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Review

# Novel catalytic reactions involving π-allylpalladium and -nickel as the key intermediates: umpolung and β-decarbopalladation of π-allylpalladium and nickel-catalyzed homoallylation of carbonyl compounds with 1,3-dienes☆

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**Abstract**

Three subjects concerning novel reactions involving π-allylpalladium and π-allylnickel as intermediates are reviewed: the first is the umpolung of π-allylpalladium, an alternation of the electrophilic nature of π-allylpalladium species into the nucleophilic one of allylzinc species, which proceeds by treating the π-allylpalladium with diethylzinc. Unique regio- and stereoselectivity of the thus-formed allylzincs toward carbonyl compounds is described. The second is the ring-opening reaction of 5-vinyl-2-oxa-1-palladacyclopentane intermediates, which furnishes aldehydes and ketones in good yields. The reaction proceeds via a novel C–C bond cleavage β to the palladium (decarbopalladation reaction). Finally, the nickel-catalyzed homoallylation of carbonyl compounds with 1,3-dienes is discussed. The reaction is promoted by triethylborane or diethylzinc and tolerates carbonyl compounds (alkyl-, arylaldehydes and ketones) and 1,3-dienes, of a wide structural variety. The reaction provides 1,2- and 1,3-disubstituted 4-pentenols with high 1,2- and 1,3-diastereoselectivity. Mechanistically, this final reaction is closely related, in a reverse manner, to the decarbopalladation reaction (second subject). 

*Keywords:* Aldehyde; Allylation; Diene; Diethylzinc; Homoallylation; Ketone; π-Allylnickel; π-Allylpalladium; Palladium; Nickel; Triethylborane; Umpolung

Palladium and nickel have proved to be versatile catalysts for a variety of reactions, particularly for C–C bond formation reactions, and these catalytic reactions are indispensable for the elegant and efficient construction of desired molecules. In this review three new catalytic reactions developed in our laboratories are described, which involve π-allylpalladium and π-allylnickel complexes as the key intermediates.

As illustrated in Scheme 1, these reactions (a)–(c) are correlated to each other by the structural similarity of the intermediates **I**–**III**. The reaction (a) is concerned with the umpolung of π-allylpalladium: an alternation of the electrophilic nature of π-allylpalladium species **I** into the nucleophilic one of allylzinc species **II**, which proceeds by treating **I** with diethylzinc. The versatility and the unique regio- and stereoselectivity associated with this methodology is described in Section 1.

The second reaction is the ring-opening reaction of 5-vinyl-2-oxa-1-palladacyclopentanes **I**, which furnishes ω-dienyl aldehydes and ketones [reaction (b), Scheme 1]. The reaction proceeds via a novel C–C bond cleavage β to the palladium (β-decarbopalladation reaction).

☆ This review is dedicated to Professor J. Tsuji on the occasion of his 70th birthday for his great contribution to the development of palladium chemistry in the synthetic field.

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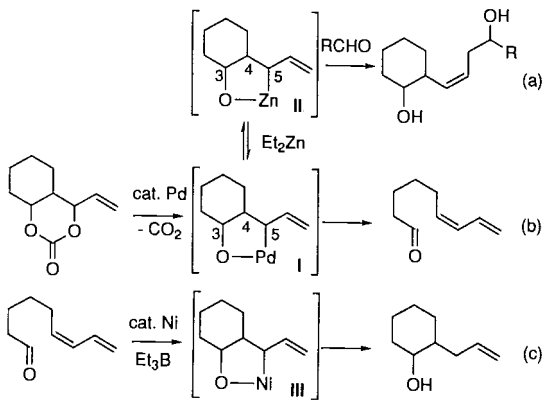


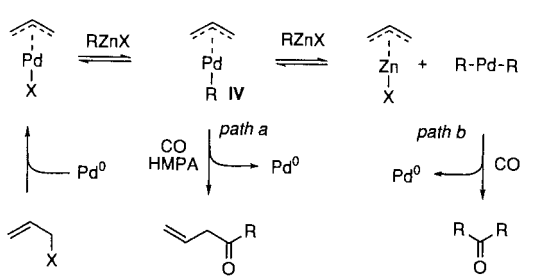

Scheme 1. Schematic presentation of (a) an allylation of aldehydes via umpolung of π-allylpalladium with diethylzinc, (b) a decarbopalladation of π-allylpalladium, providing ω-dienyl aldehydes and (c) a nickel-catalyzed intramolecular homoallylation of ω-dienyl aldehydes.

Besides being interesting from a mechanistic point of view, this reaction may be important from a synthetic point of view. The results of detailed study are described in Section 2.

The nickel-catalyzed homoallylation of aldehydes and ketones with 1,3-dienes is discussed in Section 3. The reaction is promoted by triethylborane or diethylzinc and tolerates both reaction partners, carbonyl compounds and 1,3-dienes, of a wide structural variety. In reaction (c) of Scheme 1 an example of the intramolecular version of this reaction is shown, using the product obtained in the reaction (b) as the starting material. Apparently, this reaction is closely related, in a reverse manner, to the β-decarbopalladation reaction [reaction (b)].

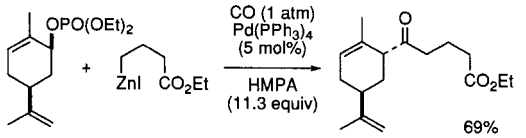
## 1. Palladium-catalyzed allylation of carbonyl compounds via umpolung of π-allylpalladium by diethylzinc

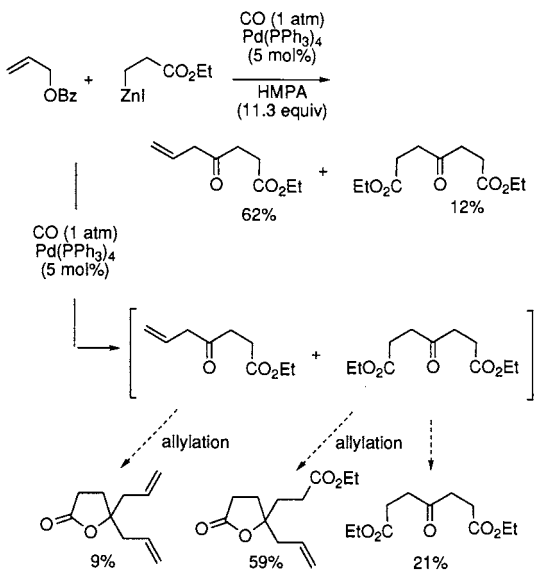
Prior to discussing the chemistry of the umpolung reaction [reaction (a), Scheme 1], here its background is reviewed briefly. Recently, we have developed an efficient method of unsymmetrical ketone synthesis based




Scheme 2. A mechanism for palladium-catalyzed ketone synthesis via three-component connection reaction of allyl benzoates, organozincs, and carbon monoxide.

on the palladium-catalyzed three-component connection reaction of allylic substrates, carbon monoxide, and alkylzincs [1]. Two typical examples are shown in Eqs. (1) and (2). These reactions smoothly proceed at room temperature (r.t.) under atmospheric pressure of carbon monoxide. For the optimization of the reaction, HMPA is essential. As shown in Eq. (3), in the absence of HMPA, the reaction feature changes dramatically, and a mixture of two kinds of γ-lactones and a symmetrical keto-diester is obtained in a good combined isolated yield.

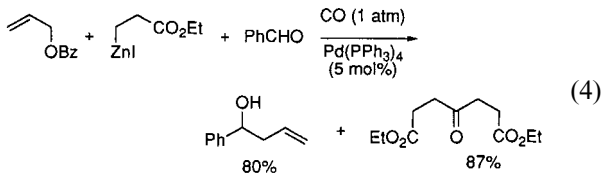



In Scheme 2 the reaction mechanism that accommodates these results is outlined; HMPA facilitates the carbonylation of π-allylalkylpalladium(II) intermediate **IV** to selectively provide an unsymmetrical ketone (path a). In the absence of HMPA, this process becomes slow and the other process becomes dominant, where the intermediate **IV** reacts with alkylzinc (being present in a large excess relative to **IV**) to give a mixture of allylzinc and dialkylpalladium(II) complexes. The thus-formed dialkylpalladium(II) species undergoes carbonylation to give a symmetrical ketone (path b) and allylzinc reacts with the thus-formed unsymmetrical ketone (path a) and symmetrical ketone (path b) to furnish the corresponding tertiary alcohols, which spontaneously cyclize to give the two kinds of lactones shown in Eq. (3). In reactions 1–3, paths a and b are regarded to operate in the ratios of 100:0, 62:12, and 9:80, respectively.

An important piece of evidence, further supporting the formation of allylzinc and dialkylpalladium intermediates, is obtained when allyl benzoate and β-zincio-

ester are reacted in the presence of benzaldehyde and in the absence of HMPA under 1 atm of carbon monoxide (Eq. (4)). In this reaction, benzaldehyde is used for two purposes: the first is to capture the allylzinc species and the second is to shift the equilibrium to the right and hence to generate the dialkylpalladium(II) species, bis-(2-ethoxycarbonylethyl)palladium(II), in maximum quantity (Scheme 2). As expected, both the allylation product, 1-phenyl-3-buten-1-ol, and the carbonylation product of the dialkylpalladium(II) species, diethyl 4-oxo-heptanedioate, are obtained in quantitative yields.



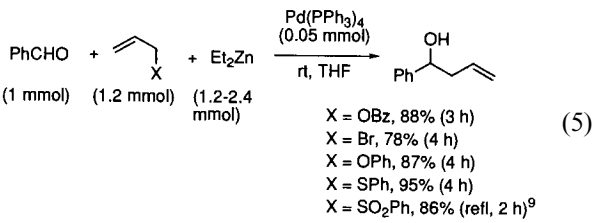
(4)

It is generally accepted that allylalkylpalladium(II) species **IV**, generated by the reaction of π-allylpalladium with alkyllithium and -magnesium compounds, are rather unstable and prone to undergo either reductive elimination or β-dehydropalladation. In this context, it is remarkable for the intermediate **IV**, generated from alkylzinc compounds, to be reluctant to these reductive elimination and β-dehydropalladation reactions [2]. Indeed, we have encountered such unusual stability of **IV** on many occasions. For instance, a stoichiometric reaction of chloro-[1-(2-phenylethyl)-π-allyl]palladium(II) dimer (0.25 mmol, 0.5 mmol/Pd) and diethylzinc (5 mmol) in the presence of triphenylphosphine (2 mmol, $PPh_3/Pd = 4/1$ mol/mol, see Eq. (7) for the structure of the π-allyl]palladium(II) dimer) in THF at 0°C for 5 h, remains almost unchanged and provides 4-phenyl-1-butene (and its regioisomer, β-dehydropalladation product) and 3-ethyl-4-phenyl-1-butene (and its regioisomer, reductive elimination product) in less than 5% yield each. The amount of triphenylphosphine, however, strongly affects the reaction; in its absence, the same reaction gives rise to 4-phenyl-1-butene and 3-ethyl-4-phenyl-1-butene in 55 and 1–2% yields, respectively.

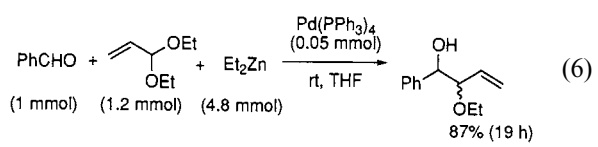
In contrast to the reluctance of alkylzinc compounds, the following organozinc compounds, characteristically possessing the polarized C–Zn bonds (and also bearing no hydrogens β to zinc metals), are known to readily react with π-allylpalladium to give the corresponding reductive elimination products in good yields: α-zincioesters (the so-called Reformatsky reagent) [3], allylzincs [4], phenylzincs [5] and perfluoroalkylzincs [6]. Intramolecularly, π-allylpalladium and alkylzinc may undergo reductive elimination, though under rather harsh conditions [7].

Whatever the reason for the unusual stability of the intermediates **IV**, a sequence of equilibria in Scheme 2 suggests the possibility of the alternation of an electrophilic nature of the allylic moiety of π-allylpalladium intermediates into a nucleophilic one of the allylzinc species by exposing the π-allylpalladium intermediates to alkylzinc compounds (umpolung). If this is the case, the present umpolung methodology may be utilized as a versatile allylation method of carbonyl compounds, since π-allylpalladium complexes are available in many ways either as isolable stable crystalline solids or as reaction intermediates in catalytic reactions.

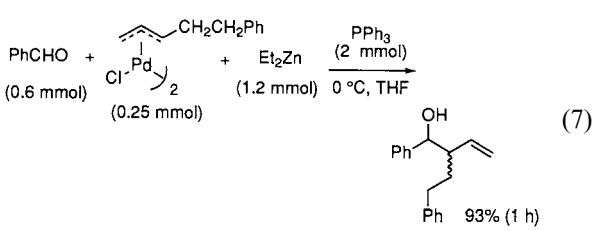
Indeed, this has proved to be the case. In Eqs. (5) and (6) typical reaction conditions successfully applied to the umpolung methodology are shown, where commercially available diethylzinc (1.2–2.4 mol equiv) is used as an alkylzinc compound and tetrakis-(triphenylphoshine)palladium(0) (0.05 equivalents) as the catalyst [8,9]. The allylation of benzaldehyde proceeds smoothly at r.t., and in most cases the reaction is completed within 1 day. Allylating agents with a wide variety of leaving groups are tolerated. The reactions using π-allylpalladium complexes as the starting materials proceed smoothly even at 0°C or below (Eq. (7)).



