PALLADIUM CATALYZED SYNTHESIS OF 1,4-DIENES

by

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ABSTRACT

1,4-dienes are ubiquitous in nature. Our aim was to develop a facile route to the stereospecific synthesis of 1,4-dienes applicable to the total synthesis of leukotrienes and macrolide insect pheromones. With this goal in mind it appeared that the palladium catalyzed cross coupling of allylic substrates with vinyl organometallic reagents was the method of choice. These processes tolerate a variety of unprotected groups and typically proceed under mild reaction conditions to give excellent yields of coupled products. However, while palladium catalyzed coupling reactions of τ,τ-*di*substituted allylic derivatives with vinyl organometallics are highly stereospecific, similar reactions with τ-*mono*substituted analogs give rise to mixtures of regio- and stereoisomers. The poor selectivity observed in the latter cases arises from the greater ease of isomerization in these sterically less crowded allylpalladium intermediates. Hydride capture of allylpalladium intermediates derived from τ-monosubstituted allylic chlorides revealed that isomerization processes giving rise to *E* and *Z* isomers can be suppressed at temperatures below -45 °C. Cross coupling of allylic chlorides with organoaluminum and organozirconium compounds has been achieved at low temperatures using a coordinatively unsaturated Pd^0 catalyst. Although these coupling reactions proceed with complete retention of stereochemistry in the allylic moiety, they are accompanied by formation of a regioisomer. The solution to this problem was based on the rationalization that the higher degree of stereoselectivity observed in coupling reactions with τ,τ-disubstituted allylic derivatives was due

to increased steric crowding at the τ position. Replacement of a τ hydrogen in the τ-monosubstituted allylic chloride with a trialkylsilyl group gave the τ,τ-disubstituted allylic derivative, which was easily coupled with an organometal. Stereospecific replacement of silicon by hydrogen in the coupled product afforded the isomerically pure 1,4-diene in good yield.

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PALLADIUM CATALYZED

SYNTHESIS OF 1,4-DIENES

INTRODUCTION

Unsaturated systems containing the 1,4-diene moiety are found in a number of biologically important compounds. Leukotrienes for instance have gained increasing attention in medical research since they have been implicated in inflammatory and hypersensitivity related ailments[1]. Lipooxygenase derived metabolites of arachidonic acid are structurally similar to the leukotrienes and cause irreversible inhibition of prostaglandin biosynthesis[2] (FIGURE 1).

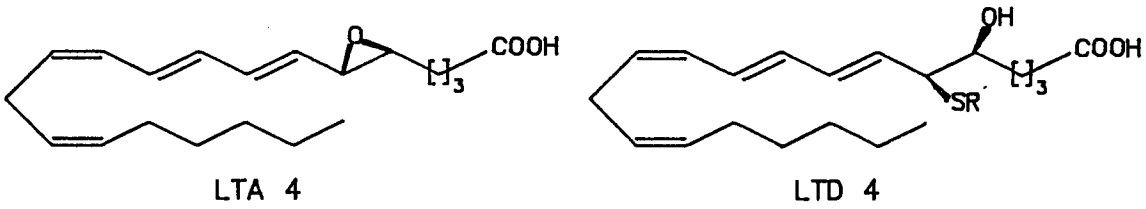


FIGURE 1: Structures of two leukotriene intermediates containing the 1,4-diene unit.

Aggregation pheromones recently isolated from two economically important species of grain beetles were identified as macrolide lactones containing the 1,4-diene unit[3] (FIGURE 2). The use of these pheromones for monitoring insect populations is a current goal of research within our group.

In order to study the biological activity of these compounds it is

important that they may readily be synthesized by convenient methods. Since the biological activity of a particular molecule is directly related to its stereochemical configuration, it is desirable that steps in the synthesis of these compounds are highly stereospecific.

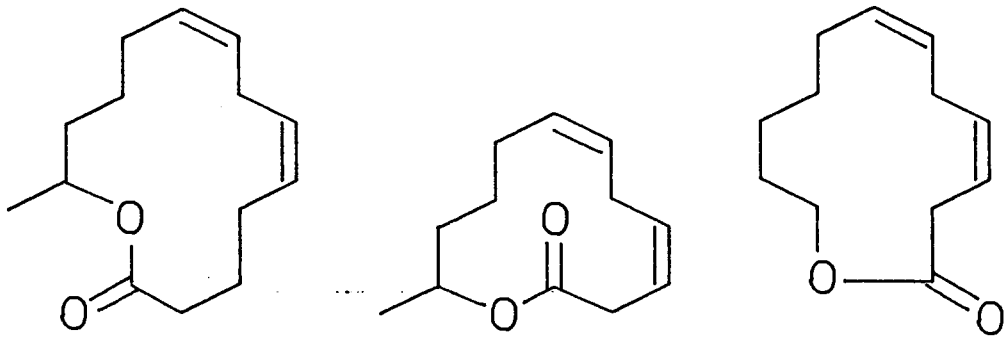
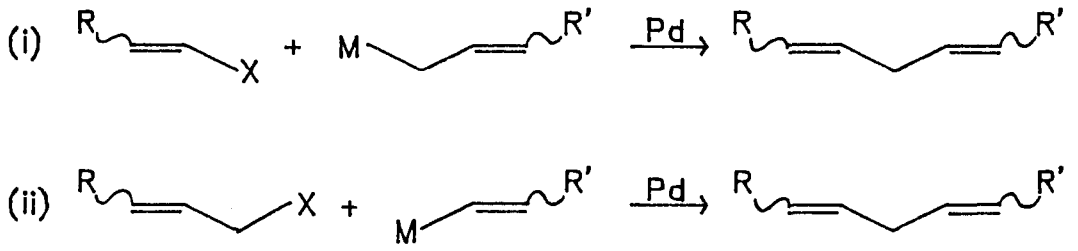


FIGURE 2: Macrolide lactones isolated from two species of grain beetles.

