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Stereochemistry of the Palladium-Catalyzed Allylic Substitution: The Syn-Anti Dichotomy in the Formation of (π-Allyl)Palladium Complexes and their Equilibration†

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Abstract: The mechanism of palladium(0)-catalyzed allylic substitution has been investigated with the aim of finding whether or not the intermediate (π-allyl)palladium complexes can arise in a *syn* fashion as an alternative to the well known *anti*-mechanism. Using (diphenylphosphino)acetate as a leaving group and stereochemically biased substrates **30b** and **35b** evidence for the *syn* stereochemistry has been acquired (**30b** → **31** and **35b** → **36**). This reversal of stereochemistry is facilitated by severe steric congestion in the starting allylic esters (which impairs the ordinary *anti*-mechanism) and is boosted by the pre-coordination of the Pd(0) reagent to the leaving group. The latter effect apparently lowers the activation entropy. With cyclohexene derivatives **10b**, **18b**, and **19b** and acyclic substrate **25b**, where steric hindrance does not operate, the *anti*-mechanism producing η^3-complexes dominates even for (diphenylphosphino)acetates. At elevated temperature, rapid equilibration of η^3-complexes (**13** ⇄ **14** and **20** ⇄ **21**) has been observed prior to the reaction with a nucleophile. This effect has been attributed to the presence of (diphenylphosphino)acetate ion acting as a ligand for palladium.

Introduction

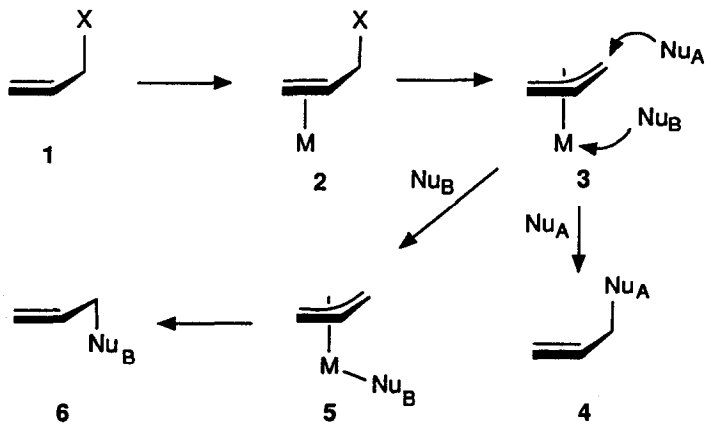
Allylic substitution, in its traditional version, is a capricious reaction that can afford a variety of products due to the competing S_N1, S_N2, S_N2', and elimination processes.[1] Moreover, the S_N2' reaction can proceed in an *anti* or *syn* fashion,[1-3] so that mixtures of products are often obtained, unless an inherent bias in the substrate molecule strongly favors one particular pathway.

In 1965 Tsuji[4] reported on the stoichiometric reaction of (π-allyl)palladium complexes with nucleophiles, effecting an overall allylic substitution. Later (in 1970), Walker[5] and Hata[6] discovered that the allylic displacement of OR groups with a variety of nucleophiles requires only a catalytic amount of palladium. These findings opened a vast area of further studies and applications. The refinement of this reaction owes much to the work of Trost,[7] Tsuji,[8] Bäckvall,[9] and others,[10] who recognized its potential. Since the mid 70-ties the palladium-catalyzed allylic substitution has evolved into a very mild, efficient

and generally stereospecific method for C-C, C-N, and C-O bond formation in both inter- and intramolecular versions[7-10] whereas investigation of the classical S_N2' reaction virtually ceased in early 80-ties.

Stereochemical studies demonstrated that formation of the intermediate (π-allyl)palladium complexes from allylic esters,[11] carbonates,[12] or phosphates[13] (oxidative addition) uniformly proceeds via an *anti*-mechanism (**1** → **2** → **3**).[14] The following reaction with stabilized C-nucleophiles (Nu_A) leads to **4**, again via an *anti*-mechanism (Scheme I).[11,12,14] In contrast, reactions of the complexes with organometallics (Nu_B),[15] such as aryl- and vinylzinc halides,[15c,16,17] and aryl- and vinyltin[18] and zirconium[15] reagents give *syn*-products in the second step (**3** → **5** → **6**).[19]

Scheme I



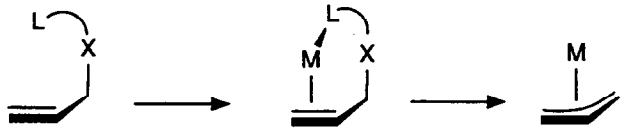
In sharp contrast to the variability of the stereochemistry of the second step, the initial oxidative addition has been found to invariably occur in an *anti* fashion.[11-14] However, a *syn*-mechanism for this step should also be stereoelectronically allowed, in spite of being apparently higher in energy. If attainable, this reversal of stereochemistry would largely broaden the synthetic scope of the palladium-catalyzed allylic substitution. Here we present a full account of our efforts to achieve the *syn*-mechanism in the oxidative addition as a follow up to our preliminary communication.[24]

Results

We reasoned that the *syn* route for the oxidative addition of Pd(0) to the allylic substrate (Scheme II) might be boosted, e.g., by pre-coordination of the Pd(0) reagent to the leaving group (**7** → **8** → **9**). This type of coordination has been observed in the reactions of allylic carbamates with organocuprates,[27] and steering a reagent by pre-coordination to a neighboring group has become an established method of stereocontrol for a number of other reactions[26] such as epoxidation,[27] cyclopropanation,[28] mercuration,[29] carbonylation,[30] hydroboration,[31] hydrogenation,[32] addition of Grignard reagents,[33] and others.[26,34] In analogy with the previous work of Trost, who used allylic acetate **10a** (Scheme III) as a model compound to elucidate the stereochemistry of the palladium-catalyzed

substitution (Table 1, entries 1, 2), we have prepared a set of carbamates[35] **10d-10g** and thiocarbamate[36] **10h** (Scheme III) and submitted them to palladium catalyzed substitution with the sodium or lithium salt of diethyl malonate. All of them, however, followed the usual reactivity of the acetate **10a** in spite of the previously reported reversal of the steric course of reaction with cuprates.[25] No substantial *syn* pathway could be detected and good yields of **15** with diastereoisomeric excess of ~10:1 were isolated in all cases (Table 1, entries 15-18).[37] Apparently, neither N nor S in our leaving groups could coordinate palladium effectively so as to induce an appreciable proportion of the *syn* pathway.

Scheme II



7 **8** **9**

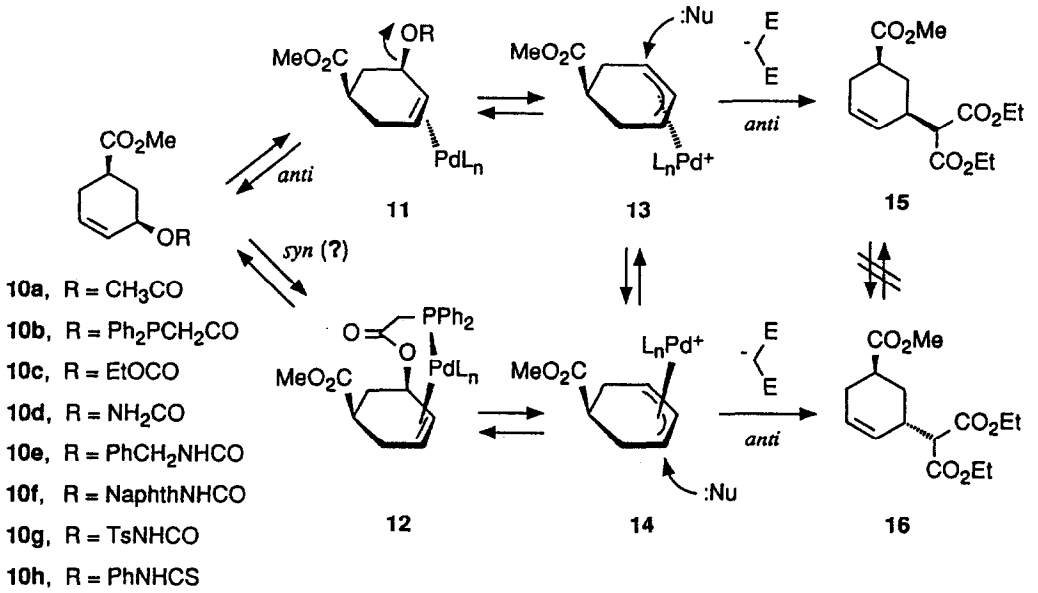
Since phosphines are known to be particularly good ligands for palladium we turned our attention to (diphenylphosphino)acetic acid (DPPAcOH)[38] and prepared the corresponding ester **10b** (Scheme III). The latter was treated with alkali salt (Li or Na) of diethyl malonate and a catalytic-(5 mol%)to-stoichiometric amount of Pd(0) in various solvents, using a range of temperature, and various ligands (Table 1). While acetate **10a** is known to predominantly afford the product of overall retention of configuration (entry 1) with high selectivity (93:7 to 98:2), we found that with our DPPAcO derivative **10b** we could achieve up to 3:2 ratio of the products **15** and **16** (entries 3-6). Since no epimerization of **10b** was detected at ca. 50% conversion, it was conceivable that the minor product **16** might really arise by the mechanism we looked for, involving pre-complexation of the palladium reagent to the Ph_2P- group and formation of the complex **12**. But still, the competing mechanism of the oxidative addition remained the dominant reaction pathway, giving eventually **15** as the major product.[39]

We next reasoned that strongly coordinating ligands in the catalyst give the DPPAcO group little chance of replacement. Therefore, we have elucidated the ligand effect (entries 6-11). Bidentate dppe is obviously coordinated even more strongly to Pd(0) than is Ph_3P and, accordingly, a higher proportion of the *anti* pathway was observed (entry 7). Turning to "weaker" ligands, such as dibenzylideneacetone (dba; entry 8) and p-benzoquinone (entries 9 and 10) we expected to shift the product distribution in favor of **16**. However, the reaction was found to return back to the usual outcome (entries 8-10); neither changing the solvent (from non-coordinating benzene to strongly coordinating DMF or MeCN) nor addition of LiCl,[9] had a pronounced effect on the reaction (see notes for entry 4). Experimenting with added external ligands, such as Ph_3P or $P(CH_2CH_2CN)_3$ (entries 6 and 11), also did not lead to a significant improvement and the best product ratio (ca. 1:1) was obtained in the presence of the latter ligand (entry 11).

