Tolylamidoplatinum(II) Complex [Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(NH(Tol-*p*))]: Regioselectivity in Addition of Acrylonitrile into the Pt-N Bond

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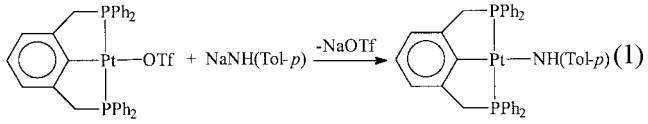
Monomeric amido complexes of late transition metals have been postulated as intermediates in many metal-catalyzed amination.[1] Such complexes, however, are rare because the inability of electron rich metal center to accept extensive π-donation from the lone pair of electrons on an amide nitrogen tends to lead amide-bridged dimeric species.[2,3] For alkylamido complexes, a facile β-hydrogen transfer is a common decomposition pathway, resulting in formation of metal hydrides or reduced species.[4] Thus the stability of neutral monomeric species of late transition metal amides varied depending not only on the ligand framework but also on substituents of the amide ligand in the complexes.

Amido complexes of square planar platinum group metals bearing a PCP pincer as an ancillary ligand are of particular interest because such complexes stabilized with the rigid ligand framework, which inhibits both phosphine dissociation and reductive elimination of the aryl group, would demonstrate that the metal-amide bond should selectively involve in stoichiometric reactions with various substrates.[5] Recently, we have reported a rare example of the monomeric dimethylamido palladium(II) complex Pd(2,6-(Ph_2PCH_2)$_2C_6H_3$)(NMe_2), which was stable only at low temperatures.[6] In this paper, we report a novel monomeric *p*-tolylamido platinum (II) complex having the pincer ligand, Pt(2,6-(Ph_2PCH_2)$_2$-C_6H_3)(NH(C_6H_4Me-*p*)). The title complex undergoes regiospecific insertion of the C=C bond of acrylonitrile into the Pt-N bond, that may be closely relevant to catalytic hydroamination of olefins as a key step in a catalytic cycle.[7] In this study, the role of amines in platinum-catalyzed hydroamination is discussed in terms of their mechanistic features in microscopic reaction pathways.

Reaction of Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(OTf) (**1**) with an excess of NaNH(C_6H_4Me-*p*) (*ca.* 3 equivalents) in tetrahydrofuran afforded the monomeric amido complex of platinum(II) Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(NH(C_6H_4Me-*p*)) (**2**) in high yields (Eq. 1). The formulation of **2** can be readily verified by the ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. In the ^{1}H-NMR spectrum of **2** in d_6-benzene, the N*H* resonance of the amide moiety N*H*(C_6H_4Me-*p*) has been observed at δ 3.06 as a broad signal with platinum satellites (^3J(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) has been observed at δ 3.63 as a pseudo-triplet "virtual coupling" along with platinum satellites (|^3J(PH) + ^4J(PH)| = 9.0 Hz, ^3J(PtH) = 26.2 Hz).[8]

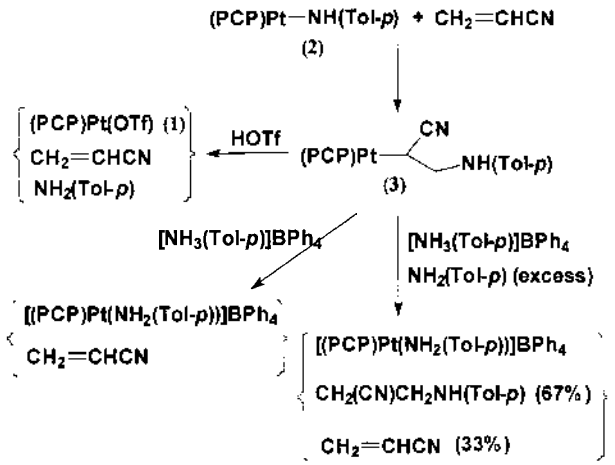
The platinum(II) amide **2** in d_6-benzene slowly reacted



(1)

with acrylonitrile to yield the regioselective addition product Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(CH(CN)CH_2NH(Tol-*p*)) (**3**). The reaction was not only highly selective but nearly quantitative as evidenced by the ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The ^{1}H-NMR spectrum of **3** in d_6-benzene shows that the C*H* resonance of Pt-C*H*(CN)CH_2NH(Tol-*p*) displays at δ 2.75 as multiplets with platinum satellites (^2J(PtH) = 80 Hz). The methylene-protons resonances of Pt-CH(CN)CH_2NH-(Tol-*p*) have been observed to be diastereotopic at δ 3.08 and δ 3.45 as multiplets, respectively. The N*H* proton, which was confirmed on the addition of D_2O, was observed at δ 3.52 as multiplets. Complex **3** was isolated from the d_6-benzene solution by reducing the volume of the solution *in vacuo* followed by the addition of *n*-hexane, giving a pale-yellow powder. It is worth noting that a d_6-benzene solution of **3** was stable for 7 days at refluxing temperatures. Even in the presence of an excess of acrylonitrile, the complex was intact for a prolonged period of time at elevated temperatures, resulting in no formation of oligomeric or decomposed species.

