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Why Platinum Catalysts Involving Ligands with Large Bite Angle Are so Efficient in the Allylation of Amines: Design of a Highly Active Catalyst and Comprehensive Experimental and DFT Study

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Abstract: The platinum-catalyzed allylation of amines with allyl alcohols was studied experimentally and theoretically. The complexes [Pt(η^3-allyl)(dppe)]OTf (**2**) and [Pt(η^3-allyl)(DPP-Xantphos)]PF_6 (**5**) were synthesized and structurally characterized, and their reactivity toward amines was explored. The bicyclic aminopropyl complex [Pt($CH_2CH_2CH_2NHBn$-κ-*C*,*N*)(dppe)]OTf (**3**) was obtained from the reaction of complex **2** with an excess of benzylamine, and this complex was shown to be a deactivated form of catalyst **2**. On the other hand, reaction of complex **5** with benzylamine and allyl alcohol led to formation of the 16-VE platinum(0) complex [Pt(η^2-C_3H_5OH)(DPP-Xantphos)] (**7**), which was structurally characterized and appears to be a catalytic intermediate. A DFT study showed that the mechanism of the platinum-catalyzed allylation of amines with allyl alcohols differs from the palladium-catalyzed process, since it involves an associative ligand-exchange step involving formation of a tetracoordinate 18-VE complex. This DFT study also revealed that ligands with large bite angles disfavor the formation of platinum hydride complexes and therefore the formation of a bicyclic aminopropyl complex, which is a thermodynamic sink. Finally, a combination of **5** and a proton source was shown to efficiently catalyze the allylation of a broad variety of amines with allyl alcohols under mild conditions.

Keywords: allylation · density functional calculations · homogeneous catalysis · platinum · reaction mechanisms

Introduction

Synthesis of allyl amines is an active area of research because of their importance as building blocks in organic synthesis and their occurrence in many biologically active and natural compounds.[1–3] Over the last two decades, many efforts have been devoted to the development of economically viable catalytic procedures allowing their production from simple and inexpensive starting materials. Among various synthetic approaches, transition-metal-catalyzed allylation processes, which involve a coupling reaction between an amine and the tertiary carbon atom of the allyl moiety, emerged as the most attractive method.[4,5] Though complexes of many transition metals (Ni, Pd, Pt, Mo, W, Ir, Ru) were shown to catalyze this coupling, most studies focused on the use of palladium complexes as catalysts and activated allylic alcohols as substrates. Initially, the introduction of a good leaving group on the allylic alcohol (carboxylate, carbonate, phosphate, or related derivatives) was necessary to overcome the poor leaving ability of the OH group. More recently, direct use of allyl alcohols as substrates was sought in order to make these C–N coupling reactions much more attractive from an environmental and economical point of view.[6] Efficient catalysts featuring palladium[7–16] and iridium,[17,18] were devised but in most cases the presence of an activator (usually a Lewis acid) was still needed to facilitate departure of the OH group.[18–34] Two years ago, we reported on a complete mechanistic study of the allylation of primary amines catalyzed by palladium(0) complexes,[35] and we showed that the use of a significant amount of Lewis acid (at least in the case of palladium) is not a prerequisite provided that the ligands employed display a strong π-accepting capacity to facilitate the release of substrates from the intermediate 16-valence-electron(VE) complexes, and that traces

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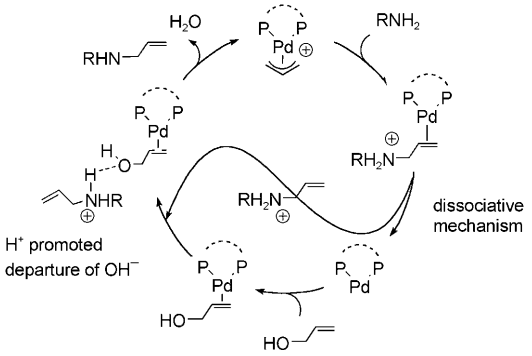
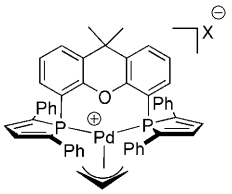
of H^+ are present to promote the release of water. The general scheme of this coupling is depicted in Scheme 1.



Scheme 1. Palladium-catalyzed allylation of primary amines.

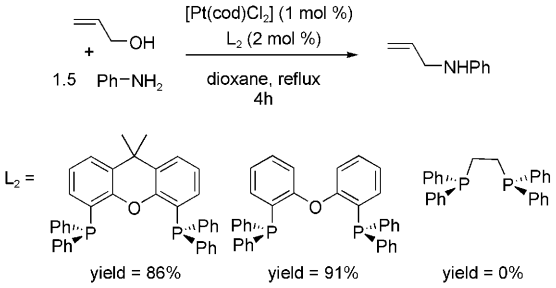


Scheme 2. [Pd(η^3-allyl)(DPP-Xantphos)]X.

On the basis of these findings we then developed a very efficient catalytic system for the allylation of aryl amines with allyl alcohols or allyl ethers.[14,36] This catalytic system, which relies on the use of large-bite-angle ligand DPP-Xantphos (Scheme 2), could achieve complete allylation of aniline at room temperature with 0.1 mol% of catalyst. However, as observed with other palladium complexes, only a very limited scope of amines (such as aryl amines and a handful of secondary amines) could be converted.

In 2007 Ohshima, Mashima et al. reported on the successful in situ combination of bidentate phosphorus ligands with the $PtCl_2$ fragment as catalyst in the direct allylation of amines with allyl alcohols in refluxing dioxane.[37,38] Contrary to palladium catalysts, these platinum complexes exhibited broad substrate compatibility, and alkyl amines could be coupled with allyl alcohols to give mono-allyl amines with a good selectivity. Importantly, they also evidenced an interesting correlation between ligand bite angle and catalytic activity. Thus, whereas complexes featuring bidentate ligands with a standard bite angle (between 85 and 95°) were found to be almost inactive (conversion yields of less than 30% for aniline after 4 h in refluxing dioxane), complexes bearing ligands such as DPEphos (106°) and Xantphos (108°) were very efficient catalysts (91 and 86%, respectively, for the conversion of aniline; Scheme 3). Though no exhaustive mechanistic studies were undertaken, Ohshima, Mashima et al. concluded that the mechanism of this transformation would probably be similar to that depicted in Scheme 1 for palladium catalysts.

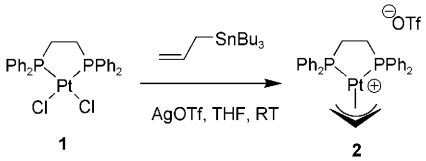
All these observations and our long-standing interest in this important synthetic transformation prompted us to launch a mechanistic study combining DFT calculations with stoichiometric and catalytic experiments. We show that 16- and 18-VE platinum(0) complexes are involved as intermediates in an associative process, contrary to the palladium-catalyzed allylation reaction, which only involves 16- and 14-VE intermediates. We also explain why the outcome of the transformation is indeed highly dependant on the geometry of the ligand, and why this geometry affects the accessibility of platinum hydride complexes. In turn, stoichiometric and catalytic reactions allowed us to establish the existence of a deactivation process involving formation of 16-VE cationic hydridopalladium complexes. Finally, experimental and theoretical findings were successfully exploited to develop the most efficient and versatile catalyst system so far.



Scheme 3. Platinum-catalyzed allylation of aniline.

Results and Discussion

Reactivity of [Pt(η^3-allyl)(dppe)]OTf toward amines: formation of a bicyclic aminopropyl complex: During their study, Ohshima, Mashima et al. found that the in situ combination of the 1,2-bis(diphenylphosphanyl)ethane (dppe) ligand with a source of $PtCl_2$ resulted in no catalytic activity.[37] However, since the [$PtCl_2$(dppe)] complex is not involved in the proposed catalytic cycle, we investigated the reactivity of the corresponding cationic platinum allyl complex [Pt(η^3-allyl)(dppe)]$^+$ (**2**).[39] Complex **2** was readily obtained from the reaction of [$PtCl_2$(dppe)] (**1**) with allyltributyltin in the presence of AgOTf as chloride abstractor in THF at room temperature (Scheme 4). Complex **2**, which was isolated as an air-stable, gray powder, was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystal structure analysis.



Scheme 4. Synthesis of [Pt(η^3-allyl)(dppe)]OTf (**2**).

