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Protonolysis of a toluidinoalkyl platinum(II) complex derived from the insertion of the C=C bond into the Pt–NHR (amido) bond: the role of amine in Pt-catalyzed hydroamination of acrylonitrile

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The complex Pt{2,6-$(R_2PCH_2)_2C_6H_3$}(OTf) [R = Ph (**1a**), Cy (**1b**)] catalyzes the hydroamination of acrylonitrile with *p*-toluidine to produce $CH_2(CN)CH_2NH$(Tol-*p*), exclusively. In the catalyzed reactions, platinum intermediates were detected by NMR spectroscopy. The *p*-tolylamido platinum complex Pt{2,6-$(Ph_2PCH_2)_2C_6H_3$}{NH(Tol-*p*)} (**4**), containing the pincer ligand, was synthesized from the reaction of **1a** and NaNH(Tol-*p*). Complex **4** reacted with acrylonitrile to yield the regiospecific insertion product Pt{2,6-$(Ph_2PCH_2)_2C_6H_3$}{$CH(CN)CH_2NH$(Tol-*p*)} (**5**), quantitatively. Reaction of **5** with HX (X = Cl, OTf) generated free acrylonitrile, *p*-toluidine and Pt{2,6-$(Ph_2PCH_2)_2$-C_6H_3}X. Reacting **5** with a proton source having a non-coordinating counter anion, $[NH_3$(Tol-*p*)$]BPh_4$, also produced free acrylonitrile along with a cationic amine complex $[Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}\{NH_2(Tol\text{-}p)\}]^+$. On the other hand, reaction of **5** with $[NH_3$(Tol-*p*)$]BPh_4$ in the presence of excess *p*-toluidine (*ca.* 30 equiv.) generated the hydroaminated product $CH_2(CN)CH_2NH$(Tol-*p*), predominantly. Treatment of **5** with $[NH_2Me_2]BPh_4$ in the absence of amine bases also released the hydroaminated product. These results apparently reveal that the amine substrate plays a critical role in driving the catalytic cycle.

Introduction

Catalytic addition of N–H bonds to olefins mediated by late transition metal complexes offers regioselective ways to prepare biologically active compounds as well as industrial chemicals.[1] Two different mechanistic pathways for these catalytic reactions have been suggested. Milstein and co-workers[2a] have demonstrated for the first time a catalytic system involving N–H bond oxidative addition to an electron-rich metal center to yield a hydrido amido complex $[MH(NR_2)]$, which proceeds *via* insertion of a C=C bond into a metal–amide bond, followed by C–H reductive elimination to give hydroaminated products.[1,2] An alternative, but more generally observed, pathway for high-valent complexes may involve the nucleophilic attack of amine on coordinated olefin, and then subsequent proton transfer to generate hydroaminated products.[1,3] Although many catalytic hydroaminations of olefins have been reported so far, the mechanistic pathways for these catalytic systems have not been fully understood. In this paper, the role of amines in platinum-catalyzed hydroamination of olefins is discussed in terms of their mechanistic features in microscopic reaction pathways. For this study, platinum(II) complexes having terdentate P,C,P-pincers have been employed, since the ligand inhibits both phosphine dissociation and reductive elimination of the aryl group.[4] As a consequence, these types of complexes stabilized with the rigid ligand framework offer regioselectivity in the stoichiometric and catalytic reactions to be probed.[5–8]

Results and discussion

The complex Pt{2,6-$(R_2PCH_2)_2C_6H_3$}(OTf) [R = Ph (**1a**), Cy (**1b**)] catalyzes the hydroamination of acrylonitrile with *p*-toluidine to produce $CH_2(CN)CH_2NH$(Tol-*p*), exclusively (eqn. 1). The reaction proceeds rather slowly (15 and 45%

$$CH_2{=}CHCN + NH_2(Tol\text{-}p) \xrightarrow{[Pt]} CH_2(CN)CH_2NH(Tol\text{-}p) \quad (1)$$

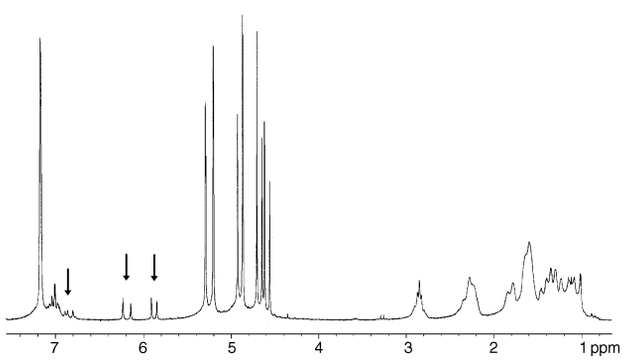

Fig. 1 The ^{1}H-NMR spectrum of a d_6-benzene solution of **1b**, at ambient temperature, in the presence of an excess amount of acrylonitrile shows resonance signals due to coordinated acrylonitrile (marked with arrows).