(5)



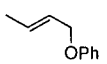
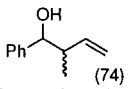
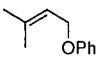
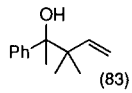
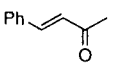
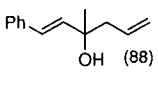
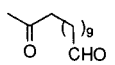
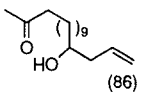
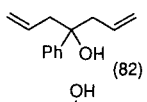
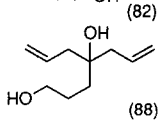
(6)



(7)

The reactions of allyl phenyl ethers and carbonyl compounds, encompassing aldehydes, ketones, esters and lactones, are summarized in Table 1. Esters and lactones provide the diallylated products in good yields (runs 5 and 6, Table 1). The reaction displays high chemoselectivity (run 4). The relative reactivity of benzaldehyde, acetophenone, and methyl benzoate is roughly determined to be $10^5:10^3:1$ based on competition experiments using allyl phenyl ether as an allylating agent (r.t.). This means, under usual reaction conditions, an exclusive allylation of acetophenone (1

Table 1
Allylation of various carbonyl compounds with allyl phenyl ethers via umpolung of π-allylpalladium with diethylzinc[a]

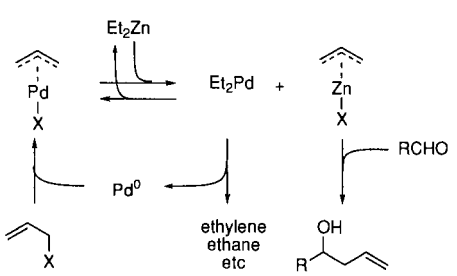
| run | carbonyl | allyl phenyl ether | $Et_2Zn$ (mmol) | time (h) | product (% yield) |
|---|---|---|---|---|---|
| 1 | PhCHO |  | 2.4 | 7 |  (74) [*syn*:*anti* = 1:2] |
| 2 | PhCOMe |  | 2.4 | 22 |  (83) |
| 3 |  |  | 2.4 | 22 |  (88) |
| 4 |  |  | 2.4 | 10 |  (86) |
| 5 | $PhCO_2Me$ |  | 4.8 | 24 |  (82) |
| 6 |  |  | 4.8 | 24 |  (88) |

[a] Reaction conditions: carbonyl (1 mmol), allyl ether (1.2 mmol for runs 1–4, 2.4 mmol for runs 5 and 6), $Pd(PPh_3)_4$ (0.05 mmol), and $Et_2Zn$ (2 M in hexane) in 3 ml of dry THF at r.t. under $N_2$.

mmol) takes place even when methyl benzoate (5 ml) is used as the solvent (acetophenone/methyl benzoate = 1/40, mol/mol).

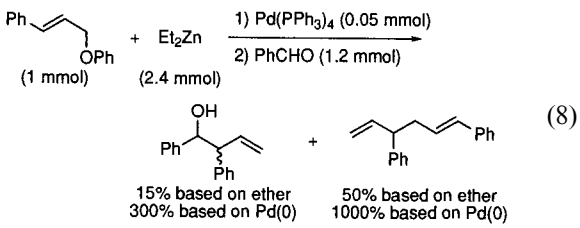
In Scheme 3 the catalytic cycle of the present umpolung reaction is outlined. According to this scheme, it is expected that 1 mol of allylzinc compound is generated from 1 mol each of an allylating agent and diethylzinc, provided that diethylpalladium(II) decomposes promptly and the π-allylpalladium(II) intermediate is supplied continuously.

In fact, allylzinc is accumulated in 15% yield at most as indicated by the following experiment (Eq. (8)). A mixture of cinnamyl phenyl ether and diethylzinc in




Scheme 3. Catalytic cycle of Pd(0) for diethylzinc-promoted allylation of aldehydes via umpolung of π-allylpalladium intermediate.

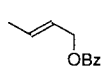
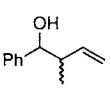
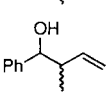
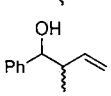
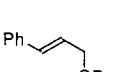
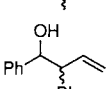
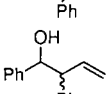
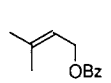
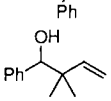
THF is heated at 50°C in the presence of $Pd(PPh_3)_4$ (0.05 equivalents) until the ether completely disappears (7 h), and then the reaction mixture is treated with benzaldehyde at −35°C for 10 min. The results shown in Eq. (8) clearly indicate that a major portion of the allylzinc generated is consumed for the reaction with the π-allylpalladium intermediate to furnish 1,4-diphenyl-1,5-hexadiene [4,10]. Accordingly, all the reactions listed in Tables 1–3 are undertaken under the Barbier conditions, i.e. with the necessary reagents all together from the beginning of the reaction.



(8)

The allylation based on the umpolung of π-allylpalladium displays unique regio- and stereoselectivity depending on the substitution pattern of the allylic moiety. The results obtained for α- or γ-substituted allylating agents are summarized in Table 2, [8]. The reactions with β,γ- and α,β,γ-substituted allylic substrates are listed in Table 3, [11,12].

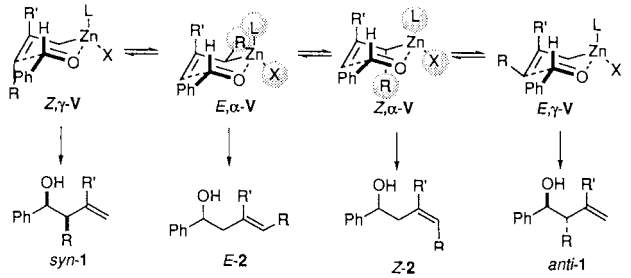
Table 2
Allylation of benzaldehyde with α- and γ-substituted allylic benzoates[a]

| run | allyl benzoate | time (h) | product (% yield) [*syn*:*anti*] |
|---|---|---|---|
| 1 |  | 2 |  (94) [1:2.4] |
| 2 |  | 2 |  (92) [1:2.4] |
| 3 |  | 5 |  (79) [3.6:1] |
| 4 |  | 5 |  (83) [1:10] |
| 5 |  | 3 |  (83) [1:10] |
| 6 |  | 2 |  (95) |

[a] Reaction conditions: benzaldehyde (1 mmol), allyl benzoate (1.2 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and $Et_2Zn$ (2.4 mmol, 2 M in hexane) in 3 ml of dry THF at r.t. under $N_2$.

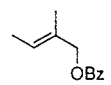
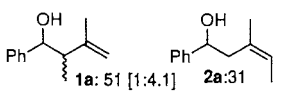
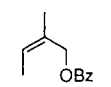
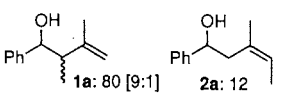
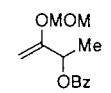
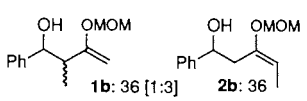
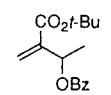
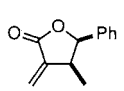
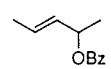
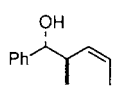
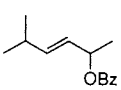
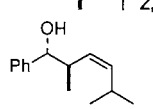
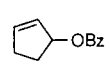
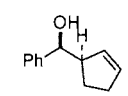
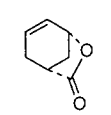
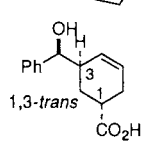
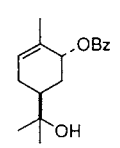
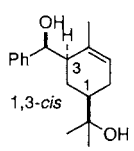
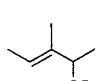
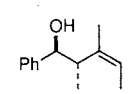
As is apparent from Table 2, between the unsymmetrically substituted allylic termini, the ones bearing the highest number of substituents react selectively (see also runs 1 and 2, Table 1).

(*E*)- and (*Z*)-cinnamyl benzoates show almost the same reactivity and stereoselectivity and provide the *anti*-isomer in a high preference over the *syn*-isomer (runs 4 and 5, Table 2), while (*E*)- and (*Z*)-crotyl benzoates show a different diastereoselectivity, providing the *anti*- and *syn*-isomers, respectively, in modest selectivity (runs 1 and 3, Table 2). These contrasting results suggest that (*E*)- and (*Z*)-cinnamylzinc compounds establish a fast equilibrium before they react with benzaldehyde, while (*E*)- and (*Z*)-crotylzinc compounds isomerize to each other more slowly than they react with benzaldehyde.




Scheme 4. Transition states for the allylation of benzaldehyde with α-mono (R′ = H) and α,β-disubstituted allylic benzoates and the corresponding products.

Table 3
Allylation of benzaldehyde with di- and tri-substituted allylic benzoates[a]

| run | allyl benzoate | time (h) | product (% yield) [*syn*:*anti*] |
|---|---|---|---|
| 1 |  | 72 |  **1a**: 51 [1:4.1] **2a**:31 |
| 2 |  | 71 |  **1a**: 80 [9:1] **2a**: 12 |
| 3 |  | 24 |  **1b**: 36 [1:3] **2b**: 36 |
| 4 |  | 4 |  **1c**: 47 [only *syn*] |
| 5 |  | 26 |  **3a**: 63 [only *Z*,*anti*] |
| 6 |  | 26 |  **3b**: 60 [1:8] |
| 7 |  | 9 |  **3c**: 61 [only *syn*] |
| 8 |  | 6 |  **3d**: 87 [only *syn*] |
| 9 |  | 9 |  **3e**: 98 [only *syn*] |
| 10 |  | 100 |  **3f**: 91 [only *anti*] |

[a] Reaction conditions: benzaldehyde (1 mmol), allyl benzoate (1.2 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and $Et_2Zn$ (2.4 mmol, 2 M in hexane) in 3 ml of dry THF at r.t. under $N_2$.

The C2 substituents of allylating agents cause a dramatic change in the regio- and stereoselectivity (runs 1–4, Table 3), [11]. (*E*)- and (*Z*)-2-methyl-2-butenyl benzoates selectively furnish *anti*-**1a** and *syn*-**1a**, respectively (runs 1 and 2, Table 3). The selectivity is apparently higher than that observed for (*E*)- and (*Z*)-crotyl benzoates (runs 1 and 3, Table 2). In addition to **1a**, these reactions provide the regioisomer, **2a**, the product being allylated at the least substituted allylic termini. The allylic ester bearing a C2 MOM substituent (run 3, Table 3) also shows similar regio- and stereoselectivity. Notably, in these reactions, *Z*-**2a** and *Z*-**2b** are obtained as single stereoisomers. The C2 *tert*-butoxycarbonyl derivative, on the other hand, gives rise to *syn*-product **1c** exclusively (run 4, Table 3).

These contrasting regio- and stereoselectivities seem to depend on the electronic nature of the C2 substituents and may be rationalized according to Scheme 4. The electron-donating C2 substituents may enhance the reactivity of all the allylzinc intermediates, especially the α-substituted *Z*,α-**V** and *E*,α-**V**, since the γ-substituents of *Z*,γ-**V** and *E*,γ-**V** may sterically hinder the reaction with benzaldehyde.

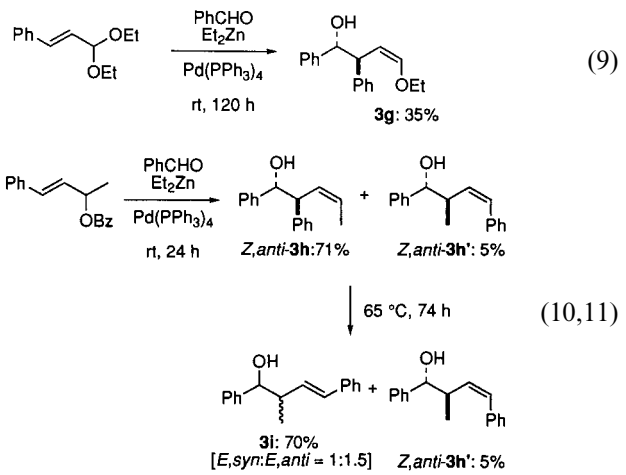
The isomer *Z*-**2** may be derived from a transition state *Z*,α-**V**. In an alternative transition state, *E*,α-**V**, leading to *E*-**2**, the substituent R suffers from gauche repulsion against both the ligand L and the counterion X on the tetrahedral zinc(II) ion. The gauche repulsion is expected to be substantial, since these ligands and counterions are sterically bulky, being either THF or triphenylphoshine and either an ethyl group or a benzoate anion, respectively [13].

The reaction of *Z*,α-**V** with benzaldehyde may interrupt the isomerization between *Z*,γ-**V** and *E*,γ-**V**; hence, a better stereochemical correlation between the starting

materials and the products results (runs 1 and 2, Table 3) than that for the (*E*)- and (*Z*)-crotyl cases (runs 1 and 3, Table 2).

