J|A|C|S
ARTICLES

Published on Web 09/17/2009

Platinum-Catalyzed Direct Amination of Allylic Alcohols under Mild Conditions: Ligand and Microwave Effects, Substrate Scope, and Mechanistic Study

Takashi Ohshima,* Yoshiki Miyamoto, Junji Ipposhi, Yasuhito Nakahara, Masaru Utsunomiya, and Kazushi Mashima*

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

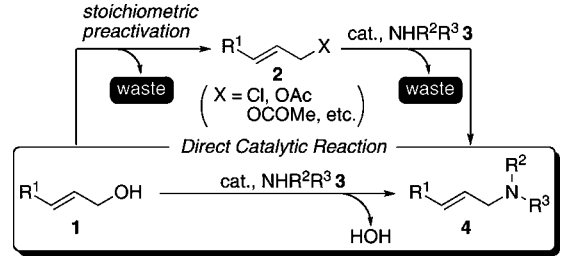
Received June 6, 2009; E-mail: ohshima@chem.es.osaka-u.ac.jp; mashima@chem.es.osaka-u.ac.jp

Abstract: Transition metal-catalyzed amination of allylic compounds via a π-allylmetal intermediate is a powerful and useful method for synthesizing allylamines. Direct catalytic substitution of allylic alcohols, which forms water as the sole coproduct, has recently attracted attention for its environmental and economical advantages. Here, we describe the development of a versatile direct catalytic amination of both aryl- and alkyl-substituted allylic alcohols with various amines using Pt-Xantphos and Pt-DPEphos catalyst systems, which allows for the selective synthesis of various monoallylamines, such as the biologically active compounds Naftifine and Flunarizine, in good to high yield without need for an activator. The choice of the ligand was crucial toward achieving high catalytic activity, and we demonstrated that not only the large bite-angle but also the linker oxygen atom of the Xantphos and DPEphos ligands was highly important. In addition, microwave heating dramatically affected the catalyst activity and considerably decreased the reaction time compared with conventional heating. Furthermore, several mechanistic investigations, including ^{1}H and ^{31}P{^{1}H} NMR studies; isolation and characterization of several catalytic intermediates, Pt(xantphos)Cl_2, Pt(η^2-C_3H_5OH)(xantphos), etc; confirmation of the structure of [Pt(η^3-allyl)(xantphos)]OTf by X-ray crystallographic analysis; and crossover experiments, suggested that formation of the π-allylplatinum complex through the elimination of water is an irreversible rate-determining step and that the other processes in the catalytic cycle are reversible, even at room temperature.

Introduction

Transition metal-catalyzed transformation of allylic compounds via a π-allylmetal intermediate is one of the most powerful and useful methods for carbon−carbon and carbon−heteroatom (N, O, and S) bond formation.[1] It is widely utilized for the synthesis of various natural and unnatural compounds. The reaction usually employs activated allylic alcohol derivatives **2**, in particular, allylic halides, carboxylates, and carbonates, because of the poor reactivity of the parent allylic alcohols **1** (Scheme 1). The use of such activated substrates, however, causes the formation of more than stoichiometric amounts of unwanted chemical waste in both the preactivation and the allylic substitution steps. Thus, a direct catalytic substitution of allylic alcohols, which forms water as the sole coproduct, has recently attracted much attention from an environmental and economical point of view.[2]

Scheme 1. Preparation of Allylamine **4** from Allylic Alcohol **1**



Allylamines are ubiquitous in various biologically active compounds,[3] such as the antifungal drug Naftifine[4a,b] and the calcium channel blocker Flunarizine,[4c,d] and are highly useful substrates for many types of reactions, such as asymmetric isomerization[5] and ring-closing metathesis.[6] Direct catalytic substitutions of allylic alcohols with amine (**1** → **4**) toward the

(1) For reviews, see: (a) Tsuji, J. *Transition Metal Reagents and Catalysis*; Wiley-VCH: Weinheim, Germany, 2000. (b) Trost, B. M.; Lee, C. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000. (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921.

(2) For review, see: (a) Muzart, J. *Tetrahedron* **2005**, *61*, 4179. (b) Muzart, J. *Eur. J. Org. Chem.* **2007**, 3077. (c) Tamaru, Y. *Eur. J. Org. Chem.* **2005**, 2647.

(3) For reviews, see: (a) Cheikh, R. B.; Chaabouni, R.; Laurent, A.; Mison, P.; Nafti, A. *Synthesis* **1983**, 685. (b) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689. (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921.

(4) (a) Petranyi, G.; Ryder, N. S.; Stütz, A. *Science* **1984**, *224*, 1239. (b) Kanno, H.; Taylor, R. J. K. *Tetrahedron Lett.* **2002**, *43*, 7337. (c) Olesen, J. J. *Neurol* **1991**, *238*, S23. (d) Marín, M. T.; Margarit, M. V.; Salcedo, G. E. *Il Farmaco* **2002**, *57*, 723.

(5) For reviews, see: (a) Akutagawa, S.; Tani, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley-VCH: New York, 1994; Chapter *3*, p 95.

(6) For reviews, see: (a) *Handbook of Metathesis*Grubbs, R. H., EdWiley-VCH: Weinheim, Germany, 2003; Vols 1−3. (b) Nicolaou, K. C.; Bulger, P. G.; Sarlar, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490.

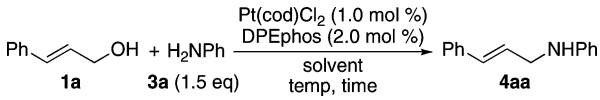
development of a highly efficient method of synthesizing allylamines in an environmentally benign manner have been studied by many research groups.[2] Most of the previous catalytic systems, however, require rather severe reaction conditions or the addition of considerable amounts of an activator, such as As_2O_3,[7] B_2O_3,[8] $SnCl_2$,[9] PPh_3-DEAD,[10] Ti(O-*i*-Pr)$_4$,[11] BPh_3,[12] BF_3•Et_2O,[13] CO_2,[14] BEt_3,[15] and 1-AdCO_2H,[16] including an efficient enantioselective variant,[17] to increase the leaving ability of the hydroxy group. Recently, palladium-catalyzed direct aminations of allylic alcohols without the use of an activator were developed by the research groups of Ozawa and Yoshifuji,[18] Ikariya,[19] Shinokubo and Oshima,[20] le Floch,[21] and Breit,[22] leading to the development of a highly atom economical synthetic process for allylamines.[23] The substrate generality of those reactions, however, remains limited. In particular, the reaction with aliphatic primary amines results only in the formation of the diallylation products[19,20] because of the higher nucleophilicity of the monoallylation product compared to that of the starting substrate. In 2007, we reported a new direct catalytic amination of allylic alcohols[24] promoted by the combination of Pt(cod)Cl_2 and a large bite-angle ligand, DPEphos[25] or Xantphos.[26] This platinum catalysis proceeded with high monoallylation selectivity of both aromatic (up to >88:1) and aliphatic (up to 30:1) primary amines. Later, le Floch et al. reported that the reactivity of the platinum-catalyzed amination was improved by using a catalytic system of [Pt(η^3-allyl)(dpp-xantphos)]PF_6 (DPP-Xantphos: 4,5-bis(2,5-diphenyl-1*H*-phosphol-1-yl)-9,9-dimethyl-9*H*-xanthene) and NH_4PF_6 (20 mol %) as an activator.[27] These platinum-catalyzed reactions, however, have much room for improvement in terms of substrate generality of the allylic alcohol because only allyl alcohol and α- or *γ-aryl*-substituted allylic alcohols afford a high yield and the reaction of *alkyl*-substituted allylic alcohol results in moderate yield because of side reactions, such as β-H elimination. Herein, we report a highly versatile direct substitution reaction of both *aryl*- and *alkyl*-substituted allylic alcohols with various amines catalyzed by Pt-Xantphos and Pt-DPEphos complexes without the need for an additional activator. We observed drastic ligand effects, and the large bite-angle as well as the linker oxygen atom of the Xantphos and DPEphos ligands were essential to achieve high catalytic activity. Microwave irradiation efficiently accelerated the reaction without a loss of selectivity, making it possible to lower the reaction temperature to 50 °C and shorten the reaction time to 1 h for arylamines and 2 h for alkylamines. In addition, the usefulness of the present direct catalysis was demonstrated by a one-step synthesis of the biologically active compounds Naftifine and Flunarizine in 95% and 94% yields, respectively. Finally, on the basis of several mechanistic investigations, including ^{1}H and ^{31}P{^{1}H} NMR studies, isolation of several catalytic intermediates, confirmation of the structure of [Pt(η^3-allyl)(xantphos)]OTf by X-ray crystallographic analysis, and crossover experiments, we present a plausible catalytic cycle in which (1) all catalytic intermediates in the cycle are in rapid equilibrium even at room temperature; (2) among them, [Pt(η^3-allyl)(xantphos)]X is the most stable species; and (3) the formation of the π-allylplatinum complex through the elimination of water, which is activated by in situ generated ammonium salt, is an irreversible rate-determining step.

Results and Discussion

Reaction Using Arylamines. The study was initiated by evaluating solvent effects using cinnamyl alcohol (**1a**) and aniline (**3a**) as representative substrates at 110 °C or the solvent reflux temperature (Table 1, entries 1−7). To clarify the solvent effects, reactions assisted by Pt(cod)Cl_2[28] (1.0 mol %) and DPEphos (2.0 mol %) in various solvents were stopped after 3 h and the yield of allylamine **4aa** was determined by gas chromatographic analysis. Among the solvents examined, dioxane (entry 3, 72%), which was used in an earlier study,[24]

