Amine and Olefin Complexes of Pt(II) Having a PCP-Pincer Ligand

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$Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ (OTf = $CF_3SO_3^-$) readily reacts with various amines to afford cationic amine complexes $[Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(amine)](OTf)$ (amine = NH_3, $NHMe_2$, NHC_4H_8, NH_2Ph, $NH_2(Tol\text{-}p)$) in high yields. These complexes have been fully characterized by IR, ^1H-, $^{19}F\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectroscopy, and elemental analyses. Reaction of $Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ with acrylonitrile quantitatively produced the π-olefinic complex $[Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2{=}CHCN)](OTf)$, which is only stable in solution in the presence of acrylonitrile. Attempt at isolating this complex in the pure solid state was failed due to partial decomposition into $Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$. The equilibrium constants (K_{eq} = $[Pt(PCP)(NH_2R)^+][CH_2{=}CHCN]/[Pt(PCP)(CH_2{=}CHCN)^-][NH_2R]$: $[Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2{=}CHCN)]^+ + NH_2R \rightleftharpoons [Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(NH_2R)]^+ + CH_2{=}CHCN$; R = Ph, *p*-tolyl) were calculated to be 0.28 (for R = Ph) and 3.1 (R = *p*-tolyl) at 21 °C. The relative stability of the σ-donor amine versus the π-olefinic acrylonitrile complex has been found largely dependent upon the amine-basicity (pK_b), implicating that acrylonitrile practically competes with amine in the platinum coordination sphere. On the contrary to the formation of the acrylonitrile complex, no reaction of $Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ with other olefins such as ethylene, styrene and methyl acrylate was observed.

Keywords : Platinum, Amine, Olefin, Equilibrium constant.

Introduction

Addition of the N-H bond of amine to the C=C bond of olefin catalyzed by late transition metal complexes has received much attention recently.[1] Although many catalytic hydroamination of olefins have been reported so far, mechanistic pathways for these catalytic systems are still a matter of controversy.[1,2] Two discerning mechanistic steps of these catalytic reactions have been suggested. One way involves the N-H bond activation of amines by low-valent metal complexes.[3] In the meanwhile a coordinated amine to a high-valent complex is to be acidic,[4] thereby being readily deprotonated by an appropriate base to yield an amido complex which is frequently involved in the N-C bond formation.[5] An alternative, but more generally observed, pathway may involve nucleophilic attack of amines to coordinated olefins on high-valent complexes.[6]

In this paper, of relevance to catalytic hydroamination of olefins with amines, a series of ammine, amine, and acrylonitrile complexes of Pt(II) particularly containing a bisphosphine PCP-pincer ligand have been reported.[7] In the employed Pt(II) complexes for this study, the terdentate ligand inhibits both phosphine dissociation and reductive elimination of the aryl group, as a consequence the rigid ligand system in a square planar Pt(II) complex allows us to explore only one alternative coordination site to be probed.[8] The relative stability of σ-donor amine versus π-olefinic complexes of Pt(II) can be evaluated by measuring equilibrium constants, which may provide valuable information relevant to catalytic hydroamination of olefin.

Experimental Section

All operations for air sensitive compounds were performed on a standard Schlenk line or in an inert atmosphere glovebox under argon or nitrogen. All solvents were properly dried and deaerated by conventional manners.[9] K_2PtCl_4 was supplied by Kojima Chemicals Co., Ltd., and used without purification. Anhydrous dimethylamine, 1,5-cyclooctadiene, AgOTf, α,α'-dibromo-*m*-xylene, and deuterated solvents were purchased from Aldrich Chemical Company, and used as supplied. Ammonia was dried by passing through a column (Drierite gas-drying unit: Aldrich Z11, 287-9) filled with anhydrous $CaSO_4$. Dicyclohexylphosphine was supplied by Strem Chemicals Inc. All other reagents were from various commercial companies. The compounds $1,3\text{-}(Cy_2PCH_2)_2C_6H_4$[7g] and $Pt(2,6\text{-}(Cy_2PCH_2)_2\text{-}C_6H_3)(OTf)$[8a] were prepared according to the literature methods.