At this stage we felt that evidence for the coordination of the Pd(0) reagent to the DPPAcO group was clearly needed. This would have been difficult in the catalytic mode and we have therefore prepared complex **17** (52%)[40] by reaction of **10b** with $[(\pi\text{-crotyl})PdCl]_2$ in the presence of maleic

anhydride. When **17** was submitted to the reaction with diethyl sodiomalonate in THF at r.t. for 30 min., a 49:51 mixture of **15** and **16** (71% isolated yield) was obtained rather than the expected pure **16**. A possible explanation could be as follows. About half of the molecules may react in an intramolecular fashion employing a *syn*-mechanism for the formation of the η^3-intermediate, which is eventually converted to **16**. The other half of the molecules react in an intermolecular way utilizing the second molecule of **17**, or the released Pd(0) species, as a reagent for the *anti*-mechanism, eventually producing **15**.[41,42]

Scheme III

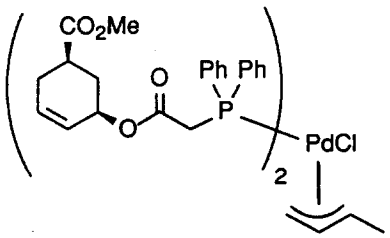


A further possibility for boosting the *syn*-mechanism would be to make Pd in **17** coordinatively unsaturated through abstracting Cl by silver.[47] This might facilitate the coordination of Pd to the neighboring carbon-carbon double bond and, possibly, shift the reaction in favor of the *syn*-mechanism. However, when **17** was treated with $NaCH(CO_2Et)_2$ in the presence of an equivalent of $AgBF_4$ at r.t. for 1 h, the product analysis showed a significant shift back toward the ordinary outcome giving an 82:18 mixture of **15** and **16** in 75% yield.[48] In a related experiment, a Pd(II) complex was first generated by reaction of **10b** with a stoichiometric amount of $(MeCN)_2PdCl_2$ and then reduced to a Pd(0)-complex by means of $Fe(CO)_5$. The latter was then treated with diethyl sodiomalonate in THF at 50°C for 48 h but, again, afforded **15** as the major product (92:8; 33% isolated yield).

Table 1. Reaction of **10** with $LiCH(CO_2Et)_2$/Pd(0) in THF at 0.03 M concentration

entry	compd	leaving group	catalyst	mol% of catalyst	temp. (°C)	time (h)	ratio **15:16** [a]	isolated yield (%)
1	**10a**	CH_3CO	$(Ph_3P)_4Pd$	5	50	16	93:7 [b]	91
2	**10a**	CH_3CO	$(Ph_3P)_4Pd$	10	50	1	82:18	60
3	**10b**	DPPAcO	$(Ph_3P)_4Pd$	10	50	1	67:33	42
4	**10b**	DPPAcO	$(Ph_3P)_4Pd$	25	50	1	58:42	95 [c,d]
5	**10b**	DPPAcO	$(Ph_3P)_4Pd$	100	50	1	57:43	78
6	**10b**	DPPAcO	$(Ph_3P)_4Pd$	25 [e]	50	1	73:27	51
7	**10b**	DPPAcO	$(dppe)_2Pd$	5	50	1	>95:5 [f]	62
8	**10b**	DPPAcO	$(dba)_2Pd$	50	50	1	>95:5 [f]	80
9	**10b**	DPPAcO	$(Ph_3P)_2Pd(BQ)$	25 [g]	20	1	94:6	92
10	**10b**	DPPAcO	(bpy)Pd(BQ)	25	20	1	95:5	90
11	**10b**	DPPAcO	$[(\pi\text{-crotyl})PdCl]_2$	50 [g,h]	20	1	53:47	93
12	**10b**	DPPAcO	$(Ph_3P)_4Pd$	25	0	1	92:8	53
13	**10b**	DPPAcO	$(Ph_3P)_4Pd$	20	20	1	72:28	87
14	**10c**	EtOCO	$(Ph_3P)_4Pd$	10 [g]	50	2	94:6	80
15	**10e**	BnNHCO	$(Ph_3P)_4Pd$	25 [g]	50	16	89:11	92
16	**10f**	NphthNHCO	$(Ph_3P)_4Pd$	25 [g]	50	16	81:19	92
17	**10g**	TsNHCO	$(Ph_3P)_4Pd$	25 [g]	50	16	87:13	93
18	**10h**	PhNHCS	$(Ph_3P)_4Pd$	25 [g]	50	16	86:14	79

[a] Determined by GC. [b] With $(dppe)_2Pd$ the ratio was 98:2 (ref 21d). [c] In DME the ratio was 57:43 at 50 °C and in dioxane 66:34. Other solvents (C_6H_6, $CHCl_3$, C_5H_5N, MeCN, and DMF) gave ≥ 90:10 ratio. [d] When the reaction was carried out at 0.003 M concentration, the ratio had changed to 8911. [e] With 100 mol% of Ph_3P as an added ligand. [f] Determined by ^1H NMR. [g] The reaction was carried out with $NaCH(CO_2Et)_2$. [h] With 100 mol% of $P(CH_2CH_2CN)_3$ as an added ligand.



17

Since not even the complex **17** was particularly prone to the *syn*-mechanism an alternative rationalization should be sought for the reactivity of our DPPAc derivatives. Bosnich has demonstrated that optically active (π-allyl)palladium complexes may be partly or fully racemized by an excess of the Pd(0)-reagent.[49] Assuming that isomerization can occur at the stage of η^3-complexes, it is conceivable that **17** is first converted to the (π-allyl) complex (one way or another) and the latter is isomerized prior to its reaction with nucleophile. Similarly, in the catalytic reaction, **10b** would initially produce a η^3-complex which would then isomerize to a mixture of **13** and **14**; this sequence would be reflected in the product ratio. In order to find which of the two diastereoisomeric η^3-complexes is formed first from **10b** (prior to the isomerization), we have elucidated the temperature effect on the catalytic reaction (entries 4, 12, and 13). At 0°C (entry 12) the reaction of **10b** gave approximately the same ratio of the products as that obtained from acetate **10a**. Raising the temperature to 20°C (entry 13) and further to 50° (entry 4) resulted in a continuing increase of the proportion of **16**. Further increase (to 80°C in DME) had no effect indicating that an equilibrium had been reached. This behavior suggests that the η^3-complex is predominantly formed via the *anti*-mechanism even for **10b** with subsequent thermodynamic equilibration **13** ⇆ **14** at elevated temperature.

To gain further support for this rationalization, it was desirable to explore the reaction with other substrates. To this end we prepared steroidal esters **18** - **19** (Scheme IV). To our surprise, we found all of them either to be inert toward the Pd-catalyzed substitution with diethyl sodiomalonate or to give complex mixtures of products under harsh conditions.[50] On the other hand, these esters reacted with PhZnCl in the presence of a catalytic amount of $(Ph_3P)_4Pd$. While 3β-derivatives **18a** and **18b** gave similar compositions of the products **22** and **23**, slightly favoring the former (Table 2, entries 1 and 2), **19a** reacted differently from **19b**. While acetate **19a** gave approximately the opposite ratio of **22** to **23** to that obtained from its epimer **18a** (Table 2, entry 3), the DPPAcO derivative **19b** clearly favored inversion to give almost pure **22** (entry 4).[52] Since organometallics are known to react stereospecifically with the (π-allyl)palladium complexes using a *syn*-mechanism, the results obtained with **18a**, **18b**, and **19a** are consistent with the existence of both diastereoisomeric Pd-complexes **20** and **21** as intermediates; the product ratio indicates that equilibration of these complexes has occurred, although apparently not to completion. In contrast, the formation of a single phenyl derivative **22** from **19b** is probably due to substantial elimination, which may well have been the major reaction pathway for the β-diastereoisomeric complex **20**.

Since all the above allylic derivatives displayed some degree of steric hindrance, further information was sought using an aliphatic substrate free of any steric congestion. Acetate (-)-**25a** (58% ee) is known to produce (-)-**28** (58% ee) via the *anti,anti* sequence (Scheme V) on a Pd(0)-catalyzed reaction with dimethyl sodiomalonate.[14a] We have prepared DPPAc derivative (+)-**25b** from the enantiomeric alcohol (+)-**24** of ≥99% ee[53] and carried out the Pd(0)-catalyzed reaction under the standard conditions (at 40°C) to get a dextrorotatory product (+)-**28**, whose optical rotation indicated about 84% optical purity,[57] while the ^{1}H NMR spectrum taken in the presence of $Eu(tfc)_3$ implied 74% ee[58] which corresponds to an 87:13 ratio. This is again in agreement with the ordinary *anti*-mechanism for the oxidative addition followed by partial racemization of the intermediate η^3-complex **27**.[59]

Scheme IV

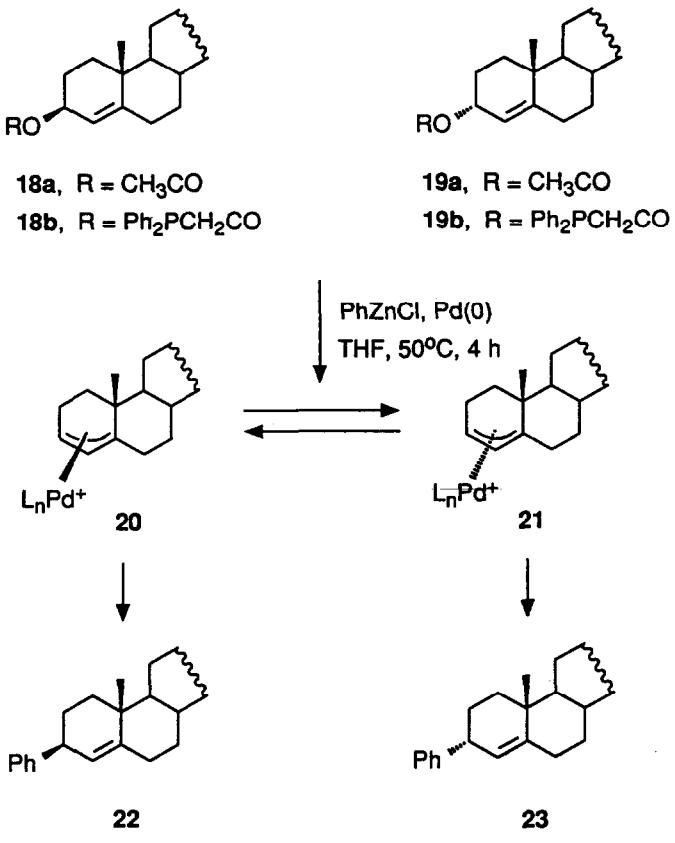
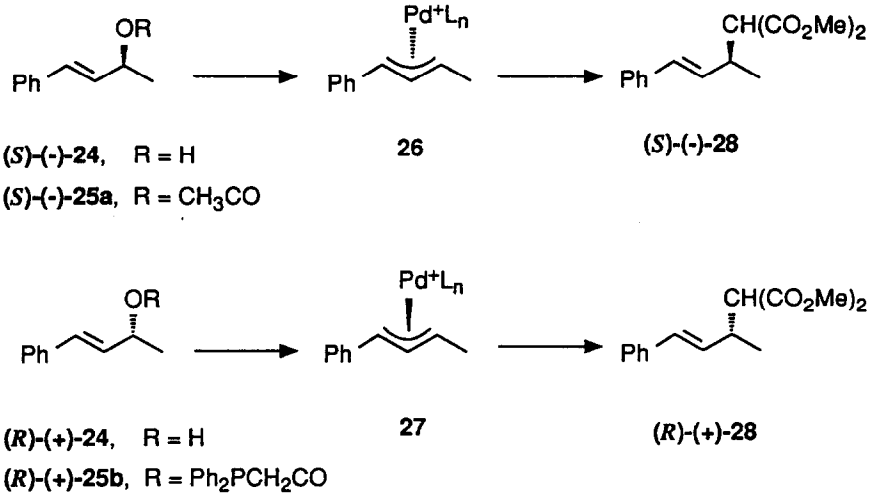


