On the Influence of the Bite Angle on the Allylic Alkylation of (*E*) and (*Z*) Substrates: Loss and Retention of Double Bond Stereochemistry

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Keywords: Allyl complexes / Homogeneous catalysis / P ligands / Palladium

The bite angle of bidentate phosphane ligands has a pronounced influence on the degree of retention of the double bond geometry of the allylic substrate in the allylic alkylation reaction. To study the effect of the ligand on the regioselectivity, (*Z*)- and (*E*)-pent-2-enyl acetate were used as substrates. The alkylation of substrates with an (*E*) conformation of the double bond results in the preferential formation of the linear (*E*) product. A larger bite angle of the ligand results in an increase of the regioselectivity to >98% for the Sixantphos ligand. Analogously, the alkylation of (*Z*) substrates results in the formation of the linear (*Z*) product. Remarkably, for (*Z*) substrates, a larger bite angle of the ligand leads to an increased regioselectivity for the formation of the branched product instead of the linear product, up to 47.5% for Sixantphos. The observed regioselectivities are rationalized in terms of: a) a competition between *syn-anti* isomerization and alkylation, and b) a combination of steric and electronic effects in the transition state of the reaction. For all ligands tested, the reaction is faster for the (*E*) than for the (*Z*) substrate. However, competition experiments using the Sixantphos ligand show a relatively fast reaction rate for the (*Z*) substrate, which indicates that the coordination of the substrate to palladium is the discriminating, but not the rate-determining, step when both substrates are present.

Introduction

Transition metal-catalyzed allylic alkylation is a useful tool in synthetic organic chemistry.[1] A total control of the stereoselectivity and regioselectivity is required for most applications of this reaction. Whereas the enantioselective alkylation of symmetrically disubstituted allyl moieties (derived from, for example, cyclohexenyl acetate) has received much attention in the literature,[1] the regioselectivity of the reaction with other types of allylic substrates has been studied less extensively.[2−6]

When nonsymmetrically substituted allylic substrates are used,[2−6] regiocontrol is required prior to enantiocontrol (Figure 1). So far, palladium catalysts are the most widely studied, and generally show for such substrates a preference for the formation of the linear product.[1a,2] With bidentate P-N ligands, however, it is possible to obtain a high regioselectivity for the chiral branched product.[3] Catalysts based on other metals,[4] such as tungsten or iridium, also show a preference for the branched product, but the rate of the reaction is much lower than that found for palladium.

Relatively few studies have been reported concerning the influence of the geometry of the starting allylic substrate on the regioselectivity of the palladium catalyzed reaction.[5] Some years ago, Åkermark et al. reported such a study in which phenanthroline-type ligands were used in the allylic alkylation reaction with sodium diethyl 2-methylmalonate as the nucleophile.[5a] It was found that the regioselectivity of the reaction is dependent on the geometry of the double bond [(*E*) or (*Z*)] of the substrate. The (*E*) substrate reacts with the Pd(ligand) fragment to form an allylic complex having a *syn* geometry, which, after reaction with the nucleophile, mainly yields the linear (*E*) product. Analogously, the (*Z*) substrate reacts to form a (ligand)Pd(allyl) complex with an *anti* geometry (see Figure 1), which results in the formation of the linear (*Z*) and the branched product. They also reported that in the catalytic reactions, the regioselectivity is determined by competition between *syn-anti* isomerization and alkylation.

Recently, we have reported on the effect of the bite angle of bidentate *phosphane* ligands on the *syn*/*anti* ratio of cationic (P-P)Pd(crotyl) complexes.[6] It was found that a large bite angle leads to a low *syn*/*anti* ratio as a result of increased steric interactions. *Stoichiometric* alkylation of these complexes showed a correlation between the bite angle and the regioselectivity: the complexes were present as *syn*/*anti* mixtures, which complicated interpretation of the data. Moreover, apart from the C1 to C3 selectivity, the regioselectivity of the *catalytic* reaction was also determined by the competition between *syn-anti* isomerization and alkylation, which obscured structure-selectivity relations.

