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Chapter 5

*Palladium Catalysed Allylic Substitution with
a Phosphine Modified Acridine*

5.1 Introduction

The objective of this thesis is to use DNA as a scaffold in asymmetric catalytic reactions based on phosphine ligands. As described in Chapter 1 transition metal ligands can be connected to DNA in a covalent or non-covalent way. In Chapter 4 the utilization of the non-covalent approach (intercalation) in the Rh hydrogenations reaction was described. It was concluded that this non-covalent approach was not suitable for the Rh catalysed hydrogenation of methylacetamidoacrylate. In this chapter the results are described using the same intercalating ligand (**3**) in Pd-catalysed allylic substitution.

The allylic substitution was discovered by Tsuji *et al.* in 1965 as a stoichiometric reaction.¹ The asymmetric Pd catalysed allylic substitution was developed twelve years later by Trost *et al.*² In these reactions typical substrates are allylic compounds with a good leaving group such as acetate. In the key intermediate, palladium is coordinated to the allyl moiety, forming a π -allyl-complex and overall the leaving group at the allyl moiety is displaced by a nucleophile forming mostly a new C–C or C–N bond (respectively alkylation or amination).^{3,4} The asymmetric version of palladium catalysed allylic substitution is often applied in total synthesis.^{5,6}

A two-phase (aqueous-organic medium) palladium catalysed substitution system with water soluble phosphine ligands was first published by Sinou *et al.* in 1991. This two-phase system allows easy recovery and recycling of the catalyst.⁷

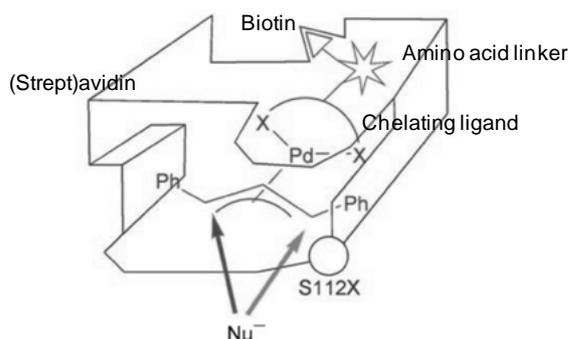


Figure 1: The postulated enantio-discrimination event in the asymmetric allylic alkylation in an artificial metalloenzyme by Ward *et al.*⁸

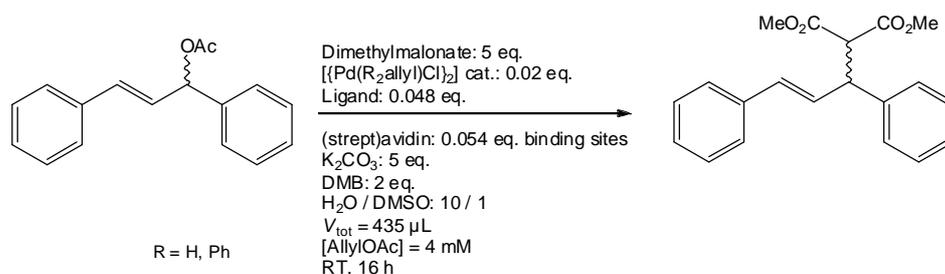


Figure 2: Reaction condition used for the asymmetric allylic alkylation catalysed by (strept)avidin-biotin artificial metalloenzymes by Ward *et al.*⁸

The first, and so far only, example of the use of artificial metalloenzymes in allylic substitution reactions was reported by Ward *et al.* in 2008 (Figure 2).⁸ They showed that a combination of chemical and genetic optimization resulted in $[\text{Pd}(\eta^3\text{-allyl})(\text{biotin-spacer-ligand})]^+\text{C}(\text{strept})\text{avidin}$ catalysts that afford both *R* and *S* alkylation products. The product of the substitution reaction of 1,3-diphenylallyl acetate and dimethyl malonate was obtained with enantiomeric excesses ranging from 90% (*R*) to 82% (*S*). Their first attempts resulted in little, if any, conversion due to hydrolysis of the starting material 1,3-diphenylallyl acetate. The application of surfactants resulted in a significant increase in yield, especially with the use of didodecyldimethylammonium bromide (DMB), but only in combination with a limited number of ligand scaffolds. It thus appears that the nature of the biotinylated ligand plays a key role in determining the activity of the resulting artificial metalloenzyme.