The palladium catalyzed cross coupling of organic halides (a^1 synthons) with d^1 synthons (stabilized carbanions, organometallic reagents) has proven to be a versatile method of carbon - carbon bond formation[4]. Contrary to conventional methods which employ lithium or Grignard reagents, these reactions are typically catalytic and tolerate a large variety of functional groups[5]. The latter feature was expected to allow direct coupling of a^1 and d^1 synthons containing unprotected functionalities, thereby significantly reducing the number of steps in the total synthesis of organic molecules. In principle, the synthesis of 1,4-dienes can be achieved by reacting vinyl substituted compounds with allylic organometallics (i; FIGURE 3) or, alternatively, by coupling vinyl organometallics with allylic compounds (ii; FIGURE 3).

Numerous vinyl and allylic organometallic reagents containing metals

of intermediate electronegativity have been reported to be the most



X = leaving group M = transition metal R = alkyl

FIGURE 3: Two possible combinations of allylic and vinyl synthons leading to 1,4-dienes.

efficient in palladium mediated cross coupling reactions[4]. Allylic organometallics based on Zn[6], Cd[7], Cr[8], Mg[9] and Cu[10] which might be expected to undergo cross coupling (i; FIGURE 3) exist either in the form of π-allyl intermediates or as equilibrium mixtures in which the metal is bonded to either allylic terminus. Therefore, these organometallic derivatives are likely to yield mixtures of *E* and *Z* olefins in cross coupling reactions. Since stereochemical integrity of the allylic organometal is required for the stereoselective synthesis of 1,4-dienes the choice of an organometallic reagent is limited to B[11], Si[12], Al[13], and Sn[14]. However, these are known to undergo allylic rearrangement via electrophilic substitution and would give rise to undesired isomers (FIGURE 4). Therefore, cross coupling of a vinyl *metal* with an allylic *substrate* (ii; FIGURE 3) seemed the most promising approach to the stereospecific synthesis of 1,4-dienes.

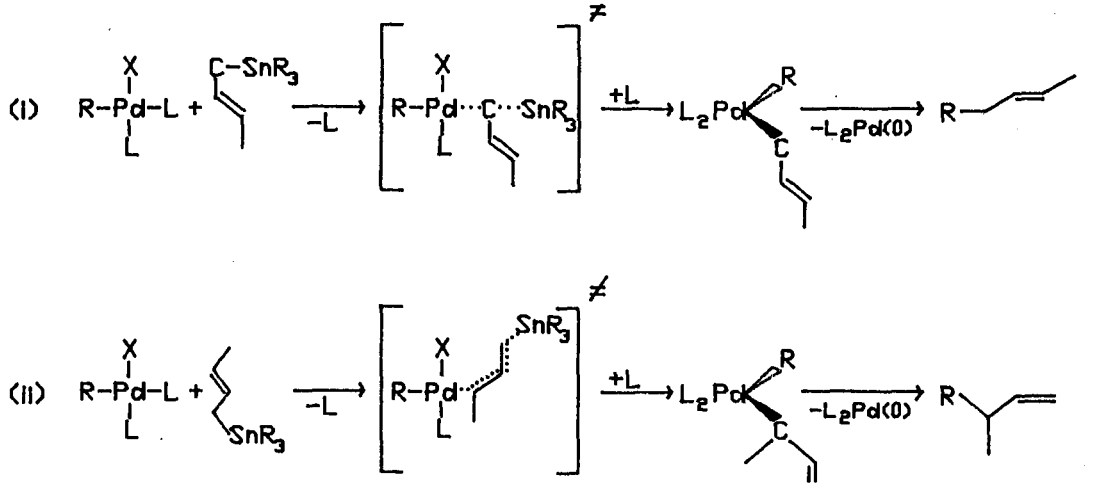


FIGURE 4: Electrophilic cleavage reactions via SE2 (i) and SE2' (ii) mechanisms

The mechanism of this coupling reaction is believed to involve several key steps. Initially, oxidative addition of the allylic substrate to palladium yields a π-allylpalladium complex. Transmetallation of this intermediate with a vinyl organometallic reagent results in the formation of a diorganopalladium species which then undergoes reductive elimination to afford the coupled product and Pd^0. It has been demonstrated that the reaction sequence described above results in overall inversion of configuration at the reacting center. Oxidative addition (inversion) followed by reductive elimination (retention) results in net inversion of configuration[15] (FIGURE 5).

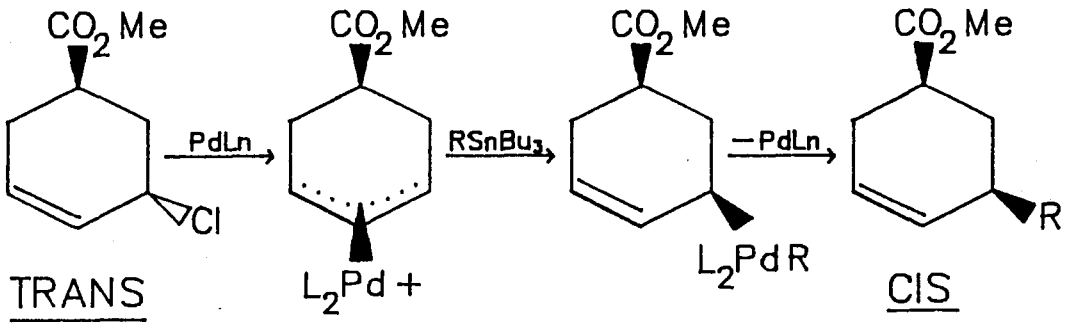


FIGURE 5: Palladium catalyzed cross coupling of allylic derivatives with organometallics.

Palladium catalyzed coupling reactions of vinyl organometallics with τ,τ-*di*substituted allylic halides or acetates proceed with high regio- and stereoselectivity and generally result in high yields[16]. Analogous reactions of τ-*mono*substituted allylic halides, however, give mixtures of regio- and stereoisomers[4c]. It is known that the π-allylpalladium adducts derived from oxidative addition of τ-*mono*substituted allylic chlorides are in rapid equilibrium between various intermediate forms at ambient temperature. Therefore, interconversion of these intermediates prior to coupling results in the loss of stereochemical integrity of the allylic double bond in the coupled product.