Table 2. Reaction of **18** and **19** with PhZnCl/Pd(0)

entry	compd	ratio[a] 22:23	isolated yield (%) substitution	elimination
1	**18a**	59:41	62	32
2	**18b**	65:35	51	19
3	**19a**	43:57	41	12
4	**19b**	> 95:5	59	39

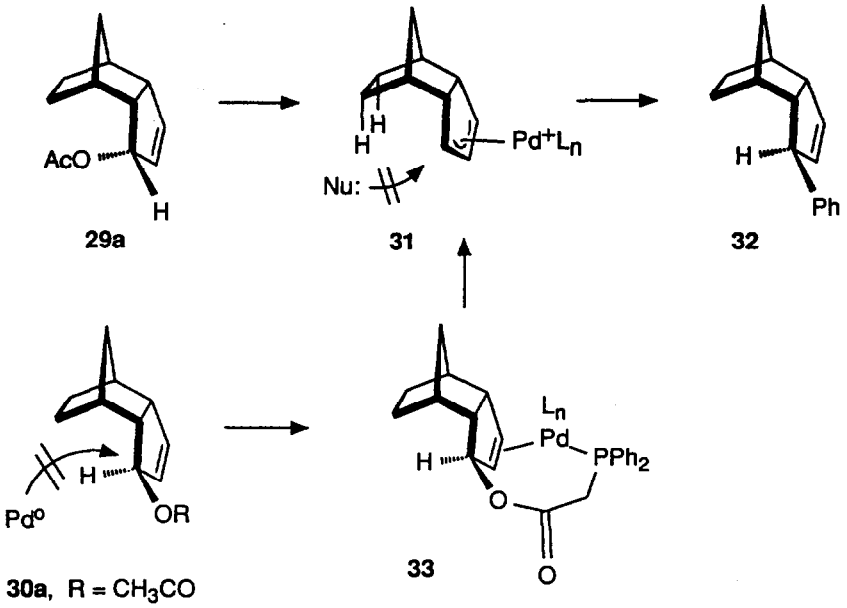
[a] Determined by ^{1}H NMR (see ref. 52).

Scheme V

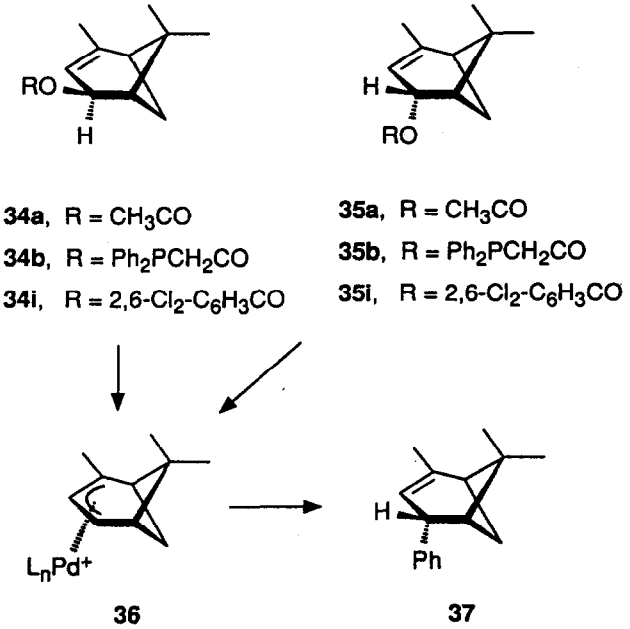


These experiments showed that although the initial results achieved with **10b** seemed to provide support for the *syn*-mechanism, those obtained later did not. Nevertheless, we wished to explore systems, where the ordinary *anti* pathway for oxidative addition would be strongly disfavored by, e.g., steric congestion, to find out if this would finally promote the *syn*-mechanism. A suitable pair of model compounds **29a** and **30a** to address this issue was found in the literature[17] (Scheme VI). The acetate **29a** is known to form the intermediate Pd complex **31** via an ordinary *anti*-mechanism and produce phenyl derivative **32** on subsequent *syn* reaction with PhZnCl; no reaction is observed with diethyl sodiomalonate, due to the severe steric hindrance the nucleophile would experience from the *anti* (i.e. *endo*) face of the double bond in **31.** In contrast to **29a**, the epimeric acetate **30a** has been reported to be inert towards Pd-catalyzed reactions, because the *endo* face of the allylic system required for the *anti*-mechanism is, again, severely hindered.[17] It turned out that the DPPAc derivative **30b**, of the same configuration as the inert acetate **30a**, readily reacted with PhZnCl/Pd(0), giving **32** as the sole product (in 80% isolated yield), identical with the compound obtained from the acetate **29a** (Scheme VI). Since the second step is known[17] to proceed stereospecifically in a *syn* fashion, the intermediate η^3-complex formed from **30b** should be the same as that arising from **29a**. Moreover, while the reaction of **29a** requires 2 h at 20°C to reach completion, **30b** reacted within 30 min at the same temperature. Since no epimerization of the starting material **30b** was observed, we believe that this example finally provided the required evidence for the *syn*-mechanism. When the reaction time of the acetate **30a** was extended to 48 h (still at 20°C), we also obtained the same phenylated product **32**, although in an appreciably lower yield (57%) due to partial decomposition and polymerization. Again, no epimerization of the starting acetate **30a** was observed so that this can also be interpreted as evidence for the *syn*-mechanism.

Scheme VI



Scheme VII



Similar steric bias to that in **29** and **30**, could be expected in *trans*- and *cis*-verbenol[60] derivatives **34** and **35**. Acetate **34a** and DPPAc **34b** turned out to react sluggishly with PhZnCl/$(Ph_3P)_4Pd$ affording, after 36 h at 20°C,[61] the phenylated product **37**[62] in 20% and 29% isolated yield, respectively. In contrast, epimeric esters **35a** and **35b** differed dramatically from one another. Whereas acetate **35a** reacted sluggishly again (20°C, 40 h, to furnish only 18% yield of **37**),[61] the reaction of **35b** was complete within 1 h at 20°C and produced **37** in 53% yield. This dramatic acceleration is in agreement with a mechanism encompassing pre-coordination of Pd to the Ph_2P- group and a *syn*-type oxidative addition to generate intermediate **36**. It appears that in the *cis*-isomers **34a** and **34b** the alignment of the C-O bond and the π-orbitals (required for the reaction to occur)[11f] is difficult to achieve due to the steric congestion imposed by the geminal dimethyl group. This seems to be the rationale for the slowing down the reaction. Even the 2,6-dichlorobenzoyloxy group, generally known to react much faster than other allylic esters,[63] did not accelerate the reaction: both **34i** and **35i** needed approximately the same time for >90% conversion as did the acetates **34a** and **35a**.[64]

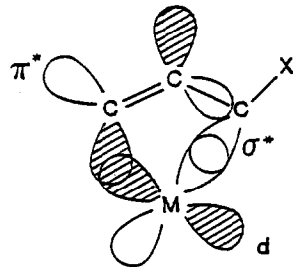
Discussion

Searching for evidence in favor of a *syn*-mechanism for the formation of (π-allyl)palladium complexes from allylic substrates, we have carried out initial experiments with **10b** (Table 1, namely entry 4) and with stereochemically biased substrates (Schemes VI and VII). While the results obtained with **10b** were tentatively interpreted as possible evidence for the *syn*-pathway (competing with the traditional *anti*-mechanism), the behavior of **30b** and **35b** was strongly supportive of the *syn* route. At this stage we have published our conclusions in a preliminary communication[24] as the first example of formation of a palladium η^3-complex in a *syn* fashion. Later, two other examples were found, namely with allylic chlorides[67,68] and certain allylic trifluoroacetates.[69,70]

Detailed investigation of the reactivity of **10b**, presented in this paper, clearly shows that some of our preliminary conclusions have to be modified. In the light of the above results, it appears that what was originally thought to be an indication of the *syn*-mechanism, was in fact a *cis-trans* isomerization of a η^3-complex. On the other hand, our DPPAc esters **30b** and **35b** demonstrate that the *syn*-mechanism of the palladium η^3-complex formation can be achieved if the ordinary *anti* reaction is precluded by strong steric congestion. Moreover, acetate **30a**, previously reported to be inert,[17] was also found to react (in a *syn* fashion),[71] but the reaction is dramatically slower than with the DPPAc ester **30b**, and the yield of the product is low. Similar behavior was observed for acetate **35a**. This indicates that pre-coordination of the Pd(0)-reagent is not a categorical prerequisite for the *syn*-mechanism to operate, but has a beneficial accelerating effect on the reaction, which is also reflected in a high yield of the product. Thus, for the substrates where the Pd-catalyzed substitution would be extremely slow, our leaving group can be used to facilitate the reaction via a *syn*-mechanism for the oxidative addition.

It appears that although the oxidative addition of palladium can really occur in a *syn* fashion, the *anti*-mechanism normally dominates unless precluded by structural effects. Clearly, the *anti*-mechanism must be lower in energy. This parallels the *anti*-stereospecificity of the substitution of allylic esters by organocuprates. The latter has been rationalized by Corey as resulting from an effective overlap

between *d* orbitals of copper with the antibonding orbitals of C=C (π^*) and C-X (σ^*) in the transition state (**41**; M = Cu).[73] We feel that similar arguments may be used to account for the preferred *anti*-stereospecificity in case of palladium (**41**; M = Pd). A higher activation energy for the *syn*-mechanism may be attributed to the lack of the orbital stabilization and to steric congestion.



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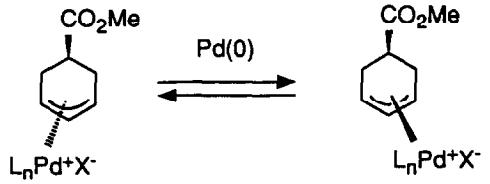
While the stereochemically biased substrates provided convincing evidence for the *syn*-mechanism of the oxidative addition, the reactivity of cyclohexene derivatives **10**, **18**, and **19** is more complex and deserves further comments. Our experiments clearly indicate that isomerization occurred at some stage. Since the thermodynamic equilibrium of the products **15** and **16** is known to be 3:1,[21d] the ratios we have obtained (3:2, 1:1, etc.; Table 1) must originate from another source. Stopping the reaction at ca. 50% conversion revealed no appreciable isomerization of the starting compound. These facts suggest that isomerization is taking place at the stage of palladium allylic complexes.

