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- 2-Phenyl-1,3-disilapropane (1): GC/MS (m/e (relative intensity)): 152 (40) (M⁺), 121 (53), 120 (100), 119 (38), 105 (33), 93 (19), 91 (15), 53 (12).

Benzylsilane: GC/MS (m/e (relative intensity)): 122 (30) (M⁺), 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⁺), 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⁺), 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⁺), 133 (18), 119 (1), 108 (80), 105 (75), 91 (100), 77 (30), 65 (20), 58 (21), 51 (20).

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

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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. Recently there has been an increasing interest in the amido complexes of transition metals because of their potential applications for catalysis.2 One class in this category is such complexes of late transition metals having unsubstituted amide ligand NH₂.3 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.⁴ Ammonia is a very weak acid ($pK_a=33$) and the N-H bond dissociation energy in ammonia is very high (107 kcal/mol).5 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 monodentated bis-triphenylphosphine has been proven not successful. When gaseous ammonia was added to a THF solution of [Pd(PPh₃)₂(THF)](ClO₄)₂ prepared in situ by the reaction of PdCl₂(PPh₃)₂ and 2 equivalents of AgClO₄, dicationic tetraammine complex [Pd(NH₃)₄](ClO₄)₂ (1) was obtained (eq. 1). The formation of 1 can be explained by a sequence of reactions involving the initial formation of [Pd (PPh₃)₂(NH₃)₂](ClO₄)₂, and then further substitution of coordinated triphenylphosphines with excess ammonia. We can not observe the intermediate complex [Pd(PPh₃)₂(NH₃)₂] (ClO₄)₂. The formulation of 1 has been confirmed by its independent synthesis from the reaction of aqueous THF solution of [PdCl₄]²⁻, 4 equivalents of AgClO₄ and ammonia (eq. 2).⁶

$$Ph(PPh_3)_2Cl_2 + 2 AgClO_4/MeOH \xrightarrow{-2AgCl}$$

$$[Pd(PPh_3)_2(THF)_2](ClO_4)_2 \xrightarrow{NH_3} (1)$$

$$[Pd(NH_3)_4](ClO_4)_2 + 2 PPh_3$$

$$Na_{2}PdCl_{4} \xrightarrow{i)} AgClO_{4} \xrightarrow{ii)} NH_{3} \longrightarrow [Pd(NH_{3})_{4}](ClO_{4})_{2}$$
(2)

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 [Pd(DPPE)(NH₃)₂](OTf)₂ (DPPE=Ph₂PCH₂CH₂ PPh₂, OTf=CF₃SO₃), (2) was synthesized by the abstraction of chloride from the compound Pd(DPPE)Cl₂ 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 ¹H and ³¹P{¹H} NMR spectroscopy, the compound containing a half molecule of ether [Pd(DPPE) (NH₃)₂](OTf)₂·1/2(OC₄H₁₀) was isolated for microanalysis by recrystalization from CH₂Cl₂/ether under argon atmosphere.⁷

$$Pd(DPPE)Cl_{2} + 2 AgOTf/MeOH \frac{-2AgCl}{THF}$$

$$[Pd(DPPE)(THF)_{2}](ClO_{4})_{2} \xrightarrow{NH_{3}}$$

$$[Pd(DPPE)(NH_{3})_{2}](OTf)_{2}$$

$$(3)$$

The IR spectrum of 2 shows characteristic three $\nu(NH)$ absorption bands at 3180, 3250 and 3330 cm⁻¹ (w, br). The absorption bands of the counter ion $CF_3SO_3^-$ have been observed ca. 1260 and 1160 cm⁻¹ with strong intensities as symmetric and antisymmetric $\nu(S=0)$, respectively. The ¹H NMR resonance for the coordinated NH₃ protons is observed at δ 3.02.8 The relative peak intensities of the coordinated ammonia, ethylene, and phenyl protons in the ¹H NMR spectrum confirms the presence of the diammine moiety Pd(NH₃)₂. The ³¹P{¹H} NMR spectrum of 2 in CDCl₃ shows a single resonance at δ 64.83. Molar conductivity measurement for 2 in acetonitrile shows that the complex 2 is 2:1 electrolyte. The calculated value of Λ_M was 250 ohm⁻¹cm²mole⁻¹ ([2]= 0.5×10^{-3} mol).

No reaction of 2 with water has been observed for 2 days in CDCl₃ by the evidence of ¹H and ³¹P{¹H} 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.9 The complex 2 has been alternatively prepared by the reaction of Pd (DPPE)Cl₂, AgOTf, and NaOH in the presence of excess ammonia. The reaction was nearly quantitative as judged by the ³¹P{¹H} NMR spectroscopy; neither the dicationic hydroxy bridged dimer [Pd(DPPE)(μ-OH)]₂²⁺ known as tetrafluoroborate salt 10 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 v(SO) and v(NH). The ¹H NMR spectrum of the solid in de-benzene showed broad signals for the coordinated DPPE. When the reaction was performed in the presence of excess dimethylacetylenedicarboxylate (DMAD), the putative complex Pd(DPPE) could be trapped with DMAD to generate Pd(DPPE)(DMAD).11 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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- The ¹H NMR resonance for the coordinated NH₃ in the platinum complex [Pt(NH₃)Me(DPPE)]⁺ was observed at δ 3.46, see ref 3 (f).
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