The currently accepted mechanism for isomerization of the allylic double bond involves interconversion of σ- and π-allyl species in the allylpalladium adduct. Rotation about the C_2-C_3 bond in the σ bonded complex followed by formation of the π-allyl intermediate allows the

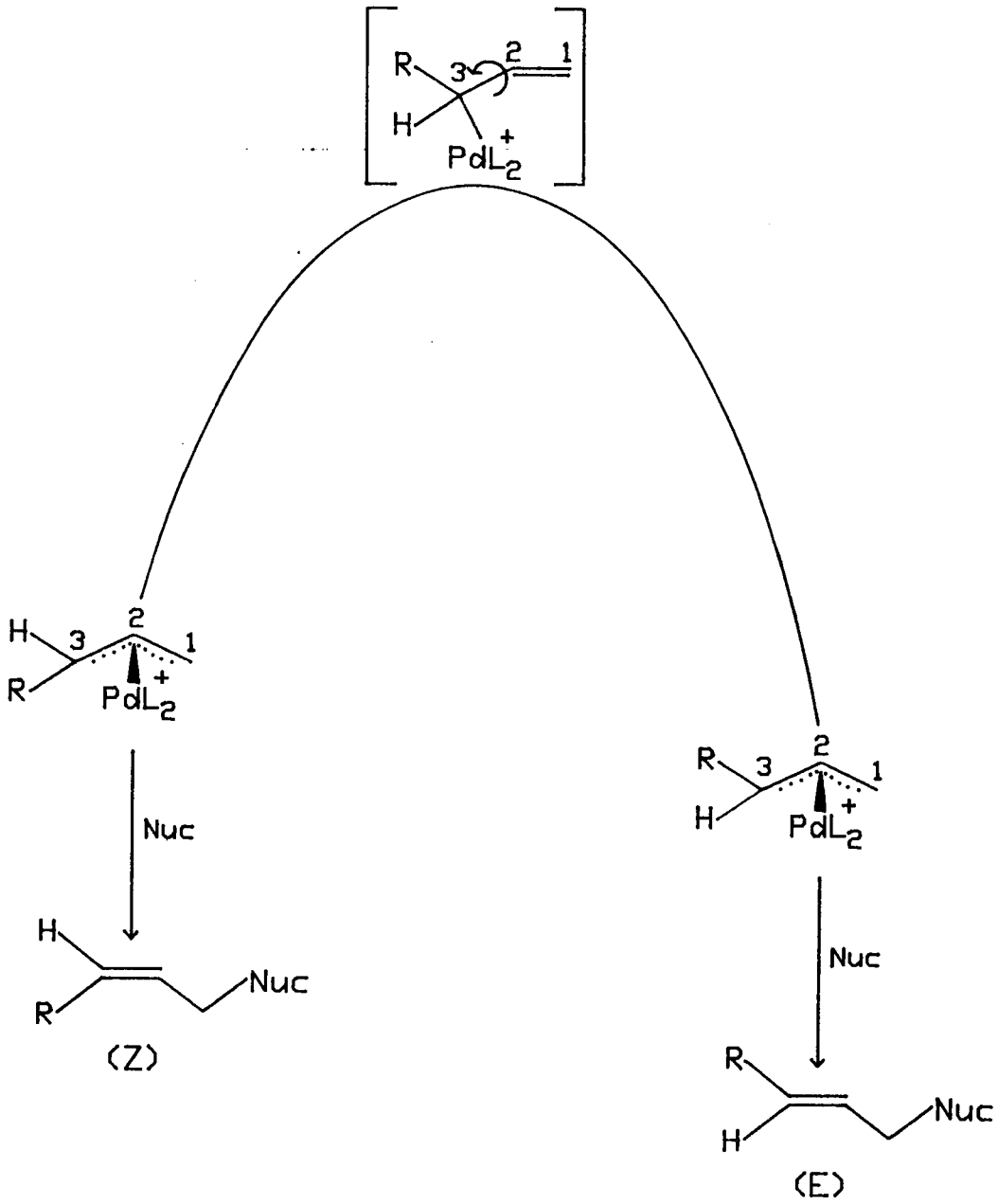


FIGURE 6: Isomerization of allylic double bonds in allylpalladium complexes

interconversion of *syn* and *anti* groups[17]. Cross coupling with these rapidly equilibrating intermediates gives rise to *E* and *Z* isomers (FIGURE 6). Variable temperature ^{1}H NMR studies indicate that the energy required for *syn-anti* exchange increases with the degree of substitution at C_3 in the allylic compound[17]. This may be rationalized in terms of greater steric repulsion in the palladium-C_3 complex between alkyl groups and the ligands on palladium. The formation of a more highly substituted double bond when palladium is bonded to the terminal allylic carbon may act as an additional driving force for preferential palladium-C_1 complexation.

The superior regioselectivity observed in coupling reactions of τ,τ-disubstituted allylic substrates is explained by the fact that processes giving rise to the branched isomer (via C_3 complexation) are energetically less favourable than pathways leading to the formation of the linearly coupled product (via C_1 complexation; FIGURE 7).