The reactivity of **2** toward primary and secondary amines such as aniline, benzylamine, *n*-butylamine, and benzylmethylamine was then examined. Only when the temperature is above 50°C does a reaction take place. In each case, a

new complex was formed quantitatively after two hours of heating, as shown by ^{31}P NMR spectroscopy. All these new complexes display similar spin system patterns with two magnetically inequivalent phosphorus atoms exhibiting very different $^{1}J_{Pt,P}$ coupling constants. For example, compound **3**, formed on reaction with benzylamine, is characterized by two singlets with platinum satellites at δ(toluene) = 49.8 ppm ($^{1}J_{Pt,P}$ = 1737 Hz) and δ(toluene) = 38.5 ppm ($^{1}J_{Pt,P}$ = 3714 Hz). According to the proposed mechanism, we first postulated that this complex could be the cationic 16-VE complex [Pt(dppe)(η^2-benzylammonium)]$^+$ resulting from nucleophilic attack of the amine on the allyl ligand. However, two important NMR data were found to be inconsistent with this proposal. First, the different magnitudes of the two $^{1}J_{Pt,P}$ coupling constants strongly suggests that the two phosphorus atoms of dppe are located *trans* to ligands having very different electronic properties.[40] Furthermore, the lack of signals for vinylic protons in the ^{1}H NMR spectrum clearly indicates that this species contains neither an allyl fragment nor a double bond. The formulation of complex **3** was established by a X-ray diffraction study on brown single crystals grown by diffusion of hexanes into a saturated solution of **3** in dichloromethane at room temperature (Figure 1). Crystal data and structural refinement details for

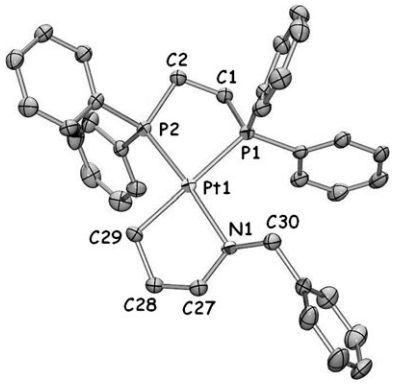
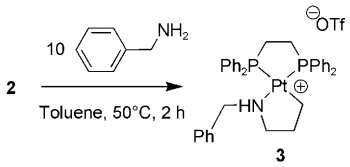


Figure 1. View of one complex cation of [Pt($CH_2CH_2CH_2$NHBn-κ-*C*,*N*)(dppe)]OTf (**3**). The numbering is arbitrary and different from that used in NMR spectra. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.3053(8), Pt1–P2 2.2307(8), P1–C1 1.830(3), C1–C2 1.542(4), P2–C2 1.837(3), Pt1–N1 2.134(2), N1–C30 1.490(4), N1–C27 1.499(4), C27–C28 1.507(4), C28–C29 1.528(4), Pt1–C29 2.096(3); P2-Pt1-P1 85.63(3), C27-N1-Pt1 109.0(2), N1-C27-C28 107.4(2), C27-C28-C29 108.6(3), C28-C29-Pt1 106.5(2), C29-Pt1-N1 82.7(1).

complex **3** are presented in Table 1. This showed that **3** is not the expected 16-VE complex but a bicyclic compound in which the dppe ligand is coordinated to a platinum aminopropyl fragment (Scheme 5). During their studies on the reactivity of cationic [Pt(allyl)(DPCB)] complexes (DPCB = diphosphinidenecyclobutene), Ozawa et al. isolated a similar complex on reaction with aniline at 50 °C,[41] the constitution of which was established on the basis of NMR data.

Table 1. Crystallographic data for **3**, **5**, and **7**.

	3	**5**	**7**
empirical formula	$C_{36}H_{37}NP_2Pt$ ·CF_3O_3S	$C_{50}H_{41}OP_2Pt$ ·PF_6·$3CH_2Cl_2$	$C_{50}H_{42}O_2P_2Pt$ ·CH_2Cl_2·C_3H_6O
M_r	890.77	1314.61	1074.87
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$Pccn$	$P\bar{1}$
a [Å]	16.778(1)	26.901(1)	12.011(1)
b [Å]	11.396(1)	15.131(1)	13.184(1)
c [Å]	18.459(1)	25.864(1)	16.089(1)
α [°]	90.00	90.00	102.534(1)
β [°]	97.226(1)	90.00	96.772(1)
γ [°]	90.00	90.00	104.360(1)
V [Å]	3501.4(4)	10527.7(9)	2369.3(3)
Z	4	8	2
ρ_{calcd} [g cm^{-3}]	1.690	1.659	1.507
μ [mm^{-1}]	0.421	0.312	0.319
crystal size [mm]	0.30×0.30×0.10	0.44×0.08×0.08	0.30×0.30×0.28
reflns collected	27902	82151	31550
unique reflns (R_{int})	10142 (0.0422)	12052 (0.0533)	13756 (0.0426)
R [$F>4\sigma(F)$]	0.0323	0.0378	0.0363
R_{wF} (all F^2)	0.0695	0.1124	0.1127
GOF	1.006	1.087	1.067



Scheme 5. Formation of the bicyclic aminopropyl platinum complex **3**.

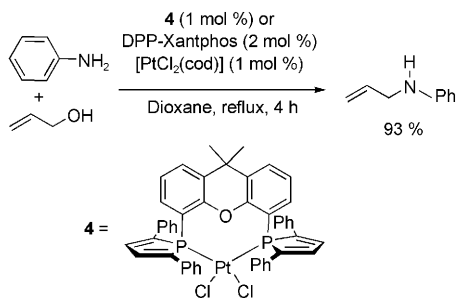
Complex **2** was subjected to catalytic conditions. Quite unexpectedly we found that, contrary to dichloro platinum complex **1**, complex **2** could catalyze the coupling reaction. Thus, benzylamine was converted to the corresponding allylbenzylamine with a low but significant yield of 15% when the reaction was conducted at 50 °C for 24 h with 1 mol% of catalyst (Scheme 6). Interestingly, 10% of the allyl amine was already formed after 2 h, but only 18% was obtained after 96 h. Two competitive pathways are clearly involved: the catalytic cycle and a deactivation process. Importantly, only the formation of complex **3** was observed during the catalysis, as shown by ^{31}P NMR spectroscopy. More drastic conditions (100 °C for 24 h) led to better conversion (47%).

Finally, similar catalytic experiments were conducted with isolated bicyclic aminopropyl complex **3**. No conversion was detectable after 24 h at 50 °C, and only 9% conversion was obtained after 24 h at 100 °C. These results prove that complex **3** is not an intermediate of the catalytic cycle but rather

Scheme 6. Complex **2** as catalyst for allylation of benzylamine.

the thermodynamically favored product of a deactivation pathway.

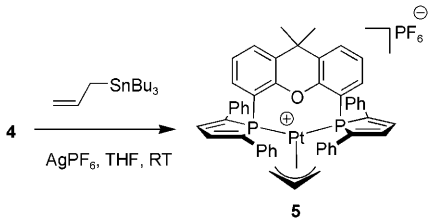
Reactivity of [Pt(η³-allyl)(DPP-Xantphos)]PF$_6$ toward benzylamine: isolation of a 16-VE complex with η²-coordinated allyl alcohol: To establish an additional experimental comparison between the dppe ligand and large-bite-angle ligands, we turned our attention to the catalytic activity of platinum complexes of DPP-Xantphos. Previous structural studies with cationic palladium allyl complexes showed that the DPP-Xantphos ligand has a wider bite angle than the classical Xantphos (116.08(4)° for [Pd(η³-allyl)(DPP-Xantphos)]OTf and 108.11(7)° for [Pd(η³-allyl)(Xantphos)]-OTf),[14,42] probably due to the steric crowding provided by the two diphenylphosphole moieties. We therefore postulated that platinum complexes of this ligand could be efficient catalysts. A first series of experiments was carried out under the same experimental conditions as those used by Ohshima, Mashima et al. in the allylation of aniline. The combination of DPP-Xantphos with [PtCl$_2$(cod)] proved to be slightly superior to the DPEphos- and Xantphos-based catalysts: 93% conversion was reached after 4 h in refluxing dioxane with 1 mol% of catalyst (Scheme 7; cf. 91% for DPEphos-based catalyst and 86% for Xantphos-based catalyst). Similar results were obtained with isolated [PtCl$_2$(DPP-Xantphos)] (**4**), prepared separately by reaction of DPP-Xantphos with [PtCl$_2$(cod)] in toluene at 100°C for 12 h. Complex **4** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystal structure analysis.



Scheme 7. Formation of allylaniline with [PtCl$_2$(DPP-Xantphos)].

Having shown, in the case of dppe, that cationic platinum allyl complexes are more efficient catalysts, we synthesized [Pt(η³-allyl)(DPP-Xantphos)]PF$_6$ (**5**). This complex was readily synthesized by using a similar procedure to that used for the synthesis of **2** and fully identified by means of NMR spectroscopy and elemental analysis (Scheme 8). Its formulation was further confirmed by X-ray structure analysis (Figure 2) on crystals grown by diffusion of hexanes into a saturated solution of **5** in dichloromethane. The most significant geometrical feature is its wide bite angle (P-Pt-P 115.98(4)°). Crystal data and structural refinement details for **5** are presented in Table 1.[43]

Reaction of **5** with ten equivalents of benzylamine in toluene at room temperature led to formation of a single new



Scheme 8. Synthesis of [Pt(η³-allyl)(DPP-Xantphos)]PF$_6$ (**5**).

