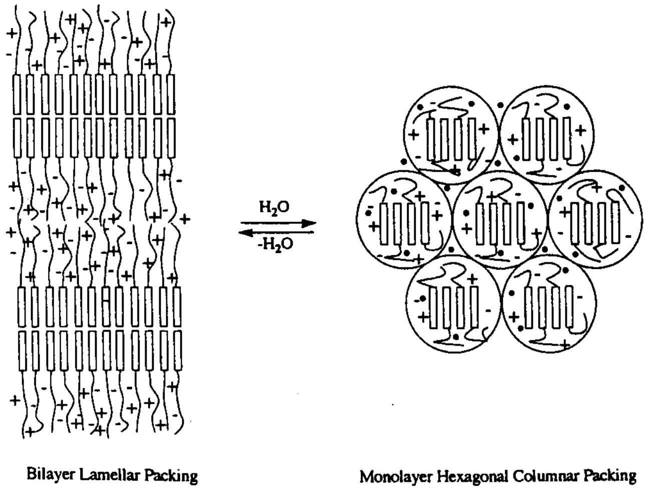

Figure 4. Schematic representation of the possible models of the structural transformation of the bilayer lamellar phase in the pure complex into the monolayer hexagonal columnar phase on addition of water; +, Li^+; −, $CF_3SO_3^-$; ●, H_2O.

llar mesophase in a concentration range from 15 to 50 weight-%. While the aquous solutions of the complex show only cylindrical micellar mesophase in a concentration range from 40 to 95 weight-%.

For morphological investigation of the lyotropic aggregation, both small angle and wide angle X-ray scattering experiments have been performed with the complex solution of 88 wt.% concentration and with the pure complex without water. As shown in Figure 3(a), the complex solution exhibits four Bragg reflections of 0.188 (strong), 0.325, 0.376 and 0.50 nm^{-1}, respectively. Bragg spacings in the ratio with 1: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$ indicate that the molecules organizes into cylindrical hexagonal structure with intercylinder distance of 6.14 nm.[11] While wide angle X-ray experiment gives only a broad halo. The X-ray scattering patterns and polarized optical microscopic observations indicate that the lyotropic mesophase exhibited by the complex solution is a monolayer hexagonal columnar structure. The pure complex without water displays the intense fundamental and its second and third harmonic reflections at Bragg spacings of 0.08 (strong), 0.267 and 0.250 nm^{-1}, respectively, as shown in Figure 3(b). The peak angles in the ratio with 1 : 2 : 3 indicate that the pure complex has a bilayer lamellar structure at room temperature.[11] Figure 4 shows the schematic representation of the structural transformation of the bilayer lamellar phase into the monolayer columnar hexagonal phase on addition of water.

The lamellar structure observed at lower water content in the rod-coil aqueous systems and at the pure complex is still the most efficient packing of coils because the volume fraction of coil parts is not large enough. At higher water content or on addition of water in the case of the complex, however, the volume fraction of coil segments is increased by selective penetration of the water molecules into the hydrophilic coil domains and the system becomes unstable due to space crowding of the coil segments. Consequently, the lamellar structure of the rod-coil oligomer will break apart into cylindrical micelles as shown in Figure 4 and predicted by theoretical work.[1,4] This might explain qualitatively the lyotropic phase behavior of this rod-coil system. Work is in progress to examine in more detail the lyotropic aggregation behavior of rod-coil oligomers containing poly(ethylene oxide).

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New Cationic Ammine Complexes of Palladium (II) Having Phenyl and Substituted Phenyl Ligands

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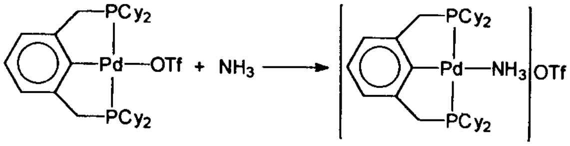
Ammine complexes of late transition metals having organic ligands are rare.[1] Recently there has been a growing interest in the amido complexes of organotransition metals because of their potential applications for catalysis.[2] One class in this category is such complexes of late transition metals having unsubstituted amide ligand NH_2.[1d-e,3] One of the synthetic methods for preparations of such complexes is deprotonation from coordinated ammonia. Ammonia is a very weak acid ($pK_a = 33$) and the N-H bond dissociation energy in ammonia is very high (107 kcal/mol).[4] Ammonia upon coordination to cationic metal center, however, becomes considerably acidic to be deprotonated by an appropriate base.[5] Recently we have reported a dicationic diammine complex of palladium(II) having a chelating DPPE ligand.[6] We herein describe palladium ammine phenyl and substituted phenyl complexes having monodentate triethylphosphines and terdentate 2,6-bis(dicyclohexylphosphinomethyl)phenyl as supporting ligands.