(7) Lu, X.; Lu, L.; Sun, J. *J. Mol. Catal.* **1987**, *41*, 245.
(8) Lu, X.; Jiang, X.; Tao, X. *J. Organomet. Chem.* **1988**, *344*, 109.
(9) (a) Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4473. (b) Masuyama, Y.; Kagawa, M.; Kurusu, Y. *Chem. Lett.* **1995**, 1121.
(10) Lumin, S.; Falck, J. R.; Capdevila, J.; Karara, A. *Tetrahedron Lett.* **1992**, *33*, 2091.
(11) (a) Itoh, K.; Hamaguchi, N.; Miura, M.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2833. (b) Satoh, T.; Ikeda, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 4877. (c) Yang, S.-C.; Hung, C.-W. *J. Org. Chem.* **1999**, *64*, 5000. (d) Yang, S.-C.; Tsai, Y.-C.; Shue, Y.-J. *Organometallics* **2001**, *20*, 5326. (e) Shue, Y.-J.; Yang, S.-C.; Lai, H.-C. *Tetrahedron Lett.* **2003**, *44*, 1481.
(12) Stary, I.; Stará, I. G.; Kocovsky, P. *Tetrahedron Lett.* **1993**, *34*, 179.
(13) Tsay, S.; Lin, L. C.; Furth, P. A.; Shum, C. C.; King, D. B.; Yu, S. F.; Chen, B.; Hwu, J. R. *Synthesis* **1993**, 329.
(14) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1065.
(15) (a) Kimura, M.; Tomizawa, T.; Horino, Y.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **2000**, *41*, 3627. (b) Kimura, M.; Horino, Y.; Mukai, R.; Tanaka, S.; Tamaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 10401. (c) Kimura, M.; Futamata, M.; Shibata, K.; Tamaru, Y. *Chem. Commun.* **2003**, 234.
(16) Yang, S.-C.; Hsu, Y.-C.; Gan, K.-H. *Tetrahedron* **2006**, *62*, 3949.
(17) Yamashita, Y.; Gopalarathnam, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 7508.
(18) (a) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968. (b) Ozawa, F.; Ishiyama, T.; Yamamoto, S.; Kawagishi, S.; Murakami, H.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1698.
(19) Kayaki, Y.; Koda, T.; Ikariya, T. *J. Org. Chem.* **2004**, *69*, 2595.
(20) Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 4085.
(21) (a) Piechaczyk, O.; Doux, M.; Ricard, L.; Le Floch, P. *Organometallics* **2005**, *24*, 124. (b) Thoumazet, C.; Grützmacher, H.; Deschamps, B.; Ricard, L.; le Floch, P. *Eur. J. Inorg. Chem.* **2006**, 3911. (c) Piechaczyk, O.; Thoumazet, C.; Jean, Y.; le Floch, P. *J. Am. Chem. Soc.* **2006**, *128*, 14306. (d) Mora, G.; Deschamps, B.; van Zutphen, S.; Le Goff, X. F.; Ricard, L.; le Floch, P. *Organometallics* **2007**, *26*, 1846.
(22) Usui, I.; Schmidt, S.; Keller, M.; Breit, B. *Org. Lett.* **2008**, *10*, 1207.
(23) Lewis acid-catalyzed direct substitution of allylic, propargylic, and benzylic alcohols with electron-deficient nitrogen nucleophiles were reported. For representative examples, see: (a) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem.—Eur. J.* **2005**, *11*, 1433. (b) Terrasson, V.; Marque, S.; Georgy, M.; Campagne, J.-M.; Prim, D. *Adv. Synth. Catal.* **2006**, *348*, 2063. (c) Qin, H.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 409. (d) Guo, S.; Song, F.; Liu, Y. *Synlett* **2007**, 964. (e) Reddy, C. R.; Madhavi, P. P.; Reddy, A. S. *Tetrahedron Lett.* **2007**, *48*, 7169. (f) Sreedhar, B.; Reddy, P. S.; Reddy, M. A.; Neelima, B.; Arundhathi, R. *Tetrahedron Lett.* **2007**, *48*, 8174. (g) Jana, U.; Maiti, S.; Biswas, S. *Tetrahedron Lett.* **2008**, *49*, 858. (h) Wang, G.-W.; Shen, Y.-B.; Wu, X.-L. *Eur. J. Org. Chem.* **2008**, 4367. (i) Huang, W.; Shen, Q.-S.; Wang, J.-L.; Zhou, X.-G. *Chin. J. Chem.* **2008**, *26*, 729.
(24) Utsunomiya, M.; Miyamoto, Y.; Ipposhi, J.; Ohshima, T.; Mashima, K. *Org. Lett.* **2007**, *9*, 3371.
(25) (a) Dube, G.; Selent, D.; Taube, R. *Z. Chem.* **1985**, *25*, 154. (b) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 3081. (c) Caporali, M.; Müller, C.; Staal, Bastiaan, B. P.; Tooke, D. M.; Spek, A. L.; van Leeuwen, P. W. N. M. *Chem. Commun.* **2005**, 3478.
(26) For a review, see: (a) Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Acc. Chem. Res.* **2001**, *34*, 895. (b) Hillebrand, S.; Bruckmann, J; Krüger, C.; Haenel, M. W. *Tetrahedron Lett.* **1995**, *36*, 75.
(27) Mora, G.; Piechaczyk, O.; Houdard, R.; Mézailles, N.; Le Goff, X.-F.; le Floch, P. *Chem.—Eur. J.* **2008**, *14*, 10047.
(28) See the Supporting Information for details.

Table 1. Effects of Solvents and Reaction Temperature on Pt-Catalyzed Direct Amination with Arylamine **3a**[a]



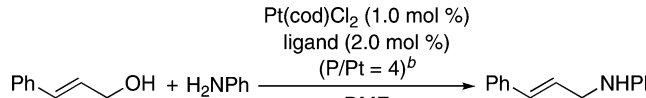
entry	solvent	temp	time (h)	yield of **4aa**[b]
1	toluene	110 °C	3	63%
2	1,2-dimethoxyethane	reflux (82 °C)[c]	3	38%
3	dioxane	reflux (101 °C)[c]	3	72%
4	DMA	110 °C	3	22%
5	DMF	110 °C	3	79%
6	DMSO	110 °C	3	63%
7	*d*	110 °C	3	57%
8	dioxane	50 °C	23	<1%
9	DMF	50 °C	23	89%
10	DMF	rt	78	52%

[a] 2.0 mmol scale, 0.4 mL of solvent was used. [b] Determined by GC analysis. [c] Boiling point of pure solvent. [d] Solvent-free conditions.

and DMF (entry 5, 79%) gave good results, in sharp contrast to the unsatisfactory result obtained with the closely related solvent DMA (entry 4, 22%). Interestingly, a marked difference between dioxane (entry 8, <1%) and DMF (entry 9, 89%) was observed at a lower temperature (50 °C) with a prolonged reaction time (23 h). Using DMF as the solvent, the direct amination of **1a** proceeded even at room temperature, although the yield was moderate even after 78 h (entry 10, 52%). Further, platinum catalysis proceeded under solvent-free conditions with reasonably good reactivity (entry 7, 57%), presenting great possibilities for the development of a more efficient and environmentally friendly catalytic synthetic process of allylamines.

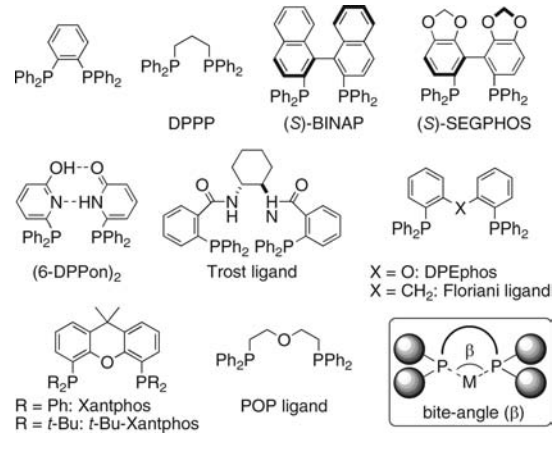
The great success in lowering the reaction temperature to 50 °C led us to examine the ligand effects under the optimized conditions (Table 1, entry 9). We previously found that the large bite-angle ligands DPEphos and Xantphos are highly effective for platinum catalysis;[24,29] therefore, we tested various large bite-angle diphosphine ligands (Table 2). Due to the lack of information about the bite-angles of Pt(η^3-allyl)(diphosphine) complexes, the bite-angles (β) shown in Table 2 were obtained by geometry optimization using the B3LYP[30] hybrid-density functional theory (LANL2DZ for Pt and 6-31G(d,p) for others).[28] Although 1,2-bis(diphenylphosphino)benzene ($\beta = 87°$), DPPP ($\beta = 96°$), BINAP ($\beta = 97°$), and SEGPHOS ($\beta = 98°$) ligands, whose bite angles are smaller than 100°, did not promote the reaction (entries 1−4), larger bite-angle ligands such as 6-DPPon,[22] which in situ dimerizes in aprotic solvent through hydrogen bonding and acts as a bidentate ligand ($\beta = 104°$),[31] and Trost ligand ($\beta = 107°$),[32] showed moderate reactivities to afford allylamine **4aa** in 40% (entry 5) and 19% (entry 6) yields,

Table 2. Effects of Diphosphine Ligands on Pt-Catalyzed Direct Amination with Arylamine **3a**[a]



entry	ligand	bite-angle (β)[c]	yield of **4aa**[d]
1	C_6H_4-1,2-$(PPh_2)_2$	87°	nd[e]
2	DPPP	96°	nd[e]
3	BINAP	97°	nd[e]
4	SEGPHOS	98°	nd[e]
5[f]	6-DPPon	104°	40%
6	Trost ligand	107°	19%
7	DPEphos	107°	71%
8	Xantphos	108°	80%
9	POP ligand	108°	nd[e]
10	Floriani ligand	111°	8%
11	*t*-Bu-Xantphos	112°	nd[e]

[a] 2.0 mmol scale, 0.4 mL of DMF was used. [b] Phosphine to platinum ratio (P/Pt). [c] Bite-angle of [Pt(η^3-allyl)(diphosphine)]$^+$ optimized with B3LYP function. [d] Determined by GC analysis. [e] Not detected in the reaction mixture. [f] 4 mol % of ligand was used to keep P/Pt to 4.



respectively. The use of DPEphos ($\beta = 107°$)[25] and Xantphos ($\beta = 108°$)[26] greatly improved catalyst activity with Xantphos giving the best result (entry 8, 80% yield). On the other hand, the use of the POP ligand ($\beta = 108°$)[33] and *t*-Bu-Xantphos ($\beta = 112°$)[34] afforded no product (entries 9 and 11) despite their large bite-angle. These findings clearly indicated that, in addition to a large bite-angle, an efficient ligand should be composed of fully aryl- or alkenyl[27]-substituted phosphines. Moreover, the very low reactivity when using the Floriani ligand ($\beta = 111°$)[35] (entry 10), which is a methylene-linked variant of DPEphos, strongly suggests the importance of the linker oxygen in DPEphos and Xantphos. The effect of the linker oxygen is discussed in the last section of this manuscript.

(29) For reviews on the influence of the bite-angle of bidentate phosphane ligands, see: (a) van Haaren, R. J.; Oevering, H.; Coussens, B. B.; van Strijdonck, G. P. F.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1999**, 1237. (b) Oestreich, M. *Eur. J. Org. Chem.* **2005**, 783. (c) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828.

(30) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(31) For a review of self-assembling ligand, see: (a) Breit, B. *Angew. Chem., Int. Ed* **2005**, *44*, 6816. (b) Breit, B.; Seiche, W. *J. Am. Chem. Soc.* **2003**, *125*, 6608. (c) Chevallier, F.; Breit, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 1599. (d) Weis, M.; Waloch, C.; Seiche, W.; Breit, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 3037. (e) Smejkal, T.; Breit, B. *Organometallics* **2007**, *26*, 2461.

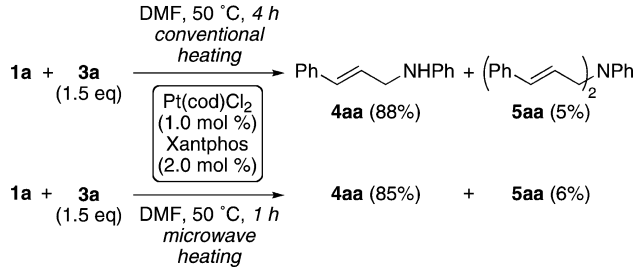
(32) For a review, see: (a) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, *39*, 747. (b) Trost, B. M.; Van Vranken, D. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 228.

(33) (a) Sacconi, L.; Gelsomini, J. *Znorg. Chem.* **1968**, *7*, 291. (b) Greene, P. T.; Sacconi, L. *J. Chem. Soc. A* **1970**, 866. (c) Dapporto, P.; Sacconi, L. *J. Am. Chem. Soc.* **1970**, *92*, 4133. (d) Dapporto, P.; Sacconi, L. *J. Chem. Soc. A* **1971**, 1914. (e) Thewissen, D. H. M. W.; Timmer, K.; Noltes, J. G.; Marsman, J. W.; Laine, R. M. *Inorg. Chim. Acta* **1985**, *97*, 143.

(34) Mispelaere-Canivet, C.; Spindler, J.-F.; Perrio, S.; Beslin, P. *Tetrahedron* **2005**, *61*, 5253.