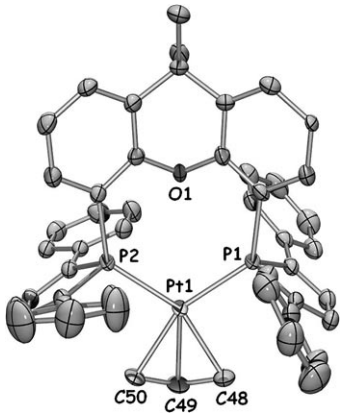
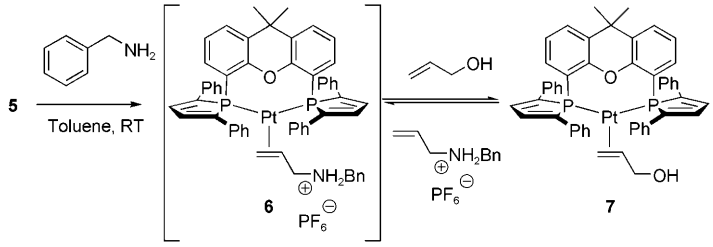


Figure 2. View of one complex cation of [Pt(η³-allyl)(DPP-Xantphos)]PF$_6$ (**5**). The numbering is arbitrary and different from that used in NMR spectra. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–C49 2.153(5), Pt1–C50 2.161(5), Pt1–C48 2.182(4), Pt1–P2 2.304(1), Pt1–P1 2.310(1), C48–C49 1.372(8), C49–C50 1.323(7); P2-Pt1-P1 115.98(4), C49-Pt1-P2 119.9(2), C49-Pt1-P1 123.4(2).

complex. Its ^{31}P NMR spectrum revealed the presence of two magnetically different phosphorus atoms exhibiting two doublets with very close chemical shifts ($\delta_{P_A}=14.1$, $\delta_{P_B}=16.4$ ppm, $^2J_{P_A,P_B}=18.8$ Hz), which suggests that the two phosphorus atoms are probably located *trans* to ligands having similar electronic properties. This complex is therefore undoubtedly not the DPP-Xantphos analogue of bicyclic aminopropyl complex **3**. The comparable magnitude of the two $^1J_{Pt,P}$ coupling constants ($^1J_{Pt,P_A}=3280$, $^1J_{Pt,P_B}=3554$ Hz) led us to propose that complex **6** could be a 16-VE complex with an η²-allylbenzylammonium ligand. The magnitudes of these $^1J_{Pt,P}$ coupling constants are also in agreement with those of reported 16-VE [Pt(η²-olefin)(PR$_3$)$_2$] complexes.[40,44,45]

Unfortunately, complex **6** could not be isolated in pure form from this reaction and could not be satisfactory characterized by means of ^{1}H and ^{13}C NMR spectroscopy because of the presence of excess benzylamine. Evaporation of excess amine from the crude reaction mixture led to slow reformation of precursor **5**. However, a partial ^{13}C NMR spectrum of the crude mixture in [D$_8$]toluene clearly shows the presence of an η²-coordinated allylic fragment (by comparison with the NMR data of complex **7**, vide infra). Further evidence for the formula of **6** was obtained from its reaction with allyl alcohol. Indeed, reaction of a toluene solu-

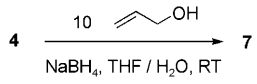
tion of **6** (containing 9 equiv of benzylamine) with 10 equiv of allyl alcohol resulted in formation of complex **7** (**6**/**7** = 30:70 after 15 min) which exhibited very similar ^{31}P NMR data to **6** (Scheme 9). In complex **7**, the two phosphorus



Scheme 9. Reaction of **5** with benzylamine and allyl alcohol.

atoms appear as two doublets with satellites at $\delta_{P_A} = 14.2$ ppm ($^1J_{Pt,P_A} = 3220$, $^2J_{P_A,P_B} = 16.6$ Hz) and $\delta_{P_B} = 15.6$ ppm ($^1J_{Pt,P_B} = 3554$ Hz). The two complexes were found to be in equilibrium, since addition of an excess of allyl alcohol (30 equiv) led to complete disappearance of the ^{31}P NMR signal of **6**. The close similarity between the ^{31}P NMR data of complexes **6** and **7** and those of analogous platinum complexes led us to propose that **7** could be the 16-VE complex [Pd(η^2-allyl alcohol)(DPP-Xantphos)].

Despite varying the experimental conditions, **7** could not be crystallized from the reaction mixture. To validate our hypothesis, **7** was synthesized by a different procedure. Reduction of **4** by $NaBH_4$ in the presence of allyl alcohol afforded **7** in 94% yield as a moderately air stable orange powder (Scheme 10). Complex **7** was fully identified by NMR spectroscopy and its X-ray crystal structure was determined on crystals grown by diffusion of hexanes into a saturated solution of **7** in dichloromethane (Figure 3). Crystal data and structural refinement details for **7** are presented in Table 1.



Scheme 10. Synthesis of **7** from **4**.

Note that heating a solution of **5** or **6** with a tenfold excess of benzylamine did not lead to the formation of a bicyclic aminopropyl analogue of **3**. Importantly, heating a mixture of **6** and **7** in the presence of equimolar amounts of benzylamine and allyl alcohol led to decreased intensity of the ^{31}P NMR signals of both complexes and concomitant appearance of the signal of platinum allyl complex **5**. Analysis of the crude mixture after 6 h by ^1H NMR spectroscopy indicated quantitative coupling of allyl alcohol and benzylamine, that is complexes **6** and **7** are catalytic intermediates. Finally, a catalytic experiment with 1 mol% of **5** confirmed that it is an excellent catalyst: quantitative conversion was obtained after 18 h at 50°C (vs. 18% conversion in 96 h with **2** as catalyst).

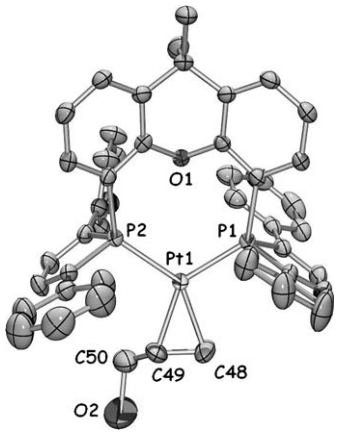


Figure 3. View of one molecule of [Pt(η^2-C_3H_5OH)(DPP-Xantphos)] (**7**). The numbering is arbitrary and different from that used in NMR spectra. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.268(1), Pt1–P2 2.2679(8), Pt1–C48 2.116(4), Pt1–C49 2.121(2), C48–C49 1.430(5); P1-Pt1-P2, 116.96(3).

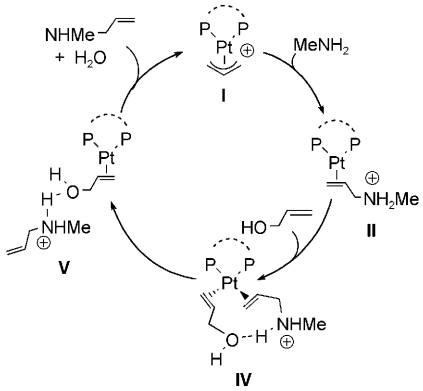
Conclusions on the reactivity of dppe- and DPP-Xantphos-based catalysts: Several conclusions could be drawn from the experiments reported above. First, as expected, cationic platinum allyl complexes are better catalysts than the corresponding $PtCl_2$ derivatives.[39] The second major result is the different reactivity of complexes **2** and **5** toward amines. The most relevant mechanistic discovery is that bicyclic aminopropyl platinum(II) complex **3** is formed from **2**, whereas 16-VE platinum(0) complex **6** is obtained from complex **5**. Complex **6** is in equilibrium with η^2-coordinated allyl alcohol platinum(0) complex **7** when allyl alcohol is added to the solution. Moreover, complex **3** was shown to be a deactivated form of catalyst **2**, while 16-VE complexes **6** and **7** were shown to be intermediates of the catalytic cycle. With these experimental data in hand, a theoretical study was carried out with two aims. First, to propose a mechanism consistent with the experimental data, and second to explain why ligands with wide bite angle are particularly suitable for this transformation.

DFT study: All calculations were carried out with the Gaussian 03 suite of programs.[46] The B3PW91 functional[47,48] was used with the 6-31+G* basis set for all nonmetal atoms and the Hay–Wadt[49] quasirelativistic effective core potential with the valence basis set (441s/2111p/21d) for platinum, augmented with an f polarization function (exponent = 0.993).[50] The structure of the intermediates and transition states were optimized without symmetry constraint. Transition states were identified by their having one imaginary frequency in the Hessian matrix. To take into account the role of the solvent, single-point calculations were carried out on the optimized structures by using the polarized continuum model (PCM)[51–54] with toluene as solvent.

We first addressed determining a catalytic cycle that explains the overall process. Since both synthesized complexes (**2** and **5**) exhibited catalytic activity for the allylation of

benzylamine, calculations on the catalytic cycle with a model of the dppe ligand were performed, because calculations on the xanthene backbone of the DPP-Xantphos ligand is very computationally demanding. The dppe ligand was modeled by the model ligand dppe-H in which the two phenyl groups are replaced by H atoms, and benzylamine is replaced by methylamine. Theoretical results are presented in Scheme 11. The overall mechanism differs significantly from that pertaining to palladium complexes. The first step of this mechanism is nucleophilic attack of the amine on the allyl ligand to form 16-VE complex **II**, which features an η^2-coordinated allylammonium ligand. This step is almost athermic ($\Delta E_{PCM} = -1.8$ kcal mol^{-1}) and requires an activation energy of $\Delta E^{\pm}_{PCM} = 11.3$ kcal mol^{-1}. This nucleophilic attack is followed by exchange of the allylammonium ligand by allyl alcohol. A dissociative mechanism, which is usually proposed for Tsuji–Trost reactions and involves transient formation of 14-VE complex **III**, was ruled out because of the considerable activation energy required to promote dissociation of the allylammonium ligand ($\Delta E^{\pm}_{PCM} = 50.7$ kcal mol^{-1}).[55] Instead, a more favorable associative mechanism was computed. In the first step, complex **II′**, which results from hydrogen bonding between the coordinated allylammonium moiety of **II** and allyl alcohol, evolves to 18-VE complex **IV**. This step is endothermic ($\Delta E_{PCM} = 12.6$ kcal mol^{-1}) and requires an activation energy of $\Delta E^{\pm}_{PCM} = 14.1$ kcal mol^{-1}. In the second step, a small activation energy ($\Delta E^{\pm}_{PCM} = 3.9$ kcal mol^{-1}) is needed to form the η^2-allyl alcohol 16-VE complex **V** via $\mathbf{TS_{IV-V}}$. The last step, which is analogous to that computed for palladium complexes, involves H^+-promoted release of water and allylamine, and reformation of catalytic precursor **I**. This is the rate-determining step and involves an energetic barrier of $\Delta E^{\pm}_{PCM} = 17.6$ kcal mol^{-1}.