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets or as a nujol mull. ^1H-, $^{31}P\{^1H\}$- and $^{19}F\{^1H\}$-NMR spectra were measured on a Varian Gemini-2000 spectrometer, using the deuterium signal of the solvent as an internal lock frequency. Chemical shifts for ^1H-, $^{31}P\{^1H\}$- and $^{19}F\{^1H\}$-NMR were reported in ppm relative to TMS, external 85% H_3PO_4 and perfluoromethylbenzene (δ = -63.73) (in a sealed capillary), respectively. GC/MS analyses were performed using a HP 6890 gas chromatograph equipped with a HP 5973 MSD and a HP-Ultra 1 column. 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.

[Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(NH$_3$)](OSO$_2$CF$_3$) (1): To a solution of Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) (300 mg, 0.36 mmol) in THF (30 mL) was added a THF solution (3 mL) of saturated NH_3. After stirring the solution for 30 min, the solution volume was reduced to *ca.* 3 mL. Addition of *n*-hexane/diethyl ether (5 mL) to the concentrated solution gave white crystals, which was isolated by vacuum filtration and dried *in vacuo*. Complex **1** for satisfactory microanalysis can be obtained by column chromatography with an eluent of CH_2Cl_2 saturated with ammonia to give colorless crystals from *n*-hexane. The isolated yield of complex **1** after column chromatography was 86% (266 mg). IR (KBr): ν(NH) = 3191, 3269, 3310 cm^{-1}, ν(SO) = 1159, 1269 cm^{-1}. ^{1}H-NMR (d_6-benzene): δ 1.0-2.5 m (44H, Cy), δ 2.88 t (4H, CH_2, $|^2J$(PH) + ^4J(PH)$|$ = 8.0 Hz, ^3J(PtH) = 23 Hz), δ 3.94 t (3H, NH_3, ^2J(PtH) = 28 Hz), δ 7.05 m (3H, Ph). ^{31}P{^{1}H}-NMR (d_6-benzene): δ 50.2 (^1J(PtP) = 2744 Hz). ^{19}F{^{1}H}-NMR (d_6-benzene): δ -79.0 s. Λ_M = 87 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ (in CH_3NO_2, [Pt] = 0.5 × 10^{-3} mol). Anal. Calcd for $C_{33}H_{54}NF_3O_3P_2PtS$: C, 46.1; H, 6.34; N, 1.63; S, 3.73. Found: C, 46.5; H, 6.48; N, 1.86; S, 3.97%.

[Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(NHMe$_2$)](OSO$_2$CF$_3$) (2): A similar procedure as for complex **1** using Pt(2,6-(Cy$_2$PCH$_2$)$_2$-C$_6$H$_3$)(OTf) (30 mg, 0.036 mmol) and $NHMe_2$ (an excess) gave complex **2**. Yield 29 mg (92%). IR (Nujol): ν(NH) = 3459 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.0-2.4 m (44H, Cy), δ 2.89 d (6H, CH_3: ^3J(HH) = 6.0 Hz), δ 3.24 t (4H, CH_2, $|^2J$(PH) + ^4J(PH)$|$ = 8.4 Hz, ^3J(PtH) = 24 Hz), δ 4.86 br (1H, NH), δ 6.96 m (3H, Ph). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 48.3 (^1J(PtP) = 2834 Hz). ^{19}F{^{1}H}-NMR ($CDCl_3$): δ -79.6 s. Λ_M = 92 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ (in CH_3NO_2, [Pt] = 0.5 × 10^{-3} mol). Anal. Calcd for $C_{35}H_{58}NF_3O_3P_2PtS$: C, 47.4; H, 6.59; N, 1.58; S, 3.62. Found: C, 47.0; H, 6.28; N, 1.75; S, 3.43%.

[Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(NHC$_4$H$_8$)](OSO$_2$CF$_3$) (3): To a solution of Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) (30 mg, 0.036 mmol) in THF (30 mL) was added an excess amount of pyrrolidine (13 mg, 0.18 mmol). After stirring the reaction mixture for 30 min, the solution volume was reduced to *ca.* 2 mL. Addition of *n*-hexane/diethyl ether (5 mL) to the concentrated solution gave white crystals, which was isolated by vacuum filtration and dried *in vacuo*. Yield 29 mg (89%). IR (Nujol): ν(NH) = 3247 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.0-2.4 m (44H, Cy), δ 3.24 t (4H, CH_2, $|^2J$(PH) + ^4J(PH)$|$ = 8.0 Hz, ^3J(PtH) = 20 Hz), δ 4.63 br (1H, NH, ^2J(PtH) = 26 Hz), δ 6.96 m (3H, Ph). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 48.7 (^1J(PtP) = 2812 Hz). ^{19}F{^{1}H}-NMR ($CDCl_3$): δ -79.7 s. Λ_M = 79 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ (in CH_3NO_2, [Pt] = 0.5 × 10^{-3} mol). Anal. Calcd for $C_{37}H_{60}NF_3O_3P_2PtS$: C, 48.7; H, 6.62; N, 1.53; S, 3.51. Found: C, 48.2; H, 6.48; N, 1.45; S, 3.33%.

[Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(NH$_2$Ph)](OSO$_2$CF$_3$) (4): A similar procedure as for complex **3** using Pt(2,6-(Cy$_2$PCH$_2$)$_2$-C$_6$H$_3$)(OTf) (30 mg, 0.036 mmol) and aniline (17 mg, 0.18 mmol) gave complex **4**. Yield 31 mg (92%). IR (Nujol): ν(NH) = 3321, 3414 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.0-2.2 m (44H, Cy), δ 3.22 t (4H, CH_2, $|^2J$(PH) + ^4J(PH)$|$ = 8.0 Hz, ^3J(PtH) = 22 Hz). δ 6.05 br (1H, NH, ^2J(PtH) = 34 Hz). δ 6.98 m (3H, Ph). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 48.2 (^1J(PtP) = 2784 Hz). ^{19}F{^{1}H}-NMR ($CDCl_3$): δ -79.5 s. Λ_M = 82 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ (in CH_3NO_2, [Pt] = 0.5 × 10^{-3} mol). Anal. Calcd for $C_{39}H_{58}NF_3O_3P_2PtS$: C, 50.1; H, 6.25; N, 1.50; S, 3.43. Found: C, 49.8; H, 6.53; N, 1.54; S, 3.65%.

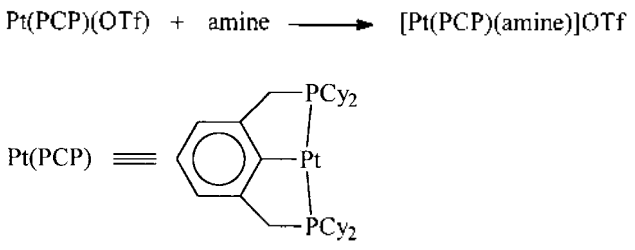
[Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(NH$_2$(C$_6$H$_4$Me-*p*)](OSO$_2$CF$_3$) (5): A similar procedure as for complex **3** using Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) (30 mg, 0.036 mmol) and toluidine (19 mg, 0.18 mmol) gave complex **5**. Yield 32 mg (94%). IR (nujol): ν(NH) = 3364, 3470 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.0-2.4 m (44H, Cy), δ 3.22 t (4H, CH_2, $|^2J$(PH) + ^4J(PH)$|$ = 8.8 Hz, ^3J(PtH) = 20 Hz), δ 5.96 br (1H, NH, ^2J(PtH) = 34 Hz), δ 6.91 m (3H, Ph), δ 7.12 d (2H, CH_2, ^3J(HH) = 8.0 Hz), δ 7.30 d (2H, CH_2, ^3J(HH) = 8.4 Hz). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 47.9 (^1J(PtP) = 2787 Hz). ^{19}F{^{1}H}-NMR ($CDCl_3$): δ -79.5 s. Λ_M = 88 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ (in CH_3NO_2, [Pt] = 0.5 × 10^{-3} mol). Anal. Calcd for $C_{40}H_{60}NF_3O_3P_2PtS$: C, 50.6; H, 6.37; N, 1.48; S, 3.38. Found: C, 50.9; H, 6.71; N, 1.58; S, 3.25%.