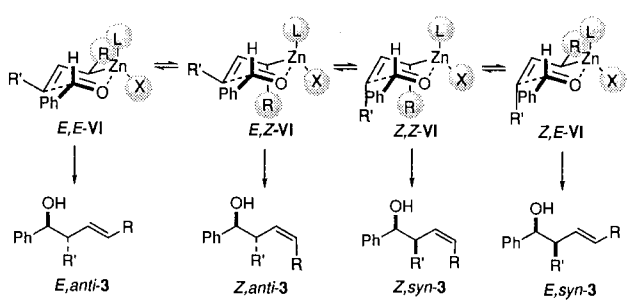
The electron-attracting C2 substituents, on the other hand, render all the allylzinc species less reactive and complete equilibrium among them may have been established before the addition to benzaldehyde takes place. Hence, only the most thermodynamically stable *Z*,γ-**V** takes part in the allylation to provide *syn*-**1c** exclusively.

Some of the typical results obtained for α,γ- and α,β,γ-substituted allylating agents are summarized in runs 5–10, Table 3 and Eqs. (9–11), [12]. All these reactions show pronounced stereoselectivity; acyclic benzoates provide *Z*,*anti*-isomers **3a**,**b**, and **3f-h** exclusively and cyclic ones *syn*-isomers **3c–e** exclusively.

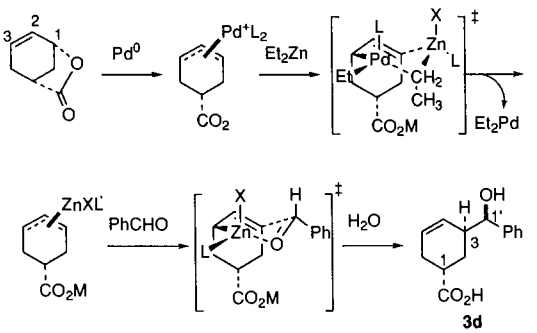



Unsymmetrical α,γ-disubstituted allylating agents display an interesting regioselectivity. The allylic termini bearing a phenyl group are generally more reactive than the others (Eqs. (9) and (10)). Marked contrast is seen in a pair of results shown in Eqs. (6) and (9), [14]. When the steric bulk of the α- and γ-substituents differs substantially, the allylic termini with the smaller substituents react preferentially (run 6, Table 3).

Although the reactions of highly substituted allylic agents sometimes require rather vigorous conditions (r.t. for 1–5 days), these reactions seem to be controlled kinetically. Indeed, when the product mixture of Eq. (10) is heated at 65°C for 3 days, the thermodynamically more stable isomers **3i** emerge at the expense of *Z*,*anti*-**3h** (Eq. (11)).




Scheme 5. Transition states for the allylation of benzaldehyde with α,γ-disubstituted allylic benzoates and the corresponding products.



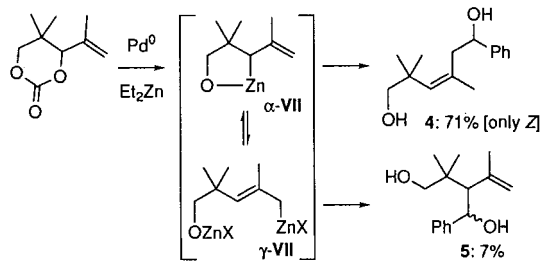

Scheme 6. A mechanistic rationale for the stereoselective formation of 1,3-*anti*-1′,3-*syn*-product, **3d**.

Four possible transition states for acyclic α,γ-disubstituted allylzincs are shown in Scheme 5. Transition states *E*,*E*-**VI** and *Z*,*E*-**VI** seem to be unfavorable, since the equatorial substituent R experiences gauche repulsion against both the ligand L and the counterion X over zinc(II) (vide supra). Of the two transition states with R in axial position, *E*,*Z*-**VI** is favored over *Z*,*Z*-**VI**, in which R and R′ have a 1,3-diaxial relationship. Thus, addition may proceed selectively through *E*,*Z*-**VI** to give *Z*,*anti*-**3**. The preference of Ph as R′ (Eqs. (9) and (10)) might be due to resonance stabilization.

The remarkably high *anti*-selectivity observed for α,γ-substituted allylating agents is attributed to the 1,3-diaxial repulsion, which makes *E*,*Z*-**VI** much more stable than *Z*,*Z*-**VI**. The moderate *anti*-selectivity observed for γ- and β,γ-substituted allylating agents (e.g. run 1, Table 2 and runs 1 and 3, Table 3) may be due to the absence of such a large energetic bias between *E*,γ-**V** and *Z*,γ-**V** (Scheme 4).

As expected from the *Z*-structure of allylzinc compounds, cyclic allylic esters furnish *syn*-products exclusively (runs 7–9, Table 3). Notably, these reactions accompany a complete inversion of configuration at the allylic stereocenters, providing 1,3-*trans*-**3d** from *cis*-lactone (run 8) and 1,3-*cis*-**3e** from 1,3-*trans*-benzoate (run 9). These results indicate that allylzinc species are generated in a stereochemically pure state [15] and they are configurationally stable under the conditions.

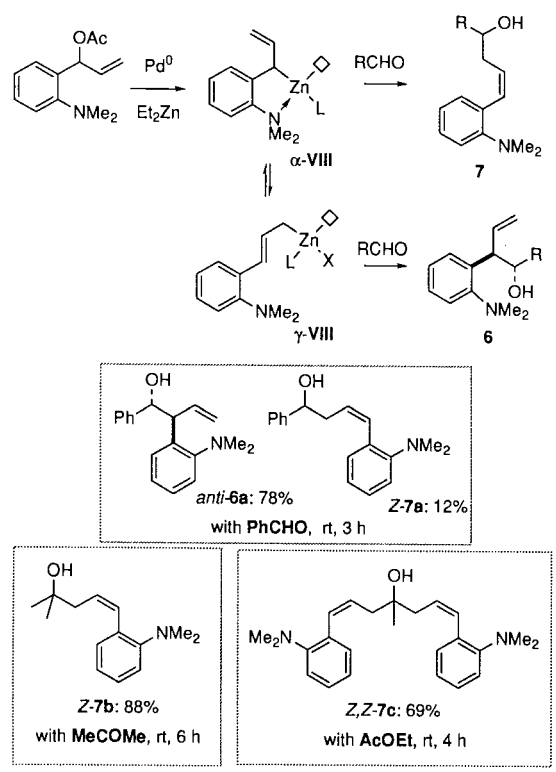
A rationale for the generation of the stereochemically defined allylzinc species and the stereochemical outcome in the allylation reaction is shown in Scheme 6, which involves an oxidative addition of the lactone C1–O bond to palladium(0) with inversion, the allyl group transfer from palladium(II) to zinc(II) with retention of configuration of the allylic moiety through a six-membered transition state, followed by the reaction of the thus-formed *trans*-allylzinc species (being *trans* with respect to Zn(II) and $CO_2M$) with benzaldehyde through a six-membered chair-like transition state, placing the phenyl group of benzaldehyde in a quasi-equatorial position.




Scheme 7. Intramolecular chelation control of regioselectivity.

In Schemes 7 and 8 some results of our attempts aimed at the reversal of regioselectivity are shown. The idea is based on an intramolecular five-membered chelation stabilization [16] of an allylzinc species like α-**VII**, which might react with aldehydes at the external allylic position to provide the regioisomer **4**. As has been discussed (Table 1), if there is no chelation stabilization, an allylzinc species like γ-**VII**, possessing a primary carbon–zinc bond, predominates in the equilibrium and provides the regioisomer **5** selectively. In fact, this idea works nicely in the case of alkoxy chelation and *Z*-**4** is obtained predominantly over **5** (Scheme 7, [17]), however, the idea can't be extended to the case of dimethylamino chelation (Scheme 8, [18a]).

Under usual umpolung conditions, 1-(*o*-dimethylaminophenyl)allyl acetate reacts with benzaldehyde to give **6a** predominantly over **7a**. The stereoselectivity is



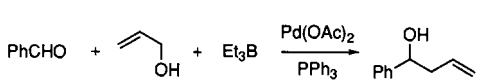

Scheme 8.

as usual, and *anti*-**6a** and *Z*-**7a** are obtained as single stereoisomers. These results seem to indicate that the *o*-dimethylamino group does not influence the regio- and stereoselectivity. Acetone, on the other hand, reacts in the way that we expected and selectively provides *Z*-**7b**. Similarly, ethyl acetate reacts to furnish *Z*,*Z*-**7c** exclusively, the product being allylated doubly in the same sense of regio- and stereoselectivity. The formation of *Z*,*Z*-**7c** as a single isomer attests to the high regio- and stereoselectivity of the present allylation.

The unique dependence of regioselectivity on the kind of carbonyl compounds may primarily be attributed to the difference in the Lewis acidity between the zinc metals of α-**VIII** and γ-**VIII** (Scheme 8). Owing to the electron donation by the amino group, the Lewis acidity of α-**VIII** is expected to be considerably lower than that of γ-**VIII**. Accordingly, α-**VIII** would accommodate only carbonyl compounds of high Lewis basicity (acetone and ethyl acetate, but not benzaldehyde) [19] into its vacant site (symbolized as ◇). That is, benzaldehyde is able to coordinate only γ-**VIII** and reacts selectively with it to furnish *anti*-**6a**. Acetone and ethyl acetate coordinate both α- and γ-**VIII**; however, owing to the overwhelming predominance of α-**VIII** over γ-**VIII**, they would react with α-**VIII** to give *Z*-**7b** and *Z*,*Z*-**7c**, respectively.

Steric repulsion between the carbonyl substituents of acetone and ethyl acetate and the *o*-dimethylaminophenyl group in a transition state leading to **6** may also contribute to retarding the reaction of γ-**VIII**. In accord with the explanation mentioned above, *p*-chlorobenzaldehyde and *p*-methoxybenzaldehyde, of lower or higher coordination ability to α-**VIII** than benzaldehyde, furnish mixtures of **6** and **7** in a ratio of ca. 9:1 and 1:1, respectively.

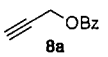
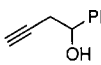
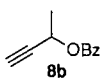
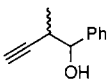
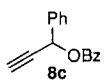
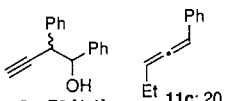
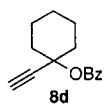
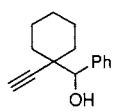
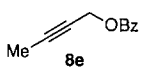
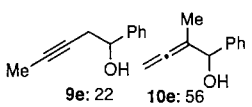
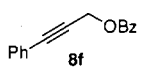
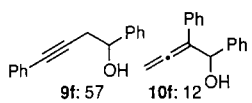
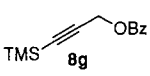
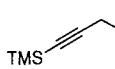
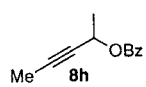
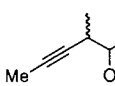
Triethylborane also promotes the allylation of benzaldehyde in the presence of catalytic amounts of $Pd(OAc)_2$ and triphenylphosphine (Eq. (12)). An interesting feature of the present reaction is that the reaction tolerates a variety of allylic alcohols as the allylating agents [17]. Allyl benzoates and allyl phenyl ethers can be utilized similarly well; however, surprisingly, allyl chlorides and bromides are entirely unreactive (Eq. (5)). The scope and mechanism of the present reaction are under investigation in the author's laboratories.




(12)

In contrast to π-allylpalladium complexes, the versatility of propargylpalladium complexes as intermediates seems to be rather limited [20]; they are present as equilibrium mixtures with allenylpalladium complexes, and generally react with hard carbon nucleophiles through the latter complexes to provide the reductive elimination products, substituted allenes [21]. Their re-

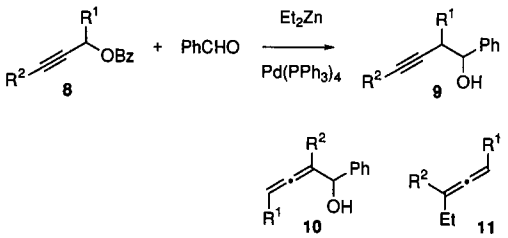
Table 4
Palladium-catalyzed propargylation of benzaldehyde via umpolung of propargylpalladium with diethylzinc[a]

| run | propargyl benzoate | $Et_2Zn$ (mmol) | time (h) | % yield of product [*syn*:*anti*] |
|---|---|---|---|---|
| 1 |  **8a** | 3.6 | 7 |  **9a**: 57 |
| 2 |  **8b** | 3.6 | 3 |  **9b**: 70 [1:1] |
| 3 |  **8c** | 3.6 | 3 |  **9c**: 79 [1:1] **11c**: 20 |
| 4 |  **8d** | 3.6 | 2.5 |  **9d**: 71 |
| 5 |  **8e** | 2.4 | 24 |  **9e**: 22 **10e**: 56 |
| 6 |  **8f** | 2.4 | 75 |  **9f**: 57 **10f**: 12 |
| 7 |  **8g** | 2.4 | 96 |  **9g**: 80 |
| 8 |  **8h** | 2.4 | 30 |  **9h**: 60 [1:1] |

[a] Reaction conditions: propargyl benzoate (1.2 mmol), benzaldehyde (1.0 mmol), diethylzinc (indicated amount), $Pd(PPh_3)_4$ (0.05 mmol), in dry THF (5 ml) at r.t. under $N_2$.

action behavior with soft carbon nucleophiles [22] has not been fully elucidated yet.