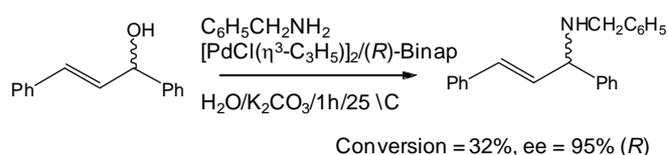


Figure 3: Allylic amination of allyl alcohol with benzylamine by Sinou *et al.*⁹

Sinou *et al.* studied the influence of the nature of the nucleophile and the allylic acetate on the activity and enantioselectivity in the catalytic asymmetric amination in water. Monitoring the conversion and the enantioselectivity versus reaction time, using benzylamine as nucleophile, they noticed the formation of 41% of allylic alcohol after 15 minutes, which was further transformed into the aminated product in the presence of the palladium catalyst. Indeed, when the allylic alcohol and benzylamine were stirred under the standard amination conditions, 32% conversion was obtained in neat water. Sinou *et al.* showed that, in the presence of surfactants, it was possible to use allylic alcohols instead of acetates as starting material.⁹

In this chapter the acridine functionalised phosphine ligand reported in Chapter 4, is applied in the palladium catalysed allylic alkylation and amination reaction. These reactions were performed in absence and presence of DNA and under DNA compatible conditions. The phosphine ligand is achiral and DNA is the only source of chirality in the mixture. If chiral induction results from the palladium catalysed allylic alkylation or amination reaction, this should come from the DNA scaffold.

5.2 Results & Discussion

5.2.1 Synthesis

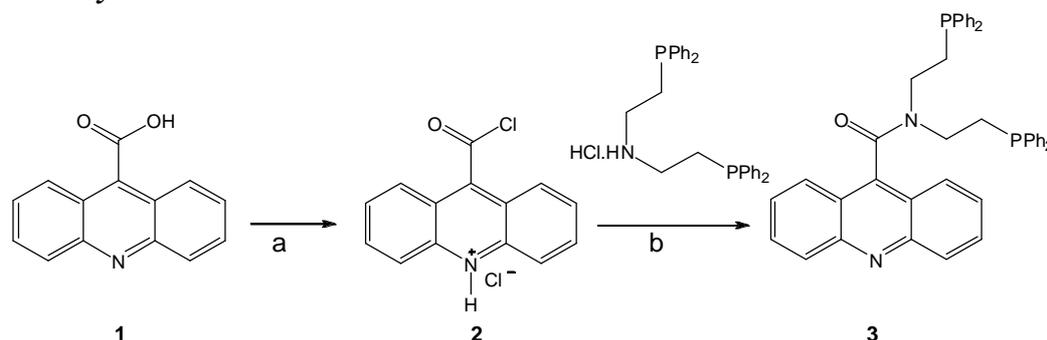
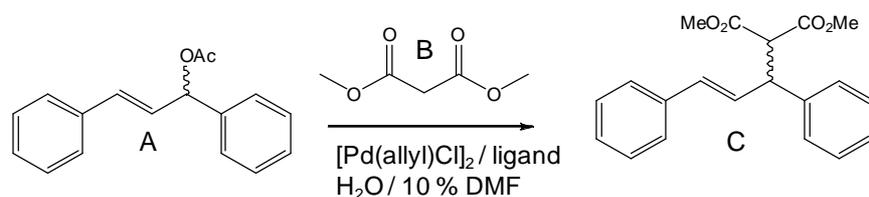


Figure 4: Synthesis of ligand **3**. Reaction conditions: a) SOCl_2 , CH_2Cl_2 , $90\text{ }^\circ\text{C}$, overnight, quantitative; b) NEt_3 , CH_2Cl_2 , r.t., overnight, 53%.

The synthesis of ligand **3** is as described in the previous chapter (Figure 4). Bis[2]-(diphenylphosphino)-ethyl]amine is selectively acylated with acridine-9-carbonyl chloride at the nitrogen atom.

5.2.2 Pd catalysed allylic alkylation



Ligand **3** was used in the palladium catalysed allylic alkylation reaction of 1,3-diphenylallyl acetate (**A**) with dimethyl malonate (**B**) as the nucleophile. The results are shown in Table 1. With 2 mol% of Pd-catalyst and 2 mM concentration of the allyl acetate substrate, the reaction reached 50% conversion after 20 hours (entry 1). The presence of base is required for deprotonation of dimethyl malonate, as is evident from the comparison of entries 1 and 2. All

the other palladium allylic alkylation reactions were performed with 5 mol% Pd-catalyst and 6 mM 1,3-diphenylallyl acetate.