(35) Lesueur, W.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1997**, *36*, 3354. Structural similarities between DPEphos and Floriani ligand were observed not only in computationally optimized structures of Pt(η^3-allyl)(diphosphine) complexes shown in Table 2 but also in crystal structure of Pd(diphosphine)Cl_2 complexes (see also ref 25c).

Scheme 2. Effects of Microwave Irradiation on Pt-Catalyzed Direct Amination

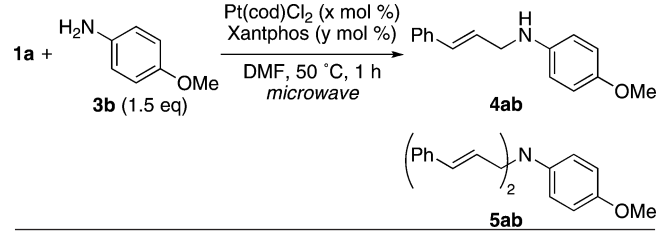


Organic synthesis assisted by microwave heating has grown rapidly since the pioneering work of Gedye in 1986.[36] In many organic transformations, microwave heating dramatically decreases reaction times and increases product yields in comparison with conventional heating methods; therefore, we examined the reaction under microwave irradiation conditions (Scheme 2). Using a CEM Discover single-mode microwave reactor, the reaction mixture was heated at 50 °C and full conversion was achieved within 1 h. Conventional heating, however, required 4 h for completion. Reaction temperature was monitored using a standard IR temperature monitoring system and controlled by microwave irradiation power (standard mode) with an air flow cooling system (20 psi). When polar DMF was used as the solvent, 5−6 W of power was sufficient to maintain the reaction temperature at 50 °C. Although the microwave reactor included a standard IR temperature monitoring system, the reaction temperature was also checked with an alcohol thermometer immediately after turning off the irradiation,[37] revealing that the error in the IR temperature monitoring system was within 5 °C. These results suggest the existence of nonthermal microwave effects.

Finally, optimization of the ligand to platinum ratio was performed using *para*-methoxyaniline (**3b**) under microwave irradiation conditions. As shown in Table 3, the presence of the extra ligand prevented the reaction (entry 1), and optimal results were obtained with a Xantphos to platinum ratio of 1:1 (entry 4), showing that the active catalyst species would be a coordinately unsaturated Pt−xantphos 1:1 complex. Under the optimal reaction conditions, the use of only 0.5 mol % of the catalyst completed the reaction within 1 h (entry 5), and a turnover number of 570 was achieved when the catalyst loading was reduced to 0.1 mol % (entry 6).

We then investigated the scope and limitations of different arylamines **3** (Table 4). Under our previously reported reaction conditions (1.0 mol % of Pt(cod)Cl_2, 2.0 mol % of DPEphos, dioxane reflux), the reaction of anilines bearing an electron-withdrawing group gave only moderate yield due to their low nucleophilicity. For example, 4-fluoroaniline (**3c**) and 4-chloroaniline (**3d**) gave the corresponding monoallylation products **4ac** and **4ad** in 55% and 41% yield, respectively, even after 42 h. Under the present optimized conditions, the reactions of aniline (**3a**) and various *para*-substituted anilines **3c**−**h** with electron-withdrawing groups were efficiently promoted by only 0.5 mol % of the catalyst to provide the desired monoallylation product **4** in high yield and high monoallylation selectivity (entries 1−7). Reaction of *para*-iodoaniline (**3f**) was the only ineffective case with 3% of the product **3af** and recovery of the unreacted **3f**, probably due to oxidative addition of **3f** onto the Pt(0) complex (entry 5). Sterically more congested *ortho*-chloroaniline (**3i**) prevented the diallylation reaction and

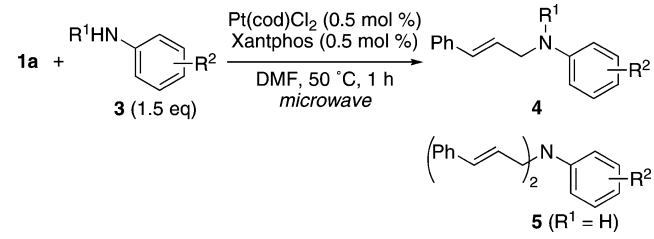
Table 3. Effects of Ligand to Platinum Ratio on Pt-Catalyzed Direct Amination with Arylamine **3b**[a]

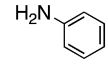
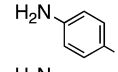
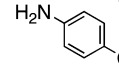
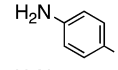
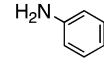
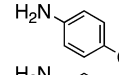
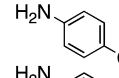
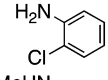
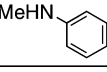


entry	Pt(cod)Cl_2x (mol %)	Xantphos y (mol %)	yield of **4ab**[b]	yield of **5ab**[b]	TON[c]
1	1.0	3.0	nd[d]	nd[d]	
2	1.0	2.0	76%	5%	86
3	1.0	1.5	80%	8%	96
4	1.0	1.0	84%	8%	100
5	0.5	0.5	85%	7.5%	200
6[e]	0.1	0.1	57%	<1%	570

[a] 2.0 mmol scale, 0.4 mL of DMF was used. [b] Isolated yield. [c] Turnover number of the platinum catalyst. [d] Not detected in the reaction mixture. [e] 4.0 mmol scale, 0.8 mL of DMF was used.

Table 4. Pt-Catalyzed Direct Amination with Various Arylamines **3**[a]



entry	arylamine **3**		yield of **4**[b]	yield of **5**[b]
1		**3a**	**4aa** (88%)	**5aa** (6%)
2		**3c**	**4ac** (85%)	**5ac** (5%)
3		**3d**	**4ad** (88%)	**5ad** (6%)
4		**3e**	**4ae** (86%)	**5ae** (5%)
5		**3f**	**4af** (3%)	**5af** (nd[c])
6[d]		**3g**	**4ag** (86%)	**5ag** (5%)
7		**3h**	**4ah** (87%)	**5ah** (4%)
8		**3i**	**4ai** (96%)	**5ai** (nd[c])
9[d]		**3j**	**4aj** (96%)	–

[a] 2.0 mmol scale, 0.4 mL of DMF was used. [b] Isolated yield. [c] Not detected in the reaction mixture [d] Reaction time was 2 h.

(36) For recent reviews, see: (a) Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250. (b) Hayes, B. L. *Aldrichimica Acta* **2004**, *37*, 66. (c) Roberts, B. A.; Strauss, C. R. *Acc. Chem. Res.* **2005**, *38*, 653. (d) Herrero, M. A.; Kremsner, J. M; Kappe, C. O. *J. Org. Chem.* **2008**, *73*, 36.

(37) Because traditional techniques for temperature measurements cannot be applied in microwave heating, the reaction temperature was measured using an alcohol thermometer immediately after turning off the microwave irradiation.

Scheme 3. Pt-Catalyzed Direct Amination with Alkylamine **6a** in DMF

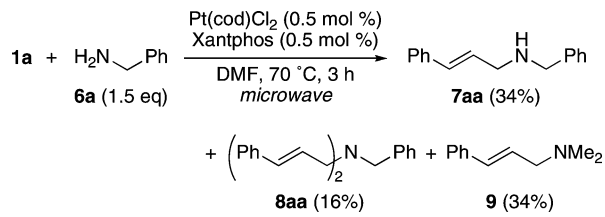
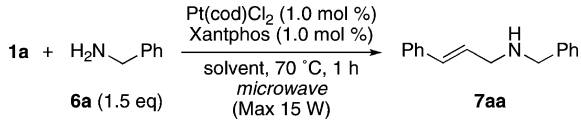


Table 5. Effects of Solvents on Pt-Catalyzed Direct Amination with Alkylamine **6a**[a]



entry	solvent	yield of **7aa**[b]
1	toluene	19%
2	1,2-dichloroethane	35%
3	$CHCl_3$	19%
4	DMSO	15%
5	CH_3CN	14%

[a] 2.0 mmol scale, 0.4 mL of solvent was used. [b] Determined by GC analysis.

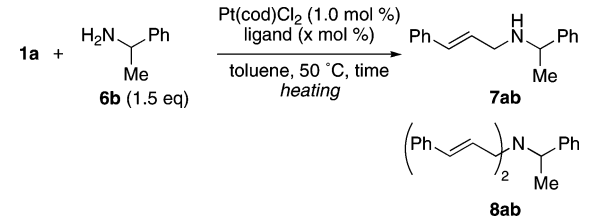
predominantly afforded the monoallylation product **4ai** (entry 7, 96%). Moreover, secondary amine **3j** was also a good substrate for this transformation (entry 8, 96%).

Reaction Using Alkylamines. We next examined the direct substitution of allylic alcohol with alkylamines, which is more challenging. When benzylamine (**6a**) was used as a nucleophile, the conditions optimized for arylamines resulted in an unsatisfactory low yield of **7aa** (34%) and **8aa** (16%) along with unexpected byproduct **9**, which is an allylation product of dimethylamine (Scheme 3). In the reaction of arylamines, this byproduct **9** was not detected at all, suggesting that dimethylamine would not be generated by simple thermal decomposition of DMF but was derived by platinum-catalyzed transamidation of DMF in the presence of highly nucleophilic benzylamine (**6a**).

To avoid such an undesirable side reaction, we re-examined the direct amination of **1a** using benzylamine (**6a**) as the nucleophile in several polar and nonpolar solvents other than DMF (Table 5). Under the standard-mode microwave irradiation conditions (70 °C, ~60 W), the reactions in all tested solvents resulted in full conversion within 1 h, making it difficult to precisely evaluate the solvent effects. Thus, the maximum irradiation power was decreased to 15 W with minimal air flow cooling to keep the reaction temperature at 70 °C. Among the tested solvents, 1,2-dicloroethane (entry 2) was best. In the case of chlorinated solvents (entries 2 and 3), however, the HCl salt of **6a** was formed, indicating that the chlorinated solvents decomposed under the reaction conditions. Thus, we used toluene (entry 1) as the solvent for further investigation of the reaction with alkylamines. For practical operation to keep the reaction temperature at 50 °C, the toluene solvent conditions required 50−60 W of power (standard mode) with standard air flow cooling.

Even after 3 h irradiation in toluene, direct amination of **1a** with **6a** resulted in a moderate yield of **7aa** (58% yield) accompanied by the formation of black precipitates due to partial

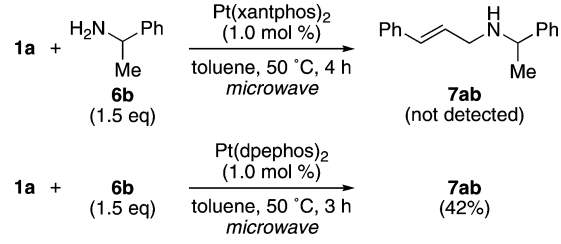
Table 6. Effects of Ligand to Platinum Ratio on Pt-Catalyzed Direct Amination with Alkylamine **6b**[a]



entry	ligand	x (mol %)	heating	time (h)	yield of **7ab**[b]	yield of **8ab**[b]
1	Xantphos	1.0	microwave	4	81%	4%
2	Xantphos	2.0	microwave	4	13%	nd[c]
3	DPEphos	1.0	microwave	3	32%	nd[c]
4	DPEphos	2.0	microwave	3	85%	3%
5	Xantphos	1.0	conventional	24	10%	nd[c]
6	Xantphos	2.0	conventional	24	nd[c]	nd[c]
7	DPEphos	1.0	conventional	24	trace	nd[c]
8	DPEphos	2.0	conventional	24	16	nd[c]

[a] 2.0 mmol scale, 0.4 mL of toluene was used. [b] Isolated yield. [c] Not detected in the reaction mixture.