In order for palladium catalyzed cross coupling of vinyl organometallics with τ-monosubstituted allylic substrates to be stereospecific coupling must: i) occur preferentially at the terminal allylic carbon (C_1) and ii) proceed below temperatures of *syn* and *anti* interconversion in the allylpalladium intermediates (*vide supra*). ^{1}H NMR studies on π-allylpalladium complexes have shown that dynamic equilibria giving rise to *E* and *Z* isomers can be suppressed at low temperatures[17]. It was reasoned that if the steps leading to coupled products (oxidative addition, transmetallation and reductive elimination) could be carried out at temperatures below interconversion of *syn* and *anti* groups in π-allyl complexes derived from τ-monosubstituted allylic compounds,

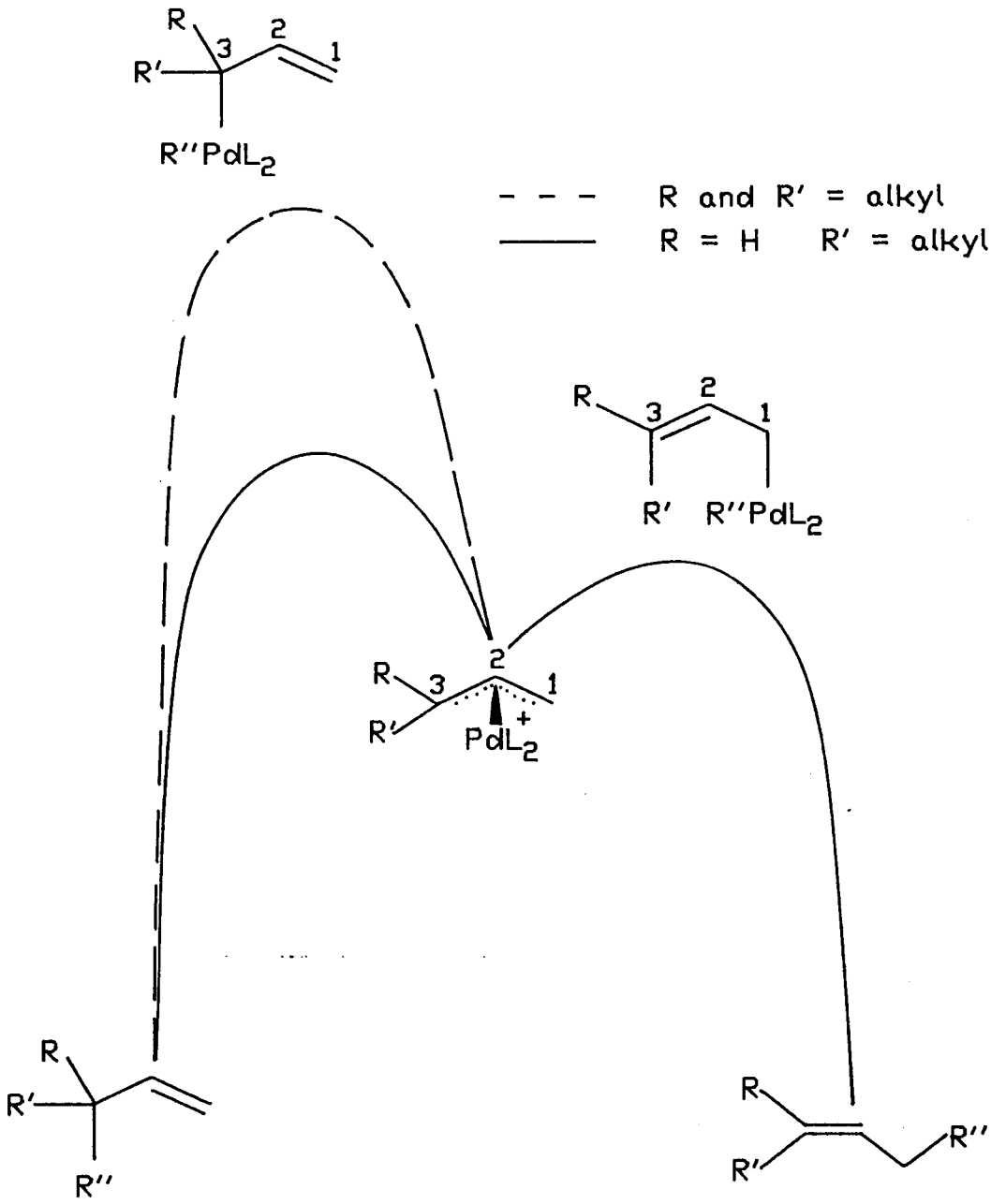


FIGURE 7: Energy profile for coupling reactions of allylic substrates with vinyl organometals.

stereospecific consumption of these organopalladium intermediates would be possible. Initial experiments were designed to probe the feasibility of this approach.

The detailed mechanism of oxidative addition of allylic substrates to palladium is still under investigation. It has been established that $Pd(P\emptyset_3)_4$ exists mainly in the the form of $Pd(P\emptyset_3)_3 + P\emptyset_3$ in polar aprotic solvents at ambient temperature[22]. While reactions catalyzed by $Pd(P\emptyset_3)_4$ require elevated temperatures, similar reactions employing preformed allylpalladium complexes proceed at or below room temperature[23].

These observations suggest that prior dissociation of $Pd(P\emptyset_3)_4$ to $Pd(P\emptyset_3)_3$ or $Pd(P\emptyset_3)_2$ is required for actual π-allyl complexation. These reactions are typically run in THF which can be assumed to occupy the sites vacated by the phosphine ligands. Oxidative addition of allylic substrates to soluble palladium catalysts is believed to be initiated by loss of metal ligands to form coordinatively unsaturated species[22].