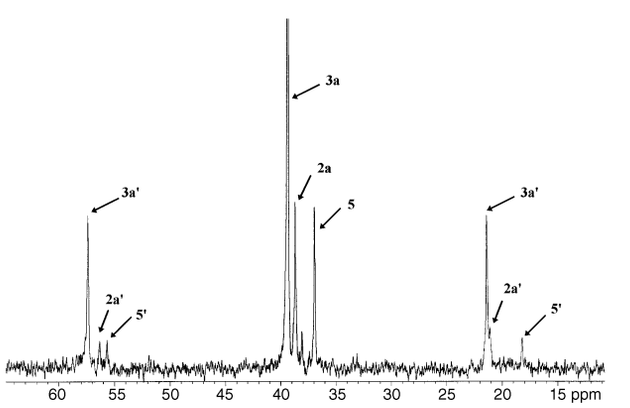

Fig. 2 The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture catalyzed by **1a** in the latter stages of the reaction shows that the solution mainly contains three platinum species, **3a**, **2a**, and **5**. The ^{195}Pt satellites are denoted **3a′**, **2a′**, and **5′**.

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yield with **1a** and **1b**, respectively; 2 days at 40 °C, 1.0 mol% [Pt]). During the course of the reaction, two main species were present in solution, as evidenced by ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy (see Fig. 1 and 2); one is an olefinic complex, [Pt{2,6-(R_2PCH_2)$_2$$C_6H_3$}($CH_2CHCN$)]OTf [R = Ph (**2a**), Cy (**2b**)], and the other an amine complex, [Pt{2,6-(R_2PCH_2)$_2$-C_6H_3}{NH_2(Tol-*p*)}]OTf [R = Ph (**3a**), Cy (**3b**)]. These complexes were verified by independent preparation from the reaction of the platinum triflates with acrylonitrile and *p*-toluidine, respectively (see Experimental). In contrast to the amine complexes, the olefinic complexes were not isolated in the pure state due to their conversion into the corresponding platinum triflate in the absence of acrylonitrile.[9]

In the reaction catalyzed by **1b**, the amine complex **3b** is predominantly observed; toluidine is favored over acrylonitrile in the platinum coordination sphere (K_{eq} = [**3b**][CH_2CHCN]/[**2b**][NH_2(Tol-*p*)] ≅ 3.1 at 21 °C: **2b** + NH_2(Tol-*p*) ⇌ **3b** + CH_2CHCN).[10] However, in the reaction catalyzed by **1a**, the olefinic complex **2a**, initially formed on addition of acrylonitrile into a d_6-benzene solution of **1a**, immediately disappeared to yield the amine complex **3a** on subsequent addition of *p*-toluidine into the solution. In the early stages of this reaction, only the amine complex was observed in solution, as monitored by the ^{31}P{^{1}H}-NMR spectroscopy. But in the later stages, a small amount of olefinic complex, besides the amine species, was observed along with the other platinum species, which was identified as the insertion product **5** (*vide infra*, see Fig. 2). The ^{31}P chemical shifts and the ^1J(^{195}Pt–P) values in the ^{31}P{^{1}H}-NMR spectrum were very advantageous for this study.

Thus, the *p*-tolylamido platinum complex Pt{2,6-(Ph_2PCH_2)$_2$-C_6H_3}{NH(Tol-*p*)} (**4**) was synthesized in the hope that an amido complex bearing a PCP-pincer as an ancillary ligand would undergo regioselective insertion of the C=C bond of acrylonitrile into the Pt–N bond to give a stable platinum(II) *p*-tolyaminoalkyl complex, whose protonolysis might provide crucial mechanistic information on one of the key steps in the catalytic hydroamination of olefins.

Preparation of *p*-tolylamido complex 4

Reaction of Pt{2,6-(Ph_2PCH_2)$_2$$C_6H_3$}(OTf) with an excess of NaNH(Tol-*p*) (*ca.* 3 equiv.) in tetrahydrofuran afforded the Pt(II) toluidinide complex Pt{2,6-(Ph_2PCH_2)$_2$$C_6H_3$}{NH(Tol-*p*)} (**4**) in high yield (eqn. 2). The formulation of **4** can be

$$\underset{(PCP = 2,6\text{-}(Ph_2PCH_2)_2C_6H_3)}{Pt(PCP)(OTf)} + NaNH(Tol\text{-}p) \xrightarrow{-NaOTf} Pt(PCP)(NH(Tol\text{-}p)) \quad (2)$$

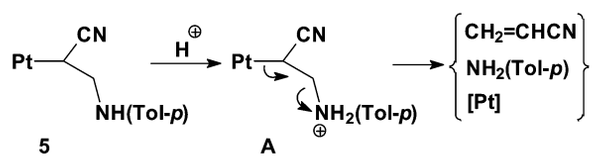
readily verified from the ^{1}H- and ^{31}P{^{1}H}-NMR spectra. In the ^{1}H-NMR spectrum of **4** in d_6-benzene, the NH resonance of the amide moiety NH(Tol-*p*) is observed at δ 3.06 as a broad signal with platinum satellites [^2J(PtH) = 14.0 Hz]. The methyl resonance of the *p*-tolyl group exhibits a single peak at δ 2.26. The resonance for the methylene protons (PCH_2) is observed at δ 3.63 as a pseudo-triplet, due to "virtual coupling", with platinum satellites ($|^2J$(PH) + ^4J(PH)| = 9.0 Hz, ^3J(PtH) = 26.2 Hz).[11] This terminal amido complex of platinum(II) bearing a PCP-pincer as an ancillary ligand is of particular interest because such complex demonstrates that the metal–amide bond should be selectively involved in stoichiometric reactions with various substrates.[12–14]

