On the Influence of the Bite Angle of Bidentate Phosphane Ligands on the Regioselectivity in Allylic Alkylation

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The natural bite angle of bidentate phosphane ligands influences the isomer distribution (*syn* and *anti*) in (1-methylallyl)(bisphosphane)Pd OTf complexes. It was found (^{31}P- and ^{1}H-NMR studies) that the *syn*/*anti* ratio changes from 12 (dppp) to 1.3 (sixantphos). Molecular orbital calculations [PM3(tm) level] indicate that for ligands inducing a large bite angle, the phenyl rings of the ligand embrace the allyl moiety, thus influencing the *syn*/*anti* ratio. This bite-angle effect on the *syn*/*anti* ratio is transferred to the regioselectivity in stoichiometric allylic alkylation. Ligands inducing large bite angles direct the regioselectivity towards the formation of the branched product **2**. Catalytic alkylation of (*E*)-2-butenyl acetate showed that for ligands with a small bite angle the regioselectivity of the catalytic and stoichiometric alkylation are in good agreement. This correspondence is worse for ligands with a larger bite angle, which is rationalised in terms of the relative rates of *syn*/*anti* isomerisation and alkylation. The ligand with the largest bite angle (sixantphos) gives the most active catalytic species.

The palladium-catalysed allylic alkylation reaction receives much interest.[1–7] Most of the research in this field focuses on asymmetric induction. Less effort is put into understanding the regioselectivity found in the alkylation of nonsymmetrically substituted allyl fragments.[5,13] Åkermark[5] has shown that the cone angle of substituted phenanthrolines has a large influence on both the isomer distribution of (1-methylallyl)Pd complexes and the regioselectivity of stoichiometric alkylation. The methyl substituents on the 2,9-dimethyl-1,10-phenanthroline ligand interfere with the methyl substituent on the allyl moiety. This causes the *anti* isomer of the complex to prevail over the otherwise more stable *syn* isomer. It was shown that stoichiometric alkylation of the *syn* complex resulted in almost exclusive formation of the linear (*E*) product (**1**). The *anti* complex reacted to the branched (**2**) and the linear *cis* product (**3**) in an approximately 1:1 ratio.

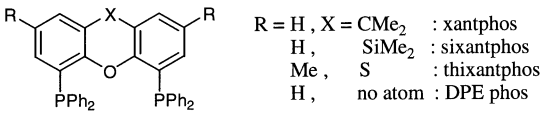

Figure 1. Generic xantphos structure

In our research group much research has been conducted concerning the effect of the natural bite angle[21] (β_n) of bidentate phosphane ligands on transition-metal-catalysed reactions.[15] This research led to the development of a new class of ligands that enforces (very) large bite angles up to 110° (the xantphos-type ligands: see Figure 1). Significant dependencies of the catalyst performance on the natural bite angle have been observed in reactions such as the rhodium-catalysed hydroformylation[8] and the nickel-catalysed hydrocyanation.[9] Recently, we communicated on the effect found in the alkylation of (*E*)-2-hexenyl acetate with sodium diethyl 2-methylmalonate.[11] Ligands with a large natural bite angle were found to direct the regioselectivity to the linear (*E*) product **1** resulting in smaller amounts of the branched product.

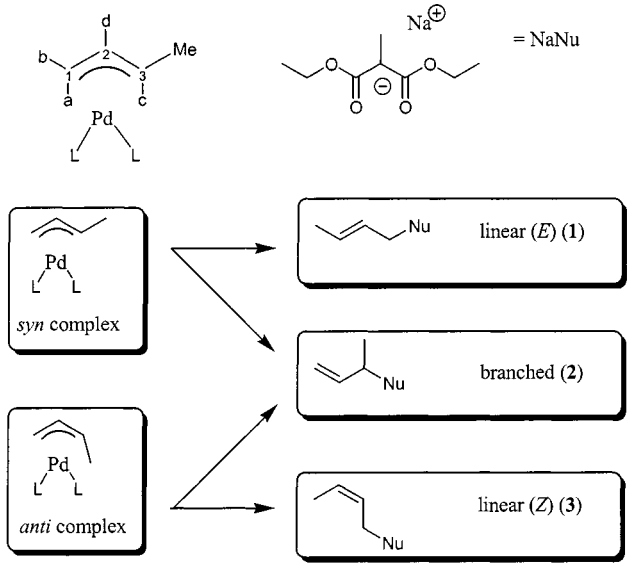

Figure 2. Numbering scheme and formation of regioisomers in the stoichiometric alkylation of (bisphosphane)(1-methylallyl)PdOTf complexes