Isomerization of η^3-complexes by added Pd(0) was first observed by Tsuji[12c] and Bosnich[49] and recently studied by Bäckvall[65] in detail.[74,75] Bäckvall has investigated equilibration of *cis* and *trans* complexes **38** and **39** (originally existing as pure compounds) and arrived at the following conclusions (Scheme VIII): (1) Free Pd(0)-reagent is responsible for the isomerization of η^3-complexes as confirmed by studies of both stoichiometric and catalytic reactions. The equilibrium of **38a**:**39a** was found to be 55:45, and can be achieved by addition of $(Ph_3P)_4Pd$ to each of the latter complexes at -14°C in less than 5 min! (2) Isomerization is inhibited by decreasing concentration of $(Ph_3P)_4Pd$ or by use of reactive allylic substrates. (3) Addition of Ph_3P is increasing equilibration due to the release of Pd(0) from the η^3-complexes. (4) Complexes with bidentate ligands, such as dppe[76] (**38b** and **39b**), isomerize very slowly (if at all).[77] This is in accord with the expected absence of "semi-naked" Pd(0) species that are required for the nucleophilic isomerization.

In view of Bäckvall's findings, our observations can be interpreted as follows. Elevated temperature and increased amount of catalyst (up to 25 mol%) expedite the *trans*/*cis* equilibration of η^3-complexes **13** and **14**. The product ratio (**15**:**16**) finally achieved with our system (58:42 or 57:43; Table 1, entries 4 and 5) closely resembles that observed for the palladium complexes **38**:**39** (55:45). Furthermore, decreasing the concentration of all components 10 times (Tab. 1, footnote *d*) resulted in considerable suppression of the isomerization (due to lowering the concentration of active Pd-reagent) as

reflected in product ratio (88:11). These results strongly support the mechanistic picture that encompasses the *anti*-mechanism producing intermediate η^3-complex **13** which is then isomerized prior to the reaction with diethyl lithiomalonate. Participation of the *syn* pathway (if any) seems negligible in this instance.

Scheme VIII: **a**, $L_n = (Ph_3P)_2$, $X = CF_3SO_3$; **b**, L_n = dppe, $X = CF_3SO_3$



38 **39**

The reactivity of the steroidal substrates **18** and **19**, as well as that of acyclic model **25b**, conforms to this mechanistic picture. The reluctance of acetate **18a** to react even under really harsh conditions apparently reflects unfavorable alignment[11f] of the C-O bond with the π-system.

Bäckvall[65] has shown that **38a** and **39a** equilibrate more quickly than the dppe complexes **38b** and **39b**. In our reaction, the equilibration is presumably also faster than previously observed. This acceleration apparently stems from the nature of ligands attached to palladium. Our DPPAcO group can probably compete with Ph_3P in the coordination sphere of Pd. Similarly to Bäckvall's triflates **38a** and **39a**, these species may be more prone to equilibration than the previously studied complexes of Ph_3P or dppe. In order to gain support for this hypothesis, we have run a Pd-catalyzed substitution with carbonate **10c** in the presence of DPPAcOH (100 mol%) as an added ligand.[78] Product analysis showed a 69:31 ratio of **15** to **16**, which is close to the 58:42 ratio obtained with **10b** (Tab. 1, entry 4) and very different from the reaction of **10c** carried out in the presence of Ph_3P (which gave a 94:6 ratio; Tab. 1, entry 14). This finding is thus in excellent agreement with the above hypothesis. Moreover, *trans*-epimer of **10a** (which normally gives mainly **16** as the product of stereohomogeneous double inversion sequence) turned out to afford a 36:64 mixture of **15** and **16** (91% yield) when the reaction was carried out in the presence of DPPAcOH. Again, this indicates a large proportion of isomerization.[79]

Conclusions

Using stereochemically biased substrates **30** and **35**, we have obtained evidence that the *syn*-mechanism of formation of palladium η^3-complexes from allylic esters may be achieved if stereochemical congestion precludes the ordinary *anti*-mechanism. Pre-coordination of the Pd(0) reagent to the leaving group (as in **30b** and **35b**) dramatically accelerates the reaction and improves the overall yield. In principle, however, this pre-coordination is not essential for the *syn*-mechanism to operate, as demonstrated by allylic acetates **30a** and **35a**.

Substrates lacking stringent stereochemical hindrance (**10**, **18**, **19**, and **25**) react via an ordinary *anti*-mechanism to produce the corresponding palladium η^3-complexes as intermediates. Apparently, the availability of pre-coordination of the Pd(0) reagent to the DPPAcO group does not compensate for the higher activation energy for the *syn*-mechanism, so that the *anti*-process still dominates.[82] At elevated temperatures the intermediate η^3-complexes isomerize prior to the reaction with a nucleophile. The isomerization can be facilitated even with allylic acetates and carbonates by addition of DPPAcOH as an external ligand.

We believe that our results, in conjunction with those obtained by other investigators, provide better insight into the mechanism of Pd(0)-catalyzed allylic substitution and broaden its applicability. Our findings show that in substrates where the classical *anti* route of complex formation is impeded by severe steric congestion, our new leaving group enables the catalytic reaction to occur readily due to the operation of *syn*-mechanism as a stereoelectronically allowed alternative.

Experimental Section

Materials and Equipment. Melting points (uncorrected) were obtained on a Kofler block. Optical rotations were measured in $CHCl_3$ at 22 °C with an error of < ±1°. The infrared spectra were obtained on a Perkin-Elmer 621 instrument in CCl_4. ^1H NMR spectra were measured on Varian XL-200 (4.7 T, FT mode) and Tesla BS 497 (2.35 T) instruments for $CDCl_3$ solutions at 25 °C with Me_4Si (for ^1H and ^{13}C) as an internal standard or 85% H_3PO_4 (for ^{31}P) as an external standard. Chemical shifts are given in δ values (ppm) relative to the signal of the standard (δ = 0.00). Coupling constants were obtained by decoupling experiments and are given in absolute values. Enantiomeric excess of **28** was determined by means of (+)-Eu(tfc)$_3$ from the relative intensities of doublets of CH_3 at 1.20 ppm (CH_3 of the dextrorotatory enantiomer appears at lower field). The mass spectra were measured on ZAB-EQ (VG Analytical) spectrometer: the EI spectra were recorded at 75 eV using the lowest temperatures enabling evaporation (100-210 °C) and perfluorokerosene for calibration; FAB spectra were measured using the thioglycerol/glycerol (3:1) matrix and MeOH as a solvent and CsI for calibration. Elemental composition of the ions was determined by high resolution techniques. GC Analysis was carried out at Hewlett-Packard 5890 instrument using capillary columns (50% OV-17, 10m x 2.65 μm). Mercury lamp with highest pressure (Narva HBO 200, Carl Zeiss Jena) was used for photochemical experiments. Standard workup of an ethereal solution means washing with 5% HCl (aqueous), water, and 5% $KHCO_3$ (aqueous), drying with Na_2SO_4, and evaporation of the solvent in vacuo. Petroleum ether refers to the fraction boiling in the range 40-60 °C. The identity of samples prepared by different routes was checked by TLC and GC and IR, mass, and NMR spectra. Yields are given for isolated product showing one spot on a chromatographic plate and no trace of impurities detectable in the NMR spectrum. Diethyl sodiomalonate in THF was prepared as follows: to sodium hydride (48 mg of 50% suspension in mineral oil; 1 mmol) in dry THF (6 mL) was added a solution of diethyl malonate (160 μL; 1.054 mmol) under argon at r.t. over 5 min. The mixture was stirred for 15 min and then used. Diethyl lithiomalonate was prepared analogously by addition of *n*-butyllithium (1.6 M solution in *n*-hexane; 630 μL; 1.008 mmol) to a solution of diethyl malonate (160 μL; 1.054 mmol) in dry THF (4 mL) at r.t. over 5 min. After stirring for another 10 min at r.t. the reagent was used. Phenylzinc chloride was prepared as follows: Phenylmagnesium bromide (2.53 M solution in ether; 400 μL; 1.012 mmol) was added to dry zinc chloride (145 mg; 1.064 mmol) in dry THF (8 mL) at 0 °C over 5 min under argon. The mixture was stirred at 0 °C for 15 min and then at r.t. for another 15 min. The resulting white suspension was used for further reactions.

General Procedure for Pd(0)-Catalyzed Substitution with Diethyl Malonate. To a solution of palladium complex (5-100 mol%; see Tab. 1 or text) in THF or another solvent (3 mL) was added a solution of allylic substrate (0.30 mmol; 1 equiv.) in 1 mL of solvent and a solution of alkali salt of diethyl malonate (3 equiv.). The mixture was stirred (for temperature and duration, see the text or Table 1) under argon and then filtered through pad of aluminum oxide using ether as eluent. The solvent was evaporated in vacuo and the residue was chromatographed on silica (12 g) with petroleum ether-ether mixture (83:17) and 25 kPa pressure. The product was analyzed by GC and ^1H NMR.

General Procedure for Pd(0)-Catalyzed Substitution with Phenylzinc Chloride. To a solution of $(Ph_3P)_4Pd$ (0.025 mmol; 10 mol%) in THF (4 mL) was added allylic substrate (25 mmol; 1 equiv.) in dry THF (4 mL). The solution was stirred at r.t. for 2 min and then phenylzinc chloride (5 equiv.) in THF was added. The mixture was stirred at r.t. for 30 min or longer (see the text) under argon. When the reaction was finished, the mixture was filtered through a pad of aluminum oxide using ether as an eluent. The filtrate was evaporated in vacuo and the residue was chromatographed on silica (10 g) with petroleum ether and 10 kPa pressure. The products were analyzed by TLC, ^1H NMR and MS.