Scheme 4. Direct Amination with Alkylamine **6b** using $Pt(xantphos)_2$ and $Pt(dpephos)_2$

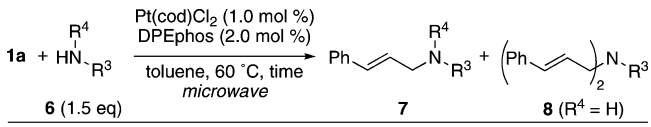


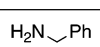
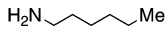
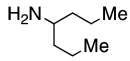
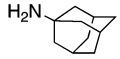
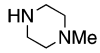
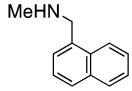
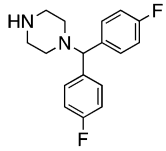
decomposition of the Pt(0) species.[38] To stabilize the Pt(0) species in the reaction mixture, we performed the reaction with an extra amount of the ligand (2.0 equiv to platinum), although we were concerned that it would generate a less active 18-electron Pt(0) complex $Pt(diphosphine)_2$ (Table 6). Surprisingly, in spite of the structural similarities of Xantphos and DPEphos, each ligand gave completely different results (entries 1−4). In the case of Xantphos, the use of 2.0 equiv of ligand to platinum substantially prevented the amination reaction (entry 2, 13%) with the formation of yellow precipitate, which was the $Pt(xantphos)_2$ complex. The reason for the low reactivity was attributed to the insolubility of this complex in toluene.[39] Moreover, this isolated 18-electron Pt(0) complex did not promote the reaction of **1a** with **6b** at all (Scheme 4). On the other hand, 2.0 equiv of DPEphos to platinum greatly improved the yield from 32% (entry 3) to 85% (entry 4) without decomposition of the platinum complex. These results clearly indicate the high solubility of the in situ generated $Pt(dpephos)_2$ complex and the easy dissociation of one DPEphos ligand or monodissociation of the bidentate bisphosphine from the 18-electron $Pt(dpephos)_2$ complex to yield the coordinately unsaturated active Pt(0) complex. In fact, the $Pt(dpephos)_2$ complex, which was prepared by the $NaBH_4$ reduction of the Pt(dpep-

(38) Because the reaction with a less congested alkylamine such as **6a** formed more black precipitates than that with a more congested alkylamine such as **6b**, decomposition of the Pt(0) species may be induced by the coordination of alkylamine to platinum. See also the Supporting Information.

(39) $Pt(xantphos)_2$ complex, synthesized by the reaction of $Pt(dba)_2$ with the Xantphos ligand (4.0 equiv), was almost insoluble, not only in toluene but also in other solvents such as $CHCl_3$, THF, and DMF.

Table 7. Pt-Catalyzed Direct Amination with Various Alkylamines **6**[a]



entry	alkylamine **6**		time (h)	yield of **7**[b]	yield of **8**[b]
1[c]		**6a**	4	**7aa** (80%)	**8aa** (10%)
2[c]		**6c**	4	**7ac** (60%)	**8ac** (17%)
3[c,d]		**6c**	7	**7ac** (65%)	**8ac** (6%)
4[c]		**6d**	6	**7ad** (74%)	**8ad** (5%)
5[c,d]		**6d**	5	**7ad** (86%)	**8ad** (5%)
6		**6e**	2	**7ae** (85%)	**8ae** (7%)
7		**6f**	6	**7af** (77%)	**8af** (10%)
8		**6g**	6	**7ag** (86%)	**8ag** (3%)
9		**6h**	3	**7ah** (96%)	–
10		**6i**	3	**7ai** (98%)	–
11		**6j**	5	**7aj** (95%)	–
12		**6k**	4	**7ak** (94%)	–

[a] 2.0 mmol scale, 0.4 mL of toluene was used. [b] Isolated yield. [c] 3.0 equiv of alkylamine **6** was used. [d] Solvent-free conditions.

hos)Cl_2 complex with the DPEphos ligand, also catalyzed the reaction in moderate yield (Scheme 4). The same tendencies as shown in entries 1−4 were observed in the conventional heating reactions (entries 5−8), but the obtained yields of the product **7ab** were quite low even after 24 h, again suggesting the existence of nonthermal microwave effects.

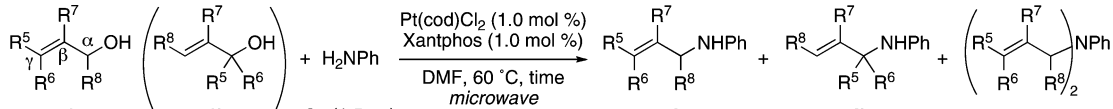
With the efficient reaction conditions for alkylamines (Table 6, entry 4) in hand, we performed the reaction with various primary and secondary alkylamines (Table 7). Although 3.0 equiv of amine was used when sterically less congested primary alkylamines were employed (entries 1−5), monoallylation products **7** were obtained in high yield along with the formation of only small amounts of diallylation products **8** (entries 1−8). To our knowledge, such high monoallylation selectivity was only achieved by platinum catalysts bearing large bite-angle diphosphine ligands.[24,27] The reactions proceeded under solvent-free conditions (entries 3 and 5), resulting in high volumetric productivity and low waste generation. Moreover, direct amination with secondary alkylamines **6h**−**k** proceeded quite efficiently to afford the desired products **7ah**−**ak**, including the antifungal drug Naftifine (**7aj**)[4a,b] and the calcium channel blocker Flunarizine (**7ak**),[4c,d] in excellent yields (entries 9−12). As compared with the previously reported conventional heating conditions in dioxane (reflux 101 °C, 18 h),[24] we succeeded in lowering the reaction temperature to 50−60 °C and decreasing the reaction time to 2−6 h while maintaining a high yield and high monoallylation selectivity.

Substrate Scope of Allylic Alcohols. Direct amination of alkyl-substituted allylic alcohols remained an unsolved target. Because microwave irradiation in DMF greatly improved the catalyst activity and lowered the reaction temperature to 50 °C, we anticipated that under such mild conditions the reaction of the alkyl-substituted allylic alcohols could be catalyzed without undergoing side reactions such as β-H elimination. Under the optimized conditions for arylamine (1.0 mol % of Pt(cod)Cl_2, 1.0 mol % of Xantphos, DMF, microwave irradiation, 60 °C, standard mode), we performed direct amination of ally alcohol (**1b**) and various aryl- and alkyl-substituted allylic alcohols **1a**-**h** with aniline (**3a**) (1.5 equiv) (Table 8). These studies also provided several new insights into the mechanism. The reaction of **1b** (entry 1) proceeded smoothly in a manner similar to γ-phenyl-substituted allylic alcohol **1a** (entry 2). Despite the moderate yield of γ-methyl-substituted **1c** under the previous reaction conditions (43% yield, dioxane, reflux, 18 h), the present reaction conditions allowed for the full conversion of **1c** to the allylated products **4ca** (77%), **4ca′** (10%), and **5ca** (6%) without proceeding to the undesired β-H elimination (entry 4). When α-substituted allylic alcohols **1a′** (entry 3) and **1c′** (entry 5) were used, the obtained regio-, stereo-, and monoallylation selectivities were almost the same as those using γ-substituted allylic alcohols **1a** (entry 2) and **1c** (entry 4), respectively, strongly suggesting that the reaction proceeds via π-allylplatinum intermediates. β-Methyl-substituted allylic alcohol **1d** (entry 6), cyclic allylic alcohol **1f** (entry 9), and α,α-disubstituted allylic alcohol **1g′** (entry 12) were also good substrates for the direct catalytic amination reaction to give the desired products in high yield. On the other hand, the reactions of α,γ-disubstituted allylic alcohol **1e** (entry 7) and γ,γ-disubstituted allylic alcohols **1g** (entry 10) and **1h** (entry 13) resulted in low to moderate yield with partial decomposition of the platinum species. Fortunately, conventional heating instead of microwave irradiation greatly improved the yield of **4ea** (entry 8, 91%), **4ga** (entry 11, 85%), and **4ha** (entry 14, 70%), though these reactions required a longer reaction time (20−48 h).[28] Based on the fact that α,α-disubstituted allylic alcohol **1g′** reacts much faster than γ,γ-disubstituted allylic alcohol **1g**, the reactivity of the platinum catalysis is more strongly affected by steric congestion around the C═C double bond in allylic alcohol than that around the hydroxy group, showing the importance of η^2-coordination of the C═C double bond to the platinum atom prior to the generation of the π-allyl intermediates. It is worth noting that all reactions of various allylic alcohols proceeded in quite high monoallylation selectivity. To the best of our knowledge, this is the first time that such broad substrate generality (both aryl- and alkyl-substituted allylic alcohols and both arylamines and alkylamines) and high monoallylation selectivity were achieved in this type of direct reaction.

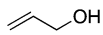
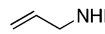
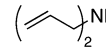
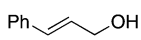
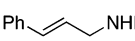
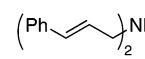
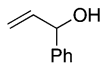
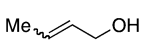
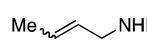
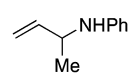
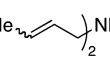
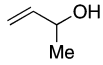
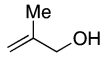
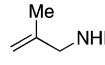
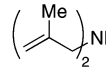
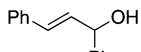
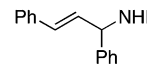
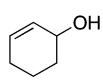
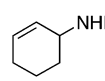
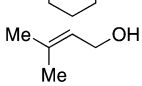
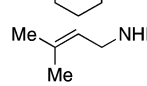
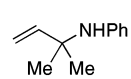
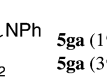
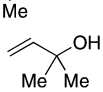
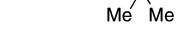
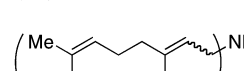
Mechanistic Studies. Based on the following intensive mechanistic studies, including ^{1}H and ^{31}P{^{1}H} NMR studies, the isolation of several catalytic intermediates, confirmation of the structure of [Pt(η^3-allyl)(xantphos)]OTf by X-ray crystallographic analysis, and crossover experiments, a plausible catalytic cycle of the platinum-catalyzed direct amination of allylic alcohol is depicted in Scheme 5.