Reaction of complex 4 with acrylonitrile

The platinum(II) amide **4** in d_6-benzene slowly reacted with acrylonitrile to yield the regioselective addition product Pt{2,6-(Ph_2PCH_2)$_2$$C_6H_3$}{$CH(CN)CH_2$NH(Tol-*p*)} (**5**). The reaction was not only highly selective, but also nearly quantitative, as evidenced by the ^{1}H- and ^{31}P{^{1}H}-NMR spectra. The formation of **5** during the course of reaction was monitored by the observation of a growing sharp single peak at δ 37.8 in the ^{31}P{^{1}H}-NMR spectrum. The ^{1}H-NMR spectrum of **5** in d_6-benzene shows the CH resonance of Pt–$CH(CN)CH_2$-NH(Tol-*p*) at δ 2.75 as a multiplet with platinum satellites [^2J(PtH) = 80 Hz]. The methylene protons of Pt–$CH(CN)$-CH_2NH(Tol-*p*) are observed to be diastereotopic, with resonances at δ 3.08 and 3.45 as multiplets. The NH proton, the assignment of which was confirmed on addition of D_2O, was observed at δ 3.52 as a multiplet. The addition of a strong coordinating ligand such as triphenylphosphine or pyridine into a d_6-benzene solution of **5** resulted in no signal changes in the ^{1}H-NMR spectrum, indicating that N-chelation of the *p*-tolylaminoalkyl ligand to platinum in the complex can apparently be excluded. Complex **5** was isolated from the d_6-benzene solution by reducing the volume of the solution under high vacuum followed by the addition of *n*-hexane, giving a pale-yellow powder. This complex can be synthesized on a preparative scale by the reaction of **4** with acrylonitrile in benzene (see Experimental). It is worth noting that a d_6-benzene solution of **5** was stable for 7 days at reflux temperatures. Even in the presence of an excess of acrylonitrile, the complex was intact for a prolonged period of time at elevated temperatures, with no formation of oligomeric or decomposed species. It was previously reported that Ir(I)- and Pt(II) anilide complexes having monodentate tertiary phosphines undergo regiospecific insertion of the C=C bonds of norbonylene and acrylonitrile, respectively, into the M–N bond.[2a,d] In the previous studies, however, the resulting anilinoalkyl complexes were unstable, undergoing further C–H reductive elimination.

Protonolysis of complex 5

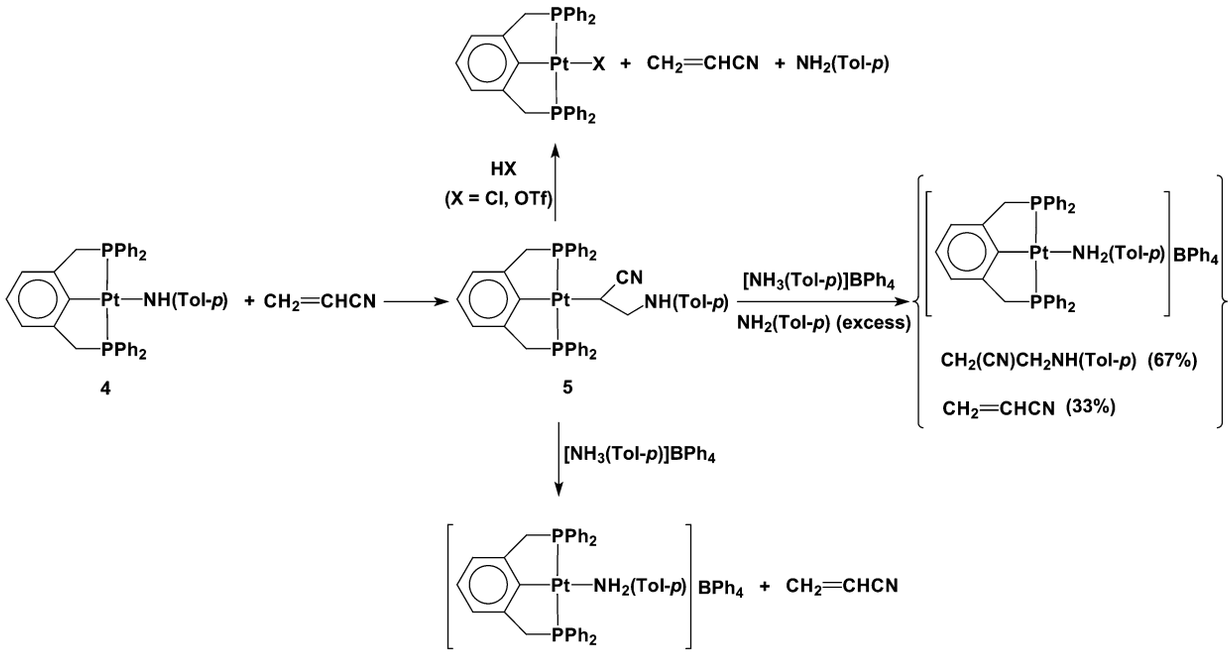
Since *p*-tolylaminoalkyl complex **5** can be isolated pure in the solid state, further stoichiometric reactions with proton sources were probed from the mechanistic viewpoint of catalytic hydroamination of acrylonitrile with *p*-toluidine. Reaction of **5** with HX (X = Cl, OTf) generated the corresponding platinum complexes Pt{2,6-(Ph_2PCH_2)$_2$$C_6H_3$}X, free acrylonitrile, and *p*-toluidine, along with [NH_3(Tol-*p*)]X. In the reaction with a proton source having a non-coordinating counter anion, [NH_3(Tol-*p*)]BPh_4, a cationic toluidine complex, [Pt{2,6-(Ph_2-PCH_2)$_2$$C_6H_3$}{$NH_2$(Tol-*p*)}]$^+$ was produced, along with free acrylonitrile.[15] These results can be indisputably explained by a sequence of reactions involving preferential protonation at the amine nitrogen rather than at the alkyl carbon in the platinum complex, and then subsequent elimination of free acrylonitrile with *p*-toluidine *via* deinsertion to give the observed products (see Scheme 1). In the latter reaction, subsequent coordination