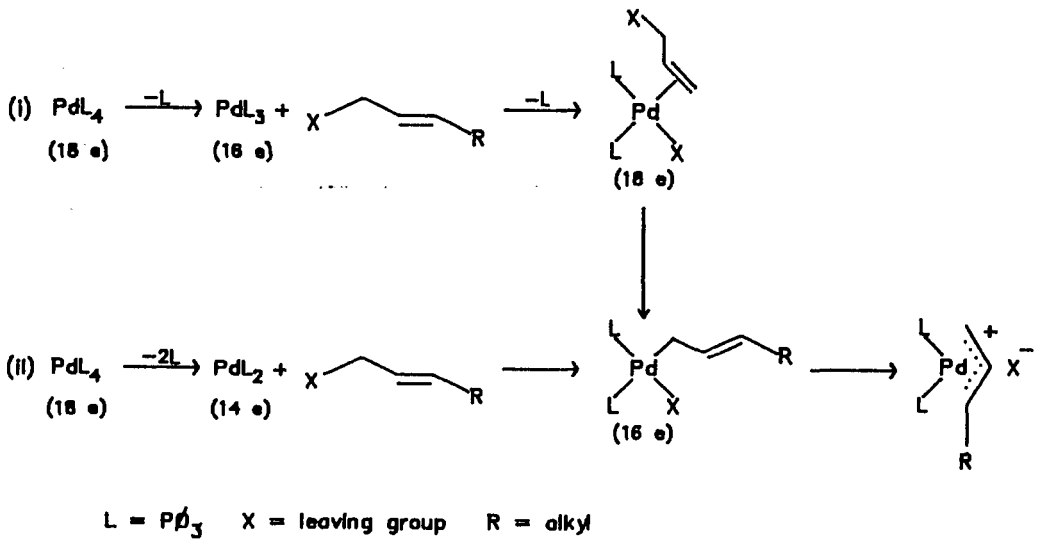


FIGURE 8: Oxidative addition of allylic substrates to coordinatively unsaturated palladium intermediates.

Formation of the oxidative adduct then proceeds via coordination of the allylic double bond to a vacant site at the metal followed by formation of the π-allylpalladium complex. Addition of the double bond may occur directly on a 14 electron species (i; FIGURE 8) or involve sequential replacement of metal ligands via 18 and 16 electron intermediates (ii; FIGURE 8). Oxidative additon occurs by backside displacement of the allylic group by the nucleophilic metal in an SN2 like fashion and is therefore quite different from the insertion of Pd^0 into carbon-halide bonds which proceeds with retention. This mechanism, in which intermediates alternate between oxidation states is common in reactions of other transition metals[24]. The mechanism of reductive elimination is still under investigation. It has been suggested that reductive elimination may be induced by formation of a octahedral palladium (IV) intermediate[25].

Based on these observations it seemed plausible that oxidative addition might be achieved at low temperatures by adding a reactive allylic substrate to a coordinatively unsaturated $Pd(P\emptyset_3)_2$ species[26]. Allylic chlorides and acetates were chosen as allylic synthons since they have been reported to be among the most reactive in cross coupling reactions[16]. In order to determine whether isomerization had occurred in the oxidative adducts (derived from τ-monosubstituted allylic substrates), these intermediates were reduced with hydride and the products analyzed. It was reasoned that if isomerization had occurred in the allylpalladium intermediates this would be reflected by the formation of product isomers. Hydride reducing agents were chosen for capturing

allylpalladium intermediates since they were readily available and were expected to be sufficiently reactive to reduce the allylpalladium complexes at low temperatures.

Various hydride donors have been reported in the reduction of π-allylpalladium complexes[27]. Reductions of τ,τ-disubstituted allylic compounds typically proceed with stereoretention of the allylic double bond. Analogous reductions of *E*-τ-monosubstituted allylic substrates yield mixtures of isomers in which the thermodynamically more stable *E* isomer generally predominates. Selective formation of either internal or terminal olefin has also been achieved by using appropriate reducing agents[28]. Since there was no precedent for the stereoselective reduction of allylpalladium intermediates derived from *Z*-τ-monosubstituted allylic compounds, reducing agents for these reductions were selected on the basis of preferential formation of internal over terminal olefins. Choice of an appropriate hydride source was therefore critical, since terminal olefin formation would of course not allow detection of isomerization in the allylpalladium intermediates. Furthermore, the transition state energies leading to olefin formation were not expected to differ substantially for *E* and *Z* allylpalladium intermediates, so it was anticipated that hydride reduction of *isomerized* allylpalladium complexes would yield a mixture of the corresponding *E* and *Z* olefins.

Several mechanisms for hydride reductions of allylpalladium complexes have been proposed[29]. It has been suggested that reductions may occur by nucleophilic attack of hydride on C_1 and C_3 in σ-bonded or π-allylpalladium complexes. Regeneration of a coordinatively unsaturated palladium species followed by further oxidative addition completes the