Methyl *cis*-[5-(diphenylphosphino)acetoxy-3-cyclohexene-1-carboxylate] (10b). To a solution of (diphenylphosphino)acetic acid (1.65g, 6.76 mmol) in a mixture of dry ether (20 mL) and acetonitrile (1 mL) was added successively 4-dimethylaminopyridine (100 mg; 0.82 mmol) in dry acetonitrile (1 mL), *cis*-(5-hydroxy-3-cyclohexen-1-carboxylate)[13b,89] (690 mg; 4.42 mmol) in dry ether (6 mL), and N,N'-dicyclohexylcarbodiimide (1.42 g; 6.88 mmol) in dry ether (10 mL) and the mixture was stirred at r.t. for 30 min. Precipitated N,N'-dicyclohexylurea was then filtered off, washed with ether and the filtrate was evaporated. The oily residue was *quickly* filtered through a pad of aluminum oxide using benzene as an eluent. The solvent was evaporated and the resulting yellowish oil was dried at 22 °C/26 Pa to yield pure **10b** (1.420 g; 84%) which could be stored under argon at -15 °C for several months without decomposition. ^{1}NMR 2.14-2.28 (m, 4 H, 2-H and 6-H), 2.63 (m, ΣJ = 31 Hz, 1 H, 1-H), 3.10 (s, 2 H, $Ph_2PCH_2CO_2$), 3.66 (s, 3 H, CO_2CH_3), 5.28 (m, ΣJ = 25 Hz, 1 H, 5-H), 5.41 (m, part of AB system, $J_{3\text{-}H,4\text{-}H}$ = 10 Hz, ΣJ = 18.2 Hz, 1 H, 4-H), 5.77 (m, part of AB system, $J_{3\text{-}H,4\text{-}H}$ = 10 Hz, ΣJ = 19.4 Hz, 1 H, 3-H), 7.23-7.70 (m, 10 H, arom.); ^{13}C NMR 27.06 and 30.19 (two s, C-2 and C-6), 34.89 (d, $J_{C,P}$ = 8.3 Hz, $Ph_2PCH_2CO_2$), 37.72 (s, C-1), 51.69 (s, CO_2CH_3), 69.75 (s, C-5), 126.53 (s, C-4), 128.40 (d, $J_{C,P}$ = 7 Hz, C_{meta} of Ph_2P), 128.85 (s, C-3), 128.94 (s, C_{para} of Ph_2P), 132.59 (d, $J_{C,P}$ = 19.8 Hz, C_{ortho} of Ph_2P), 137.03 (d, $J_{C,P}$ = 14.6 Hz, C_{ipso} of Ph_2P), 169.94 (d, $J_{C,P}$ = 7.6 Hz, $Ph_2PCH_2CO_2$), 174.31 (s, CO_2CH_3); ^{31}P NMR -15.42 (s, $Ph_2PCH_2CO_2$); IR 1656 (C=C), 1737 (C=O), 3035, 3055, and 3070 (C-H arom.) cm^{-1}. Anal. Calcd for $C_{22}H_{23}O_4P$: C, 69.10; H, 6.06; P, 8.10. Found: C, 69.04; H, 6.00; P, 8.25.

Methyl *cis*-[5-(ethoxycarbonyl)oxy-3-cyclohexene-1-carboxylate] (10c). Methyl *cis*-(5-hydroxy-3-cyclohexen-1-carboxylate) (500 mg; 3.20 mmol) in pyridine (10 mL) was treated with ethyl chloroformate (610 µL; 6.38 mol) at 0 °C for 2 h. The mixture was then decomposed with ice and water, the product was extracted with ether and the ethereal solution was worked up as usual. The residue was filtered through a pad of aluminum oxide using petroleum ether-benzene mixture (2:1). The filtrate was evaporated to furnish carbonate **10c** (570 mg; 78%) as a viscous oil: ^{1}H NMR 1.31 (t, J = 7 Hz, 3 H, CH_3CH_2O), 1.63-2.91 (m, 5 H, 1-H, 2-H, and 6-H), 3.70 (s, 3 H, CO_2CH_3), 4.19 (q, J = 7 Hz, 2 H, CH_3CH_2O), 5.25 (m, ΣJ = 27.5 Hz, 1 H, 5-H), 5.70 (dddd, part of AB system, $J_{3\text{-}H,4\text{-}H}$ = 10.5, J = 3.3, 1.5, and 1.5 Hz, 1 H, 4-H), 5.89 (dddd, part of AB system, $J_{3\text{-}H,4\text{-}H}$ = 10.5 Hz, J = 3.3, 3.3, and 1.5 Hz, 1 H, 3-H); IR 1012 and 1260 (C-O), 1654 (C=C), 1742 (C=O) cm^{-1}. Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.89; H, 7.08. Found: C, 57.71; H, 7.18.

Methyl *cis*-[5-(carbamoyl)oxy-3-cyclohexene-1-carboxylate] (10d). To a solution of methyl *cis*-5-hydroxy-3-cyclohexene-1-carboxylate (80 mg; 0.51 mmol) in abs. chloroform (2 mL) was added trichloroacetyl isocyanate (TAI, 61 µL; 0.51 mmol). The mixture was set aside under argon at r.t. for 10 min. The solution was then soaked into a pad of aluminum oxide and the product was eluted with chloroform (for the method, see ref. 90) to give carbamate **10b** (98 mg; 96%): m.p. 123-124 °C (ether); ^{1}H NMR 1.61-2.45 (m, 4 H, 2-H and 6-H), 2.72 (m, ΣJ = 33 Hz, 1 H, 1-H), 3.69 (s, 3 H, CH_3CO_2), 4.89 (br s, $W_{\frac{1}{2}}$ = 12 Hz, 2 H, H_2NCO_2), 5.27 (m, ΣJ = 26 Hz, 1 H, 5-H), 5.70 (br d, part of AB system, J = 10 Hz, 1 H, 4-H), 5.85 (m, part of AB system, ΣJ = 21 Hz, 1 H, 3-H). Anal. Calcd. for $C_9H_{13}O_4N$: C, 54.26; H, 6.58 H; N, 7.03. Found: C, 54.08; H, 6.65; N, 7.17.

Methyl *cis*-[5-(N-benzylcarbamoyl)oxy-3-cyclohexene-1-carboxylate] (10e). Methyl *cis*-(5-hydroxy-3-cyclohexene-1-carboxylate) (200 mg; 1.28 mmol) in dry chloroform (4 mL) was treated with benzyl isocyanate (500 µL; 4.06 mmol) at r.t. for 5 days. The solution was then soaked into a pad of aluminum oxide and eluted with petroleum ether-benzene mixture (2:1) and benzene. The eluate was evaporated and chromatographed on silica (25 g) using petroleum ether-ether-acetone mixture (72:18:2) as eluent and a pressure of 60 kPa. Evaporation of the corresponding fraction afforded pure **10d** (190 mg; 51%): mp 60-61 °C (methanol); ^{1}H NMR 1.48-2.95 (m, 5 H, 1-H, 2-H, and 6-H), 3.65 (s, 3 H, CO_2CH_3), 4.33 (d, J = 6 Hz, 2 H, $PhCH_2NH$), 4.70-5.60 (m, 2 H, $PhCH_2NHCO$ and 5-H), 5.75 (br d, $J_{3\text{-}H,4\text{-}H}$ = 3 Hz, 2 H, 3-H and 4-H), 7.28 (br s, 5 H, arom); IR 1506 and 1605 (C=C arom), 1726 and 1740 sh (C=O), 3035, 3065, and 3090 (C-H arom), 3450 (N-H) cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.28; H, 6.73; N, 4.65.

Methyl *cis*-{5-[N-(1-naphthyl)carbamoyl]oxy-3-cyclohexene-1-carboxylate} (10f). Methyl *cis*-(5-hydroxy-3-cyclohexene-1-carboxylate) (200 mg; 1.28 mmol) in dry chloroform (6 mL) was treated with 1-naphthyl isocyanate (230 μL; 1.60 mmol) at r.t. for 3 days. The solvent was evaporated and the residue chromatographed on silica (20 g) using petroleum ether-ether-acetone mixture (78:12:10) and a 30 kPa pressure to yield amorphous **10f** (162 mg; 39%): ^{1}H NMR 1.65-2.92 (m, 5 H, 1-H, 2-H, and 6-H), 3.70 (s, 3 H, CO_2CH_3), 5.46 (m, ΣJ = 24 Hz, 1 H, 5-H), 5.78 (br d, part of AB system, $J_{3\text{-}H,4\text{-}H}$ = 11 Hz, 1 H, 4-H), 5.94 (br d, part of AB system, $J_{3\text{-}H,4\text{-}H}$ = 11 Hz, 1 H, 3-H), 6.86-7.02 (m, 1 H, CO_2NH-Nphth), 7.36-7.98 (m, 7 H, arom); IR 1495, 1584, and 1600 (C=C, arom.), 1700 sh and 1740 (C=O), 3350 and 3460 (N-H) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 70.08; H, 5.66; N, 4.13.

Methyl *cis*-{5-[N-(4-toluenesulfonyl)carbamoyl]oxy-3-cyclohexene-1-carboxylate} (10g). Methyl *cis*-(5-hydroxy-3-cyclohexene-1-carboxylate) (41 mg; 0.26 mmol) in tetrahydrofuran (5 mL) was treated with p-toluenesulfonyl isocyanate (40 μL; 0.26 mmol) at r.t. for 30 min. The solvent was evaporated to afford a viscous oil of **10g** (91 mg; 98%): ^{1}H NMR 1.61-2.73 (m, 5 H, 1-H, 2-H, and 6-H), 2.45 (s, 3 H, 4-$CH_3C_6H_4SO_2$), 3.69 (s, 3 H, CO_2CH_3), 5.29 (m, ΣJ = 28 Hz, 1 H, 5-H), 5.55 (br d, $J_{3\text{-}H,4\text{-}H}$ = 10 Hz, 1 H, 4-H), 5.83 (m, ΣJ = 24 Hz, 1 H, 3-H), 7.34 (d, part of AB system, J = 8 Hz, 2 H, arom), 7.92 (d, part of AB system, J = 8 Hz, 2 H, arom.); IR 1495 and 1598 (C=C arom), 1654 (C=C), 1720 sh and 1740 (C=O), 3230 and 3440 (N-H) cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_6S$: C, 54.38; H, 5.42; N, 3.96; S, 9.07. Found: C, 54.26; H, 5.51; N, 3.80; S, 9.21.

Methyl *cis*-[5-(N-phenylthiocarbamoyl)oxy-3-cyclohexene-1-carboxylate] (10h). A mixture of methyl *cis*-(5-hydroxy-3-cyclohexene-1-carboxylate) (600 mg; 3.84 mmol), 4-dimethylaminopyridine (50 mg; 0.41 mmol) and phenyl isothiocyanate (600 μL; 5.02 mmol) was heated at 100 °C over 72 h under argon. The crude mixture was then chromatographed on silica (50 g) using petroleum ether-acetone mixture (91:9) and 90 kPa pressure to give **10h** (276 mg; 25%): mp 81-84 °C (chloroform); ^{1}H NMR 1.48-2.93 (m, 5 H, 1-H, 2-H, and 6-H), 3.68 (s, 3 H, CO_2CH_3), 5.40 (m, ΣJ = 26 Hz, 1 H, 5-H), 5.75 (br s, $W_{\frac{1}{2}}$ = 6.5 Hz, 2 H, 3-H and 4-H), 6.52-6.77 (m, 1 H, Ph-NH-CS), 6.98-7.50 (m, 5 H, arom); IR 1204 (C=S), 1524 and 1596 (C=C arom), 1742 (C=O), 3445 (N-H) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81; S, 11.00. Found: C, 61.93; H, 5.83; N, 4.59; S, 10.82.