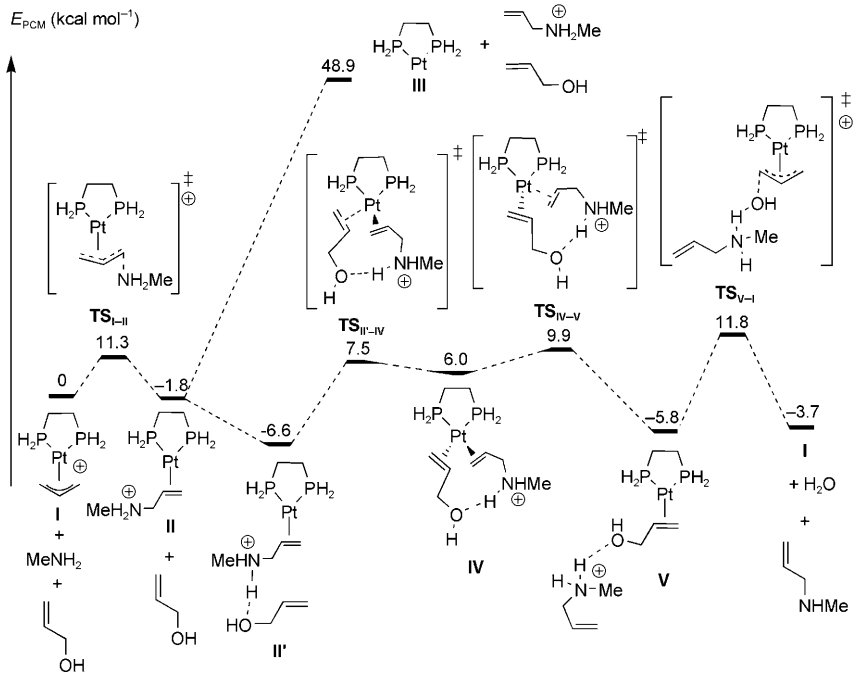
The calculated catalytic cycle is somewhat related to the mechanism proposed for the palladium-catalyzed process,[35] yet differs from it by the ligand-exchange step (Scheme 12). Indeed, it involves an associative mechanism with formation of an 18-VE platinum complex with two η^2-coordinated olefins, whereas in the case of palladium, it involves the formation of a 14-VE complex by a dissociative mechanism.



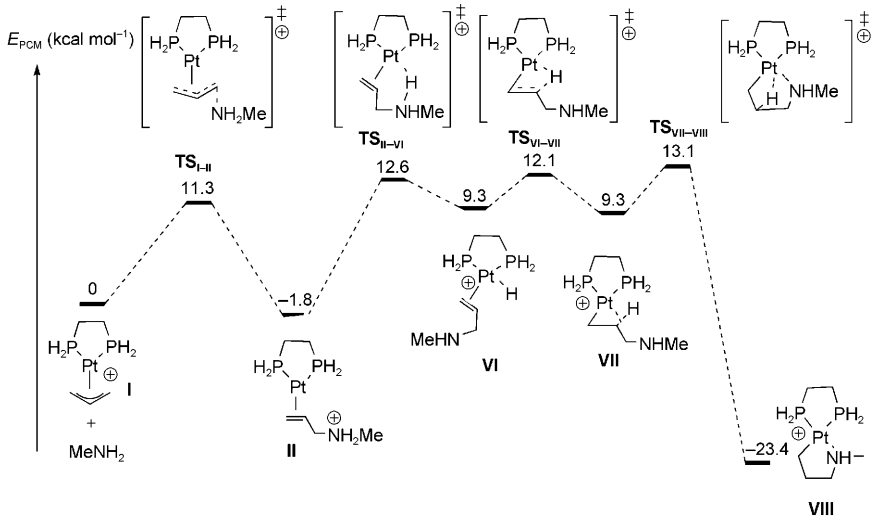
Scheme 12. Proposed mechanism for platinum-catalyzed amine allylation.

The energetic profile of this catalytic cycle (Scheme 11) is in good agreement with the experiments realized with [Pt(η^3-allyl)(DPP-Xantphos)]PF_6. Indeed, the formation of analogues of complexes **II** and **V** could be observed by ^{31}P NMR spectroscopy when benzylamine and allyl alcohol were added to a solution of [Pt(η^3-allyl)(DPP-Xantphos)]PF_6 (**5**) in toluene. Importantly, we also note that an 18-VE complex analogue of complex **IV** could neither be isolated nor even observed, since its formation is endothermic starting either from complex **II** or **V**.

We then tackled the issue of the deactivation of the catalyst observed in the case of the dppe-based complex with formation of bicyclic aminopropyl complex **3**. Formation of bicyclic aminopropyl complex **VIII** (analogue of **3**) can be decomposed into four successive steps (Scheme 13). The first step is still nucleophilic attack of the amine on the allyl fragment of complex **I**. This is followed by proton transfer from the η^2-coordinated allylammonium moiety of complex **II** to the platinum center to afford hydri-



Scheme 11. Energetic pathway accounting for formation of allylmethylamine with complex **I** as catalyst.



Scheme 13. Energetic pathway accounting for formation of bicyclic aminopropyl platinum(II) complex **VIII**.

do species **VI**. This step is endothermic ($\Delta E_{PCM} = 11.1$ kcal mol^{-1}) and requires an activation energy of $\Delta E^{\pm}_{PCM} = 14.4$ kcal mol^{-1}. A view of the transition state $\mathbf{TS_{II-VI}}$ is shown in Figure 4. The geometry of this transition state is close to T-shaped (P1-Pt-C1 96.8, P1-Pt-P2 85.2, P2-Pt-C1 178.0°) and proton transfer occurs on the vacant side of this T-shaped structure (Pt–H 1.75, H–N 1.56 Å). The third step of this process consists of retro β-hydrogen transfer to form cationic alkyl complex **VII**. This step is athermic and requires a very low activation energy ($\Delta E^{\pm}_{PCM} = 2.8$ kcal mol^{-1}). The last step, which is highly exothermic ($\Delta E_{PCM} = -32.7$ kcal mol^{-1}), involves coordination of the amine ligand to the platinum atom to finally form bicyclic aminopropyl platinum complex **VIII**. The overall process requires only small activation energies and is fully consistent with the experimental observations.

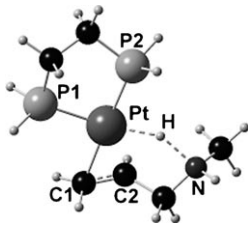
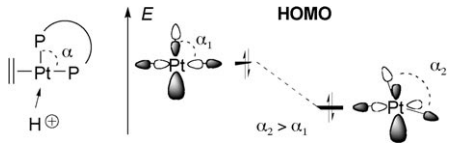


Figure 4. View of transition state $\mathbf{TS_{II-VI}}$ connecting structures **II** and **VI** as given by DFT calculations. Selected bond lengths [Å] and angles [°]: P1–Pt 2.37, P2–Pt 2.28, Pt–C1 2.18, Pt–C2 2.20, C1–C2 1.41, Pt–H 1.75, H–N 1.56; P1-Pt-P2 85.2, P1-Pt-C1 96.8, P2-Pt-C1 178.0, Pt-H-N 148.2. Imaginary frequency at −397.3 cm^{-1}.

Comparison of the two energetic pathways depicted in Schemes 11 and 13 allows the poor catalytic activity of the dppe-based catalyst to be rationalized. These calculations emphasize the importance of formation versus nonformation of complex **VIII**, since it lies at a very low energy ($E_{PCM} = -23.4$ kcal mol^{-1}) compared to all other calculated species and therefore acts as a thermodynamic sink. In the case of the dppe-H model, formation of complex **VIII** and the catalytic cycle are in competition. Indeed, the relative energy of the elimination step, which is the rate-determining step of the catalytic cycle ($\mathbf{TS_{V-I}}$), is comparable to that of formation of hydride complex **VI** ($E_{PCM} = 12.6$ kcal mol^{-1} for $\mathbf{TS_{II-VI}}$ vs. $E_{PCM} = 11.8$ kcal mol^{-1} for $\mathbf{TS_{V-I}}$) and eventually to bicyclic aminopropyl complex **VIII**. This energetic closeness explains why dppe-based complex **2** is a mediocre catalyst, since the catalytic cycle and deactivation are both competitive. Therefore, to design efficient catalysts, the formation of platinum hydride complexes must be disfavored. Experimentally, the formation of bicyclic aminopropyl derivatives was not observed in the case of [Pt(η^3-allyl)(DPP-Xantphos)]PF$_6$ (**5**), and more generally, complexes featuring wide-bite-angle ligands were shown to efficiently catalyze this reaction.[37] Thus, opening of the bite angle seems to strongly disfavor formation of platinum hydride complexes.