In order to further investigate the nature of this bite angle effect, we have prepared and isolated (bisphosphane)(1-methylallyl)PdOTf complexes of several bisphosphane ligands. NMR studies (^{1}H and ^{31}P) of these compounds show that they exist as an equilibrium mixture of the *syn*

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and *anti* isomers. The *syn*/*anti* ratio is dependent on the bite angle of the ligand and is significantly lower in complexes of ligands inducing larger bite angles (Table 1).

To understand the effect of the P−Pd−P angle[20] (β) on the structure of the (allyl)Pd complex, molecular orbital calculations [semiempirical PM3(tm) level] were carried out on the cationic (1-methylallyl)(bisphosphane)Pd^+ complexes. The P−Pd−P angle (β), taken from the calculated structures, varies from 85° (dppe) to 110° (sixantphos). The allyl moiety is found to be embraced by the phenyl rings of the ligand. When the bite angle is larger, the embracing becomes more pronounced. This is visualised in Figure 3.

In all the complexes studied using molecular modelling, the *syn* isomer has a lower energy than the *anti* isomer. The energy *difference* between the *syn* and *anti* isomer, however, decreases with larger bite angle. This is in agreement with the experimental data: a lower *syn*/*anti* ratio is observed when ligands inducing larger bite angles are applied (Table 1). The embracing effect in complexes of ligands inducing a *small* bite angle, however, is of minor influence. The relatively high *syn*/*anti* ratio of (dppp)(1-methylallyl)PdOTf is therefore the result of electronic rather than steric effects. This special case will be discussed in more detail elsewhere.[16]

The percentage of **3** remains almost constant along the bite angle range studied.

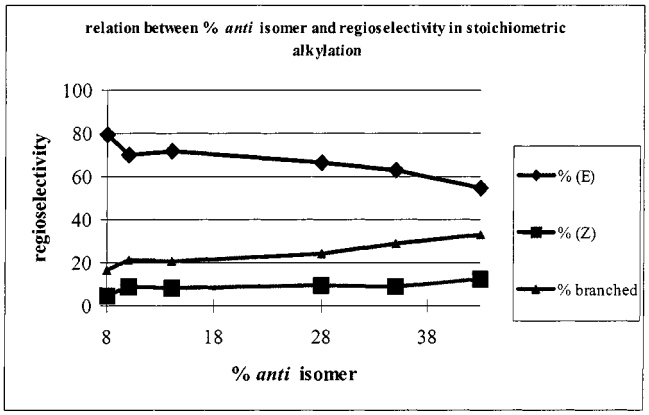

Figure 4. Relation between isomer distribution in cationic (bisphosphane)(1-methylallyl)PdOTf complexes and the regioselectivity of stoichiometric alkylation

It has been suggested[1] that in allylic alkylation reactions the structure of the allyl complex determines the (enantio)-selectivity in an early transition state. Recent developments,[4,6,12−15] however, indicate that in many cases a late transition state is more likely. In an early transition state the steric accessibility of the two carbon atoms of the allyl moiety will determine the selectivity. Due to steric hindrance between the substituent on the allyl moiety and the ligand, it will be bent out of the allyl plane, away from the palladium centre. Therefore the substituted allyl carbon atom C-3 will be less accessible for nucleophilic attack and consequently alkylation of the unsubstituted allyl carbon atom C-1 will prevail.