Reaction of 10b with Pd(II) and Fe(CO)$_5$. To a solution of (diphenylphosphino)acetate **10b** (50 mg; 0.13 mmol) in dry THF (3 mL) was added $(MeCN)_2PdCl_2$ (34 mg; 0.13 mmol) and the mixture was stirred at r.t. for 15 min under argon. To the resulting yellow solution was added diethyl sodiomalonate (0.39 mmol) in THF (3 mL) and $Fe(CO)_5$ (17 μL; 0.13 mmol). The black-greenish mixture was stirred at 50 °C for 48 h and worked up as in the general experiment to give a 92:8 (GC) mixture of **15** and **16** (13 mg; 33%).

(η^3-2-Butenyl)chlorobis{methyl-*cis*-[5-(diphenylphosphino-κP--acetoxy)-3-cyclohexene-1-carboxylate]}palladium (17). (Diphenylphosphino)acetate **10b** (50 mg; 0.13 mmol) in abs. tetrahydrofuran (2 mL) was added to a solution of [(π-crotyl)PdCl]$_2$ (27 mg; 0.065 mmol) and maleic anhydride (33 mg; 0.33 mmol) in tetrahydrofuran (2 mL), the mixture was stirred for 2 h at r.t. and then filtered through a pad of aluminum oxide using ether as eluent. The eluate was evaporated and the residue was chromatographed on silica (9 g) using petroleum ether-ether mixture (3:1) and 60 kPa pressure to furnish yellow solid **17** (64 mg; 52%): ^{1}H NMR 1.83 (dd, J = 9.0 and 6.4 Hz, 3 H, 4'-H), 1.96-2.38 (m, 8 H, 2-H and 6-H), 2.51-2.64 (m, 3 H, 1-H and 1'-H), 3.22 (m, ΣJ = 20 Hz, 4 H, Ph_2PCH_2), 3.68 (s, 6 H, CO_2CH_3), 4.23-4.67 (m, 2 H, 1'-H and 3'-H), 5.12-5.41 (m, 5 H, 4-H, 5-H, and 2'-H), 5.75 (m, ΣJ = 19.4 Hz, 2 H, 3-H), 7.28-7.88 (m, 20 H, arom.); ^{13}C NMR 17.55 (s, C-4') 27.13 and 30.12 (two s, C-2 and C-6), 34.85 (d, $J_{C,P}$ = 19.2 Hz, $Ph_2PCH_2CO_2$), 37.75 (s, C-1), 51.85 (s, CO_2CH_3), 54.41 (s, C-1'), 70.41 (s, C-5), 116.88 (s, C-2' or C-3'), 122.59 (d, $J_{C,P}$ = 10.2 Hz, C_{meta} of Ph_2P), 126.37 (s, C-4), 128.99 (s, C-3), 130.65 (s, C_{para} of Ph_2P), 131.81 (d, $J_{C,P}$ = 38.7 Hz, C_{ipso} of Ph_2P), 133.05 (d, $J_{C,P}$ = 12.5 Hz, C_{ortho} of Ph_2P), 167.77 (s, $Ph_2PCH_2CO_2$), 174.37 (s, CO_2CH_3); ^{31}P NMR 19.11 (s, Ph_2P); MS(FAB) for ^{106}Pd, m/z (rel. intensity) 925 (8%), 870 (2%), 594 (21%), 543 (100%), 488 (26%), 405 (77%), 382 (13%), 350 (62%); IR 1668 (C=C), 1730 sh and 1739 (C=O) cm^{-1}. Anal. Calcd for $C_{48}H_{53}ClO_8P_2Pd$: C, 59.95; H, 5.55; Cl, 3.69. Found: C, 60.20; H, 5.69; Cl, 3.52.

Reaction of 17 with Diethyl Malonate. To a solution of complex **17** (16 mg; 0.017 mmol) in dry THF (1.5 mL) was added a solution of diethyl sodiomalonate (0.085 mmol) in THF (0.5 mL). The mixture was stirred at r.t. for 30 min under argon and then worked up as in the general experiment to afford a 49:51 (GC) mixture of **15** and **16** (7 mg; 71%).

4-Cholesten-3β-yl-(diphenylphosphino)acetate (18b). Prepared from cholest-4-en-3β-ol in analogy with **10b** in 82% yield as an amorphous solid: $[\alpha]_D$ -1° (c 2.4); ^{1}H NMR 0.67 (s, 3 H, 18-H), 1.01 (s, 3 H, 19-H), 3.11 (s, 2 H, $Ph_2PCH_2CO_2$), 5.02 (br s, $W_{\frac{1}{2}}$ = 4.2 Hz, 1 H, 4-H), 5.15 (m, ΣJ = 24 Hz, 1 H, 3α-H), 7.23-7.55 (m, 10 H, arom.); IR 1660 (C=C), 1723 (C=O) cm^{-1}. Anal. Calcd for $C_{41}H_{57}O_2P$: C, 80.35; H, 9.37; P, 5.05. Found: C, 80.19; H, 9.45; P, 5.30.

4-Cholesten-3α-yl-(diphenylphosphino)acetate (19b). Prepared from cholest-4-en-3α-ol in analogy with **10b** in 83% yield as an oil: $[\alpha]_D$ +105° (c 2.2; benzene); ^{1}H NMR 0.68 (s, 3 H, 18-H); 0.93 (s, 3 H, 19-H); 3.11 (s, 2 H, $Ph_2PCH_2CO_2$); 5.02 (m, ΣJ = 15.8 Hz, 1 H, 3β-H), 5.27 (d, J = 5z, 1 H, 4-H), 7.24-7.56 (m, 10 H, arom.); IR 1110 and 1260 (C-O), 1586 (arom.), 1658 (C=C), 1722 (C=O) cm^{-1}. Anal. Calcd for $C_{41}H_{57}O_2P$: C, 80.35; H, 9.37; P, 5.05. Found: C, 80.29; H, 9.50; P, 4.92.

3β-Phenyl-4-cholestene (22). ^{1}H NMR (spectrum taken in a mixture with **23**) 0.67 (s, 18-H), 1.10 (s, 3 H, 19-H), 3.16-3.49 (m, 3α-H), 5.29 (br s, $W_{\frac{1}{2}}$ = 5 Hz, 1 H, 4-H), 7.09-7.57 (m, arom.).

3α-Phenyl-4-cholestene (23). ^{1}H NMR (spectrum taken in a mixture with **22**) 0.67 (s, 18-H), 1.06 (s, 3 H, 19-H), 3.16-3.49 (m, 3β-H), 5.37 (br d, $J_{3\beta\text{-H},4\text{-H}}$ = 4.5 Hz, 1 H, 4-H), 7.09-7.57 (m, arom.).

(+)-(*R*)-(*E*)-4-Phenyl-3-buten-2-ol (24). To a solution of titanium(IV) isopropoxide (4.60 mL, 15.45 mmol, 1.0 equiv.) in dry CH_2Cl_2 (150 mL) and containing molecular sieves 3Å (6 g) was added (+)diisopropyl tartrate (3.90 mL, 18.55 mmol, 1.2 equiv.) at -20 °C and the mixture was stirred under argon at this temperature for 20 min. Then a solution of (±)-*trans*-4-phenyl-3-buten-2-ol (2.29 g, 15.46 mmol) in CH_2Cl_2 (10 mL) was added followed by a dropwise addition of *t*-butyl hydroperoxide in CH_2Cl_2 (4.93 M, 1.88 mL, 9.27 mmol, 0.6 equiv.) at -20 to -30 °C over a period of 20 min. The mixture was stirred at -20 °C for 2 h, then poured into a cold mixture of acetone (350 mL) and water (4.6 mL) and stirred for 3 h (until it reached rt). The mixture was then filtered through a column of aluminum oxide (5x5 cm) and evaporated. The residue was chromatographed on silica (170 g) using a light petroleum-ether-acetone mixture (85:10:5 2 L) as eluent to afford (+)-(*R*)-(*E*)-4-Phenyl-3-buten-2-ol (**24**) (856 mg; 37%) and 3,4-epoxy-4-phenyl-3-butanol (1.20 g; 47%). The latter alcohol (**24**) had $[\alpha]_D$ +24.5° (c 3.0, $CHCl_3$, corresponding to 99% e.e.[57]); ^{1}H NMR (d, J = 6 Hz, 3 H, 1-H), 4.47 (m, ΣJ = 28 Hz, 1 H, 2-H), 6.24 (dd, J = 6 and 17 Hz, 1 H, 3-H), 6.59 (d, J = 17 Hz, 1 H, 4-H), 7.19-7.45 (m, 5 H, arom.). The epoxy alcohol: ^{1}H NMR 1.34 (d, J = 7 Hz, 3 H, 1-H), 3.23 (br d, J = 7.5 Hz, 1 H, 3-H), 4.51 (br d J = 7.5 Hz, 1 H, 4-H), 5.17 (m, ΣJ = 28 Hz, 1 H, 2-H), 7.32 (br s, 5 H, arom.).

(+)-(*R*)-(*E*)-(4-Phenyl-3-buten-2-yl)-(diphenylphosphino)acetate (25b). Prepared from the corresponding alcohol in analogy with **10b** in 69% yield: $[\alpha]_D$ +36° (c 5.1); ^{1}H NMR 1.26 (d, $J_{1\text{-H},2\text{-H}}$ = 6.4 Hz, 3 H, 1-H), 3.14 (d, $J_{gem(H,P)}$ = 0.5 Hz, 2 H, $Ph_2PCH_2CO_2$), 5.42 (ddq, $J_{2\text{-H},3\text{-H}}$ = 6.7 Hz, $J_{1\text{-H},2\text{-H}}$ = 6.4 Hz, $J_{2\text{-H},4\text{-H}}$ = 1.1 Hz, 1 H, 2-H) 6.01 (dd, $J_{3\text{-H},4\text{-H}}$ = 16 Hz, $J_{2\text{-H},3\text{-H}}$ = 6.7 Hz, 1 H, 3-H), 6.49 (dd, $J_{3\text{-H},4\text{-H}}$ = 16 Hz, $J_{2\text{-H},4\text{-H}}$ = 1.1 Hz, 1 H, 4-H), 7.18-7.49 (m, 15 H, arom.); IR 1256 (C-O), 1495 and 1586 (C=C arom.), 1728 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{23}O_2P$: C, 76.99; H, 6.19; P, 8.27. Found: C, 76.81; H, 6.20; P, 8.41.

[3a,4,5,6,7,7a-Hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-yl](diphenylphosphino)acetate (30b). Prepared from the corresponding alcohol[19] in analogy with **10b** in 42% yield: ^{1}H NMR 0.93-2.13 (m, 7 H), 2.30 (m, $W_{\frac{1}{2}}$ = 10 Hz, 2 H), 2.99 (m, ΣJ = 20 Hz, 1 H, 3a-H), 3.08 (s, 2 H, $Ph_2PCH_2CO_2$), 5.46 (m, $W_{\frac{1}{2}}$ = 5.8 Hz, 1 H, 1-H), 5.61 (ddd, $J_{2\text{-H},3\text{-H}}$ = 5.7 Hz, $J_{1\text{-H},3\text{-H}}$ = 2 Hz, $J_{3\text{-H},3a\text{-H}}$ = 2 Hz, 1 H, 3-H), 5.96 (dddd, $J_{2\text{-H},3\text{-H}}$ = 5.7 Hz, $J_{1\text{-H},2\text{-H}}$ = 2 Hz, $J_{2\text{-H},3a\text{-H}}$ = 1 Hz, $J_{2\text{-H},7a\text{-H}}$ = 0.8 Hz, 1 H, 2-H), 7.23-7.93 (m, 10 H, arom.); IR 1588 and 1614 (C=C arom.), 1724 (C=O) cm^{-1}; MS(EI), m/z (rel. intensity) 376 ($M^{+\cdot}$, 7%). Anal. Calcd for $C_{24}H_{25}O_2P$: C, 76.58; H, 6.69; P, 8.23. Found: C, 76.41; H, 6.77; P, 8.18.