1. Generation of Pt(0) Species from Pt(cod)Cl_2 (A → B). When Pt(0) species, such as Pt(PPh_3)$_4$ and Pt(dba)$_2$, were used as a catalyst precursor, only low to moderate catalyst activities were observed[28] probably due to the existence of extra ligand, which would prevent the formation of coordinatively unsaturated

Table 8. Pt-Catalyzed Direct Amination of Various Allylic Alcohols **1**[a]

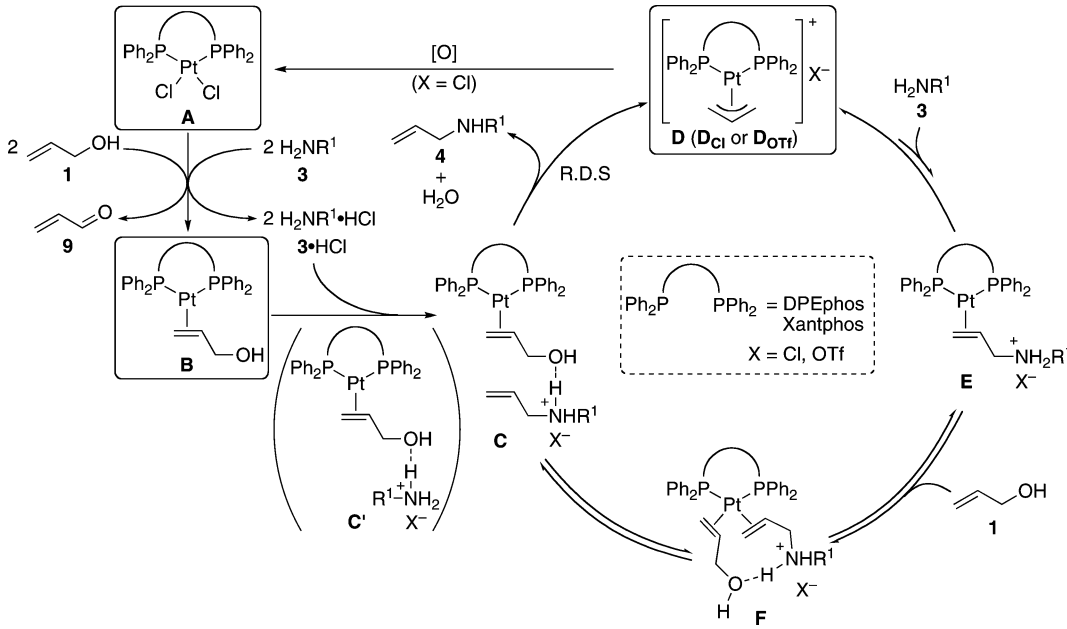


1 **1'** **4** **4'** **5**

entry	allylic alcohol **1**		time (h)	yield of **4**[b]		yield of **5**[b]
1[c]		**1b**	2	 **4ba** (85%)		 **5ba** (6%)
2[c,d]		**1a**	1	 **4aa** (88%)		 **5aa** (6%)
3		**1a'**	3	**4aa** (83%)		**5aa** (4%)
4		**1c**[e]	2	 **4ca** (77%)[f]	 **4ca'** (10%)	 **5ca** (6%)
5		**1c'**	2	**4ca** (80%)[f]	**4ca'** (11%)	**5ca** (3%)
6[g]		**1d**	4	 **4da** (82%)		 **5da** (3%)
7		**1e**	3	 **4ea** (18%)		
8[h]		**1e**	20	**4ea** (91%)		
9		**1f**	3	 **4fa** (92%)		
10		**1g**	3	 **4ga** (58%)	 **4ga'** (1%)	 **5ga** (1%)
11[h]		**1g**	48	**4ga** (85%)	**4ga'** (2%)	**5ga** (3%)
12		**1g'**	1	**4ga** (86%)	**4ga'** (1%)	**5ga** (5%)
13[g]		**1h**	3	**4ha** (28%)[i]		 **5ha** (nd[j])
14[g,h]		**1h**	24	**4ha** (70%)[i]		**5ha** (nd[j])

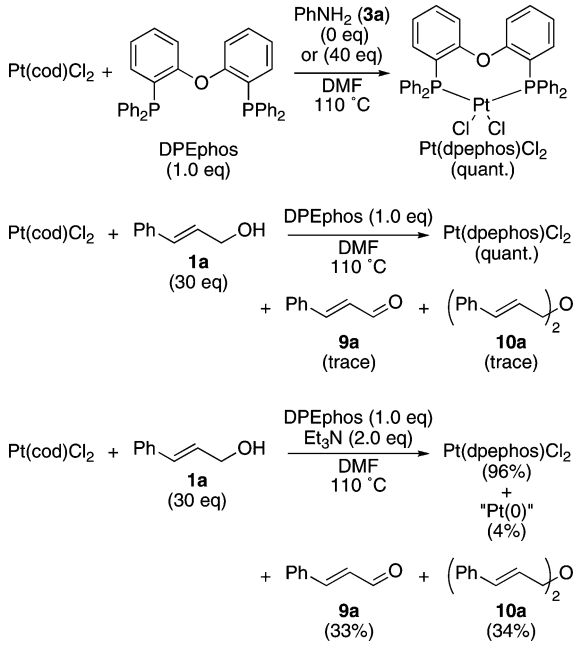
[a] 2.0 mmol scale, 0.4 mL of DMF was used. [b] Isolated yield. [c] Reaction temperature was 50 °C. [d] 0.5 mol % of $Pt(cod)Cl_2$ and 0.5 mol % of Xantphos were used. [e] *E*/*Z* mixture of **1c** (*E*/*Z* = 97/3) was used. [f] **4ca** was obtained as an *E*/*Z* mixture (10/1). [g] Reaction temperature was 80 °C. [h] Conventional heating conditions. [i] **4ha** was obtained as an *E*/*Z* mixture (5.8/1). [j] Not detected in the reaction mixture.

Scheme 5. Proposed Catalytic Cycle of the Platinum-Catalyzed Direct Amination of Allylic Alcohol[a,b]

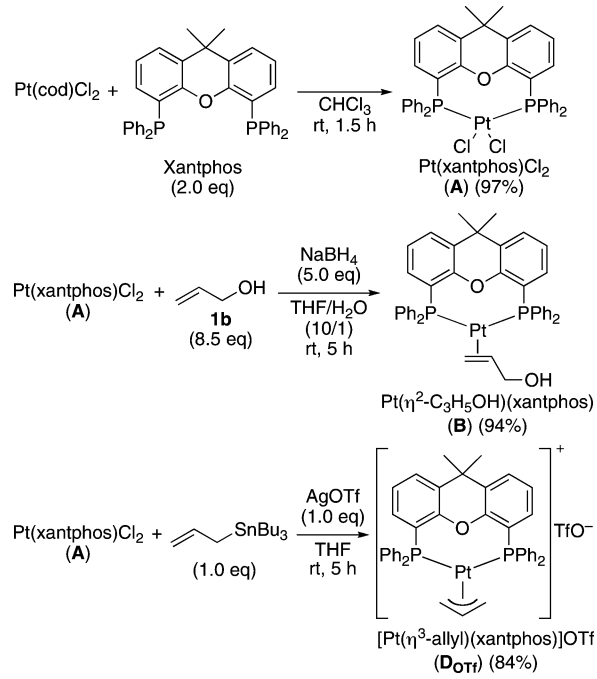


[a] Substituents of allylic alcohol **1** are omitted for clarity. [b] Structurally characterized complexes are boxed.

Scheme 6. Reaction of Pt(cod)Cl_2 with DPEphos, Amine, and Allylic Alcohol



Scheme 7. Preparation of Pt(xantphos)Cl_2 (**A**), Pt(η^2-C_3H_5OH)(xantphos) (**B**), and [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$)



active Pt(0) species. In sharp contrast, Pt(cod)Cl_2 was found to be the best precursor.[28] Our first question to be addressed was which compound reduced Pt(II) to Pt(0): phosphine ligand, amine, or allylic alcohol. Phosphine ligand can reduce $Pd(OAc)_2$ with water and amine to generate Pd(0) species and phosphine oxide. Thus, we first examined this possibility; a mixture of Pt(cod)Cl_2, 2.0 equiv DPEphos, and water in DMF was heated at 110 °C in the presence or absence of aniline (**3a**) (Scheme 6). In both cases, however, only the formation of Pt(dpephos)Cl_2 (**A**) was observed with the remaining extra DPEphos ligand, and neither the Pt(0) species nor phosphine oxide was detected. In contrast, when Pt(cod)Cl_2 and DPEphos were heated in the presence of excess cinnamyl alcohol (**1a**), trace amounts of cinnamaldehyde (**9a**) and dicinnamyl ether (**10a**), which may be produced by nucleophilic addition of **1a** to the π-allylplatinum complex, were detected. The addition of Et_3N significantly increased the yield of these products (**9a**: 33%, **10a**: 34%). Although only a small amount of Pt(0) species, assignable to Pt(η^2-PhC_3H_4OH)(xantphos) (**B**) (vide infra), was detected by $^{31}P\{^1H\}$ NMR, the results of the control reactions shown in Scheme 6 suggest that the Pt(II) species is reduced to the Pt(0) species by allylic alcohol **1** through β-H elimination, which is different from Wacker-type mechanism reported by Atwood et al.[40] We later found that we observed only a small proportion of Pt(0) species because the Pt(0) is easily reoxidized to the Pt(II) species in the presence of a chloride ligand (vide infra).

2. Syntheses, Characterization, and Catalyst Activities of Pt Complexes Pt(η^2-C_3H_5OH)(xantphos) (B) and [Pt(η^3-allyl)(xantphos)]X (D). We next examined the synthesis of putative intermediates Pt(η^2-C_3H_5OH)(L) (**B**) and [Pt(η^3-allyl)(L)]X (**D**) where L is DPEphos or Xantphos. The results using Xantphos are summarized in Scheme 7.[41] Reaction of Pt(cod)Cl_2 with 1.0 equiv Xantphos in $CHCl_3$ at room temperature led to the formation of a Pt(II) complex, Pt(xantphos)Cl_2 (**A**) ($^{31}P\{^1H\}$ NMR δ 6.60, s with Pt satellite, $^1J_{P-Pt}$ = 3694 Hz), in 97% yield. $NaBH_4$ reduction of **A** in the presence of allyl alcohol (**1b**) afforded a Pt(0) complex, Pt(η^2-C_3H_5OH)(xantphos) (**B**), in 94% yield. In the $^{31}P\{^1H\}$ NMR spectrum, two different phosphorus signals appeared as two doublets with Pt satellites at δ 19.8 (d with Pt satellite, $^2J_{P-P}$ = 51.4 Hz, $^1J_{P-Pt}$ = 3687 Hz) and 18.1 (d with Pt satellite, $^2J_{P-P}$ = 51.4 Hz, $^1J_{P-Pt}$ = 3508 Hz), suggesting the presence of two magnetically different phosphorus atoms. Moreover, significant high field shifts of alkenyl protons in ^1H NMR [δ 3.43−3.33 (m, 1 H, CH_2=C*H*-CH_2), 2.61−2.50 (m, 1 H, C*H*H=CH−CH_2), 2.50−2.34 (m, 1 H, CH*H*=CH−CH_2)] also support a η^2-coordination of **1b** to platinum metal. A π-allyl complex, [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$), was synthesized in 84% yield by the reaction of Pt(xantphos)Cl_2, allyltributylstannane (1.0 equiv), and AgOTf (1.0 equiv) and identified by $^{31}P\{^1H\}$ NMR (δ 1.24 ppm, $^1J_{P-Pt}$ = 4179 Hz), ^1H NMR, ^{19}F NMR, FAB Mass, and elemental analysis. The structure of this complex was further confirmed by X-ray crystallographic analysis (Figure 1) of crystals, which were produced by slow diffusion of hexane into the saturated CH_2Cl_2 solution of the complex at room temperature. The bite-angle of the crystal (107°) is almost the same as that obtained by DFT calculations (Table 2, 108°).

Having putative intermediates Pt(η^2-C_3H_5OH)(xantphos) (**B**) and [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$) in hand, the catalyst activities of these complexes were investigated in the reaction of **1b** and **3a**. As shown in Scheme 8, both complexes promoted the reaction to give the product, suggesting that these complexes are involved in the catalytic cycle. Reactivities of these complexes, however, differed from that of the Pt(cod)Cl_2−Xantphos system. Under conventional heating conditions at 50 °C, the Pt(0) complex **B** required 24 h to reach full conversion, while the reactions using Pt(cod)Cl_2−Xantphos and $\mathbf{D_{OTf}}$ completed in 10 and 2 h, respectively. Higher catalyst

(40) Helfer, D. S.; Phaho, D. S.; Atwood, J. D. *Organometallics* **2006**, *25*, 410.