With a higher loading of the palladium catalyst, 58% conversion was already obtained within 90 minutes (entry 3). The addition of didodecyldimethyl-ammonium bromide (DMB) as surfactant resulted in a drop of the conversion, 13% after 90 minutes (entry 4). In contrary to the artificial metalloenzyme system described by Ward *et al.*⁸ This could be explained by the solution becoming too viscous for good mixing of all the reactants.

Table 1: Asymmetric alkylation of 1,3-diphenylallyl acetate (A) with dimethyl malonate (B): the influence of incubation time, addition of base, DMB, and *st*DNA.^a

Entry	Reaction time (h)	Incubation time (h)	Additives			Conversion (%) ^d
			K ₂ CO ₃	DMB	DNA ^c	
1 ^b	20	-	+	-	-	49
2 ^b	20	-	-	-	-	0
3	1.5	-	+	-	-	58
4	1.5	-	+	+	-	13
5	1.5	19.5	+	-	-	18
6	1.5	19.5	+	-	<i>Salmon Testes</i>	3
7	20	22	+	-	-	60 ^e
8	20	22	+	-	<i>Salmon Testes</i>	15 ^e

^a Reaction conditions: [PdPP] = 0.3 mM (5 mol%), allyl / nucleophile / base / [Pd(η^3 -C₃H₅)Cl]₂ / ligand / surfactant = 20 / 60 / 60 / 0.5 / 1 / 40, solvent = H₂O / DMF (10%), 0.5 ml, room temperature. ^b Reaction conditions: [PdPP] = 0.08 mM (2 mol%), allyl / nucleophile / base / [Pd(η^3 -C₃H₅)Cl]₂ / ligand = 50 / 150 / 150 / 0.5 / 1, solvent = H₂O / DMF (10%), 0.5 ml, room temperature. ^c [*Salmon Testes* DNA] = 1.3 mg/ml. ^d Average value of duplicate experiments, no ee. ^e For the duplicate experiments conversions of 81/39 and 9/21 were obtained, respectively.

When the reaction was performed in the presence of *st*DNA, the reaction mixture was first incubated overnight before the substrate was added to allow full intercalation/interaction of ligand and DNA. From a control experiment (entry 5) it became clear that the conversion is lower after an incubation (Table 1, entry 3 vs. 5, 58% vs. 18% conversion). In the presence of *st*DNA only 3% conversion was reached in 90 minutes. No formation of palladium black was observed, indicating that catalyst decomposition is not an issue. Indeed the conversion increased when the reaction time was 20 hours. Upon performing duplicate experiments we found that there is a large difference between the experiments (entry 7 and 8), but in all experiments the conversion was higher than that of the 90 minutes experiment (entry 5 and 6). In the presence of *st*DNA and a reaction time of 20h, 15% conversion was reached (Table 1, entry 8), but no enantiomeric excess was obtained in this reaction.

The catalyst was made *in situ* by the addition of a stock-solution of free ligand **3** and the palladium precursor ($[\text{Pd}(\text{allyl})\text{Cl}]_2$). The conversions shown in Table 1 result from the palladium-ligand **3** complex, as can be concluded from the control experiments shown in Table 2. In the presence of either palladium precursor or free ligand **3** no conversion was obtained after overnight reactions (entry 1–4). The experiments shown in Table 2 were performed without pre-incubation and 20 hours reaction time. This resulted in a higher conversion of the palladium allylic alkylation reaction in the absence of *st*DNA (Table 2, entry 6, 79%) compared to the reaction with incubation time (Table 1, entry 7, 60%).

Table 2: Control experiments with only free ligand or palladium precursor for the asymmetric alkylation of 1,3-diphenylallylacetate (**A**) with dimethylmalonate (**B**).^a

Entry	[Pd] (mol%)	[Ligand] (mol%)	DNA ^b	Conversion (%) ^c
1	5	-	<i>Salmon Testes</i>	0
2	5	-	-	0
3	-	5	<i>Salmon Testes</i>	0
4	-	5	-	0
5	5	5	<i>Salmon Testes</i>	8
6	5	5	-	79

^a Reaction conditions: [Pd and / or PP] = 0.3 mM (5 mol%), allyl / nucleophile / base / $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ / ligand = 20 / 60 / 60 / 0.5 / 1, solvent = H₂O / DMF (10%), 0.5 ml, room temperature, 20h. ^b [*Salmon Testes* DNA] = 1.3 mg/ml. ^c Average value of duplo experiments, no ee.

