO}_4$  has been reported; see Coe, J. S.; Hussain, M. D.; Malik, A. A. *Inorg. Chim. Acta.* **1968**, *2*, 65.

7. Spectroscopic data for **2**: IR (KBr pellet)  $\nu(\text{NH})=3180, 3250, 3330 \text{ cm}^{-1}$  (w, br),  $\nu(\text{SO})=1260, 1160 \text{ cm}^{-1}$  (vs, br);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.02 br (6H,  $\text{NH}_3$ ),  $\delta$  2.76m (4H,  $\text{CH}_2$ ),  $\delta$  7.6-7.8m (20H, phenyl);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  64.83 s. Anal. Calcd for  $\text{C}_{30}\text{H}_{35}\text{F}_6\text{N}_2\text{O}_{6.5}\text{PdS}_2$ : C, 41.22; H, 4.04; N 3.20; S, 7.34. Found: C, 40.93; H, 4.21; N, 3.27; S, 7.37.
8. The  $^1\text{H NMR}$  resonance for the coordinated  $\text{NH}_3$  in the platinum complex  $[\text{Pt}(\text{NH}_3)\text{Me}(\text{DPPE})]^+$  was observed at  $\delta$  3.46, see ref 3 (f).
9. For the complex  $[\text{PdL}_3(\text{NH}_3)]^+$  ( $\text{L}_3=2,6\text{-bis}(\text{dicyclohexylphosphinomethyl})\text{phenyl}$ ), the coordinated ammonia slowly undergoes substitution reaction with water; unpublished result in this laboratory.
10. Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3831.
11. Precedented example of  $\text{Pd}(\text{DPPE})(\text{DMAD})$  prepared by the photolysis of  $\text{Pd}(\text{DPPE})(\text{C}_2\text{O}_4)$  in the presence of excess DMAD; see Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647.