(41) In a similar way, Pt(dpephos)Cl_2 complex **A** ($31P\{^1H\}$ NMR δ 1.97, s with Pt satellite, $^1J_{P\text{-}Pt}$ = 3796 Hz) and Pt(η^2-C_3H_5OH)(dpephos) complex **B** ($31P\{^1H\}$ NMR δ 25.7 (d with Pt satellite, $^2J_{P\text{-}P}$ = 46.6 Hz, $1J_{P\text{-}Pt}$ = 3596 Hz), 24.9 (d with Pt satellite, $^2J_{P\text{-}P}$ = 46.6 Hz, $^1J_{P\text{-}Pt}$ = 3596 Hz)) were synthesized in 89% and 58% yields, respectively.

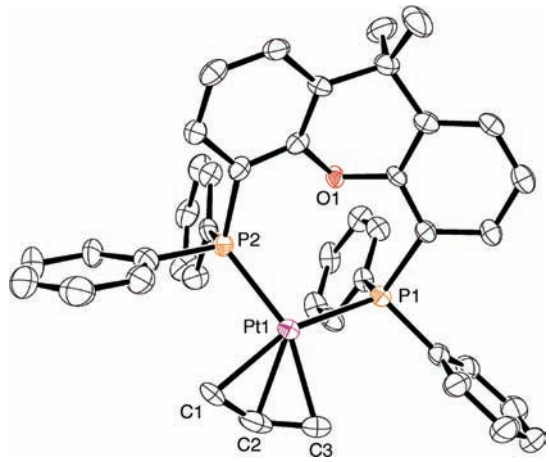
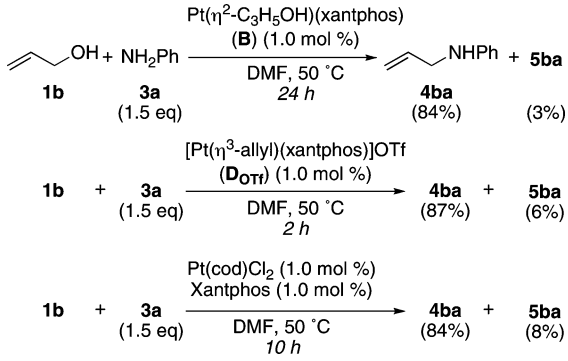


Figure 1. ORTEP drawing of [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$) with thermal ellipsoids at the 50% probability level. The hydrogen atoms, counteranions, and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1−P1 2.3302(19), Pt1−P2 2.325(2), Pt1−C1 2.195(8), Pt1−C2 2.142(9), Pt1−C3 2.182(8), Pt1−O1 3.506(4), C1−C2 1.336(14), C2−C3 1.344(15); P1−Pt1−P2 107.04(6), C2−Pt1−P1 123.6(3), C2−Pt1−P2 122.3(3).

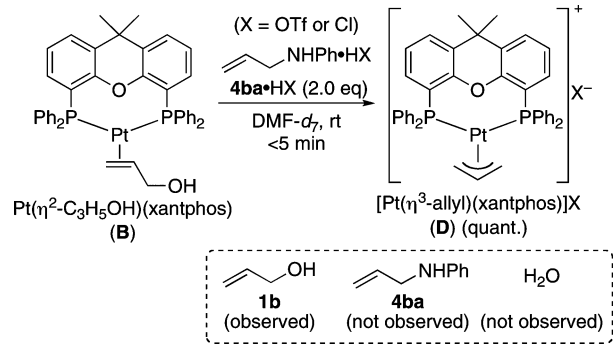
Scheme 8. Catalytic Activities of Pt(η^2-C_3H_5OH)(xantphos) (**B**) and [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$)



activities of Pt(cod)Cl_2-Xantphos and $\mathbf{D_{OTf}}$ than **B** may be attributed to the generation of ammonium salts $H_2NR^1 \cdot HCl$ and $H_2NR^1 \cdot HOTf$, which could potentially act as more efficient activators of the hydroxyl group to accelerate the elimination of hydroxide through a hydrogen bonding of ammonium salts with hydroxy group of allylic alcohol (**C′** → **D**).

3. Generation of [Pt(η^3-allyl)(xantphos)]X (D) from Pt(η^2-C_3H_5OH)(xantphos) (B) (B → C → D). To elucidate the formation of the π-allylplatinum complex **D** from the Pt(0) complex Pt(η^2-C_3H_5OH)(xantphos) (**B**), HOTf and HCl salts of *N*-allylaniline (**4ba**) were added to a solution of **B** in DMF-d_7, and these reactions were monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies (Scheme 9). The ^{31}P{^{1}H} NMR spectrum indicated that the addition of 2.0 equiv **4ba**·HOTf salt to the Pt(0) complex **B** at room temperature led to the exclusive formation of [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$) within 5 min (Figure 2). Similarly, full conversion of **B** to [Pt(η^3-allyl)(xantphos)]Cl ($\mathbf{D_{Cl}}$) was achieved within 5 min by the addition of 2.0 equiv **4ba**·HCl (Figure 3). Their ^{1}H NMR spectra, however, revealed the presence of free allyl alcohol (**1b**), but not free *N*-allylaniline (**4ba**) or water, strongly suggesting that π-allylplatinum complexes **D** were not generated through the elimination of water from allyl alcohol (**1b**) coordinated to the Pt(0) atom (**C** → **D**, Scheme 5, clockwise direction) but rationally through the elimination of aniline **3a** from *N*-allylaniline (**4ba**) (**C** → **F** → **E** → **D**, Scheme 5, counterclockwise direction). The formation of **3a** could not be confirmed due to overlapping of the signals of the aromatic protons in ^{1}H NMR.

Scheme 9. Generation of [Pt(η^3-allyl)(xantphos)]X (**D**) from Pt(η^2-C_3H_5OH)(xantphos) (**B**)



The existence of this rapid retro reaction (**C** → **F** → **E** → **D**) was further supported by the following crossover experiments (Scheme 10). We performed direct amination of cinnamyl alcohol (**1a**) with 4-methoxyaniline (**3b**) in the presence of *N*-allylaniline (**4ba**). Employing both condition A (Pt(cod)Cl_2-Xantphos) and condition B ([Pt(η^3-allyl)(xantphos)]OTf), we detected not only simple coupling product **4ab** but also significant amounts of crossover products **4aa** and **4bb**. Thus, it was confirmed that the retro reaction of complex **C**, giving complex **D**, **1a**, and **3a**, proceeded under the reaction conditions.

4. Reactivity Performance of [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$) (D → E → F → C → D). To obtain more insight into the mechanism, we next examined the reactivity of complex $\mathbf{D_{OTf}}$ toward nucleophile aniline (**3a**) (Scheme 11). ^{1}H and ^{31}P{^{1}H} NMR spectroscopic monitoring of a mixture of $\mathbf{D_{OTf}}$ and 12.0 equiv of **3a** in DMF-d_7 indicated that almost no reaction occurred even after 6 h of heating at 50 °C. In contrast, when allyl alcohol (**1b**) was added to this mixture with **3a**, clear conversion of **1b** to the allylated products **4ba** (62%) and **5ba** (38%) was detected by ^{1}H NMR, though only the starting $\mathbf{D_{OTf}}$ was detected on ^{31}P{^{1}H} NMR spectroscopy. Recently, le Floch and coauthors reported that, in the case of [Pt(η^3-allyl)(dpp-xantphos)]PF_6, addition of benzylamine (**6a**) led to the formation of a new complex, tentatively assigned as Pt(η^2-$H_2C{=}CHCH_2NH_2Bn^+PF_6^-$)(dpp-xantphos) (**E**).[27] In sharp contrast to their results, our results shown in Schemes 9−11 suggest that (1) complexes **D**, **E**, **F**, and **C** were in rapid equilibrium, even at room temperature, (2) among them, **D** was the most stable species even in the presence of excess amounts of nucleophile **3**, and (3) the formation of **D** from **C** through the elimination of water (**C** → **D**) was the rate-determining step of this catalytic cycle and required a reaction temperature of 50 °C.

Finally, we investigated the possibility of the retro reaction of $\mathbf{D_{OTf}}$ to **C** (**D** → **C**, Scheme 5, counterclockwise direction). Treatment of **D** with allylamine **4aa** and water in DMF-d_7 at 60 °C for 20 h resulted in no reaction, probably due to the low nucleophilicity of water to the π-allylplatinum complex **D**. Based on these facts, we concluded that the formation of complex **D** from complex **C** through the elimination of water is an irreversible rate-determining step.

5. Effects of Counteranion (X^-) on Stability of Pt(η^3-allyl)(xantphos)]X (D). When we examined the formation of [Pt(η^3-allyl)(xantphos)]Cl ($\mathbf{D_{Cl}}$) from Pt(η^2-C_3H_5OH)(xantphos) (**B**) by the addition of the HCl salt of *N*-allylaniline (**4ba**) (Figure 3),

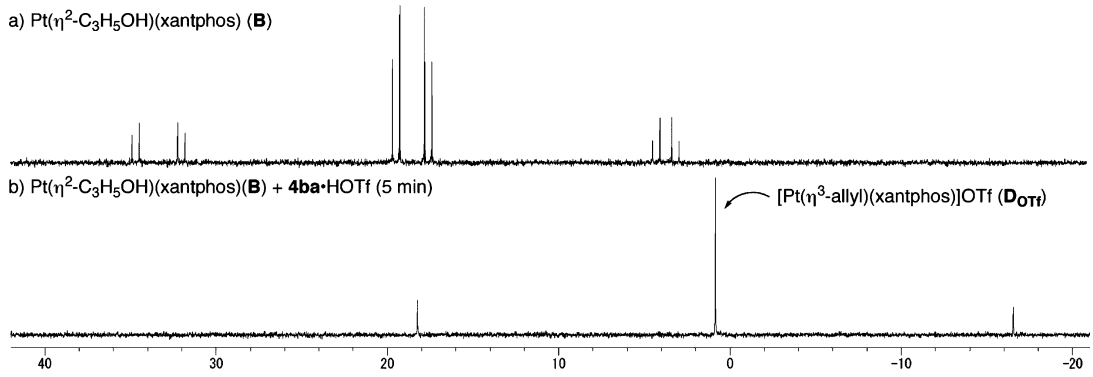


Figure 2. $^{31}P\{^1H\}$ NMR of platinum complexes in DMF-d_7: (a) Pt(η^2-C_3H_5OH)(xantphos) (**B**) and (b) **B** + **4ba**·HOTf (2 equiv), after 5 min.