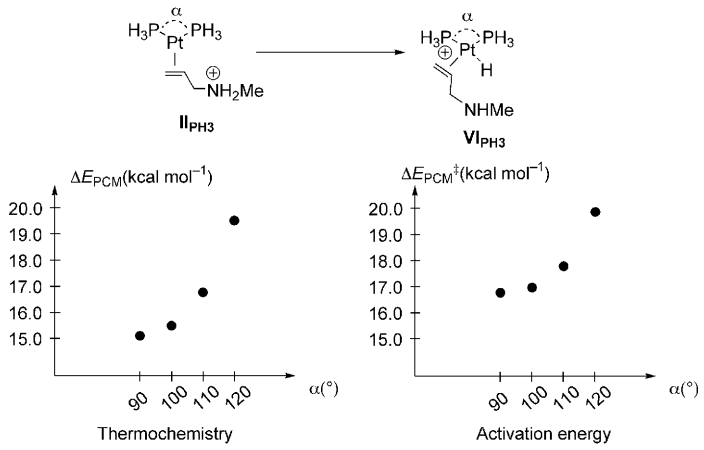
Why do ligands with wide bite angle disfavor protonation at platinum in d^{10} ML$_3$ complexes? To assess the effect of opening the P-Pt-P bite angle on formation of complex **VIII**, we focused on formation of platinum hydride complex **VI** and particularly the geometry of transition state $\mathbf{TS_{II-VI}}$, which adopts a T-shaped structure (Figure 4). A simple MO diagram reveals that, for ML$_3$ d^{10} complexes adopting such a geometry, the HOMO ($2a_1$) is a polarized $d_{x^2-y^2}$ orbital which is mainly developed in the direction of an incoming fourth ligand (H^+ in our case). Importantly, this orbital is antibonding between the ligand lone pairs and the metal d orbital. Indeed, as can be seen from the perturbation diagram in Scheme 14, opening the angle α between two neighboring ligands stabilizes this orbital and therefore reduces the susceptibility of the ML$_3$ fragment to electrophilic attack.



Scheme 14. Qualitative perturbation diagram showing stabilization of the HOMO of a T-shaped ML$_3$ d^{10} complex by increasing the angle between two neighboring ligands.

Support for this qualitative argument was obtained by DFT calculations. The influence of α on the thermodynamics and the kinetics of the proton-transfer step was computed for model complex cation [Pt(PH$_3$)$_2$(η^2-allylmethylammonium)]$^+$[56] at the same level of theory as used to determine the catalytic cycle, with the P-Pt-P angle α set as a constant

($\alpha = 90$, 100, 110, 120°). As proposed, opening of the angle between the two PH_3 ligands results in a more endothermic (from 15.2 to 19.5 kcal mol^{-1} on going from 90 to 120°) and kinetically disfavored process (activation energy ranging from 16.8 to 19.8 kcal mol^{-1} on going from 90 to 120°; Scheme 15).



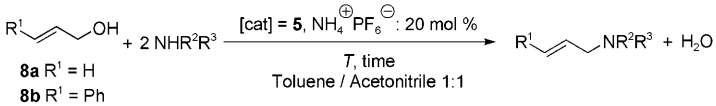
Scheme 15. Effects of opening of the bite angle on the thermochemistry of a proton-transfer process in [Pt(η^2-allylmethylammonium)(PH_3)$_2$].

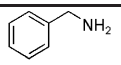
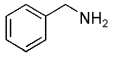
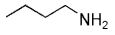
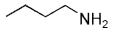
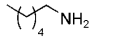
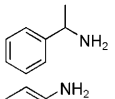
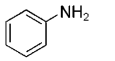
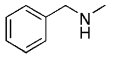
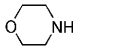
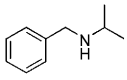
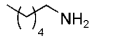
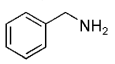
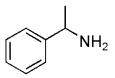
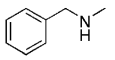
This study on the opening of the bite angle of the [(PH_3)$_2$Pt] fragment is thus in very good agreement with the nonformation of a bicyclic aminopropyl complex when DPP-Xantphos is used as ligand. Furthermore, it explains the increasing activity with increasing P-Pt-P bite angle reported by Ohshima, Mashima et al.[37] Indeed, it results from the disfavored formation of platinum hydride complexes when wide-bite-angle ligands are used and thus deactivation of the catalyst is prevented.

Scope of the allylation reaction with catalyst 5: The encouraging results obtained in the allylation of benzylamine with catalyst **5** prompted us to enlarge the scope of our experimental study. Since the rate-determining step is proton-assisted departure of water, we considered adding a proton source in catalytic amounts. Addition of an ammonium salt indeed resulted in significant enhancement of the reaction rate (optimized with 20 mol% of NH_4PF_6). Without this additive, complete conversion was also reached but with longer reaction times. To optimize the selectivity for the most valuable mono-allyl amine, two equivalents of amine were used for one equivalent of allyl alcohol.

As shown by the results in Table 2, this catalyst system is the most versatile and efficient to date. For allylation of benzylamine and butylamine (Table 2, entries 1 and 3), moderate selectivity was observed for the mono-allyl amine at 50 °C (>10% bis-allyl amine). Decreasing the temperature to 30 °C limited bis-allyl amine formation to 7% for benzylamine and 4% for butylamine, but longer reaction times were required (Table 2, entries 2 and 4). For other primary amines (Table 2, entries 5–7), high selectivity for the mono-allyl amine was observed, even though allylaniline formation required heating at 80 °C (Table 2, entry 7). All secondary amines tested in this catalytic reaction formed tertiary allyl amines in high yields (Table 2, entries 8–10, yields up to 93%), and quantitative conversions were obtained in less than 8 h with low catalyst loadings (0.1–0.5%).

Table 2. Catalytic allylation of aryl and alkyl amines with allyl alcohol (**8a**) and cinnamyl alcohol (**8b**).[a]



Entry	[Cat.] [mol%]	Alcohol	Amine	T [°C]	t [h]	Yield[b] (bis[c]) [%]
1	1.0	**8a**		50	8	66 (16)
2	1.0	**8a**		30	20	81 (7)
3	1.0	**8a**		50	16	79 (10)
4	1.0	**8a**		30	44	85 (4)
5	1.0	**8a**		50	8	81 (7)
6	0.5	**8a**		50	8	96 (<1)
7[d]	0.5	**8a**		80	3	93 (<1)
8	0.5	**8a**		50	4	96
9	0.1	**8a**		50	4	98
10	0.5	**8a**		50	8	93
11	1.0	**8b**		50	16	89 (4)
12	1.0	**8b**		50	12	73 (12)
13	0.5	**8b**		50	12	98 (<1)
14	0.5	**8b**		50	4	97

[a] Reaction conditions: 2 mmol of C_3H_5OH or C_9H_9OH, 4 mmol of R_1R_2NH in 2 mL of toluene/acetonitrile (1:1). [b] Yield of isolated mono-allyl amine. [c] Yield of isolated bis-allyl amine. [d] Only toluene as solvent.

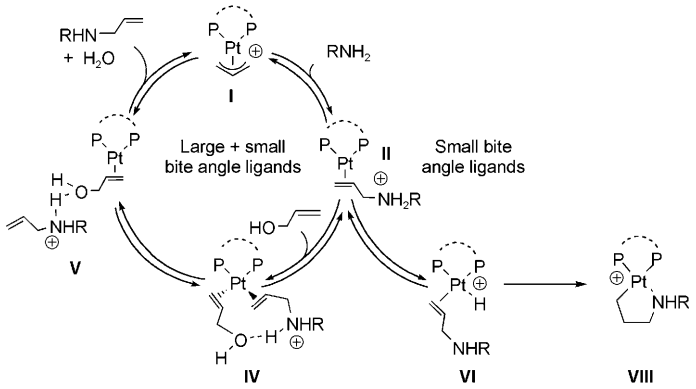
Complex **5** also efficiently promotes regioselective allylation of alkyl amines with cinnamyl alcohol (Table 2, entries 11–14) at 50 °C. Indeed the branched product was never observed in the reaction mixture. Catalyst activity is not much affected by the change in allyl alcohol: complete conversion required only slightly longer times. The selectivity for mono-allyl amine is slightly higher, probably because of the steric hindrance of the mono-allyl amine, which therefore becomes less nucleophilic.

Conclusion

A very efficient catalyst system based on [Pt(η^3-allyl)(DPP-Xantphos)]PF_6 (**5**) was devised for the allylation of amines with allyl alcohols. This system performs well even at low temperatures (30–50 °C) with a broad variety of amines and high selectivity for the desired mono-allyl amine product. To our knowledge, this complex is one of the most versatile and efficient catalysts for allylation of amines with allyl alcohol derivatives.

Moreover, stoichiometric reactions with complexes **2** and **5** allowed monitoring by NMR spectroscopy and isolation of several pertinent species, such as 16-VE platinum(0) complex **7** and bicyclic aminopropyl platinum(II) complex **3**. With [Pt(η^3-allyl)(dppe)]OTf (**2**), a deactivation pathway leading to **3** was found. On the other hand, with [Pt(η^3-allyl)(DPP-Xantphos)]PF_6 (**5**), only 16-VE catalytic intermediates could be observed.

Finally, a theoretical study allowed the experimental findings to be fully rationalized. A catalytic cycle which differs from that proposed for palladium-catalyzed coupling of amines and allyl alcohol was determined. Indeed, in the case of platinum a dissociative ligand-exchange step (via a 14-VE species) is highly unfavorable compared to the associative pathway (via 18-VE species). This theoretical study also emphasized the importance of the ligand bite angle for the activity of the catalyst. Thus, we established that a larger bite angle in diphosphine chelate ligands prevents formation of cationic platinum hydride complexes on protonation, and that formation of these complexes eventually leads to deactivation of the catalyst (Scheme 16). Further studies are underway to exploit the particular geometry of the DPP-Xantphos ligand in other catalytic processes in which the bite angle significantly affects the outcome.