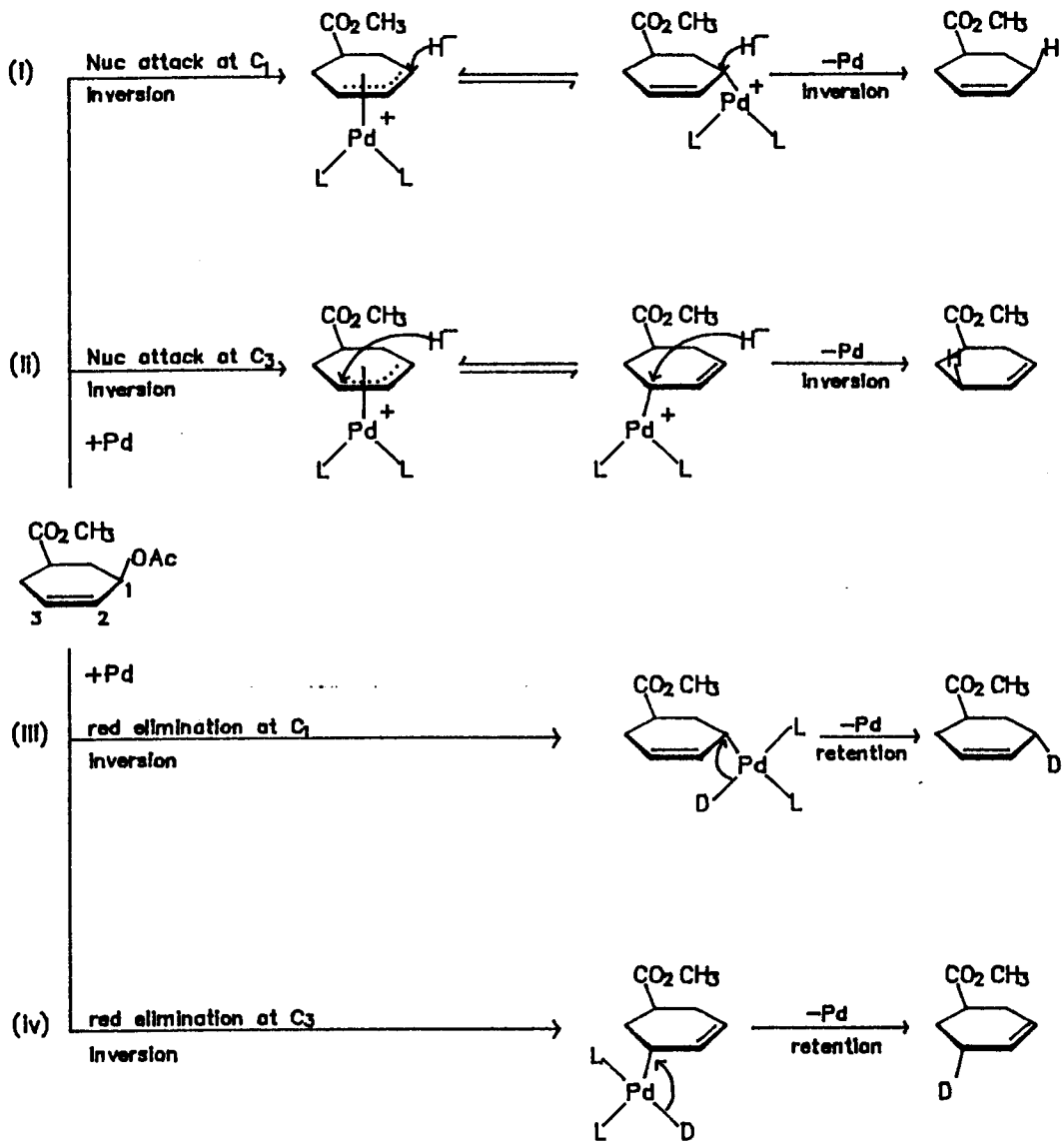


FIGURE 9: Mechanisms for hydride reduction in allylpalladium complexes.

catalytic cycle (i,ii; FIGURE 9). Studies on reductions of allylpalladium complexes using reducing agents containing deuterium have provided strong evidence for the formation of a palladium hydride intermediate. It was established that in the allylic systems investigated, reduction occurred with *net inversion* of configuration at the functionalized allylic carbon. This stereochemical outcome could not be explained by the mechanisms described above since both steps (oxidative addition and nucleophilic attack) proceed with inversion and would result in *net retention* of configuration. Therefore, it has been proposed that olefin formation occurs via reductive elimination from a palladium hydride intermediate; a process which is expected to proceed with retention. This sequence of inversion followed by retention accounts for the experimentally observed net inversion of configuration (iii; FIGURE 9).

RESULTS AND DISCUSSION

HYDRIDE CAPTURE OF π-ALLYLPALLADIUM COMPLEXES

Both *E* and *Z* allylic chlorides and acetates were readily prepared by methods described in the literature[18,19,20,21] (FIGURE 10).

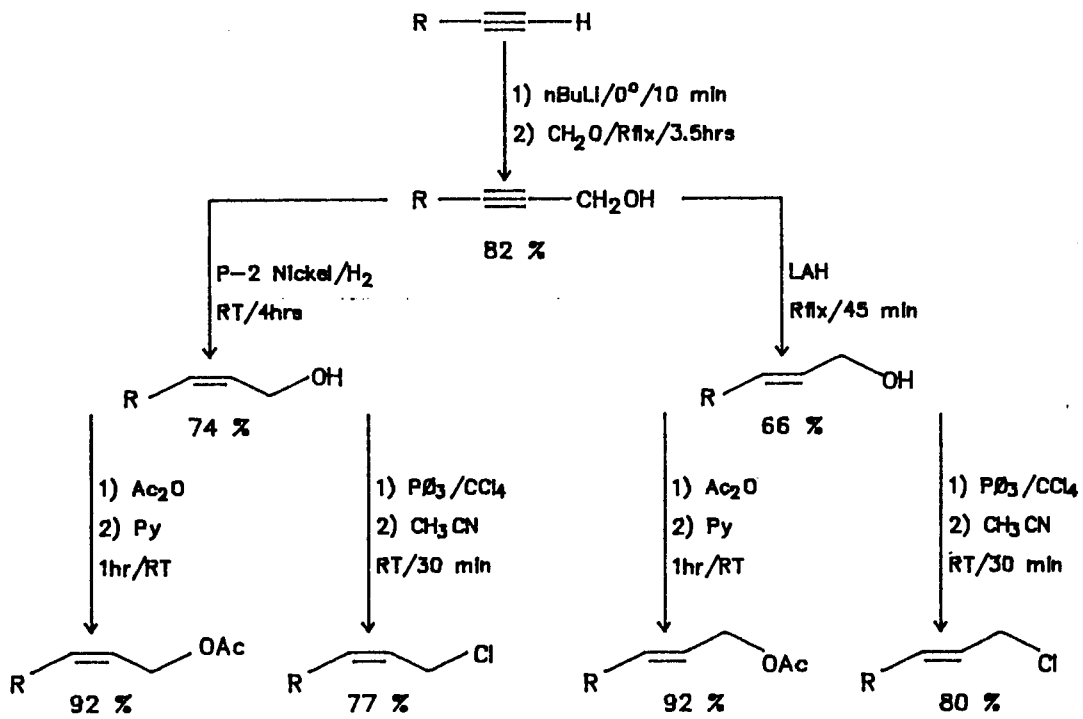


FIGURE 10: Preparation of allylic chlorides and acetates.