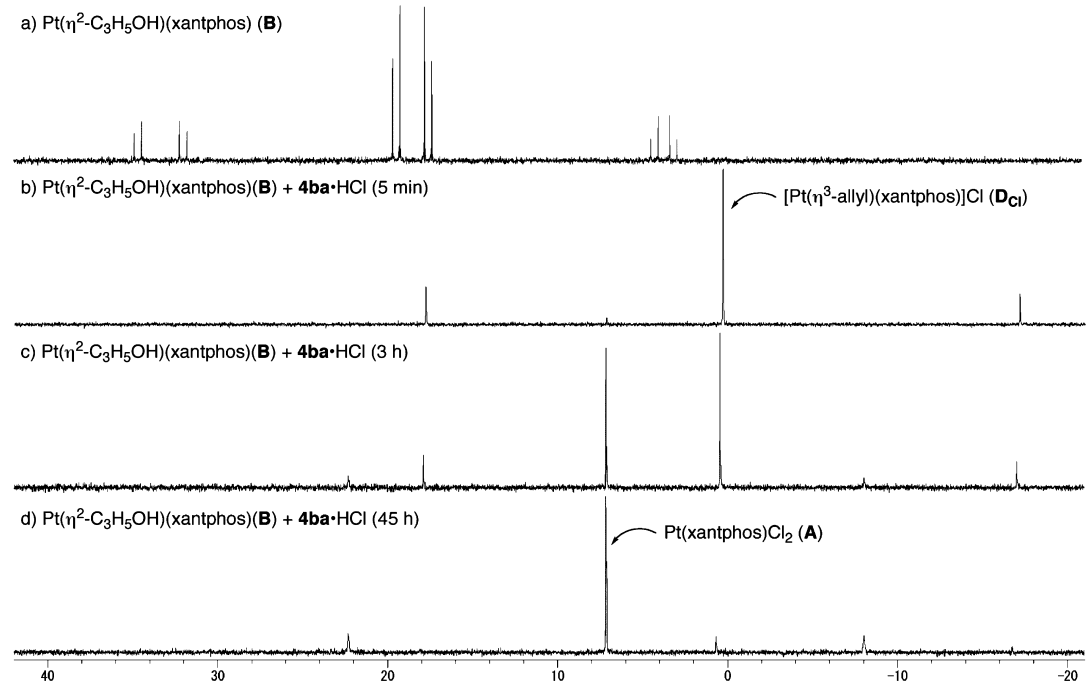


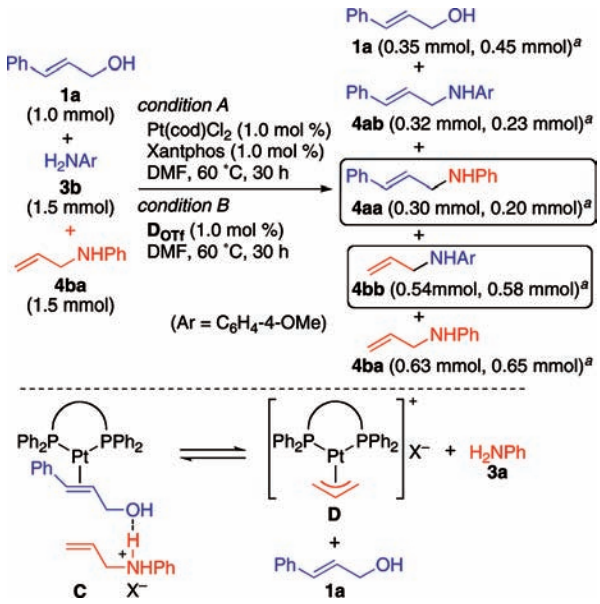
Figure 3. $^{31}P\{^1H\}$ NMR of platinum complexes in DMF-d_7: (a) Pt(η^2-C_3H_5OH)(xantphos) (**B**); (b) **B** + **4ba**·HCl (2 equiv), after 5 min, (c) after 3 h, (d) after 45 h.

we found that [Pt(η^3-allyl)(xantphos)]Cl ($\mathbf{D_{Cl}}$) was slowly converted to Pt(xantphos)Cl_2 (**A**) and the ratio of complexes $\mathbf{D_{Cl}}$ and **A** reached 10:1 after 45 h at 50 °C, even under thoroughly degassed conditions. Such an oxidation reaction[42] was not observed when **4ba**·HOTf was added to the complex **B**. In addition, $^{31}P\{^1H\}$ NMR measurement in DMF-d_7 revealed that the addition of **4ba**·HCl (2.0 equiv) gradually converted $\mathbf{D_{OTf}}$ to Pt(xantphos)Cl_2 (**A**) ($\mathbf{D_{OTf}}$: **A** = 25:75, after 18 h of heating at 50 °C). As shown in Scheme 6, the reduction of Pt(cod)Cl_2 with Xantphos by allylic alcohol **1a** resulted in the formation of only 4% of Pt(0) species together with 96% of Pt(II) complex **A**, despite the fact that **1a** was oxidized to the corresponding aldehyde in 33%. This is due to the easy reoxidation property of $\mathbf{D_{Cl}}$. The resulting Pt(II) species again requires another equivalent of allylic alcohol **1a** to participate in the catalytic cycle. These results, taken together with the fact that $\mathbf{D_{OTf}}$ has higher catalyst activity than the Pt(cod)Cl_2−Xantphos system (Scheme 8), indicate that the use of $\mathbf{D_{OTf}}$ leads to the development of a more efficient catalytic system.

6. Further Investigation of Ligand Effects of DPEphos and Xantphos. As far as we examined, only platinum complexes bearing a diphosphine ligand with a large bite-angle have efficient catalytic activity. Although the high monoallylation selectivity of Pt-DPEphos and Pt-Xantphos complexes can be explained by their large bite-angle as previously proposed,[24] it is difficult to understand their high catalyst activities on direct amination simply based on their large bite-angle. On the basis of DFT calculations, le Floch and coauthors proposed that ligands with a large bite-angle effectively prevent the formation of platinum hydride complexes and therefore the formation of an inactive bicyclic aminopropyl complex.[27] The results shown in Table 2, however, clearly demonstrated that not only the large bite-angle but also the linker oxygen in DPEphos and Xantphos are very important for achieving the high catalyst performance. Based on the X-ray crystallographic analysis of $\mathbf{D_{OTf}}$ (Figure 1), there is no direct interaction between the linker oxygen atom

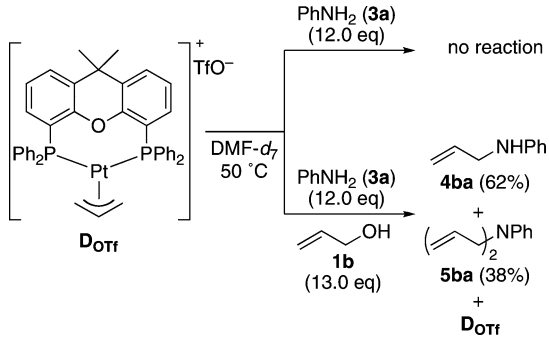
(42) Although the precise mechanism is not clear, the oxidation of [Pt(η^3-allyl)(xantphos)]Cl ($\mathbf{D_{Cl}}$) or complex **C** by the molecular oxygen remaining even after degassing may lead to the formation of Pt(xantphos)Cl_2 (**A**).

Scheme 10. Crossover Experiments[a]



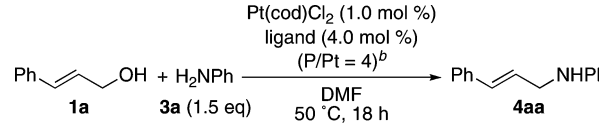
[a] Results under condition A (left) and condition B (right).

Scheme 11. Reactivity of [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$) with Amine and Allylic Alcohol



of Xantphos and the platinum atom (Pt1−O1 3.51 Å).[43] Thus, we shifted our attention to the electronic effects of the linker oxygen, which may enhance the electron density of the phosphines. To closely examine the electronic effects of the ligand on the catalyst activities, various electron-rich monophosphine ligands were used (Table 9). As compared with the benchmark ligand PPh_3 (entry 1, 41%), the use of methyl substituted ligands led to lower yields (entries 2 and 3). On the other hand, *ortho*-methoxy substituted ligand $P(C_6H_4$-2-OMe$)Ph_2$ afforded the product **4aa** in 69% yield (entry 4), whereas, very interestingly, *meta*- and *para*-methoxy substituted ligands decreased the yield to 33% (entry 5) and 11% (entry 6), respectively.[44] These results indicate that catalyst activity does not directly correlate with the electronic effects of the ligand. Introducing one more methoxy group at the other *ortho*-position somewhat decreased the yield to 45% (entry 7), and replacing a methoxy group with a methoxymethyl group (entry 8) and dimethylamino group (entry 9) resulted in almost no reaction. The exact reason for such dramatic positive effects of the oxygen atom at the *ortho*-position of triarylphosphine ligands on catalyst activity remains unclear, but the effects may be due to an increase in the leaving ability of the hydroxy group through hydrogen bonding. These findings provide highly useful information for the development of further efficient ligands including chiral variants.

Table 9. Pt-catalyzed Direct Amination Using Various Monophosphine Ligands[a]



entry	ligand	yield of **4aa**[c]
1	PPh_3	41%
2	$P(C_6H_4$-2-Me$)Ph_2$	nd[d]
3	$P(C_6H_4$-4-Me$)Ph_2$	18%
4	$P(C_6H_4$-2-OMe$)Ph_2$	69%
5	$P(C_6H_4$-3-OMe$)Ph_2$	33%
6	$P(C_6H_4$-4-OMe$)Ph_2$	11%
7	$P(C_6H_3$-2,6-$(OMe)_2)Ph_2$	45%
8	$P(C_6H_4$-2-CH_2OMe$)Ph_2$	2%
9	$P(C_6H_4$-2-$NMe_2)Ph_2$	nd[d]

[a] 2.0 mmol scale, 0.4 mL of DMF was used. [b] Phosphine to platinum ratio (P/Pt). [c] Determined by GC analysis. [d] Not detected in the reaction mixture.

Conclusion

We successfully developed a versatile direct catalytic amination of allylic alcohols with amines using Pt-Xantphos and Pt-DPEphos catalysts as a useful method to synthesize various allylamines in an environmentally friendly manner. We demonstrated that both the large bite-angle as well as the linker oxygen atom of the Xantphos and DPEphos ligands were essential to achieve high catalytic activity. Moreover, under microwave heating the reaction reached completion in a much shorter period of time compared to conventional heating, suggesting the existence of nonthermal microwave effects. Under the optimized conditions, the direct substitution reaction of both aryl- and alkyl-substituted allylic alcohols with a wide variety of aryl- and alkylamines proceeded efficiently to afford the desired monoallylamines in high yield. The usefulness of the present catalysis was successfully demonstrated by one-step synthesis of the biologically active compounds Naftifine and Flunarizine from allylic alcohol without the use of an activator. To the best of our knowledge, this is the first report of such broad substrate generality and high monoallylation selectivity for this type of direct reaction. Finally, several mechanistic investigations, including ^{1}H and ^{31}P{^{1}H} NMR studies, isolation and characterization of several catalytic intermediates, confirmation of the structure of [Pt(η^3-allyl)(xantphos)]OTf by X-ray crystallographic analysis and crossover experiments, suggested that (1) the reduction of $Pd(cod)Cl_2$ with allylic alcohol and amine H_2NR^1 generate the

(43) Weller and Willis reported that linker oxygen of DPEphos acted as a hemilabile ligand, increasing stability of the active Rh catalyst, see: (a) Moxham, G. L.; Randell-Sly, H. E.; Brayshaw, S. K.; Woodward, R. L.; Weller, A. S.; Willis, M. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7618. (b) Moxham, G. L.; Randell-Sly, H. E.; Brayshaw, S. K.; Weller, A. S.; Willis, M. C. *Chem.—Eur. J.* **2008**, *14*, 8383.