Scheme 16. Proposed mechanism for platinum-catalyzed allylation of amines with allyl alcohol.

Experimental Section

Synthesis: All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry hexanes and tetrahydrofuran were obtained by distillation from Na/benzophenone. Dry dichloromethane and dry toluene were obtained by distilling over P_2O_5 and Na metal, respectively. NMR spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks were used as reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to 85 % H_3PO_4 external reference; sat denotes platinum satellites. DPP-Xantphos was prepared as previously reported.[14] [Pt(cod)Cl_2] (cod = 1,5-cyclooctadiene) and [$PtCl_2$(dppe)] were prepared according to established procedures;[57,58] dppe, allyl alcohol, cinnamyl alcohol, allyltri-*n*-butyltin, sodium borohydride, ammonium hexafluorophosphate, silver trifluoromethanesulfonate (AgOTf), silver hexafluorophosphate, and all amines were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Service d'analyse du CNRS, at Gif sur Yvette, France.

Synthesis of [Pt(η^3-C_3H_5)(dppe)]OTf (2): Allyl(tri-*n*-butyl)tin (47 μL, 1 equiv) and AgOTf (39 mg, 1 equiv) were added to a solution of [$PtCl_2$(dppe)] (100 mg, 0.151 mmol) in THF (10 mL) at room temperature. The mixture was stirred for 4 h and completion was checked by ^{31}P NMR analysis. The solvent was removed under vacuum, dichloromethane (5 mL) was added, and after removal of the silver salts by centrifugation, the filtrate was concentrated. The resulting solid was washed five times with dichloromethane/hexanes (1:10, 10 mL) to remove Cl*S*n*Bu*$_3$ salts. The resulting solid was dried under vacuum to afford a gray solid (97 mg, 82 %). Gray needles of **2** suitable for X-ray structure analysis crystallized on slow diffusion of hexanes into a saturated dichloromethane solution of the complex at room temperature. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 45.7 (s + sat, $^1J_{Pt,P}$ = 3709 Hz); ^{1}H NMR (CD_2Cl_2): δ = 2.52–2.82 (m, ΣJ = 54.5 Hz, 4H; PCH_2), 3.00 (dd + sat, $^3J_{H,H}$ = 13.5, $^3J_{PH}$ = 9.0, $^2J_{Pt,H}$ = 45.1 Hz, 2H; H_{allyl}), 4.78 (m, ΣJ = 13.8 Hz, 2H; H_{allyl}), 5.29 (vsept, ΣJ = 45.6 Hz, 1H; H_{allyl}), 7.49–7.64 ppm (m, 20H; H_{Ph}); ^{13}C NMR (CD_2Cl_2): δ = 28.6 (vdd + sat, ΣJ = 49.4, $^2J_{C,Pt}$ = 51.6 Hz; PCH_2), 63.9 (d + sat, $^2J_{C,P}$ = 29.0 Hz, $^1J_{C,Pt}$ = 83.4 Hz; C_{allyl}), 118.7 (br s + sat, $^1J_{C,Pt}$ = 23.2 Hz; C_{allyl}), 129.3 (d + sat, $^1J_{C,P}$ = 57.0, $^2J_{C,Pt}$ = 50.0 Hz; $C_{ipso\text{-}Ph}$), 129.4 (d + sat, $^1J_{C,P}$ = 57.5, $^2J_{C,Pt}$ = 41.4 Hz; $C_{ipso\text{-}Ph}$), 130.0 (d, $^3J_{C,P}$ = 11.8 Hz; $C_{meta\text{-}Ph}$), 130.1 (d, $^3J_{C,P}$ = 11.6 Hz; $C_{meta\text{-}Ph}$), 132.8 ($C_{para\text{-}Ph}$), 132.9 (d, $^2J_{C,P}$ = 13.3 Hz; $C_{ortho\text{-}Ph}$), 133.1 ppm (d, $^2J_{C,P}$ = 14.1 Hz; $C_{ortho\text{-}Ph}$); elemental analysis calcd (%) for $C_{30}H_{29}F_3O_3P_2PtS$: C 45.98, H 3.73; found: C 46.79, H 4.00.

Synthesis of [Pt($CH_2CH_2CH_2NHBn$-κ-*C*,*N*)(dppe)]OTf (3): Benzylamine (70 μL, 10 equiv) was added to a solution of complex **2** (50 mg, 0.064 mmol) in toluene (5 mL). The mixture was stirred at 50 °C for 2 h. The solution was then totally homogeneous. The solvent was removed by pumping and the residue was washed five times with dichloromethane/hexanes (1:10, 10 mL). After centrifugation, the gray-brown solid was dried under vacuum (39 mg, 68 %). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 38.5 (s + sat, $^1J_{Pt,P}$ = 3714 Hz; *trans* to NHBn), 49.8 (s + sat, $^1J_{Pt,P}$ = 1737 Hz; *trans* to CH_2); ^{1}H NMR (CD_2Cl_2): δ = 1.43–1.72 (m, 2H; $PtCH_2CH_2$), 1.85 (br s, 1H; NH), 2.05–2.60 (m, 5H; 1H from $NHCH_2CH_2$ and 4H from PCH_2CH_2P), 2.64–2.94 (m, 1H; $NHCH_2CH_2$), 3.64–6.79 (m, 1H; $PhCH_2N$), 3.88 (br s, 1H; $PtCH_2$), 4.08–4.21 (m, 1H; $PhCH_2N$), 4.91–5.22 (m, 1H; $PtCH_2$), 6.88 (d, $^3J_{H,H}$ = 6.1 Hz, 2H; $H_{Ph(benzylamine)}$), 7.14–7.28 (m, 3H; $H_{Ph(benzylamine)}$), 7.49–7.69 (m, 14H; $H_{Ph(dppe)}$), 7.72–7.89 ppm (m, 6H; $H_{Ph(dppe)}$)); ^{13}C NMR (CD_2Cl_2): δ = 28.7 (dd, $^1J_{C,P}$ = 34.1, $^2J_{C,P}$ = 6.9 Hz; PCH_2), 29.5 (dd, $^1J_{C,P}$ = 40.5, $^2J_{C,P}$ = 15.7 Hz; PCH_2), 30.9 ($PtCH_2CH_2$), 33.8 (dd, $^2J_{C,P_{cis}}$ = 3.8, $^2J_{C,P_{trans}}$ = 78.8 Hz; $PtCH_2$), 57.6 (m, $NHCH_2CH_2$), 60.3 (m, $PhCH_2N$), 128.7 ($C_{ipso\text{-}Ph(dppe)}$), 129.0, 129.2, 129.5, 129.6 (d, $J_{C,P}$ = 11.5 Hz), 129.8 (d, $J_{C,P}$ = 11.5 Hz), 130.1 (d, $J_{C,P}$ = 10.0 Hz), 130.3 (d, $J_{C,P}$ = 10.1 Hz), 132.4 (m), 132.5 (d, $J_{C,P}$ = 1.5 Hz), 132.7 (d, $J_{C,P}$ = 2.5 Hz), 133.1 (d, $J_{C,P}$ = 11.0 Hz), 133.8 (d, $J_{C,P}$ = 12.2 Hz), 134.2 (d, $J_{C,P}$ = 10.3 Hz), 134.4 (d, $J_{C,P}$ = 9.5 Hz), 136.4 ppm ($C_{ipso\text{-}Ph(benzylamine)}$); elemental analysis calcd (%) for $C_{37}H_{38}F_3NO_3P_2PtS$: C 49.89, H 4.30; found: C 50.09, H 4.34.

Synthesis of [$PtCl_2$(DPP-Xantphos)] (4): DPP-Xantphos (181 mg, 1 equiv) was added to a solution of [$PtCl_2$(cod)] (100 mg, 0.267 mmol) in toluene (20 mL). The mixture was heated and stirred at reflux for 12 h, dried under vacuum, washed with hexanes (30 mL), and filtered. The residue was then dried to yield a yellow solid (245 mg, 97 %). Yellow needles suitable for X-ray structure analysis of complex **4** crystallized on slow diffusion of hexanes into a saturated dichloromethane solution of the complex at room temperature. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −11.8 (s +

sat, $^1J_{Pt,P}=3686$ Hz); ^{1}H NMR (CD_2Cl_2): $\delta=1.41$ (s, 6H; CH_3), 7.03 (vt, 2H, $\Sigma J=16.5$ Hz; $CH_{xanthene}$), 7.08–7.17 (m, 8H; $H_{meta\text{-}Ph}$), 7.18–7.24 (m, 8H; H_{Ph}), 7.28 (d, 2H, $^3J_{H,P}=21.1$ Hz, $H_{\beta\text{-}phosphole}$), 7.41 (d, 2H, $^3J_{H,H}=7.5$ Hz; $CH_{xanthene}$), 7.74 ppm (d, $^3J_{H,H}=7.7$ Hz, 8H; $H_{ortho\text{-}Ph}$) ; ^{13}C NMR (CD_2Cl_2): $\delta=25.5$ (CH_3), 38.7 ($C(CH_3)_2$), 126.1 (vt, $\Sigma J=7.7$ Hz; $CH_{xanthene}$), 127.8 (C_{Ph}), 128.3 (C_{Ph}), 128.4 (C_{Ph}), 129.0 (C_{Ph}), 129.4 (C_{Ph}), 134.0 (vt, $\Sigma J=13.3$ Hz; $C_{xanthene}$P), 136.4 (vt, $\Sigma J=12.6$ Hz; $C_{\beta\text{-}phosphole}$), 138.7 ($C_{Ph}$), 148.1 (d, $^3J_{P,P}=64.3$ Hz; $C_{\alpha\text{-}phosphole}$), 159.4 ppm (CO); elemental analysis calcd (%) for $C_{47}H_{36}Cl_2OP_2Pt$: C 59.75, H 3.84; found: C 60.00, H 3.89.