The *syn-anti* isomerization of the allyl moiety involves a π-σ rearrangement during which the allyl moiety is temporarily σ-bonded to the palladium through the substituted terminal allylic carbon atom (see Figure 2).[7] Rotation about the Pd−C bond and the adjacent C−C bond, followed by σ-π rearrangement then yields the other (*syn* or *anti*) isomer. As a result of increased steric hindrance, this process is slower when the substituent is larger. In order to explore the influence of the size of the allyl substituent on

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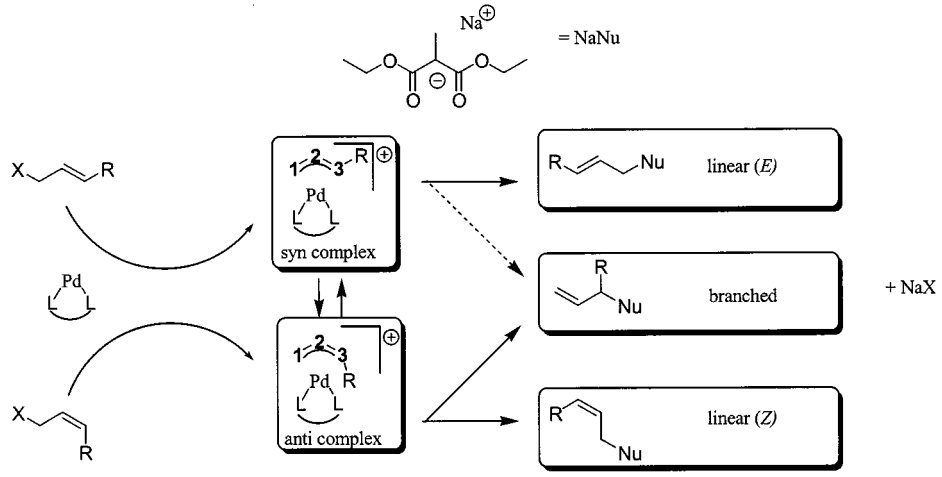


Figure 1. Regioselectivity in the allylic alkylation and numbering scheme

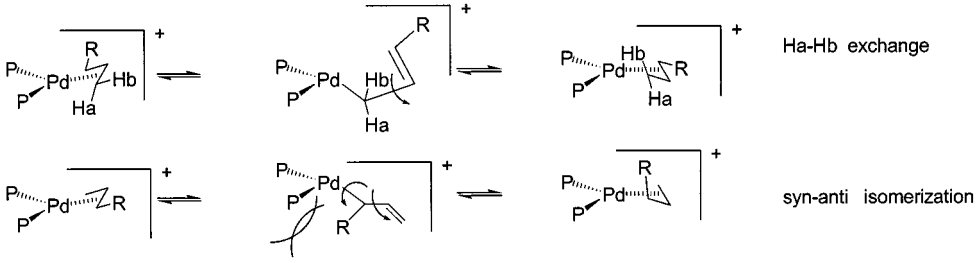
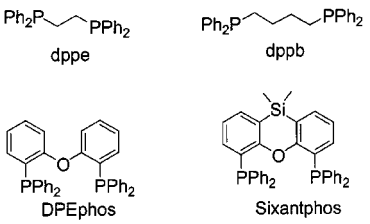


Figure 2. The π-σ rearrangement on different terminal sites of the allyl moiety (top: H_a-H_b exchange does not involve *syn-anti* isomerization of substituent R; bottom: *syn-anti* isomerization of substituent R is hampered by steric hindrance)

the regioselectivity, we have also performed the reaction with methyl-, ethyl- and propyl-substituted allylic substrates. By using (*Z*)- and (*E*)-pent-2-enyl acetate as substrates instead of (*E*)-but-2-enyl acetate, it appeared that a small change in steric size resulted in a relatively slow *syn-anti* isomerization rate (see below). This way, we have been able to study the effects of the ligands on the alkylation of the transient *syn* and *anti* isomeric complexes.