Scheme 1

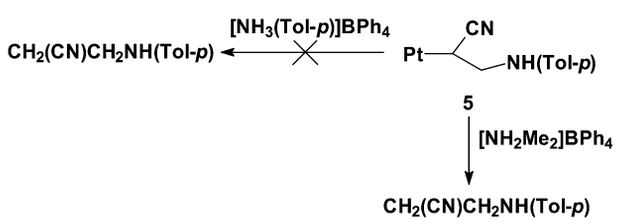
of the liberated *p*-toluidine to platinum afforded the cationic species. In the reactions, either a hydroaminated product, $CH_2(CN)CH_2$NH(Tol-*p*), or a vinylic amine (or imine), arising from β-hydrogen elimination as a competing side product, was not produced.[16] These results are not consistent with the observed catalytic reaction with the platinum triflates.

Taking account of reaction conditions in the catalytic reactions, an excess of amine would act as a base, inhibiting protonation at the amine nitrogen of the *p*-tolylaminoalkyl ligand, thereby facilitating facile proton transfer at the alkyl carbon to generate hydroaminated products. From this point of view, we have tried the reaction of **5** with [NH_3(Tol-*p*)]BPh_4 in



Scheme 2

the presence of an excess amount of *p*-toluidine (*ca.* 30 equiv.). As a result, the hydroaminated product 2-cyanoethyl(*p*-tolyl)amine $CH_2(CN)CH_2NH(Tol\text{-}p)$ was predominantly produced (67% yield) along with free acrylonitrile (33%) as evidenced by NMR and GC/MS spectroscopy. Scheme 2 represents the observed reactions. These results indicate that protonation is still competitive, occurring at both sites of the amine nitrogen and the alkyl carbon, even in the presence of a large excess of amine. In this reaction, however, the anilinoalkyl complex **5**, which is a stronger base than *p*-toluidine, favors protonation at the amine nitrogen from $[NH_3(Tol\text{-}p)]BPh_4$ to generate a transient alkylanilinium complex (**A**), which subsequently undergoes deinsertion. This explanation implies that the facile generation of the hydroaminated product in the reaction obviously depends on the the pK_a of the added ammonium salt. Thus, treatment of **5** with the dimethylammonium salt $[NH_2Me_2]BPh_4$, which is a weaker acid than the corresponding alkylanilinium complex, in the absence of base subsequently produced 2-cyanoethyl(*p*-tolyl)amine (Scheme 3).



Scheme 3

These results apparently reveal that the amine plays a critical role in driving the catalytic cycle. The amine substrate simultaneously acts as a base, deprotonating from a putative complex **A** to lead to the formation of **5**, in which facile proton transfer occurs, in turn, at the alkyl carbon to generate the hydroaminated product (see Scheme 4). As a consequence, amines inhibit reverse processes, *i.e.* deinsertion processes, in the catalytic cycle. Protonolysis of the Pt–alkyl bond probably proceeds *via* C–H elimination, preceded by protonation of the electron-rich metal center.[17]