Synthesis of [Pt(η³-C₃H₅)(DPP-Xantphos)]PF₆ (5): Allyl(tri-*n*-butyltin) (33 μL, 1 equiv) and AgOTf (27 mg, 1 equiv) were added to a solution of the complex **4** (100 mg, 0.106 mmol) in THF (20 mL) at room temperature. The mixture was stirred for 4 h and completion was checked by ^{31}P NMR analysis. The solvent was removed under vacuum, dichloromethane (5 mL) was added, and after removal of the silver salts by centrifugation, the filtrate was concentrated. The resulting solid was washed five times with dichloromethane/hexanes (1:10, 10 mL) to remove Cl*S*n*Bu*$_3$ salts. The corresponding solid was dried under vacuum to yield yellow **5** (104 mg, 92%). ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=-0.4$ (s+sat, $^1J_{Pt,P}=4080$ Hz), −146.2 (sept, $^1J_{P,F}=752$ Hz); ^{1}H NMR (CD_2Cl_2): $\delta=1.59$ (s, 3H; $C(CH_3)_2$), 1.62 (s, 3H; $C(CH_3)_2$), 2.68–2.86 (m, 2H; H_{allyl}), 3.70–3.81 (m, 2H; H_{allyl}), 4.95 (vsept, $\Sigma J=57$ Hz, 1H; H_{allyl}), 7.05–7.34 (m, 16H; H_{Ph}), 7.37–7.66 ppm (m, 14H; H_{Ph}); ^{13}C NMR (CD_2Cl_2): $\delta=26.7$ (C-$(CH_3)_2$), 38.3 ($C(CH_3)_2$), 72.3 (m+sat, $^2J_{C,P}=24$ Hz, $^1J_{Pt,C}=85$ Hz; $CH_{2\,allyl}$), 110.2 (d, $^1J_{P,C}=51$ Hz; $C_{xanthene}$P), 115.7 (CH_{allyl}), 126.5 (vt, $\Sigma J=8$ Hz; C_{Ph}), 126.9 (d, $J_{P,C}=4$ Hz; C_{Ph}), 127.0 (d, $J_{P,C}=4,4$ Hz; C_{Ph}), 129.0 (C_{Ph}), 129.7 (C_{Ph}), 129.8 (C_{Ph}), 129.9 (C_{Ph}), 133.0 (d, $^2J_{C,P}=7.9$ Hz; $C_{ipso\text{-}Ph}$), 133.1 (d, $^2J_{C,P}=7.1$ Hz; $C_{ipso\text{-}Ph}$), 134.7 (vt, $\Sigma J=14.6$ Hz; $C_{\beta\text{-}phosphole}$), 135.1 (vt, $\Sigma J=14.1$ Hz; $C_{\beta\text{-}phosphole}$), 137.7 ($C_{Ph}$), 148.0 (AXX′, $\Sigma J=40.6$ Hz; $C_{\alpha\text{-}phosphole}$), 148.7 (AXX′, $\Sigma J=40.6$ Hz; $C_{\alpha\text{-}phosphole}$), 158.1 ppm (vt, $\Sigma J=7.1$ Hz; CO); elemental analysis calcd (%) for $C_{50}H_{41}F_6OP_3Pt$: C 56.66, H 3.90; found: C 56.17, H 3.91.

Synthesis of [Pt(η²-C₃H₅NH₂(PF₆)Bn)(DPP-Xantphos)] (6): Benzylamine (21 μL, 10 equiv) was added to a solution of **5** (20 mg, 0.019 mmol) in [D$_8$]toluene (1 mL) at room temperature. After few seconds, the mixture became red and homogeneous, and ^{31}P NMR spectroscopy confirmed complete formation of the **6**. ^{31}P{^{1}H} NMR ([D$_8$]toluene): $\delta=14.1$ (d+sat, $^1J_{Pt,P}=3280$, $^2J_{P_A,P_B}=18.8$ Hz; P_A), 16.4 (d+sat, $^1J_{Pt,P}=3554$, $^2J_{P_A,P_B}=18.8$ Hz; P_B), −146.2 (sept, $^1J_{P,F}=752$ Hz); partial ^{13}C NMR ([D$_8$]toluene): $\delta=26.1$ ($CHCH_2NH_2(PF_6)$Bn), 42.5 ($CH_2NH_2(PF_6)$Bn), 50.9 ($NH_2(PF_6)CH_2$Ph), 51.6 ppm (H_2C=$CHCH_2NH_2(PF_6)$Bn).

Synthesis of [Pt(η²-C₃H₅OH)(DPP-Xantphos)] (7): Allyl alcohol (72 μL, 10 equiv) and $NaBH_4$ (20 mg, 5 equiv, in 1 mL of water) were added to a solution of complex **4** (100 mg, 0.106 mmol) in THF (20 mL) at room temperature. The solution, which became homogeneous and turned red, was stirred for few minutes until ^{31}P NMR spectroscopy indicated complete conversion. The mixture was concentrated under vacuum, and the residue was dissolved in dichloromethane and centrifuged in order to remove insoluble salts. The resultant solution was evaporated and the solid was washed with dichloromethane/hexanes (1:10), filtered off and dried to yield desired orange **7** (93 mg, 94%). ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta=14.2$ (d+sat, $^2J_{P,P}=16.6$ Hz, $^1J_{Pt,P}=3220$ Hz), 15.6 (d+sat, $^2J_{P,P}=16.6$ Hz, $^1J_{Pt,P}=3554$ Hz); ^{1}H NMR (CD_2Cl_2): $\delta=0.71$–0.74 (m, 1H; OH), 1.55 (s, 6H; $C(CH_3)_2$), 1.68 (d, 1H, $^3J_{H,H}=8.9$ Hz; H_2C=$CHCH_2OH$), 1.81 (d, 1H, $^3J_{H,H}=5.1$ Hz; H_2C=$CHCH_2OH$), 2.88–3.11 (vqt, 1H, $\Sigma J=59$ Hz; CHCH_2OH), 3.51–3.72 (m, 2H; CH_2OH), 6.95–7.19 (m, 16H; H_{Ph}), 7.21 (dd, 4H, $^3J_{HP}=20.7$ Hz; $H_{\beta\text{-}phosphole}$), 7.43 (d, 2H, $^3J_{H,H}=6.9$ Hz; H_{Ph}), 7.72 (d, 6H, $^3J_{H,H}=7.1$ Hz; H_{Ph}), 7.80 ppm (d, 2H, $^3J_{H,H}=7.1$ Hz; H_{Ph}); ^{13}C NMR (CD_2Cl_2): $\delta=27.0$ ($C(CH_3)_2$), 37.9 ($C(CH_3)_2$), 42.2 (s+sat, $^1J_{C,Pt}=174$ Hz; H_2C=$CHCH_2OH$), 62.7 (s+sat, $^1J_{C,Pt}=238$ Hz; $CHCH_2OH$), 65.4 (s+sat, $^2J_{C,Pt}=33.5$ Hz; CH_2OH), 116.7 (d, $J_{PC}=31$ Hz), 117.2 (d, $J_{P,C}=34$ Hz), 124.6 (d, $J_{P,C}=4.7$ Hz), 127.0 (d, $J_{P,C}=7.6$ Hz), 127.9 (d, $J_{P,C}=3.4$ Hz), 129.2 (d, $J_{P,C}=4.3$ Hz), 131.3 (d, $^2J_{P,C}=12.0$ Hz; $C_{\beta\text{-}phosphole}$), 131.8 (d, $^2J_{P,C}=12.2$ Hz; $C_{\beta\text{-}phosphole}$), 132.1 (d, $^2J_{P,C}=12.1$ Hz; $C_{\beta\text{-}phosphole}$), 132.3 (d, $^2J_{P,C}=9.8$ Hz; $C_{\beta\text{-}phosphole}$), 135.4–135.8 (m, $C_{xanthene}$P), 135.9 (d, $^2J_{P,C}=14.9$ Hz; $C_{ipso\text{-}Ph}$), 137.2 (d, $^2J_{P,C}=3.3$ Hz; $C_{ipso\text{-}Ph}$), 128.0–129.9 (m, $C_{\alpha\text{-}phosphole}$), 159.2 (d, $^2J_{P,C}=11.6$ Hz; CO); elemental analysis calcd (%) for $C_{50}H_{42}O_2P_2Pt$: C 64.44, H 4.54; found: C 64.36, H 4.56.