In a late transition state, nucleophilic attack of the malonate anion at the substituted allyl carbon atom C-3 will cause a change in the hybridisation on C-3 from sp^2 to sp^3. This causes the substituent to bend towards a phenyl ring of the ligand. A large bite angle results in an increase of the steric hindrance in this stage of the reaction (Figure 3), which hampers the formation of **2**.[11]

With a small group like a methyl substituent on the allyl moiety the steric hindrance during the nucleophilic attack is of less influence. Consequently, electronic factors may be-

Table 1. Relation between the bite angle and 1) Δ*E* (*syn*/*anti*) calculated by molecular modelling [PM3(tm) level] and obtained from experimental data (NMR), and 2) the regioselectivity in stoichiometric alkylation of the equilibrium mixtures of (bisphosphane)(1-methylallyl)PdOTf complexes

Complex (ligand)	β[a] [°]	% *syn*	% *anti*	Δ*E* (NMR) [kJ·mol^{-1}]	Δ*E*[b] [pm3(tm)] [kJ·mol^{-1}]	% **1**	% **3**	% **2**
I (dppe)	85	90	10	−5.4	−23.7	70.0	8.9	21.1
II (dppp)	95	92	8	−6.1	−21.9	79.2	4.6	16.2
III (dppb)	99	86	14	−4.5	−20.0	71.7	8.0	20.3
IV (dppf)	106	78	22	−3.1	−18.9	68.9	8.9	22.2
V (DPEphos)	108	72	28	−2.3	−15.4	66.4	9.6	24.0
VI (sixantphos)	110	57	43	−0.7	−12.5	54.5	12.4	33.1

[a] β Obtained from the calculated (bisphosphane)(1-methylallyl)Pd complexes. − [b] The relative large energy difference in the calculations is most likely the result of the absence of solvent and anion.

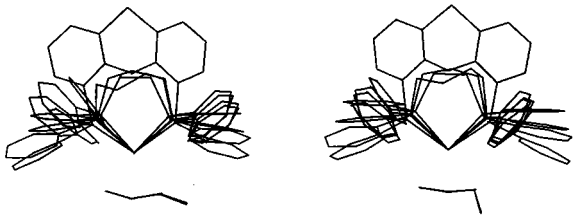

Figure 3. The embracing effect of the phenyl rings cause the substituent on the allyl moiety to bend out of the allyl plane; left = *syn*, right = *anti*

The *syn*/*anti* ratio governs the regioselectivity of the stoichiometric alkylation (Table 1, Figure 4). In (bisphosphane)(1-methylallyl)PdOTf complexes of ligands inducing a *small* bite angle the *syn* isomer largely prevails and the relative amount of the linear (*E*) product **1** is high. Going to a larger bite angle (from dppp to sixantphos), the percentage of *syn* isomer as well as the selectivity to **1** drops, whereas the selectivity to the branched product **2** increases.

come more important. This would explain the good correlation between the *syn*/*anti* ratio and the observed regioselectivity. Therefore it is concluded that in the alkylation of (bisphosphane)(1-methylallyl)PdOTf complexes the transition state of the reaction is not late. The relative importance of steric and electronic factors is dependent on the nature of the ligand and the (*syn* or *anti*) orientation of the substituents on the allyl moiety.

In addition to these stoichiometric experiments we have also carried out the *catalytic* alkylation of (*E*)-2-butenyl acetate. The catalytic experiments have been performed using the isolated (bisphosphane)(1-methylallyl)PdOTf complexes, instead of using a precursor, such as $Pd(dba)_2$, or $Pd(OAc)_2$, and the ligand. This procedure excludes an incubation step which is necessary for the formation of the catalytically active species, as well as the possibility of preequilibria by complexation of dba to Pd.[18] The retarding effect of dba is clear, if we compare the reaction rates presented in Table 2 with the reaction rates presented in a previous communication of the bite angle effect on allylic alkylation.[11] The difference in the rate of reaction is at least one order of magnitude.[16] Remarkably, the observed trend in reaction rate does not remain the same. Starting from the isolated (bisphosphane)(1-methylallyl)PdOTf complex, sixantphos is found to yield the most active catalytic species, whereas use of $Pd(dba)_2$ results in DPEphos or dppb to yield the most active catalyst.[11] Obviously, the catalytically active species is less easily formed from $Pd(dba)_2$ when a rigid ligand inducing a large bite angle is used.