We have found that the umpolung method of π-allylpalladium complexes can be directly applied to the umpolung of propargylpalladium complexes (Eq. (13), [23]) The propargylation of carbonyl compounds proceeds smoothly at r.t. by stirring a solution of propargyl benzoate **8** (1.2 mmol), a carbonyl compound (1.0 mmol), diethylzinc (2.4–3.6 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.05 mmol) in dry THF under nitrogen. Results for the reactions with benzaldehyde are listed in Table 4. Ketones react similarly well. For example, under similar conditions, **8b** reacts with acetone, cyclohexanone, and acetophenone to furnish the corresponding homopropargyl alcohols in 85, 85, and 58% yields, respectively.



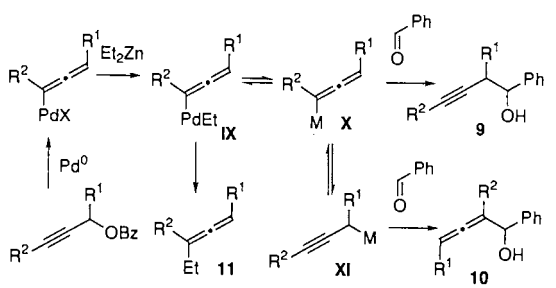
(13)

The parent compound **8a** (run 1, Table 4), α-substituted **8b-d** (runs 2–4), and α,γ-disubstituted propargyl benzoates **8h** (run 8), all provide homopropargyl alcohols **9** selectively, whereas γ-substituted compounds **8e–g** (runs 5–7) react to give allenyl alcohols **10** in addition to **9**. The ratio of **10** to **9** markedly depends on the kind of the γ-substituents $R^2$ and ranges from 72/28 for **10e**/**9e** ($R^2$ = Me, run 5) to 0/100 for **10g**/**9g** ($R^2$ = $SiMe_3$, run 7). The cross-coupling products, ethylallenes **11**, are either not detected at all or obtained only as the minor products (run 3).

The formation of **9** and **10** in good yields suggests that the reductive elimination of **IX** to **11** is slower than the transformation of **IX** to an equilibrium mixture of **X** and **XI** and the addition reactions of these complexes with benzaldehyde (Scheme 9). The metal fragment M of **X** and **XI** has not been specified yet; however, a zincate species [e.g. M = $Zn^-$(OBz)(Et) or $Zn^-(Et)_2$] is most probable judging from the formation of **9b**, **9c**, and **9h** with low stereoselectivity; M = Zn(OBz) or ZnEt is unlikely, since **X** (M = ZnCl, generated from allenyllithium and $ZnCl_2$) is known to react with aldehydes to provide *anti*-**9** selectively [24].

The selective formation of **9** (runs 1–4 and 8) may be attributed to the preponderance of **X** ($C_{sp^2}$–M bonding) over **XI** ($C_{sp^3}$–M bonding) in the equilibrium. The dramatic change in the ratio of **10**/**9** for the reactions of a series of γ-substituted **8** (runs 5–7) may owe its origin to a steric destabilization of **X** for $R^2$ = Me and Ph groups and to an electronic stabilization of **X** for $R^2 = SiMe_3$.

The hitherto reported umpolung methods of π-allylpalladium complexes are as follows: (1) reduction of π-allylpalladium either with low-valent metals [25] or by electrochemical means [26], (2) allylation of π-allylpalladium with allylstannanes, which generates a nucleo-



Scheme 9. A mechanistic rationale for the palladium-catalyzed propargylation and allenylation of benzaldehyde via umpolung of propargylpalladium intermediate with diethylzinc.

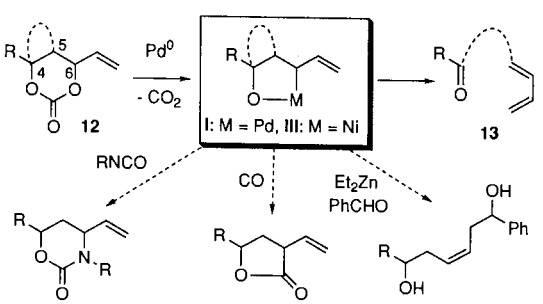
philically active bis-π-allylpalladium species [27], and (3) transformation of π-allylpalladium to allylmetalloids (e.g. allylstannanes, -silanes, -boranes) [28] that serve as nucleophiles to carbonyl compounds. The reduction method using low-valent metals may be applicable to the umpolung of propargylpalladium complexes [29].

The umpolung described here is based on a ligand exchange between π-allylpalladium(II) complexes (or propargylpalladium(II) complexes) and diethylzinc(II) and hence, is mechanistically different from the methods listed above. The utility of the present allylation may be apparent from the unique regio- and stereoselectivity, the generation of stereochemically defined allylzinc species with a clean inversion of configuration of the starting allylic benzoates, the high chemoselectivity (aldehyde:ketone:ester = $10^5$:$10^3$:1), the mild reaction conditions (r.t.), and the operational simplicity.

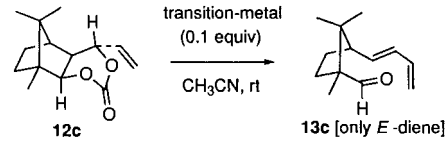
## 2. Palladium-catalyzed synthesis of ω-dienyl aldehydes and ketones via β-decarbopalladation reaction

Owing to their synthetic importance and mechanistic interest, transition metal-catalyzed or -promoted cyclization reactions of ω-ene aldehydes [30], ω-yne aldehydes [31], ω-ene carboxylic esters [32], ω-diene aldehydes [33], 1,ω-dienes [34], 1,ω-enynes [35], and so on, providing cycloalkanes and heterocycle compounds, have been developed very rapidly and studied extensively. Interestingly, however, the reverse process, ring-opening reactions, has received less attention. In this section, a novel palladium(0)-catalyzed ring-opening reaction of 6-vinyl cyclic carbonates **12** is described, which furnishes a variety of ω-diene aldehydes and ketones **13** in excellent yields (Scheme 10, [36]). The reaction most likely proceeds via a novel β-decarbopalladation reaction of π-allylpalladium intermediate **I** [37], a formal reverse process of the nickel(0)-catalyzed cyclization of **13** into **III** (Scheme 1) that will be described in Section 3.

The complexes **I** have been proposed as the common intermediate for the palladium-catalyzed conversions of **12** into six-membered cyclic carbamates (by the reaction with aryl isocyanates or arylsulfonyl isocyanates) [38] and γ-butyrolactones (by the reaction with carbon monoxide under atmospheric pressure) [39] (Scheme 10). The conversion of **I** into the corresponding allylzinc species by diethylzinc was described in Section 1.



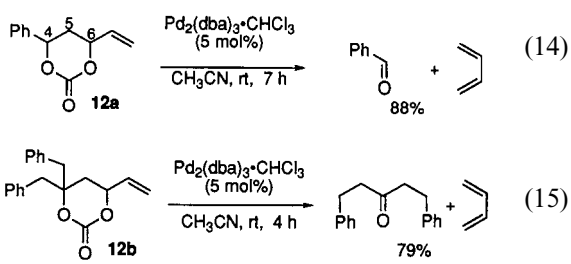

Scheme 10.




| run | transition-metal (additive)/reaction time/ yield |
|---|---|
| 1 | $Pd_2(dba)_3$•$CHCl_3$ / 72 h / 70% |
| 2 | $Pd_2(dba)_3$•$CHCl_3$ + $P(OMe)_3$ / 7 h / 82% |
| 3 | $Pd(PPh_3)_4$ / 72 h / 75% |
| 4 | $PdCl_2[P(o\text{-}Tol)_3]_2$ / 72 h / 0% |
| 5 | $Pd(OAc)_2$ / 120 h / 0% |
| 6 | $Ni(cod)_2$ + $PPh_3$ / 0.5 h / 96% |
| 7 | $Pt(PPh_3)_4$ / 12 h / 85% |

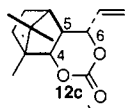
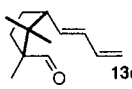
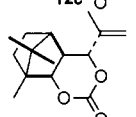
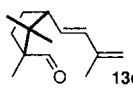
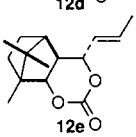
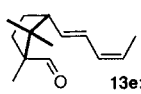
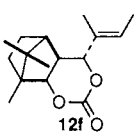
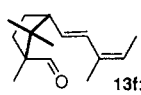
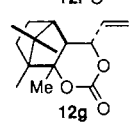
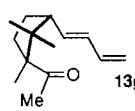
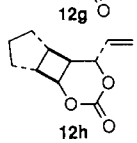
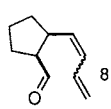
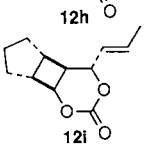
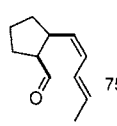
Scheme 11. Transition-metal catalyzed decarboxylative C–C bond cleavage reaction. Except for run 7 (55°C), all reactions are carried out at r.t.

Monocyclic carbonate **12a**, upon treatment with 0.05 equivalents of $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) in dry acetonitrile at r.t., spontaneously extrudes carbon dioxide and fragments into a mixture of benzaldehyde and 1,3-butadiene in good yields (Eq. (14)). Similarly, under similar conditions, **12b** gives rise to a mixture of dibenzyl ketone and 1,3-butadiene (Eq. (15)).




The reaction of tricyclic carbonate **12c** is examined extensively under various conditions. The results are summarized in Scheme 11. Typical palladium(0) complexes, irrespective of the presence or absence of phosphine and phosphite ligands, clearly promote the ring-opening reaction (runs 1–3). These reactions proceed at r.t. and provide stereochemically homogeneous *cis*-1,2,2-trimethyl-3-[(1*E*)-1,3-butadienyl]cyclopentanecarboxaldehyde (*E*-**13c**) in good yields. Palladium(II) complexes, on the other hand, are entirely ineffective (runs 4 and 5, Scheme 11). For this particular substrate, nickel(0) and platinum(0) complexes show better results than palladium(0) complexes (runs 6 and 7); however, these complexes are only marginally successful to other derivatives.

Table 5
Palladium-catalyzed decarboxylative ring-opening reaction of tricyclic carbonates[a]

| run | carbonate | temp (°C) / time (h) | product (% yield) [diene geometry] |
|---|---|---|---|
| 1 |  **12c** | 25 / 72 |  **13c**: 70 [only *E*] |
| 2 |  **12d** | 55 / 1 |  **13d**: 55 [only *E*] |
| 3 |  **12e** | 55 / 1 |  **13e**: 73 [only *E,Z*] |
| 4 |  **12f** | 25 / 30 |  **13f**: 58 [only *E,Z*] |
| 5 |  **12g** | 25 / 72 |  **13g**: 70 [only *E*] |
| 6 |  **12h** | 25 / 0.5 |  **13h**: 81 [*E*:*Z* = 1:6] |
| 7 |  **12i** | 25 / 0.2 |  **13i**: 75 [only Z,E] |

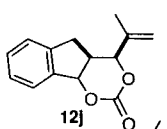
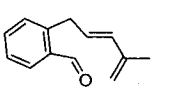
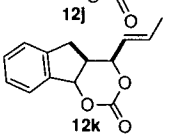
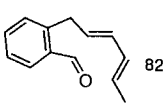
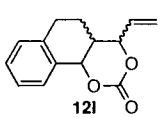
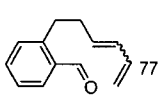
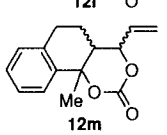
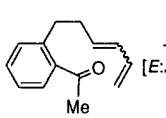
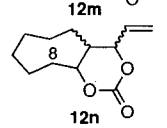
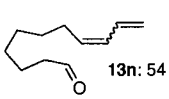
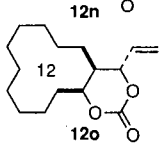
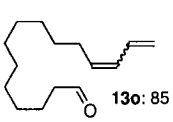
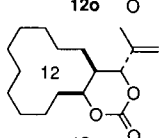
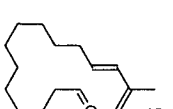
[a] Reaction conditions: cyclic carbonate (1 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ in dry acetonitrile (5 ml) under $N_2$.

In Tables 5 and 6 the results obtained for a variety of tri- and bicyclic carbonates **12**, respectively, are listed. All reactions are uniformly performed in the presence of 5 mol% of $Pd_2(dba)_3 \cdot CHCl_3$ in dry acetonitrile under $N_2$. From these tables, it is apparent that the reaction tolerates a wide structural variety of **12**, irrespective of the length of the carbon chain connecting the C4 and C5 carbons of the 1,3-dioxacyclohexan-2-one skeleton and the substitution pattern of the olefinic portion. Furthermore, these tables indicate that not only ω-dienyl aldehydes, but also ω-dienyl ketones can be obtained in reasonable yields (runs 5, Table 5 and run 4, Table 6).