1-Phenyl-3a,4,5,6,7,7a-hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (32). ^{1}H NMR 1.20-1.59 (m, 6 H), 2.37-2.49 (m, 3 H), 3.16 (m, ΣJ = 25 Hz, 1 H, 3a-H), 3.68 (m, $W_{\frac{1}{2}}$ = 7 Hz, 1 H, 1-H), 5.73 (m, ΣJ = 20 Hz, 2 H, 2-H and 3-H), 7.04-7.37 (m, 5 H, arom.); MS(EI) m/z (rel. intensity) 210 ($M^{+\cdot}$, 11%).

(+)-(1*S*)-{(1α,2β,5α)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-yl}-(diphenylphosphino)acetate (34b). To a solution of (diphenylphosphino)acetic acid (385 mg; 1.58 mmol) and (-)-*cis*-verbenol[61] (120 mg; 0.79 mmol) in a mixture of dry ether (5 mL) and dry acetonitrile (1 mL) were successively added 4-dimethylaminopyridine (30 mg; 0.25 mmol) in acetonitrile (1 mL) and N,N'-dicyclohexylcarbodiimide (326 mg; 1.58 mmol) in dry ether (5 mL). The mixture was stirred under argon at room temperature for 30 min and then worked up as given for **10b** to yield

yellowish oil of **34b** (210 mg, 70%): $[\alpha]_D$ +53° (c 2.8); ^{1}H NMR 0.90 (s, 3 H, *endo*-6-CH_3), 1.27 (s, 3 H, *exo*-6-CH_3), 1.32 (ddd, J_{gem} = 9.2 Hz, $J_{1\text{-}H,7\text{-}H}$ = 6.9 Hz, $J_{5\text{-}H,7\text{-}H}$ = 4.5 Hz, 1 H, 7-H), 1.69 (dd, $J_{2\text{-}H,4\text{-}Me}$ = 1.8 Hz, $J_{3\text{-}H,4\text{-}Me}$ = 1.6 Hz, 3 H, 4-CH_3), 1.94 (ddd, $J_{5\text{-}H,7\text{-}H}$ = 6.5 Hz, $J_{5\text{-}H,7\text{-}H}$ = 4.5 Hz, $J_{3\text{-}H,5\text{-}H}$ = 1.4 Hz, 1 H, 5-H), 2.13 (dddd, $J_{1\text{-}H,7\text{-}H}$ = 6.9 Hz, $J_{1\text{-}H,7\text{-}H'}$ = 5.5 Hz, $J_{1\text{-}H,2\text{-}H}$ = 3.4 Hz, $J_{1\text{-}H,3\text{-}H}$ = 2.0 Hz, 1 H, 1-H), 2.41 (ddd, J_{gem} = 9.2 Hz, $J_{5\text{-}H,7\text{-}H}$ = 6.5 Hz, $J_{1\text{-}H,7\text{-}H}$ = 5.5 Hz, 1 H, 7-H), 3.10 (s, 2 H, $Ph_2PCH_2CO_2$), 5.12 (dddd, $J_{2\text{-}H,3\text{-}H}$ =2.8 Hz, $J_{1\text{-}H,3\text{-}H}$ = 2.0 Hz, $J_{3\text{-}H,4\text{-}Me}$ = 1.6 Hz, $J_{3\text{-}H,5\text{-}H}$ = 1.4 Hz, 1 H, 3-H), 5.42 (ddd, $J_{1\text{-}H,2\text{-}H}$ = 3.4 Hz, $J_{2\text{-}H,3\text{-}H}$ = 2.8 Hz, $J_{2\text{-}H,4\text{-}Me}$ = 1.8 Hz, 1 H, 2-H), 7.31-7.60 and 7.75-7.88 (m, 10 H, arom.); IR 1260 (C-O), 1482 (C=C arom.), 1656 (C=C), 1734 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{27}O_2P$: C, 76.17; H, 7.19; P, 8.18. Found: C, 76.01; H, 7.39; P, 8.29.

(+)-(1*S*)-{(1α,2β,5α-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-yl}-2,6-dichlorobenzoate (34i). (-)-*cis*-Verbenol (220 mg; 1.45 mmol) was esterified in the same way as described for **35i** to afford viscous oil **34i** (420 mg; 89%): $[\alpha]_D$ +33° (c 2.1); ^{1}H NMR 1.00 (s, 3 H, *endo*-6-CH_3), 1.35 (s, 3 H, *exo*-6-CH_3), 1.49 (m, ΣJ = 20 Hz, 1 H, 5-H), 1.78 (t, J = 1.5 Hz, 3 H, 4-CH_3), 2.03 (br t, J = 5.5 Hz, 1 H, 1-H), 2.56 (t, J = 5.5 Hz, 2 H, 7-H), 5.48 (m, $W_{\frac{1}{2}}$ = 5.8 Hz, 1 H, 3-H), 5.85 (m, $W_{\frac{1}{2}}$ = 6 Hz, 1 H, 2-H), 7.22-7.40 (m, 3 H, arom.); IR 1564 and 1580 (C=C arom.), 1655 (C=C), 1737 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{18}Cl_2O_2$: C, 62.78; H, 5.59; Cl, 21.80. Found: C, 62.70; H, 5.78; Cl, 21.57.

(-)-(1*S*)-{(1α,2α,5α)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-yl}-(diphenylphosphino)acetate (35b). Prepared from (-)-*trans*-verbenol[61] in analogy with **10b** as a yellowish oil (89%) $[\alpha]_D$ -83° (c 2.6; benzene); ^{1}H NMR 0.85 (s, 3 H, *endo*-6-CH_3), 0.96-1.40 (m, 1 H, 5-H), 1.28 (s, 3 H, *exo*-6-CH_3), 1.72 (t, $J_{2\text{-}H,4\text{-}Me}$ = 1 Hz, $J_{3\text{-}H,4\text{-}Me}$ = 1 Hz, 3 H, 4-CH_3), 1.86-2.28 (m, 3 H, 1-H and 7-H), 3.10 (s, 2 H, $Ph_2CH_2CO_2$), 5.17 (m, $W_{\frac{1}{2}}$ = 6 Hz, 1 H, 2-H), 5.25 (m, $W_{\frac{1}{2}}$ = 8 Hz, 1 H, 3-H), 7.20-7.54 (m, 10 H, arom.); IR 1255 (C-O), 1586 (C=C arom.), 1655 (C=C), 1722 (C=O) cm^{-1}; MS(EI) m/z (rel. intensity) 378 ($M^{+\cdot}$, 29%). Anal. Calcd for $C_{24}H_{27}O_2P$: C, 76.17; H, 7.19; P, 8.18. Found: C, 76.03; H, 7.22; P, 8.36.

(-)-(1*S*)-{(1α,2α,5α)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-yl}-2,6-dichlorobenzoate (35i). *n*-Butyllithium (2.4 M solution in *n*-hexane; 700 μL, 1.68 mmol) was added to a solution of (-)-*trans*-verbenol[61] (200 mg; 1.31 mmol) in dry tetrahydrofuran (6 mL) and the mixture was stirred at 0 °C for 15 min under argon. 2,6-Dichlorobenzoylchloride (350 μL; 2.45 mmol) was then added and the mixture was stirred at 0 °C for 15 min, then at r.t. for 30 min, and finally at 50 °C for 4 h under argon. The mixture was then decomposed with ice, excess of $(NH_4)_2SO_4$ was added and the product was extracted five times with ether. Combined organic phase was washed with saturated NaCl, $KHCO_3$, and dried with $MgSO_4$ and evaporated in vacuo. The residue was filtered through a pad of aluminum oxide using petroleum ether-benzene mixture (1:1) as eluent. Evaporation of the filtrate furnished pure **35i** (307 mg; 72%): mp 105-108 °C (petroleum ether-ether); $[\alpha]_D$ -60° (c 2.4); ^{1}H NMR 0.98 (s, 3 H, *endo*-6-CH_3), 1.18-2.56 (m, 4 H, 1-H, 5-H, and 7-H), 1.38 (s, 3 H, *exo*-6-CH_3), 1.78 (t, $J_{2\text{-}H,4\text{-}Me}$ = 0.2 Hz, $J_{3\text{-}H,4\text{-}Me}$ = 0.2 Hz, 3 H, 4-Me), 5.47 (m, $W_{\frac{1}{2}}$ = 5.5 Hz, 1 H, 3-H), 5.71 (m, $W_{\frac{1}{2}}$ = 7.3 Hz, 1 H, 2-H), 7.09-7.38 (m, 3 H, arom.); IR 1270 (C-O), 1565 and 1580 (C=C arom.), 1654 (C=C), 1735 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{18}Cl_2O_2$: C, 62.78; H, 5.59; Cl, 21.80. Found: C, 62.54; H, 5.70; Cl, 21.65.

(-)-(1*R*)-{(1α,2α,5α)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-yl}benzene (37): $[\alpha]_D$ -104° (c 2.4); ^{1}H NMR 1.00 (s, 3 H, *endo*-6-CH_3), 1.28 (m, ΣJ = 11 Hz, 1 H, 5-H), 1.32 (s, 3 H, *exo*-6-CH_3), 1.78 (dd, $J_{2\text{-}H,4\text{-}Me}$ = 2.2 Hz, $J_{3\text{-}H,4\text{-}Me}$ = 1.6 Hz, 3 H, 4-CH_3), 2.00-2.11 (m, 2 H, 7-H), 2.13 (dddd, $J_{1\text{-}H,7\text{-}H}$ = 6.5 Hz, $J_{1\text{-}H,7\text{-}H'}$ = 4.9 Hz, $J_{1\text{-}H,2\text{-}H}$ = 2.4 Hz, $J_{1\text{-}H,3\text{-}H}$ = 1.7 Hz, 1 H, 1-H), 3.58 (m, ΣJ = 12.1 Hz, 1 H, 2-H), 5.36 (m, ΣJ = 10.6 Hz, 1 H, 3-H), 7.13-7.38 (m, 5 H, arom.); IR 1493 and 1600 (C=C arom.) cm^{-1}; MS(EI) m/z (rel. intensity) 212 ($M^{+\cdot}$, 21%). Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.33; H, 9.45.