In contrast to most literature procedures for allylic alkylation reactions only one equivalent of ligand per palladium atom is used. When a precursor, such as $Pd(OAc)_2$ is used, an additional equivalent of ligand might be required to reduce the Pd^{II} to the active Pd^0 species.[17] The presence of an excess of ligand will also reduce the rate of the reaction, by complexation to the Pd^0 species which is formed after alkylation. Before coordination of the substrate dissociation of the extra ligand is necessary. This can retard the overall reaction rate.

The bite-angle effect as observed in the *stoichiometric* alkylation of (bisphosphane)(1-methylallyl)PdOTf complexes is less obvious in the *catalytic* alkylation of (*E*)-2-butenyl acetate. The starting complex enters the catalytic cycle by alkylation of the starting (bisphosphane)(1-mehylallyl)-PdOTf complex. The next step involves oxidative addition of the substrate to the thus formed Pd^0 species. As the substrate configuration is mainly (*E*) (95%), initially the *syn*-(bisphosphane)(1-methylallyl)PdOAc complex is formed as the main product. This complex is cationic, so the acetate leaving group will remain as a counterion in the coordination sphere. Interaction of the counterion with the palladium centre is known to increase the rate of dynamic behaviour of the allyl moiety.[19] This results in an isomerisation of the *syn* complex to the *anti* complex and vice versa. The resulting regioselectivity of the catalytic reaction (Table 2) is dependent on the relative rates of *syn*/*anti* isomerisation and alkylation.

NMR experiments with the (bisphosphane)(1-methylallyl)PdOTf complexes used in the alkylation reactions, indicate that the *syn*/*anti* isomerisation in these complexes is slow relative to stoichiometric alkylation. The isomerisation, however, may play a significant role when acetate instead of the weakly co-ordinating triflate is the counterion, as is the case in the catalytic experiments.

The correlation between the regioselectivity in stoichiometric and catalytic alkylation is good for ligands inducing a small bite angle, such as dppe and dppp, but also for dppf (Table 1 and 2). Going to a larger bite angle, the selectivity follows a different trend as that in the stoichiometric reaction. The sixantphos ligand directs the regioselectivity towards 85% of the linear (*E*) product. This can be rationalised in terms of a fast alkylation rate, relative to isomerisation, of the complexes with ligands inducing a large bite angle.

In conclusion, we have shown that for (bisphosphane)(1-methylallyl)PdOTf complexes with ligands inducing a large bite angle the *syn*/*anti* ratio is much lower than in the corresponding complexes with ligands with a small bite angle. Molecular modelling studies indicate that this is caused by an increasing embracement of the allyl moiety by the phenyl rings of the ligand. This bite-angle effect on the *syn*/*anti* ratio can be transferred to the regioselectivity in stoichiometric allylic alkylation. Ligands inducing large bite angles direct the regioselectivity towards the formation of **2**. In the *catalytic* alkylation of (*E*)-2-butenyl acetate, however, the regioselectivity is also determined by the relative rates of *syn*/*anti* isomerisation and alkylation. The correlation between the regioselectivity found in the stoichiometric and

Table 2. Catalytic alkylation of (*E*)-2-butenyl acetate using the equilibrium mixtures of (bisphosphane)(1-methylallyl)PdOTf complexes

Complex (ligand)	β[a] [°]	t.o.f.[b] [$\times 10^3$ mol·h^{-1}]	Yield[c] (%)	% **1**	% **3**	% **2**
I (dppe)	85	2.0	37.3	68.8	11.1	20.0
I (dppp)	95	2.9	37.1	76.0	6.6	17.4
III (dppb)	99	8.9	90.3	79.0	3.1	17.9
IV (dppf)	106	8.0	81.5	74.1	2.5	23.4
V (DPEphos)	108	8.7	86.0	80.1	2.5	17.4
VI (sixantphos)	110	9.1	88.3	85.7	1.4	12.9