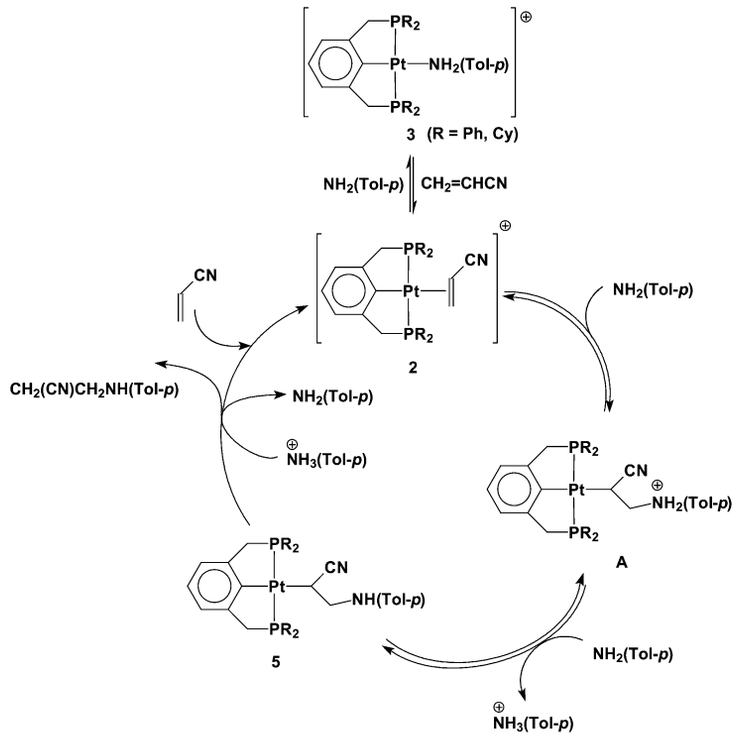
In the catalytic reactions, although a mechanism involving amine coordination to platinum followed by N-deprotonation to form amido complexes can hardly be ruled out, the present reaction may proceed *via* nucleophilic attack of amine on the olefin pre-coordinated to platinum(II). The nucleophilic addition of amines on an olefin coordinated to platinum(II)[18] and palladium(II)[19] complexes is well known. Recently, it has been reported that the nucleophilic attack of amine on coordinated olefins on highly electrophilic dicationic palladium(II) complexes leads to the formation of aminoalkyl complexes.[20] In the present study, it is noteworthy that complex **1b**, whose metal center is more basic than that of **1a**, favors the π-olefinic complex, displaying more effective catalytic activity (*vide supra*). A plausible catalytic cycle for the observed hydroamination is presented in Scheme 4.

In summary, the role of amine in catalytic hydroamination of olefins has been demonstrated, for the first time, in terms of mechanistic features in microscopic reaction pathways. Although this fact has been perceived in generally observed catalytic hydroamination of olefins, it has not yet been clearly demonstrated at a molecular scale, probably due to scarcity of amido complexes and their olefin addition derivatives.

Experimental

General procedures

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 sieves. Benzene and *n*-hexane were distilled from sodium–benzophenone ketyl with tetraglyme (tetraethylene glycol dimethyl ether). CH_2Cl_2 was dried by refluxing over sodium hydride under nitrogen. K_2PtCl_4 was supplied by Kojima Chemicals Co., Ltd., and used without purification. Potassium diphenylphosphide, 1,5-cyclooctadiene, AgOTf, α,α′-dibromo-*m*-xylene, $CDCl_3$ and C_6D_6 were purchased from Aldrich Chemical Company, and used as supplied. *p*-Toluidine was purified by subliming *in vacuo* at 50 °C. All other reagents were from various commercial companies. NaNH(Tol-*p*) was prepared from the reaction of NaH and *p*-toluidine in refluxing THF solution for 24 h, and isolated from diethyl ether. $[NH_3(Tol\text{-}p)]BPh_4$ and $[NH_2Me_2]BPh_4$ were prepared by reaction of the respective chloride salts with $NaBPh_4$ in H_2O.



Scheme 4

$Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}Cl$[4d] and $Pt\{2,6\text{-}(Cy_2PCH_2)_2C_6H_3\}(OTf)$ (**1b**)[21] were prepared as described in the literature.

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), from pressed KBr pellets. ^{1}H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$- 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 ^{1}H and $^{13}C\{^1H\}$-NMR are reported in ppm (δ) relative to TMS. Chemical shifts for $^{31}P\{^1H\}$- and $^{19}F\{^1H\}$-NMR were measured in ppm relative to external 85% H_3PO_4 (δ = 0) and perfluoromethylbenzene (δ = −63.73) (in a sealed capillary), respectively. GC/MS analyses were performed using an HP 6890 gas chromatograph equipped with an HP 5973 MSD and an HP-Ultra 1 column (crosslinked methyl silicone gum, 50 m × 0.2 mm, 0.33 μm film thickness). 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 analysis was performed at the Korea Basic Science Institute in Seoul, Korea.

Preparations

$Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}(OTf)$ (1a). A mixture of $Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}Cl$ (100 mg, 0.14 mmol) and AgOTf (43 mg, 0.17 mmol) was stirred in a mixed solvent (25 mL, THF–CH_2Cl_2 4 : 1) for 2 h. After filtering off AgCl formed during the course of the reaction, the solution volume was reduced to *ca.* 3 mL. Addition of *n*-hexane (*ca.* 20 mL) to the concentrated solution gave an off-white precipitate, which was isolated by filtration. Recrystallization of the precipitates from CH_2Cl_2–*n*-hexane gave an analytically pure compound. Yield 105 mg (90%). IR (KBr): ν(SO) = 1169, 1252 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.83 t [4H, CH_2; $|^2J(PH) + {}^4J(PH)|$ = 9.4 Hz, $^3J(PtH)$ = 25 Hz], 7.0–7.9 m (23H, Ph). ^{1}H-NMR (C_6D_6): δ 3.26 t [4H, CH_2; $|^2J(PH) + {}^4J(PH)|$ = 8.0 Hz, $^3J(PtH)$ = 32 Hz], 7.0–7.9 m (23H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 39.4 s [$^1J(PtP)$ = 3034 Hz]. $^{31}P\{^1H\}$-NMR (C_6D_6): δ 39.2 s [$^1J(PtP)$ = 3007 Hz]. $^{19}F\{^1H\}$-NMR ($CDCl_3$): δ −79.02 s. Λ_M = 66 Ω^{-1} cm^2 mol^{-1} (in $MeNO_3$, [Pt] = 1.0 × 10^{-3} mol). Anal. calc. for $C_{33}H_{27}F_3O_3P_2PtS$: C, 48.5; H, 3.33; S, 3.92; found: C, 48.4; H, 3.46; S, 3.62%.

$Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}\{NH(C_6H_4Me\text{-}p)\}$ (4). A THF solution of NaNH(Tol-*p*) (51 mg, 0.40 mmol) was slowly added to a stirred solution of **1a** (110 mg, 0.14 mmol) in THF. The reaction mixture was stirred for 2 h. The color of the solution gradually changed from colorless to deep green during the course of the reaction. Removal of volatiles from the solution under high vacuum resulted in a deep-green residue, which was washed with *n*-pentane (2 × 30 mL) to remove *p*-toluidine and then extracted with dry benzene (2 × 10 mL) to give a brownish green solution. The volume of the solution was reduced to *ca.* 5 mL under high vacuum. Addition of *n*-pentane (*ca.* 15 mL) to the concentrated solution resulted in a greenish orange solution along with the formation of a small amount of a brownish precipitate. After filtering off the precipitate, the solvent was removed from the filtrate and the residue dried *in vacuo* for 12 h to give an analytically pure greenish orange compound. Yield 78 mg (72%). ^{1}H-NMR (C_6D_6): δ 2.26 s (3H, CH_3), 3.06 br, s [1H, NH; $^2J(PtH)$ = 14.0 Hz], 3.63 t [4H, CH_2; $|^2J(PH) + {}^4J(PH)|$ = 9.0 Hz, $^3J(PtH)$ = 26.2 Hz], 6.62 d [2H, CH(Tol-*p*); $^3J(HH)$ = 8.3 Hz], 6.81 d [2H, CH(Tol-*p*)], 7.0–7.8 m (23H, Ph). $^{31}P\{^1H\}$-NMR (C_6D_6): δ 30.7 s [$^1J(PtP)$ = 3013 Hz]. Anal. calc. for $C_{39}H_{35}NP_2Pt$: C, 60.5; H, 4.55; N, 1.81; found: C, 60.9; H, 4.75; N, 1.61%.

Reaction of 4 with CH_2=CHCN to yield $Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}\{CH(CN)CH_2NH(C_6H_4Me\text{-}p)\}$ (5). To a d_6-benzene solution of **4** (*ca.* 10 mg) in a 5 mm screw-capped NMR tube (Wilmad, 528-TR) was added an excess of acrylonitrile (*ca.* 10 mg). The insertion product $Pt\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}\{CH(CN)CH_2NH(Tol\text{-}p)\}$ was quantitatively formed from the reaction, although the reaction proceeded rather slowly (for *ca.* 3 h), which was monitored by NMR spectroscopy. The product can be isolated from the concentrated d_6-benzene solution followed by the addition of *n*-hexane. A preparative scale experiment for this reaction was conducted in a glove box as follows. To a benzene solution of **4** (100 mg, 0.13 mmol) was added an excess of acrylonitrile (0.02 g, 0.38 mmol). The reaction mixture was stirred for 6 h. The solution volume was reduced to *ca.* 5 mL under high vacuum. Addition of *n*-hexane (*ca.* 20 mL) to the concentrated solution gave a beige precipitate, which was

isolated by filtration. Recrystallization of the precipitates from CH_2Cl_2–*n*-hexane gave an analytically pure compound. Yield 98 mg (92%). IR (KBr): ν(CN) = 2248, 2172 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 2.20 s (3H, CH_3), 2.75 m [1H, CH; ^2J(PtH) = 80 Hz], 3.08 m (1H, CH_a), 3.45 m (1H, CH_b), 3.52 m (1H, NH), 3.66 t [4H, CH_2; $|^2J(PH) + {}^4J(PH)|$ = 8.4 Hz, ^3J(PtH) = 30.4 Hz], 6.00 d [2H, C*H*(Tol-*p*); ^3J(HH) = 8.4 Hz], 6.86 d [2H, C*H*(Tol-*p*)], 7.0–7.8 m (23H, Ph). ^{13}C{^{1}H}-NMR (C_6D_6): δ 3.92 t [Pt–*C*H(CN)CH_2NH(Tol-*p*); ^2J(CP) = 10 Hz, ^1J(PtC) = 429 Hz], 20.73 [Pt–CH(CN)CH_2NH(Tol-*p*)], 47.53 t [P–CH_2; $|^1J(PC) + {}^3J(PC)|$ = 37.5 Hz], 49.61 t [Pt–CH(CN)*C*H_2NH(Tol-*p*); ^3J(CP) = 3.8 Hz]. ^{31}P{^{1}H}-NMR (C_6D_6): δ 37.8 s [^1J(PtP) = 2966 Hz]. Anal. calc. for $C_{42}H_{38}N_2P_2Pt$: C, 60.9; H, 4.63; N, 3.38; found: C, 61.4; H, 4.46; N, 3.58%. NMR Assignments were made on the bases of various NMR techniques: selective homonuclear decouplings and COSY.