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References and Notes

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(36) Allylic xanthates give the η^3-palladium complexes again via *anti* route (ref. 21n).

(37) Carbamate **10d** remained unreacted.

(38) Jarolím, T.; Podlahová, J. *J. Inorg. Nucl. Chem.* **1976**, *38*, 125.

(39) Since the **15**:**16** equilibrium is known to be 3:1,[21d] the ratio we have obtained clearly cannot originate from the thermodynamic equilibration of the final product.

(40) This complex was fully characterized by spectral data (see the experimental part). Diagnostically significant was the expected shift in the ^{31}P NMR spectrum: while in **10b** the phosphorus signal appears at -15.42 ppm, the latter resonates at 19.11 ppm in **17**. The mass spectrum revealed fragments of the **10b** molecule containing Pd.

(41) Allylic substitution has also been reported with complexes of W,[43] Fe,[44] Mo,[45] and Ni, Ru, Rh, and Pt.[46] Stoichiometric reaction of **10b** with $(MeCN)_2W(CO)_4$, however, afforded the corresponding product of ligand exchange, $[RO_2CCH_2(Ph)_2P]_2W(CO)_4$, (58%), inert to $NaCH(CO_2Et)_2$. Similarly, the reaction of **10b** with $Fe_2(CO)_9$ led to the corresponding complex $RO_2CCH_2(Ph)_2P$-$Fe(CO)_4$ (69%), also inert toward $NaCH(CO_2Et)_2$. However, irradiation of the latter complex by a mercury lamp in the presence of $NaCH(CO_2Et)_2$ (THF, reflux 3 h), led to a 65:35 mixture of **15** and **16** (34%) and free **10b** (48%), which indicates that dissociation precedes the formation of η^3-complexes.

(42) Low yields of substitution products were obtained on reaction of **10b** with MeCu(CN)Li (27%) and Me_3Cu_2Li (36%). While the ratio of retention/inversion products was 11:89 for the former reagent, the latter afforded a 31:69 mixture. Other cuprates, including Me_2CuLi, MeCu, and $MeCu.BF_3$, either did not react or produced complex mixtures. In contrast, **10e** and **10h** reacted readily with Me_2CuLi giving a 94:6 and 89:11 mixture, respectively, in good yields, indicating a strong pre-coordination control by the leaving group. As expected, **10b** preferred inversion, producing a 17:83 mixture.

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(47) (a) Åkermark, B.; Åkermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037. (b) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620. (c) Carturan, G.; Scrivanti, A.; Morandini, F. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 112.

(48) No solvent or temperature effect has been observed for this reaction.

(49) (a) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. (b) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046.

(50) Acetate **18a** was inert even when treated with $NaCH(CO_2Et)_2$ (4 equiv.), $(Ph_3P)_4Pd$ (10 mol%), Ph_3P (40 mol%) in Me_2SO at 120°C over 12 h![51]

(51) Under these conditions other unreactive substrates have been reported to react: Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 3435.

(52) In all cases, elimination was also observed as another competing pathway (Table 2). The configuration of Ph in **22** and **23** was determined from the signal of 4-H in the ^{1}H NMR spectra: while 3β-substituted derivatives consistently show this signal as a broad singlet, the 3α-substituted derivatives are characterized by a broad doublet with $J \approx 5$ Hz. The **22**:**23** ratio was determined by integration of the 4-H signals in the ^{1}H NMR spectrum of the mixture.

(53) We were unable to reproduce the asymmetric reduction of benzylidene acetone described in the literature (Terashima, S.; Takano, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1980**, 1026.). On the other hand, we have achieved an excellent kinetic resolution[54] of the racemic alcohol (±)-**24** via the stoichiometric Sharpless epoxidation using (+)-diisopropyl tartrate.[55] This procedure gave us (+)-**24** whose $[\alpha]_D$ +24.5° (*c* 2.8, $CHCl_3$) indicates ≥99% ee[56] in agreement with the ^{1}H NMR spectra taken in the presence of $Eu(tfc)_3$.

(54) (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. (b) Roush, W. R.; Brown, R. J. *J. Org. Chem.* **1983**, *48*, 5093.

(55) Zhou, B.; Xu, Y. *J. Org. Chem.* **1988**, *53*, 4421.

(56) Kenyon, J.; Partridge, S. M.; Phillips, H. *J. Chem. Soc.* **1936**, 85.

(57) According to ref 14a, the maximum specific rotation of (+)-**28** is $[\alpha]_D$ +68.9° (*c* 1.0, $CHCl_3$). Our product had $[\alpha]_D$ +58° (*c* 3.9, $CHCl_3$).

(58) In addition to **28**, 5% of allylic isomer was formed as revealed by ^{1}H NMR spectrum of the crude product.

(59) In view of the evidence accumulated thus far this rationalization seems to be better justified than that presented in our preliminary account (ref. 24).

(60) For the synthesis of parent alcohols, see: (a) Whitham, G. H. *J. Chem. Soc.* **1961**, 2232. (b) Cooper, M. A.; Salmon, J. R.; Whittaker, D.; Scheidegger, U. *J. Chem. Soc. (B)* **1967**, 1259. (c) Mori, K. *Agric. Biol. Chem.* **1976**, *40*, 415.

(61) Conditions necessary for >90% conversion. At higher temperature only decomposition could be observed.

(62) The configuration of Ph in **37** was determined by ^{1}H NMR spectroscopy using NOE: irradiation of 6-*endo*-CH_3 led to a 19.6% enhancement of the 3-H signal, whereas irradiation of 6-*exo*-CH_3 caused only 1.8% increase of 3-H. Accordingly, irradiation of 3-H resulted in the enhancement of the 6-*endo*-CH_3 by 3.4% while 6-*exo*-CH_3 was enhanced by 1.1%.

(63) Colobert, F.; Genêt, J.-P. *Tetrahedron Lett.* **1985**, *26*, 2779. See also: Genêt, J.-P.; Ferroud, D. *Tetrahedron Lett.* **1984**, *25*, 3579.

(64) Trifluoroacetoxyl seems to be even better leaving group for Pd-catalyzed substitution.[21j,65,66] However, trifluoroacetates derived from our verbenols are highly unstable so that their reactivity could not be tested.

(65) (a) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* in press. (b) Granberg, K. L. *Thesis*, University of Uppsala, Sweden, 1991.

(66) (a) RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3642. (b) Takahashi, T.; Nakagawa, N.; Minoshima, T.; Yamada, H.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 4333.

(67) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813.

(68) Although Kurosawa[67] has not discussed the mechanism in detail, it may be conceivable that in benzene, a coordination of halophilic palladium to chlorine in the substrate molecule **38** would boost the *syn*-mechanism.

(69) Vitagliano, A.; Åkermark, B.; Hansson, S. *Organometallics* **1991**, *10*, 2592.

(70) For further examples where a η^3-complex (Mo and W) is arising in a *syn* fashion from the allylic substrate, see ref. 45m and: Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413.

(71) This reactivity parallels that of organocuprates with allylic acetates. While *anti* stereochemistry is typical for these reactions, substrates where *anti*-mechanism is precluded by strong steric hindrance have been reported to react in a *syn* fashion.[72]

(72) (a) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422. (b) Chapleo, C. B.; Finch, M. A. W.; Lee, T. V.; Roberts, S. M.; Newton, R. F. *J. Chem. Soc., Chem. Commun.* **1979**, 676.

(73) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063. For related discussion, see: (b) Corey, E. J.; Hannon, F. J. *Tetrahedron Lett.* **1990**, *31*, 1393. (c) Hill, R. S.; Becalska, A.; Chiem, N. *Organometallics* **1991**, *10*, 2104.

(74) The possibility of isomerization of η^3-complexes through Pd-Pd exchange was first suggested by Collman and Hegedus: Collman, J. P.; Hegedus; L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 692.

(75) For isomerization, see also ref. 21l and: (a) Bäckvall, J.-E.; Vågberg, J. O.; Zercher, C.; Genêt, J.-P.; Denis, A. *J. Org. Chem.* **1987**, *52*, 5430. (b) Moreno-Mañas, M.; Ribas, J.; Virgili, A. *J. Org. Chem.* **1988**, *53*, 5328. (c) Kurosawa has reported on substitution reaction of

(π-allyl)$Pd^+(PPh_3)_2$ with $(C_2H_4)Pt(PPh_3)_2$ which occurred with inversion via an *anti* attack at the allyl ligand: Kurosawa, H.; Ogoshi, S.; Chatani, N.; Kawasaki, Y.; Murai, S.; Ikeda, I. *Chem. Lett.* **1990**, 1745.

(76) Murahashi, S. I.; Taniguchi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292.

(77) The Pd-Pd displacement with dppe as a ligand seems to be an extremely slow process, as shown by preliminary experiments quoted in ref. 65.

(78) The reaction was carried out with 0.25 mol% of $(Ph_3P)_4Pd$ in THF at 45°C for 2 h. Similar result was obtained with acetate **10a**.

(79) These effects may also play a role in the enantioselective allylic substitution catalyzed by Pd in the presence of *trans*-2-(diphenylphosphino)cycloalkaneacids reported recently.[80] Moreover, as the regioselectivity of the nucleophilic attack on η^3-complexes may be controlled electronically by the ligands (namely by their donor/acceptor properties)[81] we believe that the (phosphino)carboxylic acids might have further potential.

(80) (a) Okada, Y.; Minami, T.; Sasaki, Y.; Umezu, Y.; Yamaguchi, M. *Tetrahedron Lett.* **1990**, *31*, 3905. (b) Okada, Y.; Minami, T.; Umezu, Y.; Nishikawa, S.; Mori, R.; Nakayama, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 667.

(81) (a) Åkermark, B.; Zetterberg, K.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *J. Organomet. Chem.* **1987**, *335*, 133. (b) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620. (c) Vitagliano, A.; Åkermark, B. *J. Organomet. Chem.* **1988**, *349*, C22.

(82) Different behavior is encountered with molybdenum complexes, such as $(MeCN)_3Mo(CO)_3$ and $(C_7H_8)Mo(CO)_3$. Whereas Trost has demonstrated that allylic acetates (e.g. **10a**) follow the reaction pattern of Pd-complexes (Scheme I)[83] we have observed almost complete reversal of the stereochemical outcome (up to 93:7) with the DPPAcO derivative **10b** (which is free of any serious steric constraint).[84] Moreover, the Mo-η^3-complexes seem to be configurationally stable.[84]

(83) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543; **1983**, *105*, 3343; *Organometallics* **1983**, *2*, 1687. (b) Trost, B. M.; Lautens, M.; Peterson, B. *Tetrahedron Lett.* **1983**, *24*, 4525. (c) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, *109*, 1469. (d) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590. See, however: (e) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670.

(84) Starý, I.; Kočovský, P. to be published.

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(86) (a) Kočovský, P. *Tetrahedron Lett.* **1986**, *27*, 5521; (b) Kočovský, P.; Stieborová, I. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1969.