[a] β Obtained from the calculated (bisphosphane)(1-methylallyl)Pd complexes. – [b] t.o.f. is the initial turn over frequency, determined after 10 min of reaction time. – [c] Based on the formation of **1**, **2**, and **3**, as determined after 30 min by GC, using the internal standard method. The catalytic reactions were performed in THF (10 mL), using 0.05 mol-% of catalyst (0.00050 mmol), 1.0 mmol of substrate, and 2.0 mmol of sodium diethyl 2-methylmalonate. The reaction was monitored by GC using decane as the internal standard.

the catalytic alkylation is best for ligands inducing a small bite angle. The ligands with the largest bite angle (sixantphos) is found to result in the most active catalytic species.

Experimental Section

^{1}H- (300 MHz, TMS, $CDCl_3$) and ^{31}P-NMR spectra (121.5 MHz external 85% H_3PO_4, $CDCl_3$) were recorded with a Bruker AMX-300 spectrometer. − Elemental analyses were performed with an Elementar Vario EL (Foss Electric). − All calculations were carried out using the commercially available SPARTAN program (version 5.0.3). The geometry optimisation was performed on the semiempirical pm3(tm) level. − The product distribution was measured with an Interscience Mega2 apparatus, equipped with a DB1 column, length 30 m, inner diameter 0.32 mm, film thickness 3.0 μm, and an F.I.D detector. − All experiments were carried out using standard Schlenk techniques. All solvents were freshly distilled prior to use. − Sodium diethyl 2-methylmalonate (0.5 M in THF) was prepared from diethyl 2-methylmalonate and NaH in THF at 273 K. − The stoichiometric alkylation reactions were performed by adding an excess of sodium diethyl 2-methylmalonate (0.1 mL of a 0.5 M solution in THF) to a solution of 10 mg of the Pd complex in 1 mL of THF. Reaction was instantaneous and after 1 min, the mixture was worked up with water, filtered through silica gel, and analysed by GC. − The catalytic reactions were performed in THF (10 mL), using 0.05 mol-% of catalyst (0.00050 mmol), 1.0 mmol of substrate, and 2.0 mmol of sodium diethyl 2-methylmalonate. The reaction was monitored by taking samples from the reaction mixture which, after aqueous workup, were analysed by GC using decane as the internal standard. − The Pd complexes were prepared in CH_2Cl_2 from [(1-methylallyl)Pd(μ-Cl)]$_2$ by adding 2 equiv. of ligand and abstracting the Cl atom with AgOTf. The complexes were isolated in quantitative yield (white microcrystalline powder) as their analytically pure equilibrium mixtures and were used as such in the alkylation reaction. The syntheses of DPEphos and sixantphos have been published elsewhere.[6] Dppe, dppp, dppb, and dppf were obtained from Acros chemicals and used as received. − Analytical data of the (ligand)(1-methylallyl)-PdOTf complexes are given for their equilibrium mixtures. The NMR signals of the *syn* and *anti* isomers could easily be distinguished. The *syn*/*anti* ratio was determined by comparing the intensities of the signals of the methyl substituent on the allyl moiety. NMR data of the complexes were obtained in $CDCl_3$ (δ values).

(dppe)(1-methylallyl)PdOTf (Is+a): Obtained in a *syn*/*anti* ratio of 90:10. − $C_{32}H_{31}F_3O_3P_2PdS$ (721.005) (**Ia+s**): calcd. C 52.51, H 4.38; found C 52.08, H 4.30.

(dppe)(*syn*-1-methylallyl)PdOTf (Is): ^{1}H NMR: δ = 1.69 (ddd, J_1 = 6.3 Hz, J_2 = 8.4 Hz, J_3 = 8.4 Hz, 3 H, Me), 2.4−3.0 (m, 4 H, 2 × CH_2 bridge), 3.1 (dd, J_1 = 12.1 Hz, J_2 = 12.1 Hz, 1 H, H-a), 4.37 (m, 1 H, H-c), 4.6 (dd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 1 H, H-b), 5.7 (ddd, J_1 = 7.4 Hz, J_2 = 13.1 Hz, J_3 = 13.1 Hz, 1 H, H-d), 7.3−7.7 (m, 20 H, Ar). − ^{31}P{^{1}H} NMR: δ = 48.5 (d, J = 33 Hz), 49.6 (d, J = 33 Hz).

