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Studies on the structure and equilibration of (π-allyl)palladium complexes of phosphino(oxazolinyl)ferrocene ligands

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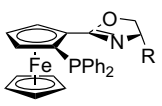
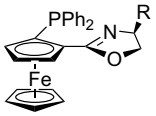
Abstract—The equilibration and catalytic efficiency of (π-allyl)Pd complexes of N,P-chelates (**L**), [Pd(**L**)(η^3-PhCHCHCHPh)]**X**, depending on their counteranions **X** have been studied by NMR spectroscopy and X-ray crystallography [**L**: 1-[4(*S*)-*tert*-butyl-2-oxazolin-2-yl]-2($_P$*S*)-(diphenylphosphino)ferrocene **1**; 1-[4(*S*)-*tert*-butyl-2-oxazolin-2-yl]-2($_P$*R*)-(diphenylphosphino)ferrocene **2**. **X**: Cl^- and PF_6^-]. Among the possible isomeric (π-allyl)Pd complexes, only *endo-syn-syn* **1n** and **2n** and *exo-syn-syn* isomers **1x** and **2x** were observed and the *endo*-isomer was found to be the major one in both cases. The *endo*/*exo* ratio determined in $CDCl_3$ at room temperature was dependent both on the counterions and more so on the N,P-chelates (Cl^-: **1n**/**1x** = 9.8/1; **2n**/**2x** = 5.3/1 vs PF_6^-: **1n**/**1x** = 8.7/1; **2n**/**2x** = 4.6/1). The counteranions significantly affected the rate as well as the enantioselectivity in the palladium catalyzed allylic substitution reaction. In the case of Cl^- counterion, the catalytic reaction proceeded much faster and also provided a higher enantioselectivity compared to the case of the PF_6^- counterion. We have also evaluated the relative thermodynamic stability of the palladium complexes depending on ligands **1** and **2** by an equilibration study and by X-ray crystal structure analysis for the corresponding (π-allyl)palladium complexes. The higher reactivity of the less stable palladium complex of **1** over the more stable palladium complex of **2** is explained by a steric strain-reactivity argument.

1. Introduction

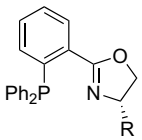
The Pd-catalyzed allylic substitution reaction has been extensively studied since the pioneering work of Tsuji showed that nucleophiles react with (π-allyl)Pd complexes in the presence of ligands.[1] A number of chiral ligands have been developed for the asymmetric version of the reaction.[2] Enantioselectivities of greater than 90% ee can be obtained for certain substrates by employing chiral ligands such as P,P-, N,N-, and N,P-chelates. Significant efforts have also been made to understand the reaction mechanism, including the factors that affect the enantioselectivity.[3] However, there are several unresolved and confusing factors in the reaction mechanism, probably owing to the inherently complex nature of the catalytic reaction. During our study on the development of new ferrocene-based N,P-chelates for the asymmetric allylic alkylation,[4] we observed a significant difference, both in the reactivity and enantioselectivity among the structurally related ligands **1**–**3**.[4a] We were particularly interested in the factors that affect the reactivity and enantioselectivity of the reaction. To understand these factors, we focused our attention on the factors that affect the relative stability and reactivity of the (π-allyl)Pd complexes, which are known to be important intermediates in the catalytic reaction. To this end, we carried out equilibration and structural (NMR and X-ray crystallographic) studies for the (π-allyl)Pd complexes of **1**–**3**. Herein, we report that the counteranions and the steric strain of the palladium complexes affect both reactivity and enantioselectivity in the Pd-catalyzed allylic alkylation reaction.



1 (R = *t*-Bu)
3 (R = *i*-Pr)



2 (R = *t*-Bu)



4 (R = *i*-Pr)

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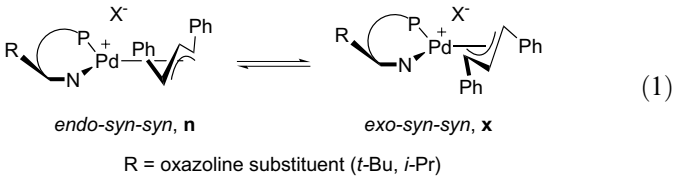
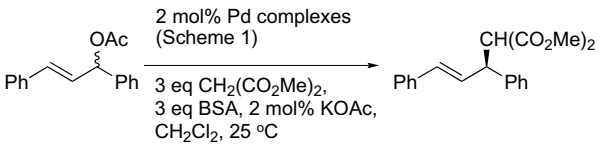
2. Results and discussion

The [(1,3-diphenyl)allyl]Pd complexes of benzene-based N,P-chelate **4** (R = *i*-Pr) undergo rapid equilibration between *endo-syn-syn* and *exo-syn-syn* (π-allyl)Pd complexes (**4n**, **4x**: $X^- = SbF_6^-$)[5] via a π–σ–π mechanism, according to Helmchen et al. (Eq. 1).[6] It has been found that *endo-syn-syn* **4n** is more stable than *exo-syn-syn* **4x** with an equilibrium ratio of 8:1 at room temperature. Based on the larger *trans influence* of the phosphorus over that of the nitrogen ligand and a π-allyl intermediate-like transition structure, the stereochemical outcome can be explained by nucleophilic attack on the allylic carbon *trans* to the phosphorus. They assumed that the *endo* isomer **4n** would be more reactive than the *exo*-isomer **4x** in order to explain the observed high enantioselectivity (98% ee) in the palladium-catalyzed allylic substitution (Eq. 2). However, this assumption may be valid in the case when the counteranion has no effect on the *endo*/*exo* ratio, because the *endo*/*exo* ratio and the enantioselectivity data were obtained by using (π-allyl)Pd complexes of different counteranions in their study (SbF_6^- vs Cl^-). Thus, we first studied how the counteranion of (π-allyl)Pd complexes affected their *endo*/*exo* equilibration and also the enantioselectivity of the catalytic reaction.



endo-syn-syn, **n** *exo-syn-syn*, **x** (1)

R = oxazoline substituent (*t*-Bu, *i*-Pr)

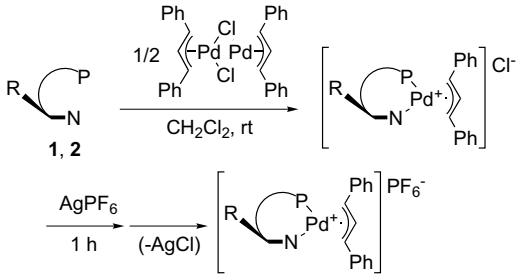


(2)

Assuming that the rate determining step is a nucleophilic attack on the allylic termini and the structural integrity of the (π-allyl)Pd complexes is maintained at the transition state (an early transition state),[3a,f,g] the enantioselectivity is determined by three factors: (1) the regioselectivity of nucleophilic attack against the two allylic termini, (2) the equilibrium ratio between isomeric (π-allyl)Pd complexes, and (3) their relative reactivity. Due to the large *trans influence* of P- over N-ligand, the nucleophiles were believed to attack the allylic carbon *trans* to the P-ligand. To predict enantioselectivity, it is therefore necessary to understand the remaining two factors, (2) and (3).

2.1. Counteranion effects on the equilibration of (π-*allyl*)Pd intermediates

We have studied the equilibration of the [π-(1,3-diphenyl)-allyl]Pd complexes of the diphenylphosphino(oxazolinyl)ferrocenes (DPOFs) **1** and **2** at room temperature by NMR spectroscopy (^1H, ^{13}C, and ^{31}P). The palladium complexes, [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 and [Pd(**2**)(η^3-PhCHCHCHPh)]PF_6, were prepared by using [(η^3-PhCHCHCHPh)PdCl]$_2$ as the palladium source[7] and DPOFs **1** and **2** via the corresponding chloride complexes, [Pd(**1**)(η^3-PhCHCHCHPh)]Cl and [Pd(**2**)(η^3-PhCHCHCHPh)]Cl, as shown in Scheme 1. In contrast to the latter chloride complexes, the former hexafluorophosphate complexes were relatively stable in air and could be isolated in a nearly pure state after a standard extractive work-up procedure. Among the various possible isomeric (π-allyl)Pd complexes due to the relative position between the N,P- and allyl ligands coordinated to Pd (*endo* vs *exo*) and geometrical isomerism of the allyl ligand[8] (*anti* vs *syn*), only two isomeric (π-allyl)Pd complexes, *endo-syn-syn* and *exo-syn-syn* isomers (Eq. 1),[9] were observed in the case of [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 from the NMR analysis. The equilibrium ratio of the *endo*/*exo*-isomers with a PF_6^- counterion was found to be 8.7/1 at room temperature,[10] which is similar to that of Helmchen's SbF_6^--complex of ligand **4**.[6] In the case of the (π-allyl)Pd complexes of Cl^- counterion, [Pd(**1**)(η^3-PhCHCHCHPh)]Cl (prepared according to Scheme 1), the corresponding *endo-syn-syn* isomer was also found to be the major species at room temperature with an *endo*/*exo* ratio of 9.8/1.[10] When we used DPOF **2**, in this case also only two isomeric complexes, *endo-syn-syn* and *exo-syn-syn*, were observed, and the *endo*/*exo* ratios were found to be 4.6/1 and 5.3/1 in the case of the PF_6^- and Cl^- counterions, respectively (Table 1). These results indicate that the counteranions affect the equilibrium ratio of the isomeric [π-(1,3-diphenyl)allyl]Pd complexes but not by as much as the ligands do.



Scheme 1. Synthesis of N,P-chelated (π-allyl)Pd complexes with Cl^- and PF_6^- counteranions.

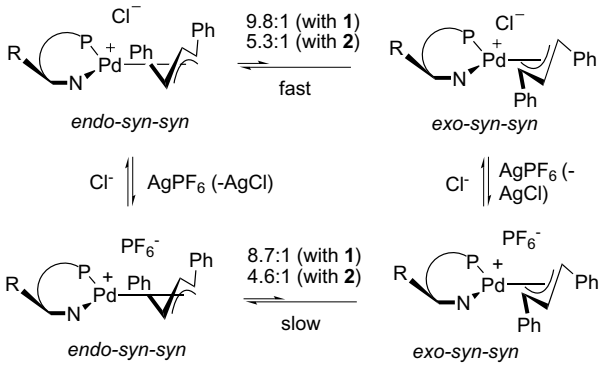
Table 1. Effects of the counteranions on the *endo*/*exo* ratio, reaction time, and enantioselectivity in the Pd-catalyzed allylic alkylation[a]

Pd catalyst[b]		*endo*/*exo*	Reaction time (h)	Yield (%)	Enantioselectivity (% ee)
Ligand	X^-				
1	Cl^-	9.8/1	2	99	78 (*S*)
1	PF_6^-	8.7/1	5	99	69 (*S*)
2	Cl^-	5.3/1	5	73	67 (*S*)
2	PF_6^-	4.6/1			

[a] The catalytic reaction was carried out according to Eq. 2.
[b] The palladium catalysts used were prepared according to Scheme 1.

Togni et al. reported that the counteranions of the (π-allyl)Pd catalysts affect enantioselectivity in the palladium catalyzed allylic amination.[11] They suggested that the counteranion would affect the rate of the equilibration between the isomeric (π-allyl)Pd complexes, which leads to

different enantioselectivities. We studied the equilibration of the (π-allyl)Pd complexes of DPOF **1** to prove experimentally the counteranion effect on the equilibration rate of the isomeric (π-allyl)Pd complexes. When the (π-allyl)Pd complex [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 prepared according to Scheme 1 was analyzed by NMR spectroscopy, the *endo*/*exo* ratio, observed 10 min after dissolving it in $CDCl_3$ (8.7/1), did not change after 7 h at room temperature. This experiment alone does not directly lead to the conclusion that the *endo*/*exo* equilibration is slow in the case of PF_6^- counterion, because the palladium complex [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 was produced from [Pd(**1**)(η^3-PhCHCHCHPh)]Cl by treatment with $AgPF_6$, followed by removal of AgCl precipitate (Scheme 1). In this case, the *endo*/*exo* ratio would gain an equilibrium value starting from the ratio initially reached with Cl^- counterion. As the chloride ion precipitates into the insoluble silver salt, a new equilibrium value would be gained at the end. In order to alleviate such ambiguity, a pure isomeric complex is required. We know that crystallization of [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 gives *endo-syn-syn* **1n** from the X-ray structure analysis (in the following section). When the single crystals were dissolved in $CDCl_3$ at room temperature and analyzed by ^{1}H NMR spectroscopy, the *endo*/*exo* ratio changed rather slowly (10.3/1 after 15 min on mixing with the NMR solvent; 9.4/1 after 1 h). When an equimolar amount of Cl^- was added into the initial palladium complexes containing PF_6^- counterion, the equilibrium ratio instantly reached to a value observed with the Cl^- counterion (9.8/1). These results experimentally confirm that the *endo*/*exo* equilibration is fast in the presence of Cl^- counterion, whereas it is much slower in the presence of PF_6^- only (Scheme 2), as proposed by Togni et al.[11,12]



Scheme 2. Counteranion effects on the equilibration of N,P-chelated (π-allyl)Pd complexes.

2.2. Counteranion effects on the reactivity and enantioselectivity in the palladium catalyzed allylic substitution

Next, we examined whether the counteranions affect the reactivity and/or enantioselectivity of the palladium catalyzed allylic substitution reaction. With 2 mol % of [Pd(**1**)(η^3-PhCHCHCHPh)]Cl prepared in situ from DPOF **1** and the palladium source, [Pd(η^3-PhCHCHCHPh)Cl]$_2$, the catalytic reaction took 2 h at room temperature to obtain the substitution product in 99% yield and with 78% ee (Eq. 2 and Table 1).[13] When [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 was employed as a catalyst in the same catalytic reaction, a longer reaction time for completion (5 h at 25 °C) and a lower enantioselectivity (69% ee) were observed when compared to the case of Cl^- counterion. Thus, the counteranion of the palladium catalysts significantly affects both the reactivity and enantioselectivity of the catalytic reaction.

2.3. Effects of steric strain on the stability and reactivity of the (π-allyl)Pd complexes

The catalytic reaction with DPOF **1** is faster than that with DPOF **3** (>99% conversion after 0.5 h vs 95% conversion after 1.5 h).[4a] The only difference between the two ligands is that the oxazoline substituents are different (*i*-Pr vs *t*-Bu), which suggests that the steric strain of the resulting (π-allyl)Pd complexes may influence the relative stability and reactivity of the reactive intermediates. In order to address how the steric strain affects the stability and reactivity of the palladium intermediates, DPOFs **1** and **2** seem to be particularly suitable: they have opposite planar chirality but same central chiralities, and the opposite planar chirality leads to a structural difference only in the relative position of the Cp–Fe moiety with respect to the N,P-chelated (π-allyl)Pd plane (Fig. 1).

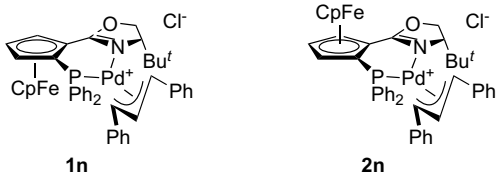
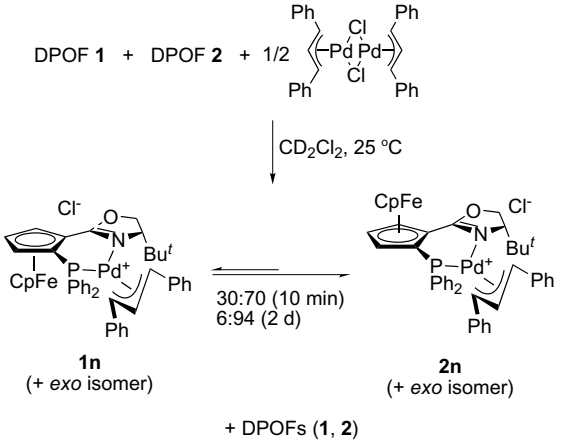


Figure 1. Structural difference between **1n** and **2n**.

As reported before,[4a] the catalytic reaction using DPOF **2** gave the substitution product with the same absolute stereochemistry but with a slower reaction rate than in the case of DPOF **1** (with 2 mol % catalysts at room temperature; <80% conversion after 5 h vs >99% conversion within 0.5 h) (Eq. 2).[14] These results indicate that the Cp–Fe moiety in both ligands may not affect the stereochemical course of the reaction but affects the reaction rate. von Matt et al. suggested that a sterically more encumbered (π-allyl)Pd complex would undergo nucleophilic substitution more readily to relieve its steric strain than a sterically less hindered one does.[3f] This 'steric strain-reactivity argument' is based on two premises: (1) the rate determining step is the nucleophilic attack at one of the allylic termini of (π-allyl)Pd complexes and (2) the structural integrity of the (π-allyl)Pd complexes is maintained at the transition state (early transition state). The difference in the catalytic reactivity in the cases of DPOFs **1** and **2** can be explained by evoking steric influence of the Cp–Fe moiety toward the Pd-bound allylic ligands, which may be relayed through the *tert*-butyl and phenyl groups in the case of DPOF **1**. Considering the structural similarities between DPOFs **1** and **2** except for the relative position of the Cp–Fe moiety,

the steric strain caused by the Cp–Fe moiety can lead to thermodynamically less stable (π-allyl)Pd complexes from DPOF **1** compared to the case of **2**. Due to the increased strain, the (π-allyl)Pd complexes of DPOF **1** undergo substitution more readily than the case of **2**, as was observed.

To assess the relative thermodynamic stability of the [π-(1,3-diphenyl)allyl]Pd complexes of DPOFs **1** and **2**, we carried out an equilibration study. DPOFs **1** and **2** were treated with a dimeric Pd source, $[(\eta^3\text{-PhCHCHCHPh})PdCl]_2$, in a molar ratio of 1.0:1.0:0.5 and the resulting mixture was immediately analyzed by NMR spectroscopy. The mixture showed N,P-chelated palladium complexes [Pd(**1**)(η^3-PhCHCHCHPh)]Cl and [Pd(**2**)(η^3-PhCHCHCHPh)]Cl in a ratio of 30:70 after 10 min at 25 °C, along with the remaining free DPOFs **1** and **2**. Both the palladium complexes contained the *endo*- and *exo*-isomers, as determined separately in the above analysis. The palladium complexes were interconvertible by a slow ligand exchange process at room temperature.[15] After 2 days at 25 °C, equilibration was reached and the portion of [Pd(**2**)(η^3-PhCHCHCHPh)]Cl increased to 94% (Scheme 3). Thus, the less reactive species [Pd(**2**)(η^3-PhCHCHCHPh)]Cl was found to be thermodynamically more stable than the more reactive complex [Pd(**1**)(η^3-PhCHCHCHPh)]Cl. The difference in the thermodynamic stability of the complexes, which is about 1.6 kcal/mol, is likely to be caused by the steric strain imposed by the Fe–Cp moiety, as argued above.



Scheme 3. Equilibration between the (π-allyl)Pd complexes of ligands **1** and **2**.

2.4. X-ray crystal structure analysis

In order to obtain structural information on the steric strain imposed by the Cp–Fe moiety, we carried out X-ray crystallographic studies on the [π-(1,3-diphenyl)allyl]Pd complexes of DPOFs **1** and **2**. Reddish-yellow crystals of the palladium complexes were obtained from CH_2Cl_2–hexanes. Crystal structures showed the *endo-syn-syn* isomers **1n** and **2n** in both cases (Fig. 2).[16] In the case of **1n**, two similar conformers were in a unit cell, which were assigned as **1n**(i) and **1n**(ii). Table 2 lists selected bond lengths and angles of the complexes. As a comparison, we listed the structural data of a simple (π-allyl)Pd complex of **1**. The bond lengths between Pd and the allylic termini [the bond *trans* to P: Pd–C1, the bond *trans* to N: Pd–C3] are similar to those of **4n** (R = *i*-Pr, SbF_6^-; 2.240 and 2.119 Å).[6] The

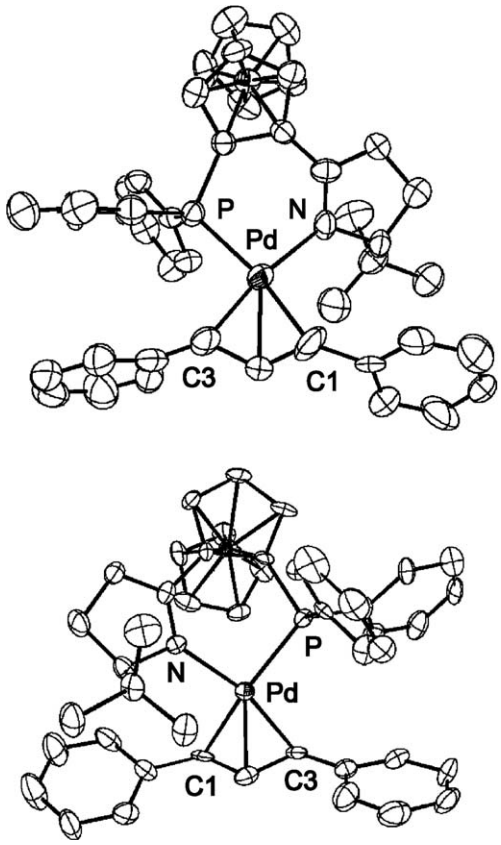


Figure 2. Crystal structures of **1n**(i) (above) and **2n** (below). Counteranion (PF_6^-) was omitted.

Table 2. Selected bond distances and angles for complexes: [Pd(**1**)-(η^3-CH_2CHCH_2)]PF_6, **1n**(i)/**1n**(ii), and **2n**

	[Pd(**1**)(π-allyl)]	**1n**(i)	**1n**(ii)	**2n**
Bond distances[a] (Å)				
Pd–N	2.096(8)	2.107(12)	2.087(14)	2.134(11)
Pd–P	2.260(2)	2.268(4)	2.273(5)	2.300(4)
Pd–C1	2.284(11)	2.300(2)	2.260(2)	2.264(13)
Pd–C3	2.112(10)	2.126(14)	2.160(2)	2.135(13)
Angles[a] (°)				
N–Pd–P	96.2(2)	94.8(4)	93.0(4)	89.7(3)
N–Pd–C1	102.8(4)	102.2(5)	102.0(7)	102.2(5)
P–Pd–C3	93.4(3)	96.2(4)	98.4(5)	104.1(4)
C1–Pd–C3	67.4(5)	66.1(5)	65.4(8)	65.8(5)
I[b]		106.5(1)	103.7(2)	105.1(9)
II[c]		1.0(1)	10.5(2)	11.1(11)
III[d]		32.9(1)	36.5(2)	22.4(16)
IV[e]		31.8(1)	26.6(1)	25.1(8)

[a] Numbers in parentheses are ESDs in the least significant digits.
[b] Angle between the allylic plane and coordination plane of Pd.
[c] Angle between the allylic plane and allylic phenyl group at Cl.
[d] Angle between the allylic plane and allylic phenyl group at C3.
[e] Angle between the allylic phenyl groups.

distinct difference in the bond lengths between the Pd and two allylic termini shows an electronic differentiation of the two allylic termini by the chelates.[17] Therefore, the assumption that the malonate nucleophile attacks the allylic carbon *trans* to the phosphorus can also be applied to our system. The bite angles of the complexes **1n**(i) and **1n**(ii) (94.8°, 93.0°, respectively) are larger than that of the complex **2n** (89.7°), which are related to steric congestion near the two allylic termini.[18]

Table 2 also lists angles between the allylic plane and coordination plane of Pd, allylic phenyl groups at C1 and C3 of the allylic termini, and angles between the allylic phenyl groups in complexes **1n** and **2n**. The Fe–Cp moiety would exert steric strain towards the equatorial phenyl group and the *tert*-butyl group in complex **1n**. Due to these steric interactions, steric strain can develop between the phenyl group of the allylic moiety and the equatorial phenyl group at P in the isomer **1n**. This may drive the allylic phenyl groups out of co-planarity with respect to the allylic systems. In particular, the allylic phenyl group near the diphenylphosphino group has significant torsional angles of 32.9° and 36.5° in the cases of the isomers **1n**(i) and **1n**(ii), respectively, compared to that of 22.4° in the case of **2n**. The angles between the two allylic phenyl rings in the isomers **1n** (31.9° and 26.6°) are also larger than that of the isomer **2n** (25.1°). The X-ray structure analysis provides the structural information that *endo-syn-syn* **1n** is thermodynamically less stable than *endo-syn-syn* **2n**, which can be explained by steric strain caused by the Cp–Fe moiety. By evoking the steric strain-reactivity argument, *endo-syn-syn* **1n** is thus expected to be more reactive than *endo-syn-syn* **2n**, as observed.

3. Conclusion

We have studied the structure and equilibration of the (π-allyl)Pd complexes of phosphino(oxazolinyl)ferrocene ligands **1** and **2**, reactive intermediates in palladium catalyzed allylic alkylations. The effects of two counteranions of the palladium complexes, Cl^- and PF_6^-, on the equilibrium ratio and rate of isomeric complexes, *endo-syn-syn* and *exo-syn-syn* isomers, have been studied by NMR spectroscopy. In the case of the Cl^- counterion, a larger *endo*/*exo* ratio was observed than in the case of the PF_6^- counterion. The equilibration between the *endo*- and *exo*-isomers was fast in the case of Cl^- counterion, whereas it was slow in the case of PF_6^- counterion. We have also carried out an equilibration study on two structurally related [π-(1,3-diphenyl)allyl]Pd complexes of the phosphino-(oxazolinyl)ferrocene ligands by NMR spectroscopy and a structural study on the two palladium complexes by X-ray crystallographic analysis. Both studies suggest that steric strain of the (π-allyl)Pd complexes affect their thermodynamic stability and also their reactivity, in line with the steric strain-reactivity argument proposed previously. The results and arguments described herein thus provide important aspects of the counteranion and steric effects on the equilibrium ratio and rate among isomeric (π-allyl)Pd complexes such as *endo* and *exo*, and their reactivity in the Pd-catalyzed allylic alkylation reaction.

4. Experimental

4.1. General methods

All reactions with air- or moisture-sensitive materials were carried out under Ar. Freshly distilled, dry, and oxygen-free solvents were used throughout the experiments. Flash column chromatography was performed with Merck silica gel (230–400 mesh) under low pressure of 5–10 psi. Tetramethylsilane and phosphoric acid (85%) were used as internal and external standard for ^1H and ^{31}P NMR, respectively. Peak assignments of ^1H NMR were assisted by COSY experiments. Chemical shifts of ^1H and ^{13}C NMR spectra are reported in ppm (δ), and multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), and app. t (apparent triplet).

4.2. [Pd(1)(η^3-PhCHCHCHPh)]PF$_6$

A solution of DPOF **1** (10.5 mg, 0.021 mmol) and di-μ-chlorobis[(η^3-1,3-diphenylallyl)palladium] (7.1 mg, 0.011 mmol) in CH_2Cl_2 (0.18 mL) was stirred at 25 °C for 1 h, then the solution was treated with $AgPF_6$ (5.4 mg, 0.021 mmol) in MeOH (63 μL). After being stirred for 1 h, the mixture was filtered through a pad of Celite and the filtrate washed with an aqueous saturated NaCl solution, dried over $MgSO_4$, and concentrated in vacuo to give a quantitative yield of the product as a reddish-yellow solid. Single crystals suitable for X-ray diffraction were grown by recrystallization from CH_2Cl_2–hexanes. The crystal structure showed only *endo*-isomer **1n**. In solution *endo*- and *exo*-isomers are in equilibrium, which can be differentiated by NMR (^{31}P, ^1H, and ^{13}C) and NOE experiments. ^{31}P NMR (121 MHz, $CDCl_3$): δ 20.2 (minor, **1x**), 16.7 (major, **1n**). ^1H NMR (300 MHz, $CDCl_3$): δ 7.8–7.7 (m, 4H), 7.5–7.2 (m, 10H), 7.0–6.7 (m, 6H), 6.4 (dd, $J = 14.1$, 10.4 Hz, 1H at allylic C2), 6.0 (dd, $J = 14.1$, 8.2 Hz, 1H at C3), 5.14 (app. t, $J = 2.5$ Hz, 0.9H, Cp, **1n**) and 5.04 (app. t, 0.1H, Cp, **1x**), 4.8 (app. t, $J = 2.5$ Hz, 0.9H, Cp, **1n**) and 4.74 (app. t, 0.10H, Cp, **1x**), 4.5 (s, 1H, Cp), 4.3 (dd, $J = 9.4$, 3.8 Hz, 1H at oxazoline C5), 4.1 (app. t, $J = 9.4$ Hz, 1H at oxazoline C5), 3.8 (s, 0.52H, Cp′, **1x**) and 3.7 (s, 4.5H, Cp′, **1n**), 3.5 (d, $J = 10.4$ Hz, 1H at allylic C1), 3.1 and 2.7 (dd, $J = 9.6$, 3.7 Hz, 1H at oxazoline C3, **1x** and **1n**), 1.1 (s, 0.93H, *t*-Bu, **1x**) and 0.8 (s, 8.07H, *t*-Bu, **1n**): This NMR spectra was recorded for the recrystallized sample after 1 h equilibration. ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3, 138.0, 136.5 (d, $J = 15.0$ Hz), 135.8 (d, $J = 5.5$ Hz), 133.0, 132.9, 132.7, 132.3, 131.8, 131.2, 130.7, 130.4, 129.3 (d, $J = 11.4$ Hz), 129.1, 128.9, 128. 6 (d, $J = 3.8$ Hz), 128.2, 111.1 (d, $J = 5.2$ Hz, $C_{\text{central allylic}}$), 104.7 (d, $J = 20.6$ Hz, C_{allylic} *trans* to P), 78.9, 78.6 (d, $J = 24.7$ Hz), 75.0 (d, $J = 6.5$ Hz), 74.5 (d, $J = 6.4$ Hz), 72.6, 72.4 (d, $J = 21.5$ Hz), 71.4, 70.9, 70.0 (d, $J = 5.8$ Hz, C_{allylic} *trans* to N), 33.7, 26.7 (–C(CH_3)$_3$, **1x**) and 25.4 (–C(CH_3)$_3$, **1n**). The splitting is due to $J_{P,C}$.

4.3. [Pd(2)(η^3-PhCHCHCHPh)]PF$_6$

A similar procedure as the one above gave the compound in a quantitative yield (12.5 mg scale) as a reddish-yellow

solid. Single crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2–hexanes. The equilibration between the major *endo* **2n** and minor *exo* **2x** isomers can be determined by NMR experiments similarly. ^{31}P NMR (121 MHz, $CDCl_3$): δ 19.2 (**2x**), 14.8 (**2n**). ^1H NMR (300 MHz, $CDCl_3$): δ 7.7–7.0 (m, 20H), 6.6 (dd, $J = 13.8$, 10.3 Hz, 1H), 6.4 (dd, $J = 11.6$, 7.5 Hz, 1H), 6.1 (dd, $J = 13.8$, 8.2 Hz, 1H), 5.2 (s, 1H, Cp), 4.84 (s, 1H, Cp), 4.81 (dd, $J = 14.7$, 10.3 Hz, 1H), 4.6 (s, 4.1H, **2n**) and 4.4 (s, 0.9H, **2x**), 4.13 (dd, $J = 14.2$, 7.1 Hz, 1H), 4.04 (s, 1H, Cp), 3.9 (app. t, $J = 8.7$ Hz, 1H), 3.1 (d, 0.18H, **2x**) and 2.2 (d, 0.82H, **2n**), 0.5 (s, 1.6H, *t*-Bu, **2x**) and 0.3 (s, 7.4H, *t*-Bu, **2n**): This NMR spectra was recorded for the recrystallized sample after 1 h equilibration, which showed an *endo*/*exo* ratio of 4.6/1. ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 138.8, 135.6 (d, $J = 5.7$ Hz), 134.0 (d, $J = 12.2$ Hz), 132.4, 132.3, 131.6, 130.9, 130.7, 129.8 (d, $J = 11.1$ Hz), 129.5, 129.3, 128.0, 127.8 (d, $J = 3.5$ Hz), 126.8, 126.2, 110.3 (d, $J = 5.4$ Hz, $C_{\text{central allylic}}$), 103.8 (d, $J = 21.9$ Hz, C_{allylic} *trans* to P), 75.4 (d, $J = 8.8$ Hz), 75.2 (d, $J = 4.7$ Hz), 73.5, 73.1, 71.1, 71.0, 70.8 (d, $J = 17.8$ Hz), 69.9 (d, $J = 14.7$ Hz), 66.2 (d, $J = 6.0$ Hz, C_{allylic} *trans* to N), 34.5 (–$C(CH_3)_3$, **2x**) and 33.8 (–$C(CH_3)_3$, **2n**), 25.6 (–C(CH_3)$_3$, **2x**) and 24.8 (–C(CH_3)$_3$, **2n**). The splitting is due to $J_{P,C}$.

4.4. [Pd(1)(η^3-PhCHCHCHPh)]Cl

A solution of DPOF **1** (9.9 mg, 0.020 mmol) and di-μ-chlorobis[(η^3-1,3-diphenylallyl)palladium] (6.5 mg, 0.011 mmol) in $CDCl_3$ (0.18 mL) was stirred at 25 °C for 30 min before being subjected to ^1H NMR analysis. ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.8 (**1x**), 19.0 (**1n**). ^1H NMR (300 MHz, $CDCl_3$): δ 7.8–6.6 (br m, 20H, 4 Ph), 6.5 (app. t, 1H at allylic C2), 6.0 (app. t, 1H at allylic C3), 5.2 (s, 1H at Cp) and 4.9 (s, 1H at Cp), 4.5 (s, 1H at Cp), 4.4 (dd, $J = 9.1$, 3.3 Hz, 1H at oxazoline C5), 4.1 (app. t, 1H at oxazoline C5), 3.7 (s, 5H at Cp′), 3.5 (d, $J = 9.9$ Hz, 1H at allylic C1), 2.6 (br s, 1H at oxazoline C3), 1.1 and 0.9 (s, 9H, *t*-Bu; **1x** and **1n**). When the same sample was prepared in CD_2Cl_2, an actual solvent of the catalytic reaction, almost the same spectrum was obtained with slight chemical shift differences. ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 137.4, 135.9 (d, $J = 14.8$ Hz), 135.3 (d, $J = 5.2$ Hz), 132.9, 132.5, 132.4, 131.9, 131.3, 130.7, 130.5, 130.2, 129.1 (d, $J = 11.5$ Hz), 128.8, 128.7, 128.2, 126.3, 110.8, 104.0, 78.7, 78.1 (d, $J = 29.3$ Hz), 74.5 (d, $J = 5.9$ Hz), 74.3 (d, $J = 5.9$ Hz), 72.4, 71.7 (d, $J = 21.5$ Hz), 71.0, 70.7, 69.6, 33.4, 25.9, and 25.6 (–C(CH_3)$_3$, **1x** and **1n**). The splitting is due to $J_{P,C}$.

4.5. [Pd(2)(η^3-PhCHCHCHPh)]Cl

^1H NMR spectrum showed a mixture of the two isomers, **2n** (84%) and **2x** (16%), which was assigned by NOE experiments. ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.6 (**1x**), 17.0 (**1n**). Although both ^1H and ^{13}C NMR spectra of the complexes show peak patterns similar to other cases, normal peak assignments were difficult due to different heights and overlaps of the isomeric mixtures, except for certain peaks for which the *exo*- and *endo*-isomers were unambiguously assigned: δ_H 4.6 and 4.4 (s, 5H, Cp′, **2n** and **2x**), 4.86 and 4.82 (t, $J = 2.5$ Hz, 1H at oxazoline C5, **2n** and **2x**), 0.51 and 0.32 (s, 9H, *t*-Bu, **2x** and **2n**); δ_C 25.6 and 24.8 (–C(CH_3)$_3$, **2x** and **2n**).

4.6. General procedure for the Pd-catalyzed allylic alkylation and determination of % ee values of products

See the procedure described in Refs. 4a,b.

4.7. Determination of the relative stability of [Pd(1)(η^3-PhCHCHCHPh)]Cl and [Pd(2)(η^3-PhCHCHCHPh)]Cl

To an equimolar mixture of DPOFs **1** (9.9 mg, 0.020 mmol) and **2** (9.9 mg, 0.020 mmol) in CD_2Cl_2 (0.5 mL) at 25 °C was added [(η^3-PhCHCHCHPh)PdCl]$_2$ (6.7 mg, 0.010 mmol). The resulting mixture was subjected to ^1H NMR analysis at 25 °C at intervals. The equilibration between [Pd(**1**)(η^3-PhCHCHCHPh)]Cl and [Pd(**2**)(η^3-PhCHCHCHPh)]Cl proceeded slowly from an initial value of 30:70 (after 10 min). It took 2 days to reach a constant value, 6:94, favoring the latter palladium complex. Two different experiments were also carried out, in which the addition sequence was changed as follows. The addition of DPOF **1** to a CD_2Cl_2 solution of [(η^3-PhCHCHCHPh)PdCl]$_2$ to form [Pd(**1**)(η^3-PhCHCHCHPh)]Cl, then addition of DPOF **2** to the mixture after 30 min; or a reverse addition sequence of the ligands. In both cases, the same results were observed.

4.8. Crystal structures of 1n and 2n

Crystal data for **1n**: $C_{88}H_{86}F_{12}Fe_2N_2O_2P_4Pd_2$, M 1879.96, monoclinic, space group $P2_1/n$, $a = 12.191(5)$, $b = 15.143(3)$, $c = 24.917(12)$ Å, $V = 4489(3)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\mu = 0.962$ mm^{-1}, 5753 independent reflections, GOF on $F^2 = 1.078$. Final R indices [$I > 2\sigma(I)$] (refinement on F^2): $R_1 = 0.0596$, $wR_2 = 0.1243$.

Crystal data for **2n**: $C_{44}H_{43}F_6FeNOP_2Pd$, M 939.98, orthorhombic, space group $P2_12_12_1$, $a = 13.027(3)$, $b = 14.155(3)$, $c = 21.934(4)$ Å, $V = 4044.5(10)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\mu = 0.946$ mm^{-1}, 2801 independent reflections ($R_{\text{int}} = 0.0000$), GOF on $F^2 = 1.033$. Final R indices [$I > 2\sigma(I)$] (refinement on F^2): $R_1 = 0.0540$, $wR_2 = 0.0830$.

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5. Compounds **4n** and **4x** denote the *endo-syn-syn* (π-allyl)Pd complex **n** and *exo-syn-syn* (π-allyl)Pd complex **x** containing the N,P-ligand **4**, respectively. Similarly **1n**, **1x**, **2n**, and **2x** denote those (π-allyl)Pd complexes containing ligands **1** and **2**, respectively. We used *endo* and *exo* notations to indicate the isomeric (π-allyl)Pd complexes (shown in Eq. 1) in which the relative positions of ligand and substrate are different: such *endo* and *exo* notations are opposite to those of Helmchen et al. (Ref. 6).
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9. By NOE experiments, we were able to make the necessary assignments. The NOEs from the *tert*-butyl protons of DPOF **1** to the nearest phenyl protons of the allyl moiety particularly differentiated the two isomers **1n** and **1x**. A strong NOE was observed (15%) in the complex **1n** but a weak NOE (1.5%) in the complex **1x**. Similarly, **2n** (1.6% NOE) can be differentiated from **2x** (0% NOE).
10. Both ^{1}H and ^{31}P NMR spectra of [Pd(**1**)(η^3-PhCHCHCHPh)]PF_6 showed two isomers **1n** and **1x** in a ratio of 8.7:1 at room temperature. Diagnostic peaks are indicated in the experimental section. Hou and co-workers reported a similar equilibration study with a different counteranion (SbF_6^-, Ref. 4g).
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13. It should be noted that when the same reaction was carried out using [(π-allyl)PdCl]$_2$ as the palladium source, a shorter reaction time and a higher enantioselectivity (0.5 h; 99% ee) were observed.[4a] Thus, the enantioselectivity and the percentage conversion are also dependent on the palladium source used. The dependency of the reaction rate and enantioselectivity on the palladium sources is not clear. A different decomposition rate of the catalysts seems to interplay, which may be dependent on the chelating ligands and also on the counteranions. With ^{1}H NMR analysis, we were able to follow the decomposition of a simple palladium complex, [Pd(**1**)(η^3-CH_2CHCH_2)]Cl, which is in a fast equilibrium between *exo* (16%) and *endo* (84%) isomers: The major *endo* isomer decomposes at such a rate: 5% after 0.5 h, 12% after 5 h, and 20% after 20 h at room tem-perature (a related decomposition experiment is mentioned below).
14. We observed a large increase in the reaction rate, yield, and enantioselectivity in the catalytic reaction by increasing catalyst loading. Thus, when a larger amount of catalyst, such as 10 mol % of DFOF **2**–Pd complex was used, the allylic substitution was nearly completed after 1.5 h, and a 98% isolated yield with 92% ee was obtained. In the case of 2 mol % loading, the same catalytic reaction gave 73% yield after 5 h (after a similar conversion) with 67% ee. These results may be due to the decomposition of the catalysts.
15. We do not know the mechanism of the interconversion. The interconversion can be assigned by following the *tert*-butyl peaks. The interconversion is faster than the NMR timescale in the case of the (π-allyl)Pd complexes that are generated from [(π-allyl)PdCl]$_2$ and DPOFs **1** and **2**. The equilibrium was reached within 30 min at 25 °C, giving a ratio of 16:84, which can be assigned from the *tert*-butyl peaks of the corresponding Pd complexes.
16. CCDC 611857-611859 contain the supplementary crystallographic data for the structures reported in this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
17. ^{13}C Chemical shifts of the terminal allylic carbons are also a measure of the different electronic environment on these centers.[3b,f,g] The carbons *trans* to P appear at much more downfield [**1n** ($X^- = PF_6^-$): 104.7 ppm; **2n** ($X^- = PF_6^-$): 103.9 ppm] than those carbons *trans* to N [**1n** ($X^- = PF_6^-$): 69.9 ppm; **2n** ($X^- = PF_6^-$): 66.3 ppm], which should stem from the larger *trans influence* of P over that of N, an important factor that controls the regioselectivity of the nucleophilic attack. The ^{13}C chemical shifts in parentheses were determined in $CDCl_3$ at 296 K; those for the minor *exo*-isomers were not assigned clearly.
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