Reaction of 5 with HCl to yield Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}Cl, CH_2=CHCN and $NH_2(C_6H_4Me$-*p*). Reaction of **5** with HCl in d_6-benzene generated Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}Cl, CH_2=CHCN and *p*-toluidine (along with the byproduct, *p*-toluidine·HCl salt).

Reaction of 5 with HOTf to yield 1a, CH_2=CHCN and $NH_2(C_6H_4Me$-*p*). Reaction of **5** with HOTf in d_6-benzene generated Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}(OTf) (**1a**), CH_2=CHCN and *p*-toluidine (along with the byproduct, *p*-toluidine·HOTf salt).

Reaction of 5 with [$NH_3(C_6H_4Me$-*p*)]BPh_4 to yield [Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}{$NH_2(C_6H_4Me$-*p*)}]$^+$ and CH_2=CHCN. Reaction of **5** with [$NH_3(C_6H_4Me$-*p*)]BPh_4 in d_6-benzene generated free acrylonitrile and [Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}{$NH_2(C_6H_4$-Me-*p*)}]$^+$. The formation of the cationic toluidine species has been confirmed by the independent synthesis of the triflate salt [Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}{$NH_2(C_6H_4Me$-*p*)}]OTf from the reaction of **1a** and *p*-toluidine (see the following experiment).

[Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}{$NH_2(C_6H_4Me$-*p*)}]OTf (3a). Reaction of **1a** (30 mg, 0.036 mmol) and *p*-toluidine (19 mg, 0.18 mmol) in dichloromethane gave the cationic amine complex **3a**, which was isolated from CH_2Cl_2–diethyl ether. Yield 31 mg (92%). IR (KBr): ν(NH) = 3362, 3469 cm^{-1}, ν(SO) = 1152, 1264 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.25 s (3H, CH_3), 3.93 t [4H, CH_2; $|^2J(PH) + {}^4J(PH)|$ = 8.5 Hz, ^3J(PtH) = 24 Hz], 5.84 br [2H, NH_2; ^2J(PtH) = 32 Hz], 6.07 d [2H, C*H*(Tol-*p*); ^3J(HH) = 7.8 Hz], 6.58 d [2H, C*H*(Tol-*p*)], 7.0–7.9 m (23H, Ph). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 40.0 s [^1J(PtP) = 2938 Hz]. ^{31}P{^{1}H}-NMR (C_6D_6): δ 39.3 s [^1J(PtP) = 2918 Hz]. Λ_M = 86 Ω^{-1} cm^2 mol^{-1} (in $MeNO_3$, [Pt] = 1.0 × 10^{-3}mol). ^{19}F{^{1}H}-NMR ($CDCl_3$): δ −79.4 s. Anal. calc. for $C_{40}H_{36}NF_3O_3P_2PtS$: C, 51.9; H, 3.92; N, 1.51; S, 3.47; found: C, 51.4; H, 4.01; N, 1.48; S, 3.32%.

[Pt(2,6-{Cy_2PCH_2)$_2C_6H_3$}{$NH_2(C_6H_4Me$-*p*)}]OTf (3b). A similar procedure as for complex **3a**, using **1b** (30 mg, 0.036 mmol) and *p*-toluidine (19 mg, 0.18 mmol) gave complex **3b**. 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), 3.22 t [4H, CH_2, $|^2J(PH) + {}^4J(PH)|$ = 8.8 Hz, ^3J(PtH) = 20.0 Hz], 5.96 br [1H, NH, ^2J(PtH) = 34.0 Hz], 6.91 m (3H, Ph), 7.12 d [2H, CH_2, ^3J(HH) = 8.0Hz], 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]. ^{31}P{^{1}H}-NMR (C_6D_6): δ 48.1 s [^1J(PtP) = 2786 Hz]. ^{19}F{^{1}H}-NMR ($CDCl_3$): δ −79.5 s. Anal. calc. 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 1b with CH_2=CHCN to generate [Pt(2,6-{Cy_2-PCH_2)$_2C_6H_3$}(CH_2=CHCN)]OTf (2b). To a d_6-benzene solution of **1b** (*ca.* 5 mg) in a 5 mm NMR tube was added acrylonitrile (*ca.* 7 mg). The formation of **2b** in solution was supported by ^{1}H-, ^{13}C{H}- and ^{31}P{^{1}H}-NMR spectroscopy. In the ^{1}H-NMR spectrum at ambient temperature, the downfield-shifted olefinic protons resonances of coordinated acrylonitrile were observed as rather broad multiplets (Fig. 1). No couplings of the coordinated acrylonitrile with ^{195}Pt in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra at ambient temperature were observed due to the lability of the acrylonitrile complex. Variable-temperature ^{1}H-NMR experiments in d_8-toluene were attempted to detect the ^{195}Pt-satellites with no success. The corresponding signals get even broader below −60 down to −85 °C. The ^{1}H- and ^{13}C{^{1}H}-NMR data observed for the coordinated acrylonitrile in the present complex are closely comparable to those of π-olefinic acrylonitrile complexes of Pt(II) [$PtMeL_2$(CH_2=CHCN)]BF_4 reported by Eisenberg *et al.*[9a] Attempts to isolate complex **2b** in the pure state were unsuccessful because of partial decomposition into **1b**; a d_6-benzene solution prepared by re-dissolving the isolated solid shows that the solution contained both **2b** and **1b** in a 3 : 1 ratio, as evidenced by ^{31}P{^{1}H}-NMR spectroscopy. On standing this solution in the absence of acrylonitrile, **2b** slowly converted into **1b**. For **2b**: ^{1}H-NMR (C_6D_6): δ 5.88 d [$CH_{cis}H_{trans}$; $^3J(HH)_{cis}$ = 12 Hz], 6.19 d [CH_{cis}-H_{trans}; $^3J(HH)_{trans}$ = 18 Hz], and 6.87 dd [CHCN; $^3J(HH)_{cis}$ = 12 Hz, $^3J(HH)_{trans}$ = 18 Hz]. ^{13}C{^{1}H}-NMR (C_6D_6): δ 106.9 (CH_2CHCN), 118.3 (CH_2CHCN), 143.0 (CH_2CHCN). ^{31}P{^{1}H}-NMR (C_6D_6): δ 54.2 s [^1J(PtP) = 2686 Hz].