When a benzene solution of *trans*-Pd(Ph)(OTf)(PEt$_3$)$_2$ (OTf=CF$_3$SO$_3^-$) was added to a methanolic solution of ammonia, *trans*-[Pd(Ph)(NH$_3$)(PEt$_3$)$_2$]OTf (**1**) was obtained (eq. 1).[7] The complex **1** for satisfactory microanalysis can be obtained by column chromatography with an eluent of THF to give colorless crystals from *n*-hexane. The isolated yield of **1** after column chromatography was 84%. The complex **1** has been fully characterized by various spectroscopic methods.[8] The IR spectrum of **1** shows three characteristic ν (NH) absorption bands at 3183, 3264 and 3319 cm^{-1}. The absorption bands for the counter ion CF$_3$SO$_3^-$ have been also observed at *ca.* 1260 and 1160 cm^{-1} with strong intensities. The peaks can be assigned to symmetric and antisymmetric ν(SO) bands, respectively. The ^{1}H NMR resonance for the coordinated NH$_3$ protons is observed at δ 2.33. The relative peak intensities of the coordinated ammonia, phenyl, and ethyl protons in the ^{1}H NMR spectrum confirms the presence of the ammine moiety Pd(NH$_3$). The ^{31}P{^{1}H} NMR spectrum of **1** in CDCl$_3$ shows a single resonance at δ 12.4. The molar conductivity measurement for **1** in nitromethane shows that the complex is 1 : 1 electrolyte (Λ_M=87 ohm$^{-1}\cdot$cm$^2\cdot$mol^{-1}, [**1**]=0.5×10^{-3} mol).[9]

$$\begin{array}{l} trans\text{-Pd(Ph)(OTf)(PEt}_3)_2+\text{NH}_3\rightarrow \\ trans\text{-[Pd(Ph)(NH}_3)(\text{PEt}_3)_2]\text{OTf} \\ \qquad\qquad \mathbf{1} \end{array} \qquad (1)$$

A cationic ammine complex of palladium(II) containing terdentate anionic ligand, [(PCP)Pd(NH$_3$)]OTf (**2**) (PCP=2,6-bis(dicyclohexylphosphinomethyl) phenyl) has been similarly prepared by the reaction of (PCP)Pd(OTf) and ammonia (eq. 2).[10] A crude product of **2** can be purified by column chromatography with an eluent of a CH$_2$Cl$_2$ solution saturated with ammonia to give an analytically pure compound.[11] The three characteristic ν(NH) bands of **2** in the IR spectrum have been similarly observed at 3179, 3263 and 3330 cm^{-1}. The ν(SO) bands for the counter anion CF$_3$SO$_3^-$ have been also observed at *ca.* 1260 and 1160 cm^{-1} with strong intensities. The ^{1}H NMR in CDCl$_3$ for **2** shows the coordinated NH$_3$ resonance at δ 2.52. The resonance for methylene protons has been observed at δ 3.27. The trans geometry of **2** has been verified by the observation of the pseudo-triplet resonance for the methylene protons due to the "virtual coupling" of *trans* phosphoruses.[12] The observed value of $|^2J(\text{PH})+^4J(\text{PH})|$ for **2** is 8.8 Hz.[13] The ammine moiety Pd(NH$_3$) in the complex has been verified by integrating the relative peak intensities of the coordinated ammonia, phenyl, methylene and cyclohexyl protons in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} NMR spectrum of **2** in CDCl$_3$ shows a single resonance at δ 52.4. The observed downfield shift in the ^{31}P{^{1}H} NMR resonance for **2** is due to the chelating ring system of PCP.[14] The Molar conductivity measurement for **2** shows that the complex is 1 : 1 electrolyte (Λ_M=89 ohm$^{-1}\cdot$cm$^2\cdot$mol^{-1} (CH$_3$NO$_2$), [**2**]=0.5×10^{-3} mol).[9] Spectral and microanalytical data for the complexes **1** and **2** are listed in ref. 8.



(2)

2

The compounds **1** and **2** are stable not only in the solid state but in solution. The phenyl substituted palladium(II) ammine complex **1** having monodentating triethylphosphines positioned mutually trans to each other is stable in solution in the presence of excess ammonia; no substitution of triethylphosphines with ammonia has been observed by ^{1}H and ^{31}P{^{1}H} NMR. On the other hand, an attempt for the preparation of analogous compounds having triphenylphosphines was not successful by a similar synthetic procedure.[15] The stability of cationic ammine complexes seems to be very sensitive to the supporting ligands in the complexes. Our previous report has showed that a diammine palladium(II) complex with a chelating DPPE ligand could be successfully prepared, while an analogous complex with monodentating triphenylphosphines could not be available by a similar method because of substitutions of triphenylphosphines with ammonia.[6] The successful preparation of **2** again showed that a cationic ammine complex of palladium(II) with a chelating PCP ligand was intact from an excess of ammonia.