It was found that addition of (*E*)- and (*Z*)-1-chloro-2-octene to $Pd(P\emptyset_3)_2$, prepared <u>in situ</u> by reduction of $PdCl_2(P\emptyset_3)_2$ with two equivalents of diisobutylaluminum hydride (DIBAH)[26], was complete after 10 minutes at -78 °C. Oxidative addition of the allylic chlorides was rapid at -78 °C as was evidenced by the disappearance of the allylic starting material within several minutes after addition. The corresponding acetates, however, required room temperature conditions and

were therefore dismissed as suitable substrates for low temperature cross coupling reactions. With the successful formation of the allylpalladium intermediate at low temperature, it remained to be determined whether isomerization of the allylic double bond had occurred. For this purpose a hydride source was required which would selectively reduce allylpalladium intermediates to yield internal olefins. It was found that π-allylpalladium complexes derived from (*Z*)-1-chloro-2-octene could be cleanly reduced to (*Z*)-2-octene in high yield using DIBAH as the hydride source. All other reducing agents employed gave rise to mixtures of 1-octene and (*E*)- and (*Z*)-2-octene under similar reaction conditions (Table I).

Table I. Hydride reduction of (*Z*)-1-chloro-2-octene[a]

Hydride	Temp/Time	1-Octene[b]		(*E*)-2-Octene[b]		(*Z*)-2-Octene[b]	Yield[c]
DIBAH	-78 °C/20min	n.d.	:	n.d.	:	1.0	100 %
$LiBEt_3D$	-78 °C/20min	1.1	:	1.0	:	3.8	88 %
LAH	-78 °C-RT[d]	1.1	:	1.0	:	3.8	58 %
$NaBH_4$	-78 °C/4.5hr	1.0	:	1.1	:	1.2	65 %

[a] reactions were run in THF using 30 % Pd^0 (generated in situ by adding 2 eq. of DIBAH to $PdCl_2(P\emptyset_3)_2$) and 5 eq. of hydride; [b] Determined by coinjection of an authentic sample; [c] By g.c.; [d] 19 % octane formed; n.d. = not detected, < 0.2 % by g.c.; DIBAH = Diisobutylaluminum hydride; $LiBEt_3D$ = Lithium triethylborodeuteride; LAH = Lithium aluminum hydride; $NaBH_4$ = Sodium borohydride

By carrying out the reductions at successively higher temperatures, it was hoped that the onset of isomerization might be detected. This information would allow the estimation of an upper temperature limit below which cross coupling could be carried out without isomerization. It

was observed that product isomers were formed when solutions of allylpalladium complexes were quenched at temperatures above -45 °C (Table II). These results corroborate the notion that reactions at C_1 in allylpalladium intermediates are energetically lower processes than similar reactions at C_3. The fact that isomers are formed above -45 °C indicates that equilibration between C_1 and C_3 palladium complexes above this temperature is much more rapid than the rate of hydride transfer. Competing processes such as β-hydride elimination may account for the somewhat lower yields in reductions carried out at elevated temperatures[29a].

Table II. Diisobutylaluminum hydride capture of π-allylpalladium complexes at various temperatures

Temp.	1-Cl-2-octene	1-Octene[b]	(*E*)-2-Octene[b]	(*Z*)-2-Octene[b]	Yield[c]
-78 °C[d]	*Z*	n.d. :	n.d. :	1	100 %
-45 °C[e]	*Z*	4.2 :	1 :	12.2	87 %
-23 °C[f]	*Z*	2 :	1 :	1.8	73 %
0 °C[g]	*Z*	3.1 :	1 :	1.4	76 %
RT	*Z*	3.7 :	1 :	2.4	69 %
-78 °C[d]	*E*	n.d. :	1 :	n.d.	82 %
-45 °C[e]	*E*	1 :	2.6 :	n.d.	90 %
-23 °C[f]	*E*	1 :	1.4 :	n.d.	95 %
0 °C[g]	*E*	1.5 :	1 :	n.d.	57 %
RT	*E*	1 :	1.4 :	trace	56 %

[a] reactions were run in THF using a stoichiometric amount of Pd^0 (generated in situ by adding 2 eq. of DIBAH to $PdCl_2(P\emptyset_3)_2$) and 5 eq. of DIBAH; [b] Determined by coinjection of an authentic sample; [c] By g.c.; [d] Dry ice / acetone; [e] $N_{2(l)}$ / CH_3CN; [f] $N_{2(l)}$ / CCl_4; [g] ice-water slurry; n.d.= not detected, < 0.2 % by g.c.

Control experiments in which reductions were carried out in the absence of palladium revealed that (Z)-1-chloro-2-octene was not reduced

at -78 °C but required room temperature conditions. This observation establishes beyond doubt the involvement of the palladium catalyst in reductions of allylic chlorides and supports the idea that activation occurs by formation of an allylpalladium intermediate. It is noteworthy that all three octene isomers were obtained when boron hydrides were used as reducing agents. This suggests that reductions using these reagents might proceed by mechanisms other than nucleophilic attack or reductive elimination (*vide supra*). Formation of isomers when LAH was employed is not surprising considering that room temperature was necessary for reduction of the allylpalladium intermediates to take place.

Table III. Hydride Reduction of (*Z*)-1-chloro-2-octene[a]

Hydride	1-Octene[b]		(*E*)-2-Octene[b]		(*Z*)-2-Octene[b]	Yield[c]
DIBAH [d]	n.d.	:	n.d.	:	n.d.	n.d.
$LiBEt_3D$	1.0	:	n.d.	:	6.7	100 %
LAH [e]	1.7	:	1.0	:	30.0	78 %
$NaBH_4$	1.0	:	1.9	:	1.6	70 %

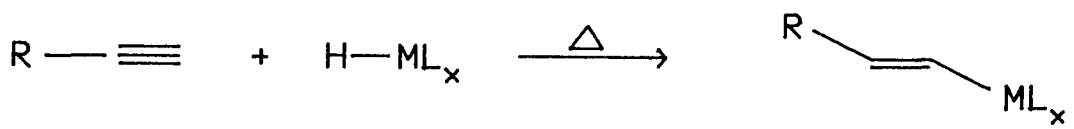
[a] reactions were run at R.T. for 12 hr in THF without a palladium catalyst. 5 eq. of hydride were added; [b] Determined by coinjection of an authentic sample; [c] By g.c.; [d] Formation of unidentified products; [e] 2.4 % octane formed; n.d. = not detected, < 0.2 % by g.c.; DIBAH = Diisobutylaluminum hydride; $LiBEt_3D$ = Lithium triethylborodeuteride; LAH = Lithium aluminum hydride; $NaBH_4$ = Sodium borohydride

It was further noted that the (*Z*)-allylic chloride was reduced more cleanly by LAH or $LiBEt_3D$ alone. This can be explained by the same arguments mentioned above: hydride reductions of allylpalladium intermediates, in which both allylic termini are susceptible to attack,

are expected to be less selective than in cases involving nucleophilic displacement of a terminal allylic chloride (Table III).