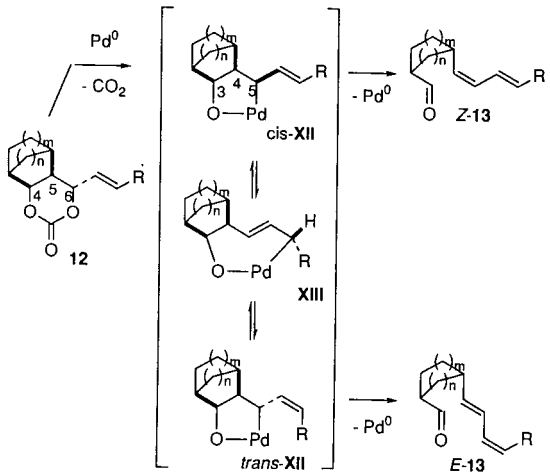
The stereochemical outcome of the dienyl moiety of **13** may be rationalized according to Scheme 12. Here we postulate that (1) *cis*-4,5-disubstituted 2-oxa-1-palladacyclopentane (*cis*-**XII**) is generated by an oxidative addition of Pd(0) into the O1–C6 bond of **12** with inversion of configuration and isomerizes to the corresponding *trans*-isomer (*trans*-**XII**) through **XIII** [σ–π–σ interconversion, which accompanies the isomerization of the double bond from *E* to *Z*] and (2) the thus-formed *cis*-**XII** and *trans*-**XII** undergo C3–C4 bond fission (*cis*-β-decarbopalladation) to give *Z*-**13** and *E*-**13**, respectively.

The intermediates *cis*-**XII** ($n = 0$, $m = 2$), generated from **12h** and **12i**, possess such strained cyclobutane C3–C4 bonds that they would readily undergo fragmentation to provide *Z*-**13h** and *Z*-**13i**, respectively (runs 6 and 7, Table 5). In the case of **12e** (run 3, Table 5), on the other hand, *cis*-**XII** ($n = 1$, $m = 1$, R = Me) possesses a less-strained C3–C4 bond, but suffers from steric repulsion between the *cis*-oriented $-CH(CMe_2)CH_2-$ and 1-(*E*)-propenyl groups. Accord-

Table 6
Palladium-catalyzed decarboxylative ring opening reaction of bicyclic carbonates[a]

| run | carbonate | temp (°C) / time (h) | product (% yield) [diene geometry] |
|---|---|---|---|
| 1 |  **12j** | 25 / 52 then 55 / 1 |  **13j**: 82 [only *E*] |
| 2 |  **12k** | 25 / 12 |  **13k**: 82 [only *E,E*] |
| 3 |  **12l** | 25 / 21 |  **13l**: 77 [*E*:*Z* = 10:1] |
| 4 |  **12m** | 25 / 21 |  **13m**: 77 [*E*:*Z* = ca. 1:1] |
| 5 |  **12n** | 25 / 7 |  **13n**: 54 [*E*:*Z* = 1:4] |
| 6 |  **12o** | 25 / 5 |  **13o**: 85 [*E*:*Z* = 1:3] |
| 7 |  **12p** | 25 / 24 then 55 / 3 |  **13p**: 63 [only *E*] |

[a] Reaction conditions: carbonate (1 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ in dry acetonitrile (5 ml) under $N_2$.




Scheme 12. Stereochemical correlation between the starting carbonates **12** and the products **13** (ω-dienyl aldehydes).

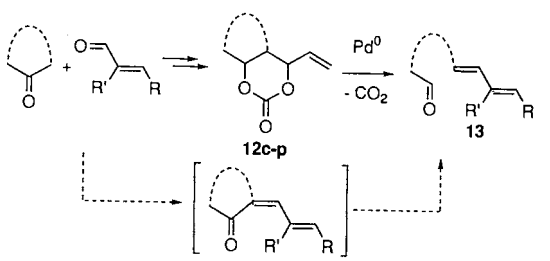
ingly, it would rather isomerize to the thermodynamically more stable *trans*-**XII** ($n = 1$, $m = 1$, R = Me) than fragment into *Z*,*E*-**13e**; the thus-formed *trans*-**XII** undergoes β-decarbopalladation to give *E*,*Z*-**13e**.

The *E*-exclusive formation of the newly formed double bonds in *E*-**13c** (run 1, Table 5), *E*-**13d** (run 2), *E*,*Z*-**13f** [run 4; note a clean isomerization of the substituent geometry, from (*E*)-1-methyl-1-propenyl of **12f** to (*Z*)-1-methyl-1-propenyl of **13f**], and *E*-**13g** (run 5) may be rationalized in a similar way.

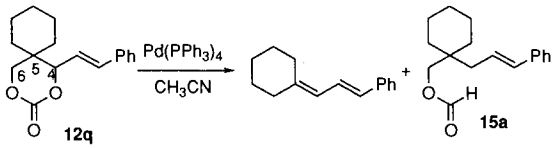
The *E*-selective formation of **13p** (run 7, Table 6), as opposed to the *Z*-selective formation of **13o** (run 6, Table 6), seems to be a natural consequence of steric repulsion between the $(CH_2)_{10}$ tether and bulky isopropenyl group in the intermediate *cis*-**XII**.

The clean and facile β-decarbopalladation of **XII** may primarily owe its origin to the C3–C4 bonds weakened by the negatively charged O2 [40] and also to their five-membered structures that conformationally make an alternative β-dehydropalladation process, providing 2-alkenylidenecycloalkanols, less favorable [41].

Bi- and tricyclic carbonates **12c–p** are prepared by the following sequence of reactions: aldol addition of lithium enolate of cyclic ketones to unsaturated aldehydes, reduction of the ketone function with $LiAlH_4$,




Scheme 13.

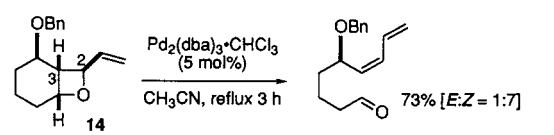



| run | additive | temp (°C)/ time (h) | % diene | % **15a** |
|---|---|---|---|---|
| 1 | none | 55/19 | 51 | 30 |
| 2 | $(CH_2O)_n$ (10 equiv) | 55/4 | 18 | 77 |
| 3 | *tert*-octylamine (1.1 equiv) | 82/1 | 81 | 0 |

Scheme 14.

followed by carbonation of the thus-obtained diols with ethyl chloroformate [39]. Accordingly, as illustrated in Scheme 13, the overall transformation of the present reaction formally comprises (1) aldol condensation of cyclic ketones with unsaturated aldehydes and (2) hydrogenolysis of the C1–C2 bonds of the thus-formed α-alkenylidenecycloalkanones. The synthetic utility of the present reaction may be augmented by the usefulness of **13** as synthetic intermediates [42] [e.g. intramolecular (hetero) Diels–Alder reaction] [43], the ready availability of the starting cyclic carbonates **12** with a wide structural variety, and the mild reaction conditions under which the reaction can be performed very easily.

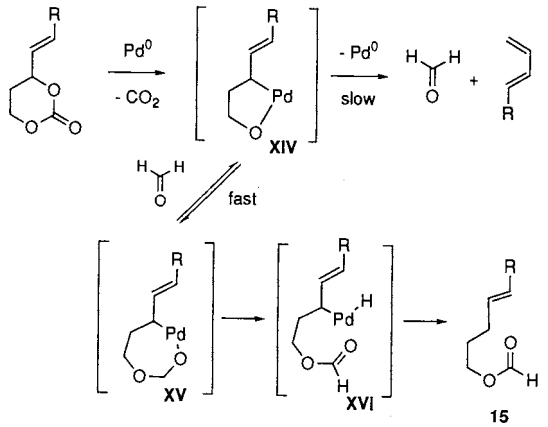
Upon refluxing in acetonitrile in the presence of 5 mol% of $Pd_2(dba)_3 \cdot CHCl_3$, 2-vinyloxetane **14** undergoes a ring-opening reaction and provides 5-benzyloxy-6,8-nonadienal in good yield (Eq. (16), [17]). This reaction may proceed in a similar way to that described for **12** via β-decarbopalladation of 2-oxa-1-palladacyclopentane intermediate **I**, which may be formed by oxidative addition of **14** at the oxetane O–C2 bond to palladium(0) complexes [44].




(16)

The reaction of 4-vinylcyclic carbonates that bear no substituents at the C6 position is rather complicated (Scheme 14). For example, the reaction of **12q** is rather slow under the usual conditions and is only promoted by heating at 55°C in the presence of 10 mol% of tetrakis(triphenylphoshine)palladium(0) (run 1, Scheme 14). In this reaction, in addition to the expected diene, a formate **15a** is obtained in a considerable amount [18b].

The formation of a mixture of **15a** and the diene is rationalized by supposing that the β-decarbopalladation of **XIV**, providing a mixture of formaldehyde and diene, is slower than the insertion of the thus-formed formaldehyde into the Pd–O bond of **XIV** (Scheme 15). The thus-formed 2,4-dioxa-1-palladacycloheptane **XV** is

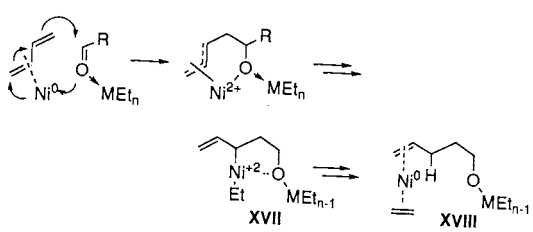



Scheme 15. Mechanistic rationale for the formation of diene and 4-pentenyl formate.

conformationally rather flexible and would readily undergo β-dehydropalladation and reductive elimination to give **15** [45].

The mechanism outlined in Scheme 15 is supported by the high-yield formation of **15a** in the reaction performed in the presence of ten equivalents of *para*formaldehyde (only a part of which is dissolved in the reaction medium, run 2, Scheme 14) and also by the quantitative formation of diene in the reaction undertaken in the presence of 1.1 equivalents of *tert*-octylamine (run 3, Scheme 14). *tert*-Octylamine may react with formaldehyde to form a Schiff-base and hence impede the formation of **XV**.

The present reaction is reminiscent of the palladium-catalyzed decarboxylative diene syntheses from 3-acetoxy-4-pentenoic acids reported by Trost et al. [46]. The formation of the C=O double bond of carbon dioxide (in Trost's case) and aldehydes and ketones (in our case) seems to make these reactions energetically favorable. The ring-opening reaction of 2-oxa-1-palladacyclopentanes **XII** into palladium(0)-olefin complexes and aldehydes contrasts with the cyclization reaction of titanium–olefin complexes and aldehydes to form cyclic 2-oxa-1-titanacyclopentane derivatives [30]. The latter reaction is stoichiometric with respect to titanium and the high oxophilic reactivity of titanium may make the cyclization favorable.




Scheme 16.

## 3. Novel and highly regio- and stereoselective nickel-catalyzed homoallylation of aldehydes and ketones with 1,3-dienes promoted by triethylborane or diethylzinc

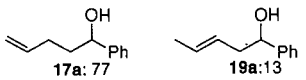
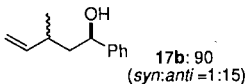
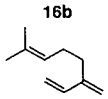
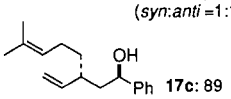
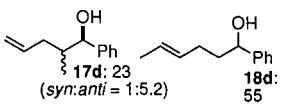
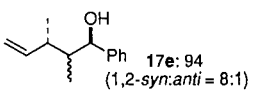
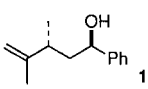
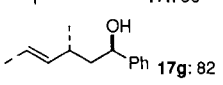
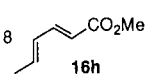
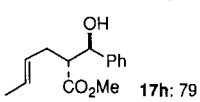
Allylation of carbonyl compounds is a fundamental process in organic syntheses and a number of efficient methodologies have been developed [47]. One such methodology is described in Section 1. Besides the allylic metals of alkali and alkaline earth metals, the allylic metals of transition-metals [27,48] and allylmetalloid species (allylstannanes, -silanes, -boranes, etc.) [49] have been utilized for the regio- and stereoselective allylation of carbonyl compounds.

Homoallylation may be similarly important for organic transformation; however, this process has received little attention, probably owing to the limited structural flexibility of the homoallylating agents ($CH_2$=$CHCH_2CH_2$–metal). The metals of the homoallylating agents may be confined to those of high electropositivity, e.g. Li, Mg, since as compared with the polarity of the allylic metal C–metal bonds, that of the homoallylic metal C–metal bonds is expected to be considerably diminished.

By analogy with a stoichiometric homoallylation of carbonyl compounds with $ZrCp_2$(1,3-diene) complexes [50], we envisaged that a catalytic homoallylation of carbonyl compounds with 1,3-dienes may be realized by an appropriate combination of a 1,3-diene–nickel(0) complex and a carbonyl–ethylmetal ($Et_nM$) complex (Scheme 16); these two might constitute an electron-push-pull system [51] and through a sequence of reactions, form a σ-allylethylnickel(II) complex **XVII**, the σ-allyl structure being stabilized by the coordination with the metal alkoxide oxygen. By virtue of this σ-allyl nature of the complex **XVII**, the ethyl group would selectively deliver hydrogen at the allylic position bound to nickel to produce a nickel(0)-bishomoallyl alcohol complex **XVIII**. Ligand exchange with 1,3-diene may regenerate the starting 1,3-diene-nickel(0) complex and liberate a metal alkoxide complex of the homoallylated product.