(dppe)(*anti*-1-methylallyl)PdOTf (Ia): ^{1}H NMR: δ = 0.9 (ddd, J_1 = 6.9 Hz, J_2 = Hz, J_3 = Hz, 3 H, Me), 2.4−3.0 (m, 4 H, 2 × CH_2 bridge), 3.5 (dd, 1 H, H-a), 4.15 (m, 1 H, H-c), 4.7 (dd, 1 H, H-b), 5.6 (m, 1 H, H-d), 7.3−7.7 (m, 20 H, Ar). − ^{31}P{^{1}H} NMR: δ = 49.9 (d, J = 35 Hz), 52.6 (d, J = 35 Hz).

(dppp)(1-methylallyl)PdOTf (IIs+a): Obtained in a *syn*/*anti* ratio of 92:8. − $C_{33}H_{33}F_3O_3P_2PdS$ (735.032) (**IIa+s**): calcd. C 53.16, H 4.60; found C 52.58, H 4.74.

(dppp)(*syn*-1-methylallyl)PdOTf (IIs): ^{1}H NMR: δ = 1.14 (ddd, J_1 = 6.7 Hz, J_2 = 8.9 Hz, J_3 = 8.9 Hz, 3 H, Me), 2.6−3.0 (m, 4 H, 2 × CH_2 bridge), 3.0 (dd, J_1,J_2 > 7 Hz, 1 H, H-a), 3.65 (dd, J_1,J_2 < 7 Hz, 1 H, H-b), 4.2 (m, 1 H, H-c), 5.5 (ddd, J_1 = 12.4 Hz, J_2 = 12.4 Hz, J_3 = 7.4 Hz, 1 H, H-d), 7.2−7.6 (m, 20 H, Ar). − ^{31}P{^{1}H} NMR: δ = 6.75 (d, J = 65.3 Hz), 8.01 (d, J = 65.3 Hz).

(dppp)(*anti*-1-methylallyl)PdOTf (IIa): ^{1}H NMR: δ = 0.88 (ddd, J_1 = 7.1 Hz; J_2 = 7.1 Hz, J_3 = 7.1 Hz, 3 H, Me), 2.6−3.0 (m, 4 H, 2 × CH_2 bridge), 3.2 (dd, J_1,J_2 > 7, 1 Hz, 1 H, H-a), 4.0 (dd, J_1 = 6.9 Hz, J_2 = 6.9 Hz 1 H, H-b), 4.0 (dd, J_1 = 6.9 Hz, J_2 = 6.9 Hz, 1 H, H-b), 4.7 (m, 1 H, H-c), 5.5 (m, 1 H, H-d), 7.2−7.6 (m, 20 H, Ar). − ^{31}P{^{1}H} NMR: δ = 7.1 (d), 7.9 (d).

(dppb)(1-methylallyl)PdOTf (IIIs+a): Obtained in a *syn*/*anti* ratio of 86:14. − $C_{34}H_{35}F_3O_3P_2PdS$ (749.059) (**IIIa+s**): calcd. C 53.78, H 4.79; found C 52.60, H 4.73.

(dppb)(*syn*-1-methylallyl)PdOTf (IIIs): ^{1}H NMR: δ = 1.15 (ddd, J_1 = 9.4 Hz, J_2 = 7.2 Hz, J_3 = 7.2 Hz, 3 H, Me), 1.7−2.0 (m, 4 H, 2 × CH_2 bridge), 2.5−2.8 (m, 4 H, 2 × CH_2 bridge), 2.95 (dd, J_1 = 11.3 Hz, J_2 = 11.3 Hz, 1 H, H-a), 3.7 (dd, J_1 = 6.5 Hz, J_2 = 6.5 Hz, 1 H, H-b), 4.85 (m, 1 H, H-c), 5.5 (ddd, J_1 = 7.4 Hz, J_2 = 13.0 Hz, J_3 = 13.0 Hz, 1 H, H-d), 7.4−7.7 (m, 20 H, Ar). − ^{31}P{^{1}H} NMR: δ = 20.4 (d, J = 20.8 Hz), 21.2 (d, J = 20.8 Hz).