PREPARATION OF VINYL ORGANOMETALLIC REAGENTS

Initial cross coupling experiments were carried out using (*E*)-vinyl organometals which were readily prepared by the hydroalumination of terminal acetylenes (FIGURE 11). It was reasoned that having established optimum coupling conditions using the easily obtainable (*E*)-vinyl organometals, analogous reactions with the less readily prepared *Z* isomers might be explored. At the time a likely route to the preparation of *Z*-vinylorganometallics seemed possible by the lithiation of *Z*-vinyl halides followed by transmetallation with a metal halide. However, initial attempts failed to yield the desired product. Instead, a complex mixture of unidentified products was obtained.



R = alkyl M = Al,B,Zr L = metal ligands

FIGURE 11: Hydrometallation of terminal acetylenes

REACTIVITY ENHANCEMENT USING COORDINATIVELY UNSATURATED PALLADIUM

Literature reports indicated that coordinatively unsaturated palladium species were more reactive than their saturated counterparts. In earlier experiments we demonstrated that oxidative addition to

coordinatively unsaturated palladium was rapid at low temperatures and that isomerization in these complexes was negligible below -45 °C. As discussed above, for cross coupling to be stereospecific it is essential that the remaining steps in the coupling sequence (transmetallation, reductive elimination) proceed below temperatures of isomerization. It was hoped that $Pd(P\emptyset_3)_2$ would be sufficiently reactive to catalyze cross coupling under these stringent reaction conditions. In order to gauge the feasibility of such an approach the reactivities of $Pd(P\emptyset_3)_2$ and $Pd(P\emptyset_3)_4$ were compared in a model system. For this purpose allylbromide was chosen as the allylic coupling partner since it was readily available, but more importantly, because analysis of the coupled product was not complicated by the formation of regio- and stereoisomers (FIGURE 12).

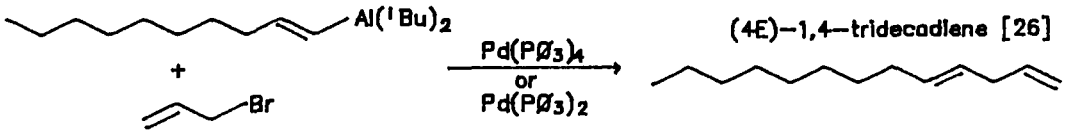


FIGURE 12: Cross coupling using two different palladium catalysts

Reactions catalyzed by $Pd(P\emptyset_3)_4$ required refluxing conditions and therefore this catalyst was not suitable for low temperature cross coupling. Reactions with $Pd(P\emptyset_3)_2$ were extremely sluggish at 0 °C and required warming to room temperature for completion (TABLE IV).

Based on this observation it seemed doubtful that $Pd(P\emptyset_3)_2$ was suitable for stereospecific coupling of vinyl organoaluminum reagents with allylic chlorides. This suspicion was confirmed by the $Pd(P\emptyset_3)_2$

Table IV. Efficacy of coordinatively unsaturated palladium[a] in cross coupling of allylbromide with (*E*)-1-decenyldiisobutylalane.[b]

Catalyst	Reaction Conditions	Yield(%)
$Pd(P\emptyset_3)_4$	1 hr/RT	n.d.
	30 min/Rflx	75 %[c]
$Pd(P\emptyset_3)_2$ [a]	0 °C - RT	90 %[c]

[a] Prepared <u>in situ</u> by adding 2 equivalents of DIBAH to $PdCl_2(P\emptyset_3)_2$ in THF; [b] Prepared according to reference 38; [c] Isolated yields; n.d.= not detected, < 2 % by g.c.

Table V. $Pd(P\emptyset_3)_2$[a] catalyzed coupling of allylic chlorides[b] with nonenylalane.[c]

Allylic chloride[b]	Reaction conditions	Regio-isomer[d]	*E*,*E*[e]	*Z*,*E*[f]
E-Cl	0 °C - RT	1.0	: 5.5	: n.d.
Z-Cl	0 °C - RT	1.5	: 7.6	: 1

[a] Prepared <u>in situ</u> by adding 2 equivalents of DIBAH to $PdCl_2(P\emptyset_3)_2$ in THF; [b] *E* or *Z*-1-chloro-2-octene; [c] Prepared according to reference 38; [d] (4*E*)-3-pentyl-1,4-dodecadiene; [e] (6*E*,9*E*)-6,9-heptadecadiene; [f] (6*Z*,9*E*)-6,9-heptadecadiene; Product ratios determined by g.c.; n.d.= not detected, < 2 % by g.c.

mediated cross coupling of (*E*)- and (*Z*)-1-chloro-2-octene with (*E*)-1-nonenyldiisobutylalane which resulted in the formation of regio- and stereoisomers (TABLE V). Processes giving rise to formation of the diene isomers are depicted in Figure 13.

$Pd(P\emptyset_3)_2$ CATALYZED CROSS COUPLING OF ALLYLIC CHLORIDES WITH VINYL ORGANOMETALS

In search of a solution to this problem a variety of vinyl organometals were prepared and subjected to cross coupling in the hope of finding a metal that would allow transmetallation and reductive elimination to proceed at lower temperatures. The highest yields were achieved with organometals based on aluminum (entries 1-4; TABLE VI) followed by those based on zirconium (entries 9,10; TABLE VI).