In the reaction of **1** with carbon monoxide, no substitution of the coordinated ammonia with CO has been observed but phenyl migration occurs to give a Pd(C(O)Ph) moiety.[16] On the contrary, the reaction of **2** with carbon monoxide yields a carbonyl derivative [(PCP)Pd(CO)]OTf (**3**) (eq. 3).[17] The formation of **3** has been confirmed by its independent synthesis from reacting a CDCl$_3$ solution of (PCP)PdBr and silver triflate followed by treatment of carbon monoxide.[18] Addition of ammonia to a chloroform solution of **3** immediately undergoes back to **2**. The reaction is quantitative by the evidences of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy; no other complex such as [(PCP)Pd(C(O)NH$_3$)]$^+$ derived from nucleophillic attack of ammonia to the coordinated CO has been observed. The reactivity difference observed from **2** and carbon monoxide can be explained by the steric congestion of the rigid chelating PCP ligand, which resulted the substitution of the coordinated ammonia by CO instead of the insertion of CO into the Pd-C bond yielding benzoyl derivative. The complexes of **1** and **2** do not react with CH$_2$CHCN and/or dimethyl maleate.

$$[\text{(PCP)Pd(NH}_3)]\text{OTf}+\text{CO} \rightleftarrows \underset{\mathbf{3}}{[\text{(PCP)Pd(CO)}]\text{OTf}}+\text{NH}_3 \qquad (3)$$

Cationic ammine complexes of palladium(II) containing tertiary phosphines as supporting ligands can be prepared by employing large *trans*-influence phenyl and substituted phenyl ligands. Preparations of palladium(II) amides from these new cationic ammine complexes are currently under investigation.

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8. Spectral data for **1** and **2**. **1**: IR (KBr pellet); ν(NH)= 3183, 3264, 3319 cm^{-1} (w, br), ν(SO)=1260, 1160 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$); δ 1.14 m (18H, CH_3), δ 1.43 m (12H, CH_2), δ 2.33 br (3H, NH_3), δ 6.94 t (1H, phenyl-*p*), δ 7.01 t (2H, phenyl-*m*), δ 7.18 d (2H, phenyl-*o*). $^{31}P\{^1H\}$ NMR ($CDCl_3$); δ 12.4 s. Λ_M=87 $ohm^{-1}cm^2mole^{-1}$ (in CH_3NO_2, [**1**]=0.5×10^{-3} mol). Anal. Calcd for $C_{19}H_{38}F_3NO_3P_2PdS$: C, 38.95; H, 6.54; N 2.39; S, 5.47. Found: C, 38.62; H, 6.68; N, 2.62; S, 5.20. **2**: IR (KBr pellet); ν(NH)=3179, 3263, 3330 cm^{-1} (w, br), ν(SO)=1260, 1160 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$); δ 1.1-2.3 m (44H, cyclohexyl), δ 2.52 br (3H, NH_3), δ 3.27 t (4H, CH_2, $|^2J(PH)+^4J(PH)$(= 8.8 Hz), δ 6.99 m (3H, phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$); δ 52.4 s. Λ_M=89 $ohm^{-1}cm^2mole^{-1}$ (in CH_3NO_2, [**2**]=0.5×10^{-3} mol). Anal. Calcd for $C_{33}H_{54}F_3NO_3P_2PdS$: C, 51.46; H, 7.07; N 1.82; S, 4.00. Found: C, 51.13; H, 6.68; N, 1.50; S, 4.00.
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11. Without treatment of ammonia to the CH_2Cl_2 eluent, dissociation of ammonia from **2** does occur on column chromatography (spectral data for **2**; see ref 8).
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15. Uncharacterized several complexes have been observed from the reaction of a benzene solution of *trans*-Pd(Ph)I $(PPh_3)_2$ and silver triflate followed by ammonia.
16. The observations of the ν(CO) at 1629 cm^{-1} in the IR and the downfield shifted phenyl protons resonances at δ 8.1 and δ 7.5 in the ^1H NMR are indicative of the Pd(C(O)Ph) moiety in the complex.
17. The coordinated ammonia on **2** has not been completely replaced by the atmospheric pressure of CO to yield **3** at ambient temperature; the respective amount of **3** and **2** observed in solution was in the ratio of 1/4 by integrating the corresponding triplet resonances of the methylene protons in the ^1H NMR.
18. The complex **3** can not be isolated from the solution because of decomposition yielding uncharacterized species with no carbonyl ligand in the IR spectrum. Spectral data for **3** in solution: IR (in $CDCl_3$); ν(CO)=2105 cm^{-1} (s, sh), ν(SO)=1270, 1160 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$); δ 1.1-2.4 m (44H, cyclohexyl), δ 3.62 t (4H, CH_2, $|^2J(PH)+^4J(PH)|$=9.5 Hz), δ 7.1-7.4 m (3H, phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$); δ 73.2 s.