(dppb)(*anti*-1-methylallyl)PdOTf (IIIa): ^{1}H NMR: δ = 0.64 (ddd, J_1 = 6.7 Hz, J_2 = 6.7 Hz, J_3 = 6.7 Hz, 3 H, Me), 1.7−2.0 (m, 4 H, 2 × CH_2 bridge), 2.5−2.8 (m, 4 H, 2 × CH_2 bridge), 3.05 (dd, 1 H, H-a), 4.0 (dd, 1 H, H-b), 5.7 (m, 1 H, H-d), 7.4−7.7 (m, 20 H, Ar). − ^{31}P{^{1}H} NMR: δ = 20.7 (d, overlap with signals of *syn* complex), 21.2 (d, overlap with signals of *syn* complex).

(dppf)(1-methylallyl)PdOTf (IVs+a): Obtained in a *syn*/*anti* ratio of 78:22. − $C_{40}H_{35}F_3FeO_3P_2PdS$ (876.973) (**IVa+s**): calcd. C 54.15, H 4.05; found 53.71, H 4.11.

(dppf)(*syn*-1-methylallyl)PdOTf (IVs): ^{1}H NMR: δ = 1.08 (ddd, J_1 = 6.7 Hz, J_2 = 6.7 Hz, J_3 = 10.3 Hz, 3 H, Me), 3.23 (dd, J_1 = 11.0 Hz, J_2 = 11.0 Hz, 1 H, H-a), 3.50 (dd, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 1 H, H-b), 3.83 (s, 1 H, Cp-H), 3.94 (s, 1 H, Cp-H), 4.27 (s, 1 H, Cp-H), 4.32 (s, 1 H, Cp-H), 4.35−4.55 (m, contains Cp-H and H-c), 4.37 (s, 1 H, Cp-H), 4.46 (s, 1 H, Cp-H), 4.63 (s, 1 H, Cp-H), 4.83 (s, 1 H, Cp-H), 5.64 (ddd, J_1 = 12.9 Hz, J_2 = 12.9 Hz, J_3 = 7.4 Hz, 1 H, H-d), 7.3−7.8 (m, 20 H, Ar, *syn* and *anti*). − ^{31}P{^{1}H} NMR: δ = 24.9 (d, J = 47.5 Hz), 23.6 (d, J = 47.5 Hz).

(dppf)(*anti*-1-methylallyl)PdOTf (IVa): ^{1}H NMR; some signals appear as shoulders on signals of **IVs**, others appear as separate signals: δ = 0.90 [ddd, J_1 = J_2 = J_3 = 6.8 Hz, 3 H, Me], 3.2 [shoulder on signals of **IVs** (H-a), H-a], 3.93 (s, 1 H, Cp-H), 4.35−4.55 (m, contains Cp-H), 4.40 (s, 1 H, Cp-H), 4.43 (s, 1 H, Cp-H), 4.51 (s, 1 H, Cp-H), 4.56 (s, 1 H, Cp-H), 4.66 (s, 1 H, Cp-H), 4.74 (ddd, J_1 = J_2 = J_3 = 6.8 Hz, 1 H, H-c), 7.3−7.8 (m, 20 H, Ar, *syn* and *anti*). − ^{31}P{^{1}H} NMR: signals appear as shoulders on signals of **IVs**.

(DPEphos)(1-methylallyl)PdOTf (Vs+a): Obtained in a *syn*/*anti* ratio of 72:28. − $C_{42}H_{35}F_3O_4P_2PdS$ (861.148) (**Va+s**): calcd. C 57.99, H 4.15; found C 57.60, H 4.08.

(DPEphos)(*syn*-1-methylallyl)PdOTf (Vs): ^{1}H NMR: δ = 1.1 (ddd, J_1 = 10.7 Hz, J_2 = 6.6 Hz, J_3 = 6.6 Hz, 3 H, Me), 3.4 (m, 2 H, H-a and H-b), 4.4 (m, 1 H, H-c), 5.6 (ddd, J_1 = 7.4 Hz, J_2 = 12.7 Hz, J_3 = 12.7 Hz, 1 H, H-d), 6.4−7.6 (m, Ar). − ^{31}P{^{1}H} NMR: δ = 10.3 (d, J = 39.6 Hz), 17.1 (d, J = 39.6 Hz).

(DPEphos)(anti-1-methyl-allyl)PdOTf (Va): ^{1}H NMR: δ = 0.9 (ddd, J_1 = 6.6 Hz, J_2 = 6.6 Hz, J_3 = 6.6 Hz, 3 H, Me), 3.0 (dd, J_1 = 9.1 Hz, J_2 = 14.1 Hz, 1 H, H-a), 4.2 (dd, J_1 = 6.4 Hz, J_2 = 6.1 Hz, 1 H, H-b), 4.4 (m, 1 H, H-c), 5.8 (ddd, J_1 = 14.0 Hz, J_2 = 7.7 Hz, J_3 = 7.7 Hz, 1 H, H-d), 6.4−7.6 (m, Ar). − ^{31}P{^{1}H} NMR: δ = 10.6 (d, J = 40 Hz), 16.4 (d, J = 40 Hz).

(sixantphos)(1-methylallyl)PdOTf (VIs+a): Obtained in a *syn*/*anti* ratio of 57:43. − $C_{44}H_{39}F_3O_4P_2PdSSi$ (917.287) (**VIa+s**): calcd. C 55.88, H 4.46; found C 56.31, H 4.35.

(sixantphos)(*syn*-1-methylallyl)PdOTf (VIs): ^{1}H NMR: δ = 0.57 (s, 3 H, MeSi), 0.61 (s, 3 H, MeSi), 0.8 (ddd, J_1 = 11.3 Hz, J_2 = 6.3 Hz, J_3 = 6.3 Hz, 3 H, Me), 3.4 (dd, J_1 = 11.7 Hz, J_2 = 11.7 Hz, 1 H, H-a), 3.55 (dd, J_1 = 6.4 Hz, J_2 = 6.4 Hz, 1 H, H-b), 4.4 (m, 1 H, H-c), 5.4 (ddd, J_1 = 12.8 Hz, J_2 = 12.8 Hz, J_3 = 7.3 Hz, 1 H, H-d), 6.9−7.5 (m, Ar, *syn* and *anti*), 7.7 (q, Ar, *syn* and *anti*). − ^{31}P{^{1}H} NMR: δ = 9.8 (d, J = 39.3 Hz), 10.6 (d, J = 39.3 Hz).

(sixantphos)(*anti*-1-methylallyl)PdOTf (VIa): ^{1}H NMR: δ = 0.57 (s, 3 H, MeSi), 0.61 (s, 3 H, MeSi), 0.9 (ddd, J_1 = 6.2 Hz, J_2 = 6.2 Hz, J_3 = 6.2 Hz, 3 H, Me), 3.4 (dd, J_1 = 11.7 Hz, J_2 = 11.7 Hz, 1 H, H-a), 3.7 (dd, J_1 = 7.1 Hz, J_2 = 7.1 Hz, 1 H, H-b), 4.65 (m, 1 H, H-c), 5.9 (ddd, J_1 = 13.8 Hz, J_2 = 8.0 Hz, J_3 = 8.0 Hz, 1 H, H-d), 6.9−7.5 (m, Ar, *syn* and *anti*), 7.7 (q, Ar, *syn* and *anti*). − ^{31}P{^{1}H} NMR: δ = 5.8 (d, J = 35.2 Hz), 7.0 (d, J = 35.2 Hz).

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