The palladium catalysed allylic alkylation reaction of 1,3-diphenylallyl acetate and dimethyl malonate in the absence and presence of *st*DNA was also monitored in time. Reaction conditions were kept the same except a higher concentration of 1,3-diphenylallyl acetate (24 mM) and a larger reaction volume (2 ml instead of 0.5 ml) were used. At the indicated times, a sample of 0.5 ml was withdrawn from the reaction mixture, quenched with NH₄Cl (aq), extracted with diethyl ether and analysed. The higher concentration of 1,3-diphenylallyl acetate resulted in a higher conversion, 71% after one hour (Table 3, entry 1) than the one with only 6 mM 1,3-diphenylallyl acetate, 58% after 20 hours (Table 1, entry 3). After 2 ½ hour the reaction was almost complete (entry 2) and complete conversion was obtained after 20 hours.

In these experiments the reactions were started without any incubation time. The palladium catalyst is still not very active in the presence of *st*DNA. Only 19% conversion was obtained after 20 hours (Table 3, entry 6). Also with this higher loading of palladium no enantiomeric excess was obtained in the presence of *st*DNA. The reaction conditions should be optimized

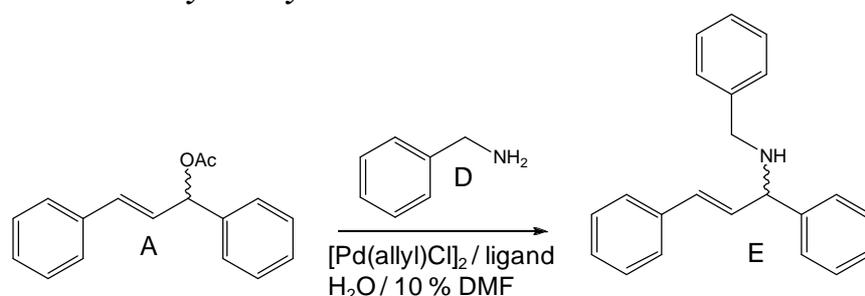
regarding the incubation time, to overcome the problem of bad reproducibility and lower activity compared to the reactions without incubation time.

Table 3: Asymmetric alkylation of 1,3-diphenylallylacetate (**A**) with dimethyl malonate (**B**) followed in time.^a

Entry	Reaction time (h)	DNA ^b	Conversion (%) ^c
1	1	-	71
2	2.5	-	95
3	20	-	>99
4	1	<i>Salmon Testes</i>	3
5	2.5	<i>Salmon Testes</i>	13
6	20	<i>Salmon Testes</i>	19

^a Reaction conditions: [Pd] = 1.2 mM (5 mol%), allyl / nucleophile / base / [Pd(η^3 -C₃H₅)Cl]₂ / ligand = 20 / 75 / 60 / 0.5 / 1, solvent = H₂O / DMF (10%), 2 ml, room temperature. ^b [*Salmon Testes* DNA] = 1.3 mg/ml. ^c no ee.

5.2.3 Pd catalysed allylic amination



Ligand **3** was also used in the palladium allylic amination reaction of 1,3-diphenylallyl acetate (**A**) with benzylamine (**D**). The results are shown in Table 4. With 2 mol% Pd-catalyst and 2 mM 1,3-diphenylallyl acetate (**A**) concentration, the reaction was halfway after stirring overnight (entry 1). With the use of benzylamine as nucleophile (**D**) there is no need to use a base during the amination reaction; the benzylamine is basic and nucleophilic enough by itself. This is evident from the results shown in Table 4, as there is no difference between the conversion when the reaction is carried out in the absence or presence of K₂CO₃. All reactions were carried out with an allyl/nucleophile ratio of 1:3, thus there is enough base and nucleophile (both benzylamine) for the allylic amination and formation of benzylammonium acetate as side-product.

Except the first two entries of Table 4, all other palladium catalysed allylic amination reactions were performed with 5 mol% Pd-catalyst and 6 mM 1,3-diphenylallyl acetate (**A**). With the higher loading of palladium more than 80% conversion was obtained in 90 minutes (entry 3 and 4). The presence of DMB as surfactant has also a negative influence on the amination reaction, but to a lesser extent than for the alkylation reactions, the conversion

dropped by 20 percent. No other surfactants were tested for the palladium catalysed allylic substitution reaction using ligand **3**.