Results

All experiments were carried out with cationic (crotyl)Pd(ligand) complexes as catalyst precursors using four ligands that differ significantly in the calculated bite angle[6] (dppe, dppb, DPEphos and Sixantphos, see Figure 3).



ligand	calculated bite angle[a] (°)
dppe	85
dppb	99
DPEphos	108
Sixantphos	110

Figure 3. The ligands {[a]: the bite angle has been determined by pm3(tm) geometry optimization of the cationic (crotyl)Pd(ligand) complexes that have been employed in the catalytic experiments[6]}

(*Z*) *and* (*E*) *Allylic Substrates*

To study the effect of the double bond geometry of the substrate we performed the allylic alkylation of (*Z*)- and (*E*)-pent-2-enyl acetate with sodium diethyl 2-methylmalonate as the nucleophile (Table 1). Starting from the (*E*) substrate, the linear (*E*) product is formed primarily. When the bite angle of the ligand is larger, the regioselectivity for the formation of this product increases. In contrast, the (*Z*) substrate reacts to form both the linear (*Z*) and the branched product. In this case, a larger bite angle of the ligand results in an increase of the regioselectivity to the branched product. With dppe, the reaction rate is low compared to the other ligands and, remarkably, the linear (*E*) product is formed in high regioselectivity, even starting from the (*Z*) substrate. The fastest reactions are observed using the relatively flexible ligands dppb and DPEphos. For all ligands, the alkylation of the (*Z*) allylic substrate is slower than that of the (*E*) allylic substrate.

Competition Experiments

To gain more insight into the different courses the reaction takes for the (*E*)- and (*Z*)-pent-2-enyl acetate, competition experiments were carried out with the ligands dppb and Sixantphos (Table 2). It was found that in the separate experiments the alkylation of the (*Z*) substrate is much slower than that of the (*E*) substrate. With dppb in the com-

Table 1. Alkylation of (*Z*)- and (*E*)-pent-2-enyl acetate

Substrate geometry	Complex (ligand)	TOF_{ini} [a] (mole/mole/h)	% branched[b]	% linear *E*[b]	% linear *Z*[b]
E	dppe	2100	1.9	94.2	3.9
E	dppb	7200	1.4	96.9	1.7
E	DPEphos	16900	1.1	98.1	0.8
E	Sixantphos	5500	1.0	98.3	0.6
Z	dppe	160	3.1	86.4	10.5
Z	dppb	1400	15.6	7.3	77.1
Z	DPEphos	3200	26.7	1.1	72.3
Z	Sixantphos	950	47.5	0.8	51.7

[a] Determined after 2 minutes reaction time (the reaction conditions are described in the Experimental Section). – [b] Determined after complete conversion.

Table 2. Competition experiment using (*E*)- and (*Z*)-pent-2-enyl acetate

Complex (ligand)	Time (min.)	% *Z* substrate[a]	% *E* substrate[a]	% branched[b]	% linear *E*[b]	% linear *Z*[b]
dppb	2	5	11	7	40	53
dppb	5	12	16	9	43	48
dppb	10	28	33	9	43	48
dppb	30	56	58	9	47	44
dppb	60	75	77	9	48	43
dppb	180	88	92	9	50	41
Sixantphos	2	12	8	36	23	41
Sixantphos	5	36	21	35	26	39
Sixantphos	10	65	38	34	29	37
Sixantphos	30	95	82	28	42	30
Sixantphos	60	100	98	25	48	27
Sixantphos	180	100	100	24	50	26

[a] Percentage of substrate consumed (the reaction conditions are described in the Experimental Section). – [b] Regioselectivity, percentage of total yield.

petition experiments, however, a much smaller difference in conversion rate is observed between the (*E*) and (*Z*) substrates. Furthermore, when Sixantphos is used as the ligand, the (*Z*) substrate is consumed at a higher rate than the (*E*) substrate. The initially predominating consumption of the (*Z*) substrate results in the formation of primarily the linear (*Z*) and the branched product. The regioselectivity of the reaction is dependent on the conversion and, as the reaction proceeds, the fraction of linear (*E*) product increases.

Influence of the Size of the Allyl Substituent

The results with (*E*)-pent-2-enyl acetate show a different regioselectivity than previously found for (*E*)-but-2-enyl acetate.[6] The results of the allylic alkylation of (*E*)-substituted allylic substrates bearing substituents of different size (methyl, ethyl and propyl) are compared in Table 3. In all cases there is a preference for the formation of the linear (*E*) product. The selectivity for the formation of the (*E*)

Table 3. Alkylation of various (*E*)-substituted allylic acetates (but-2-enyl acetate, pent-2-enyl acetate, hex-2-enyl acetate)