(44) Our preliminary DFT calculations (LANL2DZ for Pt and 6-31G for others) suggested that P−O−P angle of {[Ph_2(2-MeO-C_6H_4)P]$_2$Pt(η^3-allyl)}$^+$ is in the 102° to 106° range (the P−O−P angle of [$(Ph_3P)_2$Pt(η^3-allyl)]$^+$ obtained by DFT optimizations (102°) is almost the same as that of crystal (101°)[45]). The direct amination of **1a** with **3a** using $Pt(cod)Cl_2$ (0.5 mol %) and $P(C_6H_4$-2-OMe$)Ph_2$ (1 mol %, P/Pt = 2 or 2 mol %, P/Pt = 4) in DMF at 50 °C for 1 h with microwave irradiation (standard mode) afford the product **4aa** in only 25% (1 mol % of ligand) and 4% (2 mol % of ligand) yields, respectively, with recovery of the starting materials. These results indicate the partial decomposition of Pt[$P(C_6H_4$-2-OMe$)Ph_2]_n$ complex under microwave irradiation conditions and confirm the advantage of bidentate DPEphos and Xantphos ligands over monodentate $Ph_2P(C_6H_4$-2-OMe) ligand.

(45) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657.

active Pd(0) species along with the ammonium salt $H_2NR^1 \cdot HCl$ and the aldehyde, (2) Pt(η^2-C_3H_5OH)(xantphos) (**B**) and [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$) are involved in the catalytic cycle, (3) the ammonium salt $H_2NR^1 \cdot HCl$ acts as more efficient activatiors of the hydroxyl group to accelerate the elimination of hydroxide through a hydrogen bonding, (4) formation of the π-allylplatinum complex **D** through the elimination of water (**C** → **D**) is an irreversible rate-determining step, and (5) the other processes in the catalytic cycle are reversible, even at room temperature. Further mechanistic studies, especially on the ligand effects, further investigation of the scope of the syntheses of highly functionalized bioactive natural and unnatural compounds, and application to enantioselective variants are ongoing in our group.

Experimental Section

General Procedure for the Pt-Catalyzed Direct Amination Using Arylamines (Table 4). To a solution of Pt(cod)Cl_2 (3.8 mg, 0.010 mmol, 0.5 mol %) and Xantphos (5.9 mg, 0.010 mmol, 0.5 mol %) in DMF (0.4 mL) were added cinnamyl alcohol (**1a**, 265.4 mg, 2.0 mmol) and aniline (**3a**, 278.4 mg, 3.0 mmol, 1.5 equiv). The reaction was heated using a CEM Discover single-mode microwave reactor (standard mode) for 1 h. The resulting mixture was directly purified by flash column chromatography (silica gel, hexane/EtOAc = 45/1) to afford **4aa** as a colorless oil (387.2 mg, 88%) and **5aa** as a colorless oil (38.8 mg, 6%).

General Procedure for the Pt-Catalyzed Direct Amination Using Alkylamines (Table 7). To a solution of Pt(cod)Cl_2 (7.6 mg, 0.020 mmol, 1.0 mol %) and DPEphos (21.6 mg, 0.040 mmol, 2.0 mol %) in toluene (0.4 mL) were added cinnamyl alcohol (**1a**, 265.0 mg, 2.0 mmol) and cyclohexylamine (**6e**, 295.4 mg, 3.0 mmol, 1.5 equiv). The reaction was heated using CEM Discover single-mode microwave reactor (standard mode) for 2 h. The resulting mixture was directly purified by flash column chromatography (silica gel, hexane/EtOAc/Et_3N = 20/5/1) to afford **7ae** as a colorless oil (357.8 mg, 85%) and **8ae** as a colorless oil (48.2 mg, 7%).

Synthesis of Pt(xantphos)Cl_2 (A). Pt(cod)Cl_2 (120 mg, 0.32 mmol) and Xantphos (186 mg, 0.32 mmol, 1.0 equiv) were dissolved in $CHCl_3$ (20 mL). After being stirred at room temperature for 1.5 h, the solvent was removed under reduced pressure. The residue was washed with hexane/CH_2Cl_2 (10/1) (10 mL × 3) and dried to afford Pt(xantphos)Cl_2 as a white solid (264 mg, 0.31 mmol, 97%); ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 7.62 (d, J = 7.7 Hz, 2H), 7.48−7.34 (m, 10 H), 7.26−7.19 (m, 2H), 7.16−7.08 (m, 4H), 7.06−6.97 (m, 8H), 1.86 (s, 6H, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 35 °C): δ 6.60 (s with Pt satellite, $^1J_{P-Pt}$ = 3694 Hz); ^{31}P{^{1}H} NMR (121 MHz, DMF-d_7, 35 °C): δ 7.14 (s with Pt satellite, $^1J_{P-Pt}$ = 3669 Hz); MS (FAB) m/z 773 ([M-Cl_2]$^+$); IR (KBr, ν/cm^{-1}) 3054, 3019, 2970, 2924, 2857, 1480, 1434, 1403, 1220, 1096, 753, 740, 706, 692, 533; mp >300 °C (measurement limit); Anal. Calcd for $C_{39}H_{32}Cl_2OP_2Pt_4 \cdot CH_2Cl_2$: C, 51.68; H, 3.69; Found: C, 52.04; H, 3.35.

Synthesis of Pt(η^2-C_3H_5OH)(xantphos) (B). A solution of Pt(xantphos)Cl_2 (244 mg, 0.29 mmol) and allyl alcohol (**1b**, 142 mg, 2.5 mmol, 8.5 equiv) in THF (4.5 mL) was stirred at room temperature for 30 min. Then, an aqueous solution (2.0 mL) of $NaBH_4$ (55 mg, 1.5 mmol, 5.0 equiv) was added to the solution. After being stirred at the same temperature for 5 h, the mixture was concentrated under reduced pressure and the resulting solid was extracted with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the resulting brown solid was washed with hexane/CH_2Cl_2 (10/1) (5 mL × 2) to give Pt(xantphos)(η^2-C_3H_5OH) as a brown solid (239 mg, 0.27 mmol, 94%); ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 7.58−7.44 (m, 8H, *aromatic*), 7.25−7.05 (m, 8H, *aromatic*), 7.00−6.85 (m, 6H, *aromatic*), 6.82−6.70 (m, 4H, *aromatic*), 4.06−3.93 (m, 1H, C*H*HOH), 3.65−3.49 (m, 1H, CH*H*OH), 3.44−3.33 (m, 1H, CH_2=C*H*CH_2), 2.61−2.50 (m, 1H, C*H*H=CH), 2.50−2.34 (m, 1H, CH*H* = CH_2), 1.47 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 0.96 (dd, J = 8.0, 3.5 Hz, 1H, O*H*); ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 35 °C): δ 19.8 (d with Pt satellite, $^2J_{P-P}$ = 51.4 Hz, $^1J_{Pt-P}$ = 3687 Hz), 18.1 (d with Pt satellite, $^2J_{P-P}$ = 51.4 Hz, $^1J_{P-Pt}$ = 3508 Hz); ^{31}P{^{1}H} NMR (121 MHz, DMF-d_7, 35 °C): δ 19.5 (d with Pt satellite, $^2J_{P-P}$ = 52.1 Hz, $^1J_{Pt-P}$ = 3679 Hz), 17.6 (d with Pt satellite, $^2J_{P-P}$ = 51.1 Hz, $^1J_{Pt-P}$ = 3490 Hz); IR (KBr, ν/cm^{-1}) 3419, 3053, 2967, 2922, 1434, 1408, 1230, 1096, 744, 693, 534, 512; MS (FAB) m/z 815 ([M−OH+H]$^+$), 773 (M -C_4H_5OH); mp. 217.2−219.4 °C (decompose); Anal. Calcd. for $C_{42}H_{38}O_2P_2Pt$: C, 60.65; H, 4.60. Found: C, 60.31; H, 4.43.

Synthesis of [Pt(η^3-allyl)(xantphos)]OTf ($\mathbf{D_{OTf}}$). Allyltributylstannane (55 mg, 0.165 mmol, 1.1 equiv) was added to a suspension of Pt(xantphos)Cl_2 (136 mg, 0.161 mmol) in THF (20 mL) at room temperature. This solution was added to AgOTf (42 mg, 0.161 mmol, 1.0 equiv) in a Schlenk tube. After being stirred at the same temperature for 5 h, the mixture was concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and the filtrate was concentrated. The resulting solid was washed with $CHCl_3$/hexane (1/10) (10 mL × 5) to remove $ClSnBu_3$ salt and then dried under reduced pressure to afford [Pt(xantphos)(η^3-allyl)]OTf as a white solid (130 mg, 0.135 mmol, 84%); ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 7.65 (d, J = 7.7 Hz, 2H, aromatic), 7.50−6.98 (m, 20H, aromatic), 6.61 (t, J = 8.3 Hz, 2H, aromatic), 5.75−5.45 (m, 1H, allylic C*H*), 3.59−3.48 (br, 2H, allylic CH_2), 3.06−2.82 (m, 2H, alllylic CH_2), 1.81 (s, 3H, CH_3), 1.59 (s, 3H, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 35 °C): δ 1.24 (s with Pt satellite, $^1J_{P-Pt}$ = 4179 Hz); ^{31}P{^{1}H} NMR (121 MHz, DMF-d_7, 35 °C): δ 0.85 (s with Pt satellite, $^1J_{Pt-P}$ = 4210 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, 35 °C); δ −79.1; IR (KBr, ν/cm^{-1}) 3069, 3055, 2965, 2925, 1436, 1413, 1266, 1223, 1150, 1097, 1030, 753, 695, 637; MS (FAB) m/z 814 ([M-OTf]$^+$), 773; mp. 257.0−257.8 °C (decompose); Anal. Calcd for $C_{43}H_{37}F_3O_4P_2SPt \cdot CHCl_3$: C, 48.79; H, 3.54; Found: C, 48.70; H, 3.31.

Structure Determination and Refinement. The structure was solved by direct methods (SIR-92) and expanded using Fourier techniques (DIRDIF-99). The structure was refined on F^2 by full-matrix least-squares methods, using SHELXL-97. The non-hydrogen atoms were anisotropically refined and all H-atoms were isotropically refined using the riding model. The function minimized was $[\Sigma\omega(F_o^2 - F_c^2)^2]$ ($\omega = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.0149P]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with σ^2 (F_o^2) from counting statistics. The function $R1$ and $\omega R2$ were $(\Sigma||F_o| - |Fc||)/\Sigma|Fo|$ and $[\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma(\omega F_o^4)]^{1/2}$, respectively, and $R1$ and $wR2$ are 0.0616 and 0.1612 for 9521 reflections with $I > 2.0\sigma(I)$, respectively. All hydrogen atoms for each complex were placed in calculated positions (C-Hsp^2 = 0.95 Å, U_{iso}(H) = 1.2*U_{eq}(C) Å^2, $C_{sp}{}^3$-H(CH_2) = 0.98 Å, U_{iso}(H) = 1.2U_{eq}(C) Å^2) and kept fixed. All calculations ware performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research in a Priority Area (No. 20037040, "Chemistry of Concerto Catalysis") and Grant-in-Aid for Scientific Research (B) (21390003) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and Mitsubishi Chemical Corporation Foundation. Some preliminary calculations were performed on the IBM p570 server in Mitsui chemicals Inc. through the courtesy of its computational science department.

Supporting Information Available: Experimental procedures, characterization of the products with ^{1}H and ^{13}C NMR spectra, ^{1}H and ^{31}P{^{1}H} NMR studies, computational data, other detailed results and discussion (PDF); X-ray crystallographic data of $\mathbf{D_{OTf}}$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9046075