Table 4: Asymmetric amination of 1,3-diphenylallyl acetate (A) with benzylamine (D) regarding the influence of incubation time, addition of base, DMB and *st*DNA.^a

Entry	Reaction time (h)	Incubation time (h)	Additives			Conversion (%) ^d
			K ₂ CO ₃	DMB	DNA ^c	
1 ^b	20	-	-	-	-	52
2 ^b	20	-	+	-	-	52
3	1.5	-	-	-	-	87
4	1.5	-	+	-	-	87
5	1.5	-	-	+	-	62
6	1.5	-	+	+	-	64
7	1.5	19.5	-	-	-	69
8	1.5	19.5	+	-	-	73
9	1.5	19.5	-	-	<i>Salmon Testes</i>	17
10	1.5	19.5	+	-	<i>Salmon Testes</i>	17
11	20	22	-	-	-	82
12	20	22	-	-	<i>Salmon Testes</i>	27

^a Reaction conditions: [PdPP] = 0.3 mM (5 mol%), allyl / nucleophile / base / [Pd(η^3 -C₃H₅)Cl]₂ / ligand / surfactant = 20 / 60 / 60 / 0.5 / 1 / 40, solvent = H₂O / DMF (10%), 0.5 ml, room temperature. ^b Reaction conditions: [PdPP] = 0.08 mM (2 mol%), allyl / nucleophile / base / [Pd(η^3 -C₃H₅)Cl]₂ / ligand = 50 / 150 / 150 / 0.5 / 1, solvent = H₂O / DMF (10%), 0.5 ml, room temperature. ^c [*Salmon Testes* DNA] = 1.3 mg/ml. ^d Average value of duplicate experiments, no ee.

The incubation, which was applied to obtain a better intercalation/interaction of the ligand into/with DNA, had also a negative effect on the conversion for the amination reaction (Table 4, entry 3/4 vs. 7/8). Improved conversions were obtained when the reaction time was extended to 20 hours (entry 11). Again the *st*DNA is inhibiting the catalytic reaction for this system. Conversions around 20% were obtained and for the allylic amination reaction no enantiomeric excess was obtained either. It can be noted that for the palladium-catalysed allylic amination reaction the reproducibility is better than for the alkylation reaction, especially when one considers the reactions with an incubation time.

Also for the amination reactions, the catalyst was made *in situ* by the addition of a stock-solution of the free ligand **3** and the palladium precursor ([Pd(allyl)Cl]₂). Control experiments were done with only palladium precursor or only free ligand (Table 5). Remarkably, the conversion with only ligand (Table 5, entry 4, 84%) instead of the palladium-phosphine complex (Table 5, entry 6, 83%) in the absence of DNA is more or less the same. This result

could not be explained and should be repeated. It is very interesting indeed if the reaction would take place without catalyst. The amination reaction was not performed without palladium and ligand and only in the presence of DNA.

In the presence of DNA there was also conversion with only ligand or the palladium precursor, but the conversion with the palladium-phosphine complex is still higher. It should be noted that these reactions were performed without an incubation time. Comparison of these results (Table 5) with the ones with incubation time and DNA (Table 4), suggests that indeed the incubation time can be one of the causes for the decrease in activity of the complexes.

Table 5: Control experiments with only free ligand or palladium precursor for the asymmetric amination of 1,3-diphenylallylacetate (**A**) with benzylamine (**D**).^a

Entry	[Pd] (mol%)	[Ligand] (mol%)	DNA ^b	Conversion (%) ^c
1	5	-	<i>Salmon Testes</i>	43
2	5	-	-	67
3	-	5	<i>Salmon Testes</i>	51 ^d
4	-	5	-	84
5	5	5	<i>Salmon Testes</i>	90
6	5	5	-	83

^a Reaction conditions: [Pd and / or PP] = 0.3 mM (5 mol%), allyl / nucleophile / [Pd(η^3 -C₃H₅)Cl]₂ / ligand = 20 / 60 / 0.5 / 1, solvent = H₂O / DMF (10%), 0.5 ml, room temperature, 20h. ^b [*Salmon Testes* DNA] = 1.3 mg/ml ^c Average value of duplo experiments, no ee. ^d For the duplo experiments conversion were obtained of 34/68.