Since the *p*-tolylaminoalkyl complex **3** can be isolated in the pure solid state, protonolysis of this complex with proton sources have been probed from the mechanistic viewpoint of catalytic hydroamination of acrylonitrile with *p*-toluidine. Reaction of **3** with a stoichiometric amount of HOTf generated the platinum triflate Pt(2,6-(Ph_2PCH_2)$_2C_6H_3$)(OTf) along with free *p*-toluidine and acrylonitrile. 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)$_2C_6H_3$)(NH_2(Tol-*p*))]$^+$ was produced along with free acrylonitrile. 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 and *p*-toluidine *via* deinsertion to give observed products. In the latter reaction, subsequent coordination of liberating *p*-toluidine to platinum resulted in the formation of the cationic species. In the reactions, either a hydroaminated product CH_2(CN)CH_2NH(Tol-*p*) or vinylic amine (or imine), likely arising from β-hydride elimination as a competing side product, was not produced. These results are not



Scheme 1

consistent with the observed catalytic reaction with the platinum triflate **1**. Taking account of reaction conditions in catalytic reaction, an excess amount of amine would act as a base inhibiting protonation at the amine nitrogen of the *p*-tolylaminoalkyl ligand, thereby facilitating a facile proton-transfer at the alkyl carbon to generate hydroaminated products. From this point of view, we have tried the latter stoichiometric reaction of **3** with $[NH_3(Tol\text{-}p)]BPh_4$ in the presence of an excess amount of *p*-toluidine (*ca.* 30 equivalents). As a result, the hydroaminated product 2-cyanoethyl(*p*-tolyl)-amine $CH_2(CN)CH_2NH(C_6H_4Me\text{-}p)$ was generated predominantly. The observed reaction pathways are shown in Scheme 1.

In summary, a novel monomeric amido complex of platinum(II) with a PCP pincer ligand has been synthesized. The complex undergoes regiospecific insertion of the C=C bond of acrylonitrile into the Pt-N(amide) bond to yield the *p*-tolylaminoalkyl platinum(II) complex. In the study on protonolysis of this alkyl complex, a critical role of amine substrates 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, but not yet clearly demonstrated in details probably due to scarcity of amido complexes and their olefin addition derivatives.

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Supplementary Material Available: Full characterization data and experimental details for complexes **2**, **3** and $[Pt(2,6\text{-}(Ph_2PCH_2)_2C_6H_3)(NH_2(Tol\text{-}p))]OTf$. Supplementary materials are available from the author upon request (Fax: +82-54-770-2518; Tel: +82-54-770-2219; e-mail: shpark@mail.dongguk.ac.kr).

References

1. (a) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (b) Roundhill, D. M. *Catal. Today* **1997**, *37*, 155. (c) Muller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (d) Brunet, J.-J.; Neibecker, D.; Niedercorn, F. *J. Mol. Catal.* **1989**, *49*, 253.
2. (a) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (b) Brynza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, 1980.
3. (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 973. (b) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1991**, *10*, 615. (c) Koelliker, R.; Milstein, D. *J. Am. Chem. Soc.* **1991**, *113*, 8524. (d) Lee, S. W.; Trogler, W. C. *Inorg. Chem.* **1990**, *29*, 1099. (e) Srivastava, R. S.; Singh, G.; Nakano, M.; Osakada, K.; Ozawa, F.; Yamamoto, A. *J. Organomet. Chem.* **1993**, *451*, 221. (f) Ruiz, J.; Martinez, M. T.; Vicente, C.; Garcia, G.; Lopez, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321. (g) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708. (h) Van der Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319. (i) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1092. (j) Cuevas, J. V.; Garcia-Herbosa, G.; Munoz, A.; Garcia-Granda, S.; Miguel, D. *Organometallics* **1997**, *16*, 2220. (k) Brunet, J.-J.; Daran, J.-C.; Neibecker, D.; Rosenberg, L. *J. Organomet. Chem.* **1997**, *538*, 251. (l) Li, J. J.; Li, W.; James, A. J.; Holbert, T.; Sharp, T. P.; Sharp, P. R. *Inorg. Chem.* **1999**, *38*, 1563.
4. (a) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55. (b) Brynza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939. (c) Park, S.; Pontier-Johnson, M.; Roundhill, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 3101. (d) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794.
5. (a) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6. (b) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (c) Ohff, M.; Ohff, A.; Van der Boom, M. E.; Milstein D. *J. Am. Chem. Soc.* **1997**, *119*, 11687. (d) Creaser, C. S.; Kaska, W. C. *Inorg. Chim. Acta* **1978**, *30*, L325. (e) Bennett, M. A.; Jin, H.; Willis, A. C. *J. Organomet. Chem.* **1993**, *451*, 249.
6. Ryu, S. Y.; Kim, H.; Kim, H. S.; Park, S. *J. Organomet. Chem.* **1999**, *592*, 194.
7. (a) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (b) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (c) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4206. (d) Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744. (e) Beller, M.; Eichberger, M.; Trauthwein, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2225. (f) Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Herwig, J.; Muller, T. E.; Thiel, O. R. *Chem. Eur. J.* **1999**, *5*, 1306. (g) Yamamoto, Y.; Radhakrishnan, U. *Chem. Soc. Rev.* **1999**, *28*, 199.
8. (a) Verkade, J. G. *Chem. Rev.* **1972**, *9*, 1. (b) Verstuyft, A. W.; Nelson, J. H.; Cary, L. W. *Inorg. Chem.* **1976**, *15*, 732. (c) Pregosin, P. S.; Kunz, R. W. *^{31}P- and ^{13}C-NMR of Transition Metal Phosphine Complexes*; Springer: Berlin, 1979; p 65.