Substrate	Complex (ligand)	TOF_{ini} [a] (mole/mole/h)	% branched[b]	% linear *E*[b]	% linear *Z*[b]
Butenyl	dppe	2000	20.0	68.8	11.1
Butenyl	dppb	8900	17.9	79.0	3.1
Butenyl	DPEphos	8700	17.4	80.1	2.5
Butenyl	Sixantphos	9100	12.9	85.7	1.4
Pentenyl	dppe	2100	1.9	94.2	3.9
Pentenyl	dppb	7200	1.4	96.9	1.7
Pentenyl	DPEphos	16900	1.1	98.1	0.8
Pentenyl	Sixantphos	5500	1.0	98.3	0.6
Hexenyl	dppe	150	1.1	97.3	1.7
Hexenyl	dppb	1900	0.8	98.9	0.3
Hexenyl	DPEphos	200	0.6	99.3	0.1
Hexenyl	Sixantphos	700	0.7	99.2	0.1

[a] Determined after 2 minutes reaction time (the reaction conditions are described in the Experimental Section). – [b] Determined after complete conversion.

product increases when ligands with a larger bite angle are used. As expected, the regioselectivity is also influenced by the size of the substituent. The selectivity increases when the substituent is larger, leading to 99.3% linear (*E*) product in the alkylation of (*E*)-hex-2-enyl acetate (R = propyl) by a Sixantphos-ligated palladium complex. The size of the substituent also has a pronounced effect on the rate of the reaction: the larger the substituent, the slower the reaction.

Discussion

Several studies have been devoted to the origin of regioselectivity in the palladium-catalyzed allylic alkylation.[1a,2−6,8−10] Two different effects have been reported: 1) in the case of an *early* transition state, the regioselectivity is determined by the relative electrophilicity of the terminal allylic carbon atoms and steric hindrance is of minor importance;[8] 2) in the case of a *late* transition state, the degree steric hindrance encountered during the nucleophilic attack and the subsequent rotation of the allyl moiety becomes important.[2a,9] The route to the formation of the linear product is then favored over that of the branched product.

From theoretical[10] and experimental studies it is known that the allylic alkylation reaction proceeds by attack of the nucleophile on the cationic (π-allyl)Pd(ligand) species (Figure 4). This results in the formation of a single bond between the attacked allylic carbon atom and the nucleophile (stage **a**). A C=C double bond is then formed between the other two allylic carbon atoms (stage **b**). During these processes, the allyl moiety rotates, forming a transient neutral (olefin)Pd(P-P) complex (stage **b**).

In a recent theoretical study, a combined explanation is presented for the apparent occurrence of either an early or a late transition state.[10c] The nucleophilic attack at the most electrophilic terminal allylic carbon atom (early transition state) results in a lowering of the energy barrier of stage **b** of the reaction.

Influence of the Alkene Geometry

The alkylation of (*E*)-pent-2-enyl acetate does not yield more than 4% of the linear (*Z*) product and 2% of the branched product (Table 1), thus giving almost complete retention of alkene geometry. The linear (*E*) product can only be formed from the *syn* isomer (see Figure 1), indicating that for each of the tested palladium(ligand) complexes, oxidative addition of the (*E*) substrate yields mainly the *syn* isomer. Analogously, the results obtained for (*Z*)-pent-2-enyl acetate (Table 1) indicate that after its oxidative addition to palladium, the *anti* isomer is formed, which then reacts to form the linear (*Z*) product. However, reaction of the (*Z*) substrate leads to the formation of a relatively large amount of the linear (*E*) product. These mixtures of products can only be formed after isomerization from *anti* to *syn* (or vice versa) has occurred. Thus, the regioselectivity is a result of: (i) the *syn*/*anti* equilibrium, (ii) the competition between isomerization and alkylation, and (iii) the C1 to C3 regioselectivity for attack on the *syn* and the *anti* isomer.[5a] These points will be discussed individually below.