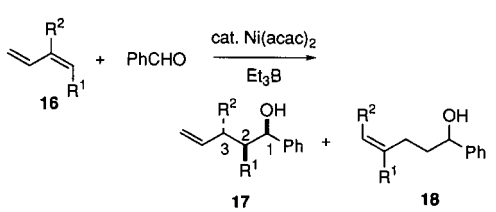
In accord with the scenario outlined above, we have found that triethylborane, as an $Et_nM$, nicely serves not only as a Lewis acid to activate carbonyl compounds but also as a reducing agent to promote the nickel-catalyzed homoallylation (reductive coupling) of benzaldehyde with 1,3-dienes (Eq. (17), [52]). By this catalytic reaction, 1-phenyl-4-pentenols **17** are obtained in excellent yields and with pronounced regio- and stereoselectivities. For example, as exemplified in run 2, Table 7, when a mixture of isoprene (4 mmol), benzaldehyde (1 mmol), $Ni(acac)_2$ (0.1 mmol), and $Et_3B$ (2.4 mmol) in dry THF (5 ml) is stirred at r.t. under nitrogen for 35 h, 3-methyl-1-phenyl-4-pentenol (**17b**) is obtained in 90% isolated yield. The same reaction, using $Ni(cod)_2$

Table 7
Nickel-catalyzed homoallylation of benzaldehyde with acyclic 1,3-dienes

| run | diene | time (h)[a] | products (% isolated yield)[b] |
|---|---|---|---|
| 1 |  **16a** | 21 |  **17a**: 77 **19a**:13 |
| 2 |  **16b** | 35 |  **17b**: 90 (*syn*:*anti* =1:15) |
| 3 |  **16c** | 43 |  **17c**: 89 |
| 4 |  **16d** | 50 |  **17d**: 23 (*syn*:*anti* = 1:5.2) **18d**: 55 |
| 5 |  **16e**[c] | 41 |  **17e**: 94 (1,2-*syn*:*anti* = 8:1) |
| 6 |  **16f** | 23 |  **17f**: 86 |
| 7 |  **16g** | 46 |  **17g**: 82 |
| 8 |  **16h** | 47 |  **17h**: 79 |

[a] Reaction conditions: Diene (4.0 mmol), benzaldehyde (1.0 mmol), $Ni(acac)_2$ (0.1 mmol), and $Et_3B$ (2.4 mmol, 1 M in hexane) in dry THF (5 ml) at room temperature under $N_2$. [b] The *syn*-*anti* mixture is not separated and their structures are assigned on the basis of the mixture. [c] A mixture of *Z*:*E* = 1.9:1 is used.

(cod = cyclooctadiene) (0.1 mmol), proceeds much faster and furnishes **17b** in 88% isolated yield within 3 h at r.t. The use of 2.4 mmol of $Et_3B$ seems to be essential; with 1.2 mmol, the reaction is not completed (80% isolated yield of **17b** based on 70% conversion after 71 h). In the absence of $Et_3B$, the reaction provides neither **17b** nor the oligomers of isoprene are obtained at all.



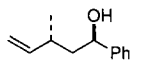
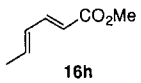
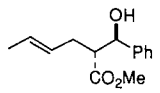
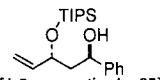
(17)

The reaction is remarkable in many respects. First, isoprene reacts with benzaldehyde exclusively at the C1 position of the diene moiety with an exclusive delivery of hydrogen at C2. No other products that might stem from the C–C bond formation at C4 and the hydrogen delivery to the other allylically related positions, providing the corresponding allylation products (e.g. **19a**, run 1, Table 7), are detected [33,53]. Thus, the reaction formally corresponds to a reductive coupling of the C1–C2 double bond of isoprene and the C=O double bond of benzaldehyde, whereby $Et_3B$ serves as a reducing agent. Second, the reaction exhibits high 1,3-diastereoselectivity, providing 1,3-*anti*-**17b** in preference to 1,3-*syn*-**17b** (15:1). 1,3-Dienes with a similar substitution pattern, e.g. **16c** and **16f** (runs 3 and 6, Table 7) show higher 1,3-asymmetric induction than **16b**, giving rise to 1,3-*anti*-**17c** and 1,3-*anti*-**17f** as single diastereomers, respectively. Third, the selective and high yield formation of a 1:1 adduct of diene and aldehyde is surprising in light of the propensity of nickel complexes to promote oligomerization of simple dienes [54]. In fact, it has been reported that nickel catalyzes or promotes the coupling reaction of isoprene and aldehyde (or ketone) to furnish alcohols as a mixture of 1:1, 2:1, and 3:1 adducts, each of which consists of many possible regio- and stereoisomers [55].

1,3-Pentadiene (**16d**) exhibits a different reaction feature (run 4, Table 7), where both termini of the diene moiety take part in the reaction, providing **18d** (C1 addition product) as a major product together with **17d** (C4 addition product, as a 5.2:1 diastereomeric mixture). Judging from the exclusive formation of **17e** (C4 addition product) from 3-methyl-1,3-pentadiene (**16e**, run 5), however, the C-3 methyl group is apparently more influential than the C4 methyl group in controlling the regioselectivity. In this regard, both methyl groups of **16g** are properly arranged to cooperatively promote the selective C1 addition reaction (run 7). Indeed, the expected isomer, 1,3-*anti*-**17g**, is obtained exclusively. Together with these results, the selective reaction of **16h** at the terminus carrying an electron-withdrawing group (run 8) suggests that the butadiene terminus bearing higher electron density undergoes an addition reaction to benzaldehyde in a nucleophilic fashion.

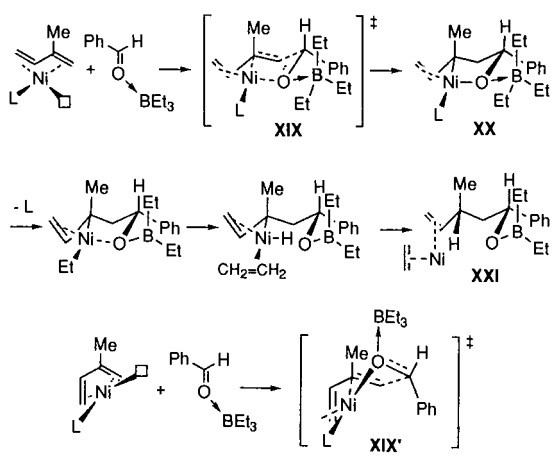
For convenience of the experimental procedure, we have routinely examined the reaction with four equivalents of diene and 0.1 equivalents of $Ni(acac)_2$ relative to benzaldehyde. The homoallylation, however, is successful with reduced amounts of dienes and the catalyst (Table 8). The initial mole ratio of diene to benzaldehyde can be minimized virtually to unity without serious deterioration of the yields (runs 4 and 6, Table 8). This aspect is beneficial, especially when dienes are expensive or prepared with difficulty. Furthermore, the amount of the catalyst can be reduced to as little as 1 mol% (runs 2 and 3, Table 8), under which neither the yields nor the reaction rates discernibly decrease.

Table 8
Nickel-catalyzed homoallylation of benzaldehyde with dienes with reduced amounts of $Ni(acac)_2$ and dienes[a]

| run | diene (equiv) | Ni cat (mol%) | time (h) | major products (% isolated yield) [isomer ratio] |
|---|---|---|---|---|
| |  **16b** | | |  **17b** [1,3-*syn*:*anti* = 1:15] |
| 1 | 4.0 | 10.0 | 35 | 90 |
| 2 | 4.0 | 1.0 | 48 | 82 |
| |  **16h** | | |  **17h** [1,2-*syn*:*anti* = 1:>25] |
| 3 | 4.0 | 1.0 | 66 | 91 |
| 4 | 1.1 | 2.5 | 75 | 75 |
| |  **16j** | | |  **17j** [1,3-*syn*:*anti* = 1:>25] |
| 5 | 2.0 | 5.0 | 65 | 65 |
| 6 | 1.1 | 5.0 | 65 | 62 |

[a] A mixture of diene (indicated amount, relative to benzaldehyde), benzaldehyde, $Ni(acac)_2$ (indicated amount), and $Et_3B$ (2.4 equivalents) in dry THF at r.t. under $N_2$.

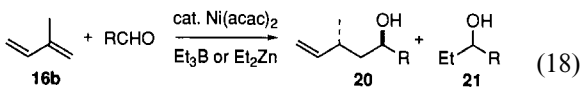
In Scheme 17 our working hypothesis is outlined, using isoprene as a representative of 1,3-dienes. Since, under the usual reaction conditions, styrene is unreactive and cyclic dienes (1,3-cyclohexadiene and 1,3-cyclooctadiene) react very slowly to provide intractable mixtures of products in low yields, an *s-trans*-diene–Ni(0) complex is considered to be a reactive species. An oxanickellacyclopentane intermediate **XX** might be formed through a cyclic transition state **XIX**, where benzaldehyde is arranged in such a way to place the oxygen to the vacant site of the *s-trans*-diene–Ni(0) complex (symbolized as ◇) and the phenyl group in a quasi-equatorial position so as to avoid a quasi-1,3-diaxial repulsion that an alternative orientation of benzaldehyde might experience. Apparently, a cyclic transition state **XIX′**, led from a *s-cis*-diene–nickel(0) complex, is less favorable than **XIX**, since in the transition state **XIX′**, a large dihedral angle O–Ni–C2–C1 (ca. 90°, isoprene numbering) poses severe strain for the oxanickellacyclopentane ring moiety. One of the ethyl groups of **XX** might migrate from borane to nickel(II), then undergo β-hydrogen elimination to deliver the hydrogen, through reductive elimination, at the allylic position bound to the nickel with retention of configuration to finally produce a nickel(0)(ethylene)(1,3-*anti*-**17b**) complex **XXI**. The nickel(0) metal of **XXI** may be reused for a new catalytic cycle.




Scheme 17. A proposed mechanism for the $Et_3B$–$Ni(acac)_2$-promoted regio- and stereoselective homoallylation of benzaldehyde with isoprene.

The 1,2-diastereoselectivity, providing 1,2-*syn*-**17e** (from *Z*-diene, Table 7), 1,2-*anti*-**17d** (from *E*-diene), and 1,2-*anti*-**17h** (from *E*-diene), may be explained similarly according to this Scheme.

The cyclization reaction that forms **XX** from nickel(0), diene, and aldehyde formally corresponds to the reverse process of the ring-opening reaction that 5-vinyl-2-oxapalladacyclopentane, the palladium(II) analog of **XX**, undergoes to give a mixture of palladium(0), diene, and aldehyde (Scheme 1 and Section 2).

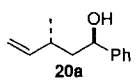
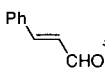
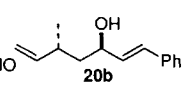
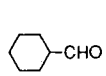
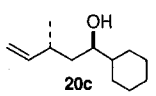
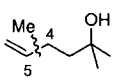


(18)

In the column on the far right in Table 9, are listed the results obtained for the homoallylation of carbonyl compounds other than benzaldehyde under the $Et_3B$–$Ni(acac)_2$ catalytic conditions. In these reactions, isoprene is used as a representative of 1,3-dienes (Eq. 18). The reaction is successful for aromatic and unsaturated aldehydes and provides 1,3-*anti*-**20a** and 1,3-*anti*-**20b** with excellent regio- and stereoselectivities (runs 1 and 2, Table 9). Unfortunately, however, the reaction is only marginally successful for saturated aldehydes (run 3). Ketones are entirely unreactive and no expected products are obtained at all (run 4).

Under similar conditions, diethylzinc, in place of triethylborane, also promotes the homoallylation of aromatic aldehydes (the second column from the right, Table 9 [18c]. The reaction, however, is plagued with the ethylation of aldehydes and hence with diminished yields of the desired products (e.g. run 1, Table 9). Apparently, the nickel catalyst takes part in the ethylation [56]; in the absence of the catalyst, neither the ethylation product **21a** nor the homoallylation product **20a** is produced at all. The reaction of cinnamaldehyde provides a complex mixture of products, among which a conjugate addition product, 3-phenylpentanal (**21b**), is the only product identified (run 2, Table 9).