Reaction of Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) with CH$_2$=CHCN to yield [Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(CH$_2$=CHCN)]OTf. To a d_6-benzene solution of Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)-(OTf) (*ca.* 5 mg) in a 5-mm NMR tube was added acrylonitrile (*ca.* 7 mg). The formation of [Pt(2,6-(Cy$_2$PCH$_2$)$_2$-C$_6$H$_3$)(CH$_2$=CHCN)]OTf in solution was supported by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy. In the ^{1}H-NMR spectrum at ambient temperature, the downfield-shifted olefinic proton resonances of the coordinated acrylonitrile were observed at δ 5.88 d ($^3J(HH)_{cis}$ = 12 Hz), δ 6.19 d ($^3J(HH)_{trans}$ = 18 Hz), and δ 6.87 dd ($^3J(HH)_{cis}$ = 12 Hz, $^3J(HH)_{trans}$ = 18 Hz). The isolation of this complex in the pure state was unsuccessful because of partial decomposition into Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf): a d_6-benzene solution prepared by re-dissolving the isolated solid shows that the solution contained both [Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(CH$_2$=CHCN)]OTf and Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(OTf) in a 3/1 ratio as evidenced by ^{31}P{^{1}H}-NMR spectroscopy. On standing this solution in the absence of acrylonitrile, [Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)-(CH$_2$=CHCN)]OTf slowly converted into Pt(2,6-(Cy$_2$PCH$_2$)$_2$-C$_6$H$_3$)(OTf). For [Pt(2,6-(Cy$_2$PCH$_2$)$_2$C$_6$H$_3$)(CH$_2$=CHCN)]-OTf: ^{31}P{^{1}H}-NMR (C_6D_6): δ 54.2 s (^1J(PtP) = 2686 Hz). ^{13}C{^{1}H}-NMR (C_6D_6): δ 106.9 (CH_2CHCN), δ 118.3 (CH_2-$CHCN$), δ 143.0 (CH_2CHCN).

Equilibrium constant measurements. The equilibrium constants (K_{eq} for [Pt(PCP)(CH$_2$=CHCN)]$^-$ + NH_2R ⇌ [Pt(PCP)(NH_2R)]$^-$ + CH$_2$=CHCN, where PCP = (2,6-(Cy$_2$-PCH$_2$)$_2$C$_6$H$_3$). R = Ph, *p*-Tol) were calculated by integration ratios of the corresponding resonance peaks in the NMR spectra: the ^{1}H-NMR resonances for [CH_2CHCN]/[NH_2R], and the ^{31}P{^{1}H}-NMR resonances for [Pt(PCP)(NH_2R)$^+$]/[Pt(PCP)(CH$_2$=CHCN)$^-$].

Results and Discussion

Ammine and amine complexes. Reaction of Pt(2,6-(Cy$_2$-PCH$_2$)$_2$C$_6$H$_3$)(OTf) with various amines readily produced



Scheme 1

cationic amine complexes [Pt(2,6-$(Cy_2PCH_2)_2C_6H_3$)(amine)]-(OTf) (amine = NH_3 (1), $NHMe_2$ (2), NHC_4H_8 (3), NH_2Ph (4), NH_2(Tol-*p*) (5)) in high yields (Scheme 1). These complexes have been fully characterized by IR and NMR spectroscopy, and microanalyses. In the IR spectra, the characteristic ν(NH) bands of the amine ligand in complexes 1-5 were observed in the range of 3200-3470 cm^{-1}. The ν(NH) absorption bands of coordinated ammonia and amines show a number of peaks corresponding to the symmetric and *anti*-symmetric N-H stretching modes (*i.e.* three bands for coordinated ammonia, two for primary amine, and one for secondary amine).[10] The ν(SO) bands associated with the counter anion $^-OSO_2CF_3$ were observed around 1160 and 1270 cm^{-1} with strong intensities as a symmetric and *anti*-symmetric stretching frequency, respectively. Molar conductivity measurements for cationic amine complexes in nitromethane solution showed that all complexes are 1 : 1 electrolytes as expected. The calculated values of Λ_M are in the range of 75-90 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ (in CH_3NO_2, [Pt] = 0.5×10^{-3} mol), that are well consistent with the literature data.[11]

In the $^{31}P\{^1H\}$-NMR spectra, complexes **1-5** resonate at around 50 ppm as a clean single peak flanked with ^{195}Pt-satellites, indicating that only one single compound was formed from the respective reaction. The observed values of ^1J(PtP) are in the range of 2700-2800 Hz, being in good agreement with the reported data for square planar Pt(II) complexes in a mutual *trans*-phosphorus geometry.[12] The presence of triflate as a counter anion in these complexes was also supported by the $^{19}F\{^1H\}$-NMR resonance observed at δ -79. In the ^{1}H-NMR spectra, the N*H* proton resonances of the coordinated ammonia and amine displayed at δ 3.94-6.05 as a broad signal, being accompanied with ^{195}Pt-satellites (^2J(PtH) = 26-34 Hz), that are considerably shifted to downfield upon coordination. These N*H* signals were confirmed on the addition of D_2O, and no ligand exchange with D_2O or H_2O was observed. The resonances for the methylene protons (PCH_2) have been observed at δ 2.88-3.63 as a pseudo-triplet due to "virtual coupling" of *trans*-phosphorus, along with platinum satellites ($|^2J(PH) + {}^4J(PH)|$ = 8.0-8.8 Hz, ^3J(PtH) = 20-24 Hz).[13] All isolated cationic amine complexes **1-5** gave satisfactory microanalytical data (see Experimental Section).