Concerning the *syn*/*anti* ratio, we have shown before that for cationic (crotyl)Pd(ligand) complexes (ligand = dppe, dppb, DPEphos and Sixantphos), the *syn* isomer is more stable than the *anti* isomer.[6] The crotyl substrate yields an allyl group with a relatively small methyl substituent. After oxidative addition of a pentenyl substrate, an allyl moiety bearing a larger ethyl group (*syn* or *anti*) is formed which will show more steric interaction of both the *syn* and the *anti* isomer with the ligand. The data obtained from the catalytic experiments (Table 1) indicate that the relatively small difference in size between a methyl and an ethyl substituent has a large effect on the *syn*/*anti* ratio of the transient allyl complexes. Because the results indicate that the *anti*-to-*syn* isomerization prevails over the *syn*-to-*anti* isomerization (Table 1), it is concluded that for larger substituents on the allyl group, the preferred *syn*/*anti* ratio is higher than that previously observed for the methyl substituent.

The occurrence of a competition between *syn*-*anti* isomerization and alkylation is supported by the concurrence

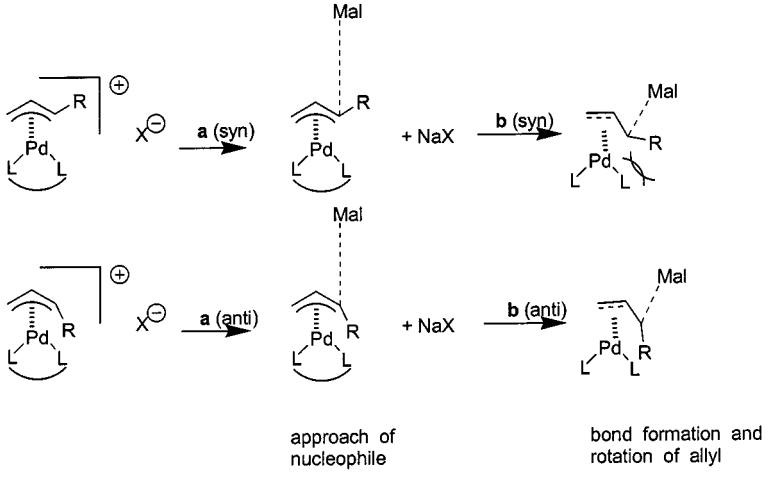


Figure 4. *Syn* and *anti* complexes: comparison of the consecutive steps of the reaction

of a low reaction rate and a low regioselectivity. Thus, the alkylation of the (*Z*) substrate occurs at a lower rate than that of the (*E*) substrate, allowing *anti*-to-*syn* isomerization to take place prior to nucleophilic attack, which lowers the overall regioselectivity. The rate of isomerization is especially fast for dppe relative to the rate of alkylation; the reaction of the (*Z*) substrate leads almost exclusively to the formation of the (*E*) product.

The effect of the bite angle on the C1 to C3 regioselectivity of the alkylation is different for the *syn* and the *anti* isomer. The selectivity of the *syn* isomer to the formation of the linear (*E*) product increases when the bite angle is larger. This can be explained in terms of steric hindrance during both stages **a** and **b** of the reaction. The linear C1 position is more accessible for the approaching nucleophile than the branched C3 position. Furthermore, during the bond formation the substituent has to bend away from the nucleophile in the direction of the sterically crowded Pd(ligand) fragment. Nucleophilic attack on the allyl moiety results in the formation of a transient palladium-olefin complex,[9c] in which the C=C double bond is located in the P−Pd−P plane and the malonate-substituted C3 atom below this plane (see Figure 4). When the branched product has been formed, the substituted C3 site, bearing the ethyl group and the malonate, is rotated out of the P−Pd−P plane (stage **b**). In a *syn*-substituted allyl moiety, the ethyl group points in the direction of the phenyl rings of the ligand. The steric interactions thus encountered are more pronounced when the bite angle of the ligand is larger. So, during both stages **a** and **b** of the reaction, steric hindrance directs the regioselectivity to the formation of the linear (*E*) product.

In contrast, the effect of the bite angle on the regioselectivity of the alkylation of the *anti* isomer shows the opposite trend. It is known that in palladium complexes of disubstituted allylic substrates, the branched *anti* position is relatively electrophilic and consequently more reactive than the branched *syn* position.[5b] The geometrical distortion resulting from steric interactions with the ligand are relatively large for the *anti* compared to the *syn* isomer. An increase of the bite angle will enhance the geometrical distortion of the allyl moiety and thereby[2c][10c] enhance the relative electrophilicity of the allylic carbon atom at the branched C3 position compared to the C1 position. Thus, during the approach of the nucleophile (stage **a** of the reaction) the electronic effects may prevail over the steric hindrance giving the branched product. During the rotation of the allyl moiety after the nucleophilic attack has taken place (stage **b**), the ethyl group of the *anti* isomer will point downward, i.e. not in the direction of the phenyl rings of the ligand, and steric hindrance will be less than in the case of the *syn* isomer (stage **b**). So also for the *anti* isomer, in both stage **a** and **b** of the reaction, the regioselectivity is directed to the formation of the same regioisomer, i.e. the branched product for the *anti* isomer and the linear (*E*) product for the *syn* isomer.