Table 9
Nickel-catalyzed homoallylation of aldehydes and ketones with isoprene promoted by diethylzinc or triethylborane[a]

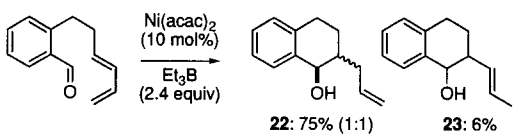
| run | carbonyl | product | $Et_2Zn$ time (h); % yield (*syn*:*anti*) | $Et_3B$ time (h); % yield (*syn*:*anti*) |
|---|---|---|---|---|
| 1 | PhCHO |  **20a** | 4; **20a**: 63 (1:15) **21a**: 16[b] | 35; **20a**: 90 (1:15) **21a**: 0[b] |
| 2 |  |  **20b** | 0.5; **20b**: 0 **21b**: 28[b] | 70; **20b**: 81 (1:20) **21b**: 0[b] |
| 3 |  |  **20c** | 0.5; **20c**: 83 (1:>20) | 10; **20c**: 28 |
| 4 | $CH_3COCH_3$ |  **20d**: 4-Me **20e**: 5-Me | 1; **20d**, **20e**: 69 (5:1) | 46; **20d**, **20e**: 0 |

[a] A mixture of $Ni(acac)_2$ (0.1 mmol), isoprene (4 mmol), aldehyde or ketone (1 mmol), and $Et_2Zn$ (2.4 mmol, 1 M hexane) or $Et_3B$ (2.4 mmol, 1 M hexane) is stirred at room temperature under $N_2$.
[b] **21a**: 1-Phenylpropan-1-ol; **21b**: 3-phenylpentanal.

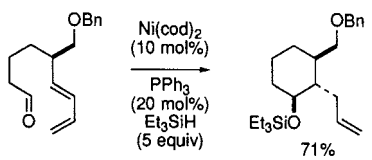
In sharp contrast to these results, the $Et_2Zn$–$Ni(acac)_2$ system has turned out to be very effective for the reactions with saturated aldehydes and ketones [18c]. In most cases, the reactions are completed within 1 h at r.t. and provide the homoallylation products in excellent yields (runs 3 and 4, Table 9). Interestingly, in these reactions no ethylation products are produced at all. The reaction is highly stereoselective and 1,3-*anti*-**20c** is obtained almost exclusively for the reaction with cyclohexanecarboxaldehyde (run 3).

For the reaction with ketones, partial erosion of regioselectivity is observed. For example, acetone provides an inseparable mixture of **20d** (C1 addition product) and **20e** (C4 addition product) in a ratio of 5:1 (run 4). In this reaction, a 1,3-diaxial repulsion between the two methyl groups of isoprene and acetone is inevitable in a cyclic transition state like **XIX**; hence, a sterically less demanding C4 addition of isoprene may compete with the electronically favored C1 addition.

In Eq. (19) an intramolecular version of the reductive coupling reaction of aldehydes and dienes is shown [17]. The yield is good; however, the regio- and stereoselectivity is still not satisfactory: In addition to the expected homoallylation product **22**, the allylation product **23** is obtained as a minor product. The alcohol **22** is obtained a mixture of *cis*- and *trans*-isomers in a ratio of 1:1. The reaction contrasts with the $Et_3SiH$–$Ni(cod)_2$-promoted intramolecular allylation of ω-dienyl aldehydes reported by Mori et al. (Eq. (20), [33a,c]) which may proceed via Markovnikov addition of '$Et_3SiNi$–H' to the diene and an intramolecular nucleophilic addition of the thus-formed π-allylnickel(II) to the aldehyde. A selective intramolecular homoallylation of ω-dienyl aldehydes takes place by employing a stoichiometric amount of 'Ni–H' complexes generated under sophisticated conditions (anti-Markovnikov addition of 'Ni–H' to the diene) [33b].



(19)



(20)

In conclusion, the $Et_3B$–$Ni(acac)_2$ catalytic system allows us to obtain the homoallylation products of aromatic and unsaturated aldehydes with acyclic 1,3-dienes of a wide structural variety. The utility of the reaction may be apparent from (1) the usefulness of the products (bis-homoallyl alcohols), which are obtained in excellent yields and with high 1,2-, 1,3-, and 1,2,3-diastereoselectivities, (2) the mildness of the reaction conditions (r.t.), (3) the ease of the experimental procedure, and (4) the high catalytic turnover number over 80. The low cost of the reagents [$Ni(acac)_2$ and $Et_3B$] and a 1:1 stoichiometry of the reaction partners (1,3-dienes and aldehydes) are important aspects from an economic point of view. This $Et_3B$-$Ni(acac)_2$ system, however, is only marginally successful for alkyl aldehydes and entirely unsuccessful for ketones. The $Et_2Zn$–$Ni(acac)_2$ catalytic system, on the other hand, is effective particularly for the homoallylation of saturated aldehydes and ketones. Hence, these two systems, $Et_3B$–$Ni(acac)_2$ and $Et_2Zn$–$Ni(acac)_2$, complement each other and cover the homoallylation of a wide range of aldehydes and ketones.

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## References


[1] (a) Y. Tamaru, in: J.M. Coxon (Ed.), Advances of Detailed Reaction Mechanisms, JAI, London, 1995, Ch. 2. (b) Y. Tamaru, J. Syn. Org. Chem. Jpn 53 (1995) 1102. (c) K. Yasui, K. Fugami, S. Tanaka, Y. Tamaru, J. Org. Chem. 60 (1995) 1365. (d) Y. Tamaru, K. Yasui, H. Takanabe, S. Tanaka, K. Fugami, Angew. Chem. Int. Ed. Engl. 31 (1992) 645.

[2] For the reaction with arylpalladium(II) and vinylpalladium(II) intermediates, alkylzinc compounds provide the reductive elimination products in much better yields than alkyllithium and-magnesium compounds: (a) E. Negishi, L.F. Valente, M. Kobayashi, J. Am. Chem. Soc. 102 (1980) 3298. (b) E. Negishi, A.O. King, N. Okukado, J. Org. Chem. 42 (1977) 1821. For a mechanistic rationale for the contrasting reactivity between alkylzinc and alkyl metal compounds of more electropositive metals, see: (c) E. Negishi, K. Akiyoshi, T. Takahashi, J. Chem. Soc. Chem. Commun. (1987) 477. (d) E. Negishi, K. Akiyoshi, T. Takahashi, J. Organomet. Chem. 334 (1987) 181.

[3] G.P. Bolbrini, M. Mengoli, E. Tagliavini, C. Trombini, A. Umani-Ronchi, Tetrahedron Lett. 27 (1986) 4223.

[4] S. Sasaoka, T. Yamamoto, H. Kinoshita, K. Inomata, H. Kotabe, Chem. Lett. (1985) 315.

[5] M. Lautens, P.H.M. Delanghe, Angew. Chem. Int. Ed. Engl. 33 (1994) 2448. (b) J.-C. Fiaud, J.-Y. Legros, J. Org. Chem. 52 (1987) 1907. (c) T. Hayashi, A. Yamamoto, T. Hagihara, J. Org. Chem. 51 (1986) 723. (d) S. Chatterjee, E. Negishi, J. Org. Chem. 50 (1985) 3406. An intramolecular allylation of vinylzincs: (e) J. van der Louw, J.L. van der Baan, F.J.J. de Kanter, F. Bichelhaupt, G.W. Klumpp, Tetrahedron, 48 (1992) 6087, 6105.

[6] T. Kitazume, N. Ishikawa, J. Am. Chem. Soc. 107 (1985) 5186.

[7] (a) J.L. van der Baan, T.A.J. van der Heide, J. van der Louw, G.W. Klumpp, Synlett (1995) 1. (b) J. van der Louw, J.L. van der Baan, H. Stieltjes, F. Bickelhaupt, G.W. Klumpp, Tetrahedron Lett. 28 (1987) 5929.

[8] K. Yasui, Y. Goto, T. Yajima, Y. Taniseki, K. Fugami, A. Tanaka, Y. Tamaru, Tetrahedron Lett. 34 (1993) 7619.

[9] J. Clayden, M. Julia, J. Chem. Soc. Chem. Commun. (1994) 1905.

[10] H. Ochiai, Y. Tamaru, K. Tsubaki, Z. Yoshida, J. Org. Chem. 52 (1987) 4418.

[11] M. Shimizu, M. Kimura, S. Tanaka, Y. Tamaru, Tetrahedron Lett. 39 (1998) 609.

[12] Y. Tamaru, A. Tanaka, K. Yasui, S. Goto, S. Tanaka, Angew. Chem. Int. Ed. Engl. 34 (1995) 787.

[13] A similar mechanism is proposed for the *Z*-selective allylation of carbonyl compounds with α-substituted allyl(dialkyl)boranes and allyl(trialkyl)stannanes: (a) D. Behnke, S. Hamm, L. Henning, P. Welzel, Tetrahedron Lett. 38 (1997) 7059. (b) D.S. Matteson, Tetrahedron 45 (1989) 1859. (c) D.S. Matteson, Synthesis (1986) 973.

[14] The regioselectivity of allylation of carbonyl compounds with allylmetal species bearing an ether function at the allylic positions markedly depends on the kind of the metal ions: (a) A. Yanagisawa, K. Yasue, H. Yamamoto, Synlett (1993) 686, and references therein. (b) D.A. Evens, G.C. Andrews, B. Buckwalter, J. Am. Chem. Soc. 96 (1974) 5560.

[15] (a) A. Yanagisawa, S. Habaue, H. Yamamoto, J. Am. Chem. Soc. 113 (1991) 5893, 8955. For alkylzincs, see: (b) L. Micouin, M. Oestreich, P. Knochel, Angew Chem. Int. Ed. Engl. 36 (1997) 245. (c) R. Duddu, M. Eckhardt, M. Furlong, P. Knoese, S. Berger, P. Knochel, Tetrahedron. 50 (1994) 2415.

[16] P. von Matt, A. Pfaltz, Angew. Chem. Int. Ed. Eng. 32 (1993) 566.

[17] Unpublished results that will be published in due course.

[18] (a) M. Kimura, Y. Ogawa, M. Shimizu, M. Sueishi, S. Tanaka, Y. Tamaru, Tetrahedron Lett. 39 (1998) 6903. (b) H. Harayama, K. Kimura, S. Tanaka, Y. Tamaru, Tetrahedron Lett. 39 (1998) 8475. (c) M. Kimura, H. Fujimatsu, A. Ezoe, K. Shibata, M. Shimizu, S. Matsumoto, Y. Tamaru, Angew. Chem. Int. Ed. Engl. 38 (1999) 397.

[19] A. Streitwieser, C.H. Heathcock, E.M. Kosower, Introduction to Organic Chemistry, 4th edn, Macmillan, New York, 1992 Appendix IV.

[20] J. Tsuji, Tetrahedron 42 (1986) 4361.

[21] (a) M.S. Sigman, B.E. Eaton, J. Am. Chem. Soc. 118 (1996) 11783. (b) T. Mandai, T. Nakata, H. Murayama, H. Yamaoki, M. Ogawa, M. Kawada, J. Tsuji, Tetrahedron Lett. 31 (1990) 7179. (c) E. Keinan, E. Bosch, J. Org. Chem. 51 (1986) 4006. (d) C.J. Elsevier, P.M. Stehouwer, H. Westmijze, P. Vermeer, J. Org. Chem. 48 (1983) 1103.

[22] (a) C.-C. Su, J.-T. Chen, G.-H. Lee, Y. Wang, J. Am. Chem. Soc. 116 (1994) 4999. (b) J. Tsuji, H. Watanabe, I. Minami, I. Shimizu, J. Am. Chem. Soc. 107 (1985) 2196.

[23] Y. Tamaru, S. Goto, A. Tanaka, M. Shimizu, M. Kimura, Angew. Chem. Int. Ed. Engl. 35 (1996) 878.

[24] (a) G. Zweifel, G. Horn, J. Org. Chem. 49 (1984) 4567. See, also: (b) H. Shinokubo, H. Miki, T. Yokoo, K. Oshima, K. Utimoto, Tetrahedron, 51 (1995) 11681.

[25] Reduction with Sn(II): (a) Y. Masuyama, in: J.M. Coxon (Ed.), Advances in Metal-Organic Chemistry, JAI, London, 1994, pp. 255–303. (b) J.P. Takahara, Y. Masuyama, Y. Kurusu, J. Am. Chem. Soc. 114 (1992) 2577. Reduction with Sm(II): (c) T. Tabuchi, J. Inanaga, M. Yamaguchi, Tetrahedron Lett. 27 (1986) 1195. Reduction with Zn: (d) Y. Masuyama, N. Kinugasa, Y. Kurusu, J. Org. Chem. 52 (1987) 3702.

[26] (a) P. Zhang, W. Zhang, T. Zhang, Z. Wang, W. Zhou, J. Chem. Soc. Chem. Commun. (1991) 491. (b) W. Qiu, Z. Wang, J. Chem. Soc. Chem. Commun. (1989) 356. (c) S. Torii, H. Tanaka, T. Katoh, K. Morisaki, Tetrahedron Lett. 25 (1984) 3207.

[27] (a) H. Nakamura, K. Nakamura, Y. Yamamoto, J. Am. Chem. Soc. 120 (1998) 4242. (b) H. Nakamura, J.-G. Shim, Y. Yamamoto, J. Am. Chem. Soc. 119 (1997) 8113. (c) H. Nakamura, H. Iwama, Y. Yamamoto, J. Am. Chem. Soc. 118 (1996) 6641. (d) H. Nakamura, H. Iwama, Y. Yamamoto, J. Chem. Soc. Chem. Commun. (1996) 1459.

[28] Sn: (a) S. Matsubara, K. Wakamatsu, Y. Morizawa, N. Tsuboniwa, K. Oshima, H. Nozaki, Bull. Chem. Soc. Jpn 58 (1985) 1196. Si: (b) Y. Tsuji, M. Funato, M. Ozawa, H. Ogiyama, S. Kajita, T. Kawamura, J. Org. Chem. 61 (1996) 5779. B: (c) T. Ishiyama, T. Ahiko, N. Miyaura, Tetrahedron Lett. 37 (1996) 6889.