X-ray crystallography of 2–5 and 7: Crystals were grown as described in the text for **3**, **5**, and **7**, and as in the Experimental Section for **2** and **4**. Data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) at 150 K. The crystal structures were solved with SIR 97[59] and SHELXL97,[60] and ORTEP drawings were made with ORTEP III for Windows.[61] CCDC-687179 (**2**), CCDC-687180 (**3**), CCDC-687181 (**4**), CCDC-687182 (**5**), and CCDC-687183 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for allylation of amines: Complex **5** (21 mg for 1 mol%, 10.5 mg for 0.5 mol%, 2.1 mg for 0.1 mol%) was placed in a Schlenk tube with 65 mg of NH_4PF_6 (20 mol%) and toluene/acetonitrile (1:1, 2 mL). Allyl alcohol (136 μL, 2 mmol) and amine (4 mmol) were then added. The mixture was stirred at the given temperature and for the indicated time (see Table 2). The reaction mixture was then concentrated, water was added (3 mL), and the product was extracted with diethyl ether (3 mL). After conventional workup, the organic layer was purified by flash column chromatography to yield the allyl amines listed in Table 2. The NMR data obtained for the coupling products are in agreement with the corresponding literature (allylbenzylamine,[62] allylbutylamine,[63] allylhexylamine,[64] allyl-1-phenylethylamine,[65] allylbenzylmethylamine,[66] allylmorpholine,[67] allylbenzylisopropylamine,[68] allylaniline and all the coupling products between amines and cinnamyl alcohol[37]).

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[1] R. Bencheikh, R. Chaabouni, A. Laurent, P. Mison, A. Nafti, *Synthesis* **1983**, 685.
[2] M. Johannsen, K. A. Jorgensen, *Chem. Rev.* **1998**, *98*, 1689.
[3] B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921.
[4] J. Tsuji, *Transition Metal Reagents and Catalysis*, Wiley-VCH, Weinheim, **2000**.
[5] B. M. Trost, C. Lee, *Catalytic Asymmetric Synthesis*, Wiley-VCH, New York, **2000**.
[6] J. Muzart, *Eur. J. Org. Chem.* **2007**, 3077.
[7] H. Bricout, J. F. Carpentier, A. Mortreux, *J. Mol. Catal. A* **1998**, *136*, 243.
[8] L. Usui, S. Schmidt, M. Keller, B. Breit, *Org. Lett.* **2008**, *10*, 1207.
[9] Y. Yokoyama, H. Hikawa, M. Mitsuhashi, A. Uyama, Y. Murakami, *Tetrahedron Lett.* **1999**, *40*, 7803.
[10] Y. Yokoyama, H. Hikawa, M. Mitsuhashi, A. Uyama, Y. Hiroki, Y. Murakami, *Eur. J. Org. Chem.* **2004**, 1244.
[11] H. Kinoshita, H. Shinokubo, K. Oshima, *Org. Lett.* **2004**, *6*, 4085.
[12] Y. Kayaki, T. Koda, T. Ikariya, *J. Org. Chem.* **2004**, *69*, 2595.
[13] F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 10968.
[14] G. Mora, B. Deschamps, S. van Zutphen, X. F. Le Goff, L. Ricard, P. Le Floch, *Organometallics* **2007**, *26*, 1846.
[15] O. Piechaczyk, M. Doux, L. Ricard, P. le Floch, *Organometallics* **2005**, *24*, 1204.
[16] C. Thoumazet, H. Grutzmacher, B. Deschamps, L. Ricard, P. le Floch, *Eur. J. Inorg. Chem.* **2006**, 3911.
[17] C. Dubs, T. Yamamoto, A. Inagaki, M. Akita, *Chem. Commun.* **2006**, 1962.
[18] Y. Yamashita, A. Gopalarathnam, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 7508.
[19] Y. Masuyama, J. P. Takahara, Y. Kurusu, *J. Am. Chem. Soc.* **1988**, *110*, 4473.
[20] Y. Masuyama, M. Kagawa, Y. Kurusu, *Chem. Lett.* **1995**, 1121.

[21] S. C. Yang, C. W. Hung, *Synthesis* **1999**, 1747.
[22] S. C. Yang, C. W. Hung, *J. Org. Chem.* **1999**, *64*, 5000.
[23] S. C. Yang, Y. C. Tsai, *Organometallics* **2001**, *20*, 763.
[24] S. C. Yang, Y. C. Hsu, K. H. Gan, *Tetrahedron* **2006**, *62*, 3949.
[25] M. Kimura, Y. Horino, R. Mukai, S. Tanaka, Y. Tamaru, *J. Am. Chem. Soc.* **2001**, *123*, 10401.
[26] M. Kimura, M. Futamata, K. Shibata, Y. Tamaru, *Chem. Commun.* **2003**, 234.
[27] Y. Tamaru, *Eur. J. Org. Chem.* **2005**, 2647.
[28] Y. Tamaru, Y. Horino, M. Araki, S. Tanaka, M. Kimura, *Tetrahedron Lett.* **2000**, *41*, 5705.
[29] X. Y. Lu, L. Lu, J. H. Sun, **1987**, *41*, 245.
[30] X. Y. Lu, X. H. Jiang, X. C. Tao, *J. Organomet. Chem.* **1988**, *344*, 109.
[31] S. C. Tsay, L. C. Lin, P. A. Furth, C. C. Shum, D. B. King, S. F. Yu, B. L. Chen, J. R. Hwu, *Synthesis* **1993**, 329.
[32] I. Stary, I. G. Stara, P. Kocovsky, *Tetrahedron Lett.* **1993**, *34*, 179.
[33] K. Itoh, N. Hamaguchi, M. Miura, M. Nomura, *J. Chem. Soc. Perkin Trans. 1* **1992**, 2833.
[34] T. Satoh, M. Ikeda, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 4877.
[35] O. Piechaczyk, C. Thoumazet, Y. Jean, P. le Floch, *J. Am. Chem. Soc.* **2006**, *128*, 14306.
[36] G. Mora, O. Piechaczyk, X. F. Le Goff, P. Le Floch, *Organometallics* **2008**, *27*, 2565.
[37] M. Utsunomiya, Y. Miyamoto, J. Ipposhi, T. Ohshima, K. Mashima, *Org. Lett.* **2007**, *9*, 3371.
[38] Very few examples of platinum catalyzed allylation of amines with allyl alcohol were found in the literature; they all require the use of Lewis acids: Y. Tsuji, R. Takeuchi, H. Ogawa, Y. Watanabe, *Chem. Lett.* **1986**, 293–294; S-C. Yang, Y-C. Tsai, Y-J. Shue, *Organometallics* **2001**, *20*, 5326–5330.
[39] Platinum allyl complexes have been proposed as active species in this process.[37]
[40] P. S. Pregosin, R. W. Kunz, *Phosphorus and Carbon NMR of Transition Metal Phosphine Complexes*, Springer-Verlag, Berlin, **1979**.
[41] F. Ozawa, T. Ishiyama, S. Yamamoto, S. Kawagishi, H. Murakami, *Organometallics* **2004**, *23*, 1698.
[42] P. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, *J. Am. Chem. Soc.* **2003**, *125*, 5523.
[43] Note that, like in the case of complex **2**, the triflate complex was also prepared but was reluctant to crystallize.
[44] M. Camalli, F. Caruso, S. Chaloupka, E. M. Leber, H. Rimml, L. M. Venanzi, *Helv. Chim. Acta* **1990**, *73*, 2263.
[45] T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, S. Otsuka, *J. Am. Chem. Soc.* **1978**, *100*, 2063.
[46] Gaussian 03, revision C.02, M. J. Frisch, et al. Gaussian, Inc., Pittsburgh, PA, **2004**.
[47] A. D. J. Becke, *J. Phys. Chem.* **1993**, *97*, 5648.
[48] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.
[49] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[50] A. W. Ehlers, M. Bohme, S. Dapprich, A. Gobbi, A. Hollwarth, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111.
[51] V. Barone, R. Improta, N. Rega, *Theor. Chem. Acc.* **2004**, *111*, 237.
[52] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327.
[53] M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, *117*, 43.
[54] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117.
[55] This considerable activation energy results from the significant amount of π backbonding from the 14-VE [$Pt(L)_2$] fragment to the olefin ligand.
[56] We also considered a model of the Xantphos ligand in which the phosphole moieties and the methyl groups are replaced by hydrogen atoms. This Xantphos-PH_2 model is not suitable to reproduce the large bite angle of DPP-Xantphos. Indeed, the calculated [Pt(η^3-allyl)(Xantphos-PH_2)] complex has a P-Pt-P angle of only 99.5° (cf. 115.94(4) for **5**).
[57] G. K. Anderson, H. C. Clark, J. A. Davies, *Inorg. Chem.* **1981**, *20*, 3607.
[58] H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411.
[59] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single-crystal data.
[60] G. M. Sheldrick, SHELXL-97, Göttingen, Germany, **1997**.
[61] L. J. Farrugia, ORTEP-3.
[62] L. Blackburn, R. J. K. Taylor, *Org. Lett.* **2001**, *3*, 1637.
[63] G. B. Gill, G. Pattenden, S. J. Reynolds, *J. Chem. Soc. Perkin Trans. 1* **1994**, 369.
[64] S.-I. Murahash, T. Shimamur, I. Moritani, *J. Chem. Soc. Chem. Commun.* **1974**, 931.
[65] S. G. Davies, J. F. Fox, S. Jones, A. J. Price, M. A. Sanz, T. G. R. Sellers, A. D. Smith, F. C. Teixeira, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1757.
[66] A. R. Abreu, I. Costa, C. Rosa, L. M. Ferreira, A. Lourenco, P. P. Santos, *Tetrahedron* **2005**, *61*, 11986.
[67] Z. Novak, Z. Vincze, Z. Czegeny, G. Magyarfalvi, D. M. Smith, A. Kotschy, *Eur. J. Org. Chem.* **2006**, 3358.
[68] X. L. Hou, B. F. Li, L. X. Dai, *Tetrahedron: Asymmetry* **1999**, *10*, 2319.

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