Competition Experiments

The competition experiments carried out to gain more mechanistic insight in the reaction course of the (*E*) and the (*Z*) substrate showed a relatively high reaction rate for the latter. Because the overall reaction rate in the separate experiments is higher for the (*E*) substrate than for the (*Z*) substrate, the discrimination in the competition experiments has to take place in an early stage of the catalytic cycle of the reaction. As a result of the better accessibility of the (*Z*) double bond relative to the (*E*) double bond, the coordination of the substrate to palladium will be faster for the (*Z*) than for the (*E*) substrate. As the (*E*) substrate is found to react faster, we conclude that the next steps of the reaction proceed at a higher rate for the (*E*) substrate than for the (*Z*) substrate (Figure 5).

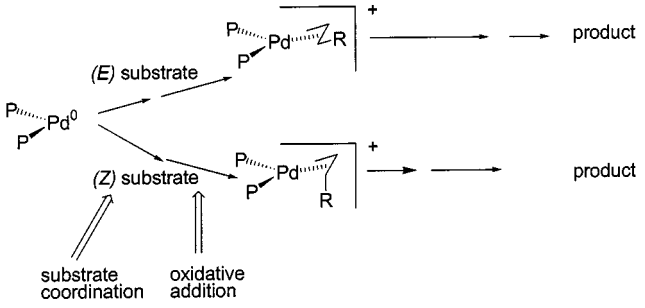


Figure 5. Schematic representation of the origin of kinetic resolution (the size of the arrows indicates the relative rate)

The change in rate difference in the competition experiments compared to the separate experiments is larger for Sixantphos, the ligand with the largest bite angle (Table 2). Upon coordination of the substrate to a Pd^0(Sixantphos) complex, the steric hindrance will be larger than for the analogous complex with the dppb ligand, and therefore the discrimination between the (*E*) and (*Z*) substrate will be more pronounced for Sixantphos. It is possible that, for dppb, the substrate discrimination does take place at this stage, but its effect may be compensated by a rate difference in the next steps of the reaction.

It can be argued that the discriminating step, coordination of the olefin, is not the rate determining step of the reaction. If the coordination of the (*E*) substrate were rate limiting, and thus slower than the coordination of the (*Z*) substrate, the (*E*) substrate would not react faster in the *separate* experiments. Analogously, if the coordination to palladium were the rate determining step for the (*Z*) substrate, it would not be found to react faster in the *competition* experiments.

On the other hand, if the rate determining step for the *E* substrate is indeed the substrate coordination and for the *Z* substrate, the subsequent oxidative addition would be rate determining and the latter being slower than the substrate coordination of the (*E*) substrate, the above arguments are not true. Unfortunately, the coordination of the substrate and the subsequent oxidative addition cannot be distinguished in kinetic experiments.

Effect of the Size of the Substituent

The alkylation of the (*E*) substrates with different substituents all show the same trend (Table 3). Both a larger bite angle of the ligand and a larger substituent on the allyl moiety result in an increase of the regioselectivity to the formation of the linear (*E*) product. As has been described above, the *syn*/*anti* isomer ratio will be lower for small groups, which accounts for the relatively large amount of linear (*Z*) product formed from alkylation of (*E*) but-2-enyl acetate. Furthermore, the relatively large size of the ethyl and propyl groups relative to the methyl group, hinders the attack of the nucleophile on the branched position. This explains the smaller amounts of branched product formed when either the substituent or the bite angle of the ligand is larger.