The palladium-catalysed allylic amination reaction of 1,3-diphenylallyl acetate and benzylamine in the absence and presence of *st*DNA was also followed in time, see Table 6. Reaction conditions were kept the same except a higher concentration of 1,3-diphenylallyl acetate (24 mM) and a larger reaction volume (2 ml instead of 0.5 ml) were used. At the indicated times, a sample of 0.5 ml was withdrawn from the reaction mixture, quenched with NH₄Cl (aq), extracted with diethyl ether and analysed. Without *st*DNA full conversion was reached after 2 ½ hours, while in the presence of *st*DNA the conversion was 88%. After stirring overnight, full conversion was obtained in the presence of *st*DNA, but again no enantiomeric excess was obtained. It should be noted that these reactions were performed without incubation time. It can be concluded that in this case also the incubation time causes a decrease in activity of the palladium catalyst.

Table 6: Asymmetric amination of 1,3-diphenylallylacetate (**A**) with benzylamine (**D**) followed in time.^a

Entry	Reaction time (h)	DNA ^b	Conversion (%) ^c
1	1	-	63
2	2.5	-	>99
3	20	-	>99
4	1	<i>Salmon Testes</i>	45
5	2.5	<i>Salmon Testes</i>	88
6	20	<i>Salmon Testes</i>	>99

^a Reaction conditions: [Pd] = 1.2 mM (5 mol%), allyl / nucleophile / [Pd(η^3 -C₃H₅)Cl]₂ / ligand = 20 / 75 / 0.5 / 1, solvent = H₂O / DMF (10%), 2 ml, room temperature. ^b [*Salmon Testes* DNA] = 1.3 mg/ml. ^c no ee.

5.2.4 Circular dichroism

One way to investigate if there is an interaction of the ligand/complex with DNA,^{10,11} is to measure circular dichroism (CD).^{12,13,14} CD spectra were recorded between 250 and 500 nm at different palladium complex concentrations (Figure 5). The complex was made *in situ* by mixing palladium precursor [Pd(allyl)Cl]₂ and ligand **3**. The DNA concentration is kept constant. There were no signals above 310 nm and thus for clarity this part is not displayed in the graph. It is shown that upon increasing the Pd-complex the CD signal around 275 nm is decreased. No extra signal or shifting of the band is shown. The change in CD signal around 275 nm suggests that there is interaction of the palladium complex with the DNA. The signal is lowered which could be due to the stretching of the DNA helix by the interaction of the palladium complex. This stretching will result in changes in the pitch of the helix which can result in a lower CD signal. A decrease in CD intensity was also observed when binding DNA to nanotubes.¹⁵ It was shown that the conformation of the backbone changed and the stacking between bases was disrupted upon adsorption onto the nanotubes.

Importantly, the palladium complex does not show a CD effect at the wavelength where only the palladium complex absorbs, which means that there is no significant transfer of chirality of the DNA to the palladium complex.

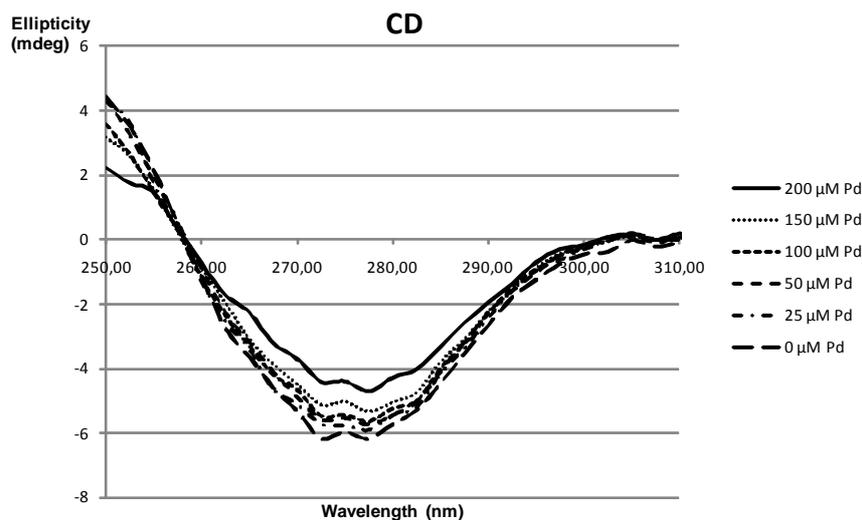


Figure 5: Circular dichroism spectra of *Salmon Testes* DNA in the presence of different concentration complexes of palladium precursor $[\text{Pd}(\text{allyl})\text{Cl}]_2$ with ligand **3**.