Reaction of 1a with CH_2=CHCN to generate [Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}(CH_2=CHCN)](OTf) (2a). To a d_6-benzene solution of **1a** (*ca.* 5 mg) in a 5 mm NMR tube was added acrylonitrile (*ca.* 7 mg). The formation of [Pt{2,6-(Ph_2PCH_2)$_2$-C_6H_3}(CH_2=CHCN)](OTf) in solution was also supported by ^{1}H-, ^{13}C{H}- and ^{31}P{^{1}H}-NMR spectroscopy. The NMR data of **2a** were similarly observed to those of complex **2b**. The isolation of this complex from the solution was unsuccessful due to complete decomposition to **1a**. For **2a**: ^{1}H-NMR (C_6D_6): δ 5.22 d [$CH_{cis}H_{trans}$; $^3J(HH)_{cis}$ = 12 Hz], 5.41 d [$CH_{cis}H_{trans}$; $^3J(HH)_{trans}$ = 18 Hz], 6.15 dd [CHCN; $^3J(HH)_{cis}$ = 12 Hz, $^3J(HH)_{trans}$ = 18 Hz]. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 105.8 (CH_2-$CHCN$), 117.6 (CH_2CHCN), 143.9 (CH_2CHCN). ^{31}P{^{1}H}-NMR (C_6D_6): δ 38.9 s [^1J(PtP) = 2822 Hz].

Reaction of 5 with [$NH_3(C_6H_4Me$-*p*)]BPh_4 in the presence of excess *p*-toluidine to produce $CH_2(CN)CH_2NH(C_6H_4Me$-*p*). [NH_3(Tol-*p*)]BPh_4 (*ca.* 15 equiv.) was added to a d_6-benzene solution of **5** (*ca.* 10 mg) with *p*-toluidine (*ca.* 30 equiv.) in a 5 mm NMR tube. The hydroaminated product (*ca.* 67%) was predominantly produced from the reaction, along with free acrylonitrile, as evidenced by NMR and GC/MS spectroscopy. For $CH_2(CN)CH_2NH$(Tol-*p*): GC/MS: *m*/*z* = 160, 120, 91.

Reaction of 5 with MeI to yield {2,6-(Ph_2PCH_2)$_2C_6H_3$}PtI, CH_2=CHCN and amines. Reaction of **5** and MeI in d_6-benzene slowly (for 12 h) generated Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}I, acrylonitrile, and a mixture of amines [*p*-toluidine (17%), *N*-methyl-*p*-tolylamine (46%), *N*,*N*-dimethyl-*p*-tolylamine (37%)], which were identified by NMR and GC/MS spectroscopy. For Pt{2,6-(Ph_2PCH_2)$_2C_6H_3$}I: ^{1}H-NMR (C_6D_6): δ 3.55 t [4H, CH_2; $|^2J(PH) + {}^4J(PH)|$ = 9.0 Hz, ^3J(PtH) = 25.4 Hz], 7.0–7.9 m (23H, Ph). ^{31}P{^{1}H}-NMR (C_6D_6): δ 35.4 s [^1J(PtP) = 2860 Hz]. GC/MS: *p*-toluidine [$NH_2(C_6H_4Me$-*p*)]: *m*/*z* = 107, 106, 91. *N*-methyl-*p*-tolylamine [$NHMe(C_6H_4Me$-*p*)]: *m*/*z* = 121, 120, 106, 91. *N*,*N*-dimethyl-*p*-tolylamine [$NMe_2(C_6H_4Me$-*p*)]: *m*/*z* = 135, 120, 105, 91.

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