The rate of the reaction is also affected by the size of the substituent. The lower rate of reaction when larger substrates are used can be explained in terms of steric hindrance. During the oxidative addition and the nucleophilic attack, a larger allylic substrate will experience more steric hindrance than a small allylic substrate and the reaction may therefore proceed at a lower rate. The product dissociation will probably not be rate limiting, but, nevertheless, the coordination of a larger product will be more hindered than that of a small one, and therefore it may dissociate faster than a small product. Which of these effects prevails depends on the nature of the rate limiting step of the reaction, which may be determined by the size and orientation of the substituent and the bite angle of the ligand.

In the absence of significant steric interactions, a larger bite angle of the ligand results in an increase of the rate of reaction. Thus, the alkylation of (*E*)-but-2-enyl acetate occurs at the highest rate when the Sixantphos ligand is used. The rate of alkylation of the larger substrates is the highest for catalysts bearing a flexible ligand favoring a relatively large bite angle, such as dppb or DPEphos.

Conclusion

We separated the effect of the bite angle on the regioselectivity resulting from the *syn* and the *anti* isomeric complex. The regioselectivity of the reaction of the *syn* isomer is determined by steric effects in both the first and the second stage of the reaction, resulting in almost exclusive formation of the linear (*E*) product. The geometry of the allyl moiety in the *anti* isomer is presumably distorted to a large extent and the electrophilicity of the branched position is large relative to the linear position. The regioselectivity of its alkylation is, in the first stage of the reaction, mainly governed by electronic factors, and in the second stage by steric effects. For *syn* complexes of ligands with a large bite angle, the *linear* product is favored both in the first and the second stage of the reaction, whereas for the *anti* isomer, the *branched* product becomes the favored regioisomer in both stages of the reaction.

In competition experiments between the (*E*) and (*Z*) substrates, the (*Z*) substrate is found to react at a rate that is similar to or faster than that of the (*E*) substrate, whereas in separate experiments the reaction with the (*E*) substrate is faster. This effect is more pronounced for Sixantphos than for dppb. The substrate discrimination presumably takes place in the stage of coordination of the olefin to the metal center, prior to oxidative addition and prior to the rate determining step. Therefore, in a system in which both the (*E*) and (*Z*) substrate are present, the latter dominates the reaction rate.

Experimental Section

^{1}H NMR (300 MHz, TMS, $CDCl_3$), $^{31}P\{^1H\}$ (121.5 MHz external 85% H_3PO_4, $CDCl_3$), ^{13}C NMR (75.4 MHz, TMS, $CDCl_3$) were recorded on a Bruker AMX-300 spectrometer. The product distribution of the alkylation experiments was measured on an Interscience Mega2 GC 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 and allylic substrates were freshly distilled prior to use. Diethyl 2-methylmalonate, NaH, and (*E*)-hex-2-enyl acetate were obtained from Aldrich.

General Synthetic Procedures: Sodium diethyl 2-methylmalonate (0.5 M in THF) was prepared from diethyl 2-methylmalonate (20 mmol, 3.48 g) and NaH (20 mmol, 0.48 g) in THF at 273 K. The synthesis and characterization of all complexes,[6] crotyl acetate,[6] and the alkylation products of the coupling of crotyl acetate and (*E*)-hex-2-enyl acetate to sodium diethyl 2-methylmalonate are described elsewhere.[5a]

Alkylation Reactions: The *catalytic* reactions were performed at 292 K in THF (5 mL), using 0.05 mol-% of catalyst (0.25 μmol), 0.5 mmol of substrate (0.064 g) and 1.0 mmol of sodium diethyl 2-methylmalonate (0.20 g). All reagents were added from stock solutions. The reaction was monitored by taking samples from the reaction mixture which, after aqueous work up, were analyzed by GC using decane (0.0142 g) as the internal standard. − NMR spectroscopic data were obtained in $CDCl_3$ (δ in ppm).