[29] (a) K. Mikami, A. Yoshida, Angew. Chem. Int. Ed. Engl. 36 (1997) 858. (b) K. Mikami, A. Yoshida, S. Matsumoto, F. Feng, Y. Matsumoto, A. Sugino, T. Hanamoto, J. Inanaga, Tetrahedron Lett. 36 (1995) 907. (c) T. Tabuchi, J. Inanaga, M. Yamaguchi, Tetrahedron Lett. 27 (1986) 5237.

[30] (a) N.M. Kablaoui, F.A. Hicks, S.L. Buchwald, J. Am. Chem. Soc. 119 (1997) 4424, and references therein. (b) W.E. Crowe, A.T. Vu, J. Am. Chem. Soc. 118 (1996) 5508. (c) W.E. Crowe, A.T. Vu, J. Am. Chem. Soc. 118 (1996) 1557.

[31] (a) N. Chatani, T. Morimoto, Y. Fukumoto, S. Murai, J. Am. Chem. Soc. 120 (1998) 5335. (b) W.E. Crowe, M.J. Rachita, J. Am. Chem. Soc. 117 (1995) 6787.

[32] (a) S. Okamoto, M. Iwakubo, K. Kobayashi, F. Sato, J. Am. Chem. Soc. 119 (1997) 6984. (b) J. Lee, J.D. Ha, J.K. Cha, J. Am. Chem. Soc. 119 (1997) 8127. (c) J.S. U, J. Lee, J.K. Cha, Tetrahedron Lett. 38 (1997) 5233. (d) J. Lee, H. Kim, J.K. Cha, J. Am. Chem. Soc. 118 (1996) 4195, and references therein.

[33] (a) Y. Sato, N. Saito, M. Mori, Tetrahedron Lett. 38 (1997) 3931. (b) Y. Sato, M. Takimoto, M. Mori, Tetrahedron Lett. 37 (1996) 887. (c) Y. Sato, M. Takimoto, K. Hayashi, T. Katsuhara, K. Takagi, M. Mori, J. Am. Chem. Soc. 116 (1994) 9771.

[34] (a) R.A. Widenhoefer, M.A. Decarli, J. Am. Chem. Soc. 120 (1998) 3805. (b) Y. Yamaura, M. Hyakutake, M. Mori, J. Am. Chem. Soc. 119 (1997) 7615. (c) W.J. Zuercher, M. Hashimoto, R.H. Grubbs, J. Am. Chem. Soc. 118 (1996) 6634. (d) K.H. Shaughnessy, R.M. Waymouth, J. Am. Chem. Soc. 117 (1995) 5873. (e) G.A. Molander, P.J. Nichols, J. Am. Chem. Soc. 117 (1995) 4415. (f) H.-G. Schmalz, Angew. Chem. Int. Ed. Engl. 34 (1995) 1833. (g) D.F. Taber, J.P. Louey, Y. Wang, W.A. Nugent, D.A. Dixon, R.L. Harlow, J. Am. Chem. Soc. 116 (1994) 9457. (h) E. Negishi, D. Choueiry, T.B. Nguyen, D.R. Swanson, J. Am. Chem. Soc. 116 (1994) 9751. (i) J.P. Morken, M.T. Didiuk, M.S. Visser, A.H. Hoveyda, J. Am. Chem. Soc. 116 (1994) 3123. (j) E. Negishi, M.D. Jensen, D.Y. Kondakov, S. Wang, J. Am. Chem. Soc. 116 (1994) 8404.

[35] (a) J.-L. Montchamp, E. Negishi, J. Am. Chem. Soc. 120 (1998), 5345. (b) O. Geis, H.-G. Schmalz, Angew. Chem. Int. Ed. Engl. 37 (1998) 911, and references therein. (c) H. Yamada, S. Aoyagi, C.C. Kibayashi, Tetrahedron Lett. 38 (1997) 3027. (d) J.-C. Galland, M. Savignac, J.-P. Genet, Tetrahedron Lett. 38 (1997) 8695. (e) H. Urabe, K. Suzuki, F. Sato, J. Am. Chem. Soc. 119 (1997) 10014. (f) T. Kondo, N. Suzuki, T. Okada, T. Mitsudo, J. Am. Chem. Soc. 119 (1997) 6187. (g) T. Morimoto, N. Chatani, Y. Fukumoto, S. Murai, J. Org. Chem. 62 (1997) 3762. (h) F.A. Nicks, S.L. Buchwald, J. Am. Chem. Soc. 118 (1996) 11688. (i) F.A. Hicks, N.M. Koblaoui, S.L. Buchwald, J. Am. Chem. Soc. 118 (1996) 9450. (j) H. Yamada, S. Aoyagi, C. Kobayashi, J. Am. Chem. Soc. 118 (1996) 1054.

[36] H. Harayama, T. Kuroki, M. Kimura, S. Tanaka, Y. Tamaru, Angew. Chem. Int. Ed. Engl. 36 (1997) 2352.

[37] Catalytic β-decarbometallation: (a) T. Kondo, K. Kodoi, E. Nishinaga, T. Okada, Y. Morisaki, Y. Watanabe, T. Mitsudo, J. Am. Chem. Soc. 120 (1998) 5587. (b) K. McNeill, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 11244. (c) M. Murakami, K. Takahashi, H. Amii. Y. Ito, J. Am. Chem. Soc. 119 (1997) 9307. (d) H. Nemoto, M. Yoshida, K. Fukumoto, J. Org. Chem. 62 (1997) 6450. (e) M. Lautens, C. Meyer, A. Lorenz, J. Am. Chem. Soc. 118 (1996) 10676. (f) M. Catellani, M.C. Fagnola, Angew. Chem. Int. Ed. Engl. 33 (1994) 2421, and references therein.

[38] (a) T. Bando, H. Harayama, Y. Fukazawa, M. Shiro, K. Fugami, S. Tanaka, Y. Tamaru, J. Org. Chem. 59 (1994) 1465. (b) Y. Tamaru, T. Bando, Y. Kawamura, K. Okamura, Z. Yoshida, J. Chem. Soc. Chem. Commun. (1992) 1498.

[39] T. Bando, S. Tanaka, K. Fugami, Z. Yoshida, Y. Tamaru, Bull. Chem. Soc. Jpn. 65 (1992) 97.

[40] (a) M.L. Steigerwald, W.A. Goddard, D.A. Evans, J. Am. Chem. Soc. 101 (1979) 1994. Oxy-Cope rearrangement: (b) L.A. Paquette, C.F. Sturino, X. Wang, J.C. Prodger, D. Koh, J. Am. Chem. Soc. 118 (1996) 5620, and references therein. Oxygen anion accelerated ring-opening reaction: (c) J.X. Harberman, C.-J. Li, Tetrahedron Lett. 38 (19970 4735. (d) S. Ando, K.P. Minor, L.E. Overman, J. Org. Chem. 62 (1997) 6379. (e) C.-J. Li, D.-L. Chem, Y.-Q. Lu, J.X. Harberman, J.T. Mague, J. Am. Chem. Soc. 118 (1996) 4216. (f) H. Nemoto, M. Shiraki, K. Fukumoto, Synlett (1994) 599. (g) M. Takayanagi, N. Umamori, K. Tanino, I. Kuwajima, J. Am. Chem. Soc. 115 (1993) 12635.

[41] (a) T. Fujinami, T. Suzuki, M. Kamiya, S. Fukazawa, S. Sakai, Chem. Lett. (1985) 199. β-Dehydropalladation of a similar intermediate: (b) K. Ohno, T. Mitsuyasu, J. Tsuji, Tetrahedron 28 (1972) 3705.

[42] Chemical and Engineering News, Nov. 10, 1997, p. 23.

[43] S.D. Burke, D.M. Armistead, K. Shankaran, Tetrahedron Lett. 27 (1986) 6295.

[44] R.C. Larock, S.K. Stolz-Dunn, Tetrahedron Lett. 30 (1989) 3487.

[45] Similar reaction behavior of alkoxynickel(II) complexes: R. Han, G.L. Hillhouse, J. Am. Chem. Soc. 119 (1997) 8135.

[46] B.M. Trost, J.M. Fortunak, J. Am. Chem. Soc. 102 (1980) 2841.

[47] (a) Y. Yamamoto, N. Asao, Chem. Rev. 93 (1993) 2207. (b) W.R. Roush, in: B.M. Trost, I. Fleming, C.H. Heathcock (Eds.), Comprehensive Organic Synthesis, vol. 2, Pergamon, Oxford, 1991, Ch. 1.1.

[48] (a) Y. Takayama, S. Okamoto, F. Sato, Tetrahedron Lett. 38 (1997) 8351. (b) S.-J. Shieh, R.-S. Liu, Tetrahedron Lett. 38 (1997) 5209. (c) A.M. Wilson, F.G. West, A.M. Arif, R.D. Ernst, J. Am. Chem. Soc. 117 (1995) 8490. (d) H. Ito, Y. Ikeuchi, T. Taguchi, Y. Hanzawa, J. Am. Chem. Soc. 116 (1994) 5469. (e) H. Ito, Y. Motoki, T. Taguchi, Y. Hanzawa, J. Am. Chem. Soc. 115 (1993) 8835.

[49] (a) S. Itsuno, K. Watanabe, K. Ito, S.A. El-Shehawy, A.A. Sarhan, Angew. Chem. Int. Eng. Engl. 36 (1997) 109. (b) P.V. Ramachandran, G.-M. Chem, H.C. Brown, Tetrahedron Lett. 38 (1997) 2417. (c) Y.N. Rubnov, M.A. Misharin, A.V. Ignatenko, Tetrahedron Lett. 38 (1997) 6259. (d) J.S. Panek, P. Liu, Tetrahedron Lett. 38 (1997) 5127. (e) N.F. Jain, N. Takenaka, J.S. Panek, J. Am. Chem. Soc. 118 (1996) 12475.

[50] (a) H. Yasuda, K. Tatsumi, A. Nakamura, Acc. Chem. Res. 18 (1985) 120. (b) G. Erker, K. Engel, J.L. Atwood, W.E. Hunter, Angew. Chem. Int. Engl. 22 (1983) 494. (c) G. Erker, U. Dorf, Angew. Chem. Int. Engl. 22 (1983) 777.

[51] A similar election relay mechanism is proposed for the nickel(0)-catalyzed reduction coupling of aldehydes and alkynes that provides allylic alcohols: (a) E. Oblinger, J. Montgomery, J. Am. Chem. Soc. 119 (1997) 9065. For The related Ni(0)-promoted alkylation (1,2-and 1,4-addition), see: (b) S. Ikeda, N. Mori, Y. Sato, J. Am. Chem. Soc. 119 (1997) 4779. (c) J. Montgomery, E. Oblinger, A.V. Savchenko, J. Am. Chem. Soc. 119 4911. (d) J. Montgomery, A.V. Savchenko, J. Am. Chem. Soc. 118 (1996) 2099. (e) S. Ikeda, K. Kondo, Y. Sato, J. Org. Chem. 61 (1996) 8248. (f) S. Ikeda, H. Yamamoto, K. Kondo, Y. Sato, Organometallics 14 (1995) 5015. (g) S. Ikeda, Y. Sato, J. Am. Chem. Soc. 116 (1994) 5975.

[52] M. Kimura, A. Ezoe, K. Shibata, Y. Tamaru, J. Am. Chem. Soc. 120 (1998) 4033.

[53] 1,3-Butadiene, as one exception among 1,3-dienes examined, furnishes the allylation product, **19a**, as a minor product (run 1, table 7). Transition metal-catalyzed (or -promoted) allylation with 1, 3-dienes: (a) K. Takai, N. Matsukawa, A. Takahashi, T. Fuji, Angew Chem. Int. Ed. Engl. 37 (1998) 152. (b) M. Suginome, H. Nakamura, T. Matsuda. Y. Ito, J. Am. Chem. Soc. 120 (1998) 4248. (c) Y. Obara, Y. Tsuji, T. Kawamura, J. Am. Chem. Soc. 117 (1995) 9814. (d) K. Kitayama, H. Tsuji, Y. Uozumi, T. Hayashi, Tetrahedron Lett. 37 (1996) 4169. (e) Y. Gao, H. Urabe, F. Sato, J. Org. Chem. 59 (1994) 5521. (f) S. Kobayashi, K. Nishio, J. Org. Chem. 59 (1994) 6620.

[54] S.G. Davies, Organotransition Metal Chemistry: Application to Organic Synthesis, Pergamon, Oxford, 1982, Ch. 6.

[55] (a) R. Baker, M.J. Crimmin, J. Chem. Soc. Perkin Trans. 1 (1979) 1264. (b) S. Akutagawa, Bull. Chem. Soc. Jpn. 49 (1976) 3646. For palladium(0)-catalyzed oligomerization of butadiene and aldehydes, see Ref. [41b].

[56] T. Stüdemann, M. Ibrahim-Ouali, G. Cahiez, P. Knochel, Synlett (1998) 143.