It is noteworthy that attempt at preparation for an analogous pyrrole complex from the reaction of the platinum(II) triflate with pyrrole by a similar preparative manner as for other amine complexes was not successful. This rather unpredicted result of no complex formation with pyrrole can not be apparently perceived by simple σ-donor strength of pyrrole as compared with those of other amines in steric or electronic factors. However, this disfavored σ-amine complexation can be likely explained by a competitive π-interaction through the C=C bond of pyrrole, which presumably impedes coordination of pyrrole through the amine-nitrogen to Pt(II) (*vide infra*).

Acrylonitrile complex. When Pt(2,6-$(Cy_2PCH_2)_2C_6H_3$)(OTf) reacted with acrylonitrile in d_6-benzene solution, the π-olefinic complex [Pt(2,6-$(Cy_2PCH_2)_2C_6H_3$)(CH_2=CHCN)]-(OTf) was quantitatively produced as evidenced by ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy (Eq 1). The $^{31}P\{^1H\}$-NMR spectrum of the d_6-benzene solution showed one sharp resonance at δ 54.2 accompanied with ^{195}Pt-satellites (^1J(PtP) = 2686 Hz), revealing that only single Pt(II) compound was formed in solution. In the ^{1}H-NMR spectrum, the downfield-shifted olefinic proton resonances of the coordinated acrylonitrile were observed at δ 5.88 d ($^3J(HH)_{cis}$ = 12 Hz), δ 6.19 d ($^3J(HH)_{trans}$ = 18 Hz), and δ 6.87 dd ($^3J(HH)_{cis}$ = 12 Hz, $^3J(HH)_{trans}$ = 18 Hz) (Figure 1). In comparison of coordinated and free acrylonitrile in its ^{1}H-NMR spectrum, all resonances of the olefinic protons shifted to downfield upon π-coordination through the C=C bond. Among these, the α-proton is most significantly shifted. Eisenberg and his co-workers have recently reported the cationic Pt(II) complexes with the π-olefinic bonding acrylonitrile [PtMeL(CH_2=CHCN)]BF_4 in which similar chemical shifts for the coordinated acrylonitrile were observed in its ^{1}H- and $^{13}C\{^1H\}$-NMR spectra.[14] The observed chemical shifts for coordinated acrylonitrile in the present complex

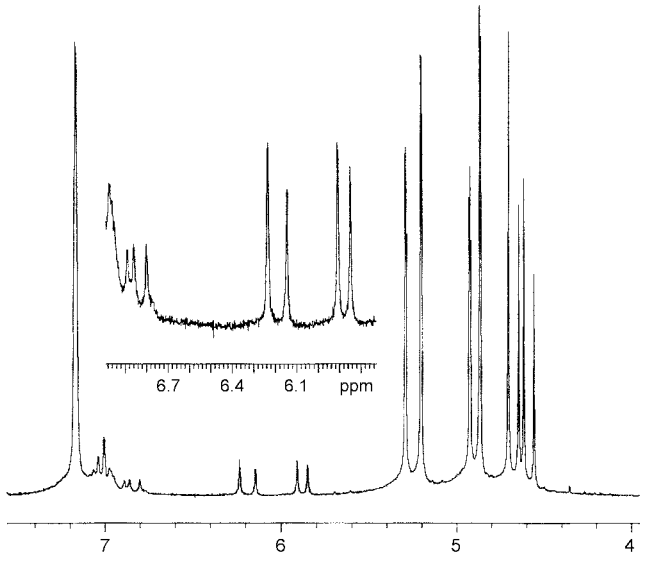


Figure 1. The ^{1}H-NMR spectrum of a d_6-benzene solution of [Pt(2,6-$(Cy_2PCH_2)_2C_6H_3$)(CH_2=CHCN)]OTf at ambient temperature in the presence of an excess amount of acrylonitrile shows that the olefinic proton-resonances of the coordinated acrylonitrile appeared at significantly downfield-shifted as compared to those of free acrylonitile.

are also closely comparable to those of other olefin complexes reported previously.[15]

$$Pt(PCP)(OTf) + CH_2=CHCN \rightarrow Pt(PCP)(CH_2=CHCN)]OTf \quad PCP = 2,6\text{-}(Cy_2PCH_2)_2C_6H_3 \quad (1)$$

On the contrary to amine complexes, the acrylonitrile complex was only stable in solution in the presence of acrylonitrile. Attempt at isolation of this complex in the pure solid state was unsuccessful because of partial decomposition into the corresponding platinum triflate. A d_6-benzene solution prepared by re-dissolving the isolated solid shows that the solution contains both $[Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(CH_2=CHCN)]OTf$ and $Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ in a 3/1 ratio as evidenced by $^{31}P\{^1H\}$-NMR spectroscopy. On standing this solution in the absence of acrylonitrile, the acrylonitrile complex gradually converted into the platinum (II) triflate. In contrast to the formation of the acrylonitrile complex, no reaction of $Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ with other olefins such as ethylene, styrene and methyl acrylate was observed.

Relative stability of amine versus acrylonitrile complexes. Addition of amine such as aniline or *p*-toluidine into a d_6-benzene solution of the acrylonitrile complex in the presence of free acrylonitrile immediately produced the amine complex. The ligand exchange reaction was equilibrated in a short time, and neither addition products nor hydroaminated derivatives were produced in the course of measuring the equilibrium constant by NMR spectroscopy.[16] Thus, the relative stability of the π-olefinic acrylonitrile complex versus the σ-donor amine species can be evaluated by determining the equilibrium constants, using NMR spectroscopy. In the following equilibrium reaction (Eq 2), the concentration-ratios of $[CH_2CHCN]/[NH_2R]$ and $[Pt(PCP)(NH_2R)^-]/[Pt(PCP)(CH_2=CHCN)^+]$ were approximately calculated by integrating the corresponding resonance peaks in the ^1H- and the $^{31}P\{^1H\}$-NMR spectrum, respectively.

$$[Pt(PCP)(CH_2=CHCN)]OTf + NH_2R \rightleftharpoons [Pt(PCP)(NH_2R)]OTf + CH_2=CHCN$$

$$K_{eq} = \frac{[Pt(PCP)(NH_2R)^+][CH_2=CHCN]}{[Pt(PCP)(CH_2=CHCN)^+][NH_2R]} \quad (R = Ph, p\text{-Tol}) \quad (2)$$

The determined equilibrium constants (K_{eq}) were to be 0.28 (for R = Ph) and 3.1 (R = *p*-tolyl) at 21 °C. Thus, the relative stability of the acrylonitrile complex versus the amine complex has been found largely dependent upon the amine-basicity (pK_b). This result reveals that acrylonitrile practically competes with amine in the coordination sphere of the cationic Pt(II) particularly containing the sterically hindered pincer ligand, *i.e.* the platinum species favors coordination of acrylonitrile over aniline, in contrast to *p*-toluidine. For a precedent, a palladium(II) complex with a crowded binding site, $Pd(CH_3)((t\text{-}Bu)_2P(CH_2)_2CH(CH_2)_2\text{-}P(t\text{-}Bu_2))$ favors coordination of acrylonitrile over aniline, showing high activity for catalytic amination of acrylonitrile with aniline, in contrast to the chelating bis-phosphine complex $Pd(CH_3)_2(dmpe)$.[17] Recently it has been reported that highly electrophilic dicationic palladium(II) species having a PNP-pincer readily complex with various olefins to afford stable π-olefinic complexes $[Pd(2,6\text{-}(Ph_2PCH_2)_2C_5H_3N)(olefin)]^{2-}$, which undergo the nucleophilic amine addition to the coordinated olefin to give aminoalkyl complexes.[18] In the reactions, no ligand exchange was observed. The present results along with precedents are also comparable with our recent studies for Pt(II)-catalyzed hydroamination of acrylonitrile in which the more sterically demanding Pt(II) complex $Pt(2,6\text{-}(Cy_2PCH_2)_2C_6H_3)(OTf)$ displays higher catalytic activity as compared to $Pt(2,6\text{-}(Ph_2PCH_2)_2C_6H_3)(OTf)$ bearing the less hindered phenyl substituents.[8c,16]

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