Diethyl 2-Methyl-[(2*E*)-pent-2-en-4-yl]malonate (linear *E*): ^{1}H: δ = 0.90 (t, ^3J = 7.3 Hz, 3 H, C*H*$_3$−CH$_2$−CH=), 1.22 (t, ^3J = 7.0 Hz, 6 H, O−CH$_2$−C*H*$_3$), 1.32 (s, 3 H, C$_{quat.}$−CH$_3$), 2.0 (m, 2H, CH$_3$−C*H*$_2$−CH=), 2.50 (d, ^3J = 6.9 Hz, 2 H, C$_{quat.}$−C*H*$_2$−CH=), 4.12 (q, ^3J = 7.0 Hz, 4 H, O−C*H*$_2$−CH$_3$), 5.25 (m, 1 H, olefinic H), 5.50 (m, 1 H, olefinic H). − $^{13}C\{^1H\}$: δ = 14.1 (*C*H$_3$−CH$_2$−CH=), 14.5 (O−CH$_2$−*C*H$_3$), 20.1 (C$_{quat.}$−*C*H$_3$), 26.0 (CH$_3$−*C*H$_2$−CH=), 39.2 (C$_{quat.}$−*C*H$_2$−CH=), 54.3 (*C*$_{quat.}$−CH$_3$), 61.5 (O−*C*H$_2$−CH$_3$), 123.1 (CH$_3$−CH$_2$−*C*H=), 137.4 (CH$_3$−CH$_2$−CH=*C*H), 172.5 (C=O).

Diethyl 2-Methyl-[(2*Z*)-pent-2-en-4-yl]malonate (linear *Z*): ^{1}H: δ = 0.90 (t, ^3J = 7.5 Hz, 3 H, C*H*$_3$−CH$_2$−CH=), 1.20 (t, ^3J = 7.0 Hz, 6 H, O−CH$_2$−C*H*$_3$), 1.33 (s, 3H, C$_{quat.}$−CH$_3$), 2.05 (m, 2H, CH$_3$−C*H*$_2$−CH=), 2.56 (d, ^3J = 7.5 Hz, 2 H, C$_{quat.}$−C*H*$_2$−CH=), 4.12 (q, ^3J = 7.0 Hz, 4 H, O−C*H*$_2$−CH$_3$), 5.15 (m, 1H, CH$_3$−CH$_2$−CH=C*H*), 5.45 (m, 1H, CH$_3$−CH$_2$−C*H*=CH). − $^{13}C\{^1H\}$: δ = 13.9 (*C*H$_3$−CH$_2$−CH=), 14.4 (O−CH$_2$−*C*H$_3$), 17.4 (C$_{quat.}$−*C*H$_3$), 20.0 (CH$_3$−*C*H$_2$−CH=), 33.4 (C$_{quat.}$−CH$_2$-CH=), 51.3 (*C*$_{quat.}$−CH$_3$), 61.6 (O−*C*H$_2$−CH$_3$), 122.7 (CH$_3$−CH$_2$−*C*H=), 135.9 (CH$_3$−CH$_2$−CH=*C*H), 172.5 (C=O).

3-(Diethyl 2-Methyl [(1*E*)-pent-1-ene malonate) (branched): ^{1}H: δ = 0.82 (t, ^3J = 7.5 Hz, 3 H, C*H*$_3$−CH$_2$−CH=], 1.20 (t, ^3J = 7.0 Hz, 6 H, O−CH$_2$−C*H*$_3$), 1.21 (m, 2H, CH$_3$−C*H*$_2$−CH), 1.32 (s, 3H, C$_{quat.}$−CH$_3$), 3.38 (m, 1H, CH$_3$−CH$_2$−C*H*), 4.12 (q, ^3J = 7.0 Hz, 4 H, O−C*H*$_2$−CH$_3$), 5.01 (d, ^3J = 16.8 Hz, 1 H, *E*−CH=C(H)*H*), 5.05 (d, *J* = 10.2 Hz, 1 H, *Z*−CH=C(H)*H*), 5.6 (m, 1H −C*H*=C(H)H). − ^{13}C{^{1}H}: δ = 12.8 (*C*H$_3$−CH$_2$−CH), 14.4 (O−CH$_2$−*C*H$_3$), 17.4 (C$_{quat.}$−*C*H$_3$), 21.0 (CH$_3$−*C*H$_2$−CH), 46.5 (CH$_3$−CH$_2$−*C*H), 51.3 (*C*$_{quat.}$−CH$_3$), 61.6 (O−*C*H$_2$−CH$_3$), 118.9 (−CH−CH=*C*H$_2$), 137.2 (−CH−*C*H=CH$_2$), 172.5 (C=O).

Acknowledgments

This research was carried out with financial support from DSM Research B.V. and with a subsidy from the Ministerie van Onderwijs, Cultuur en Wetenschappen as part of the E. E. T. program for clean chemistry.

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Received July 28, 2000
[I00299]