5.3 Conclusions

From the palladium-catalysed allylic alkylation reactions it can be concluded that the complex formed *in situ* by the palladium allyl chloride dimer and the diphosphinoacridine ligand **3** are active, but should be used directly after preparation and it is better not to incubate overnight in a mixture of water and DMF (10%). The *st*DNA has definitely an influence on the activity of the catalyst, because the conversions are much lower in the presence of *st*DNA and only 20% conversion was reached. In none of the experiments an enantiomeric excess was obtained. Future experiments could include performing the reaction at lower temperature or using other sources of DNA, for instance smaller (synthetic) strands.

The palladium ligand **3** system is more active in the allylic amination reaction than in the reaction with malonate and full conversion could be obtained without incubation. Still, in the presence of *st*DNA no enantioselectivity was obtained.

The circular dichroism experiments suggest that there is interaction of the palladium complex with the *st*DNA, as the CD intensity of the *st*DNA decreases. There is no CD effect in the window where only the Pd-complex absorbs, providing no proof for the transfer of chirality from the DNA to the metal complex.

5.4 Experimental

General remarks. Unless stated otherwise, reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. THF, diethyl ether and hexanes were distilled from sodium/benzophenone. Tertiary amines, CH_2Cl_2 and methanol were distilled from CaH_2 and toluene was distilled from sodium. Deuterated solvents were distilled from the appropriate drying agents. Unless stated otherwise, all chemicals were obtained from commercial suppliers and used as received.

General procedure for the asymmetric substitution of 1,3-diphenylallyl acetate.

The substitution experiments were carried out in (small) glass vials equipped with Teflon mini stirring bars. For a typical substitution reaction separate stock-solutions were made in H_2O or DMF of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ (DMF), ligand **3** (DMF), 1,3-diphenylallyl acetate (DMF), nucleophile (DMF; dimethyl malonate or benzylamine), K_2CO_3 (H_2O), DMB (H_2O) and *Salmon Testes* DNA (H_2O). The vials were charged with the appropriate amounts of the stock-solutions in the order: Pd, ligand, nucleophile, base, surfactant, DNA (incubation) and 1,3-diphenylallyl acetate (reaction time). The reaction was stirred for the indicated incubation or reaction time after the addition of *st*DNA or 1,3-diphenylallyl acetate respectively.

After the addition of saturated NH_4Cl (250 μl), the mixture was extracted with diethyl ether (3 x 0.5 ml). The combined organic phases were dried over Na_2SO_4 and evaporated to dryness. The conversion was determined by chiral HPLC analysis using for the alkylation: Chiralcel OD-H (0.46x25 cm) with 0.5% 2-propanol in *n*-hexane as eluent and a flow rate of 0.7 ml/min.; $\lambda = 254$ nm; t_{R} (1,3-diphenylallyl acetate) = 11.50 / 12.70 min, t_{R} (**C_R**) = 15.27 min, t_{R} (**C_S**) = 16.28 min. For the amination: Chiralcel AD-H (0.46x25 cm) with 1.0% 2-propanol in *n*-hexane as eluent and a flow of 1.0 ml/min.; $\lambda = 254$ nm; t_{R} (1,3-diphenylallylacetate) = 10.35 min, t_{R} (**E_R**) = 15.36 min, t_{R} (**E_S**) = 15.67 min.

General procedure for the circular dichroism experiments.

Circular Dichroism spectra were measured on a Olis DSM 1000 monochromator, with a temperature control attachment. MOPS:DMF, 2:1 was used as baseline and 100 iterations were done measuring between wavelengths 250–500 nm. Two stock-solutions were made with degassed solvents: $[\text{Pd}(\text{allyl})\text{Cl}]_2$ (3.28 μmol) and ligand **3** (6.21 μmol) were dissolved in DMF (10 ml); *Salmon Testes* DNA (17.707 mg) was dissolved in MOPS-buffer (15 ml, pH 6.5, 20 mM). The stock-solutions were added together in the appropriate amounts and mixed and incubated 30 minutes before measuring the CD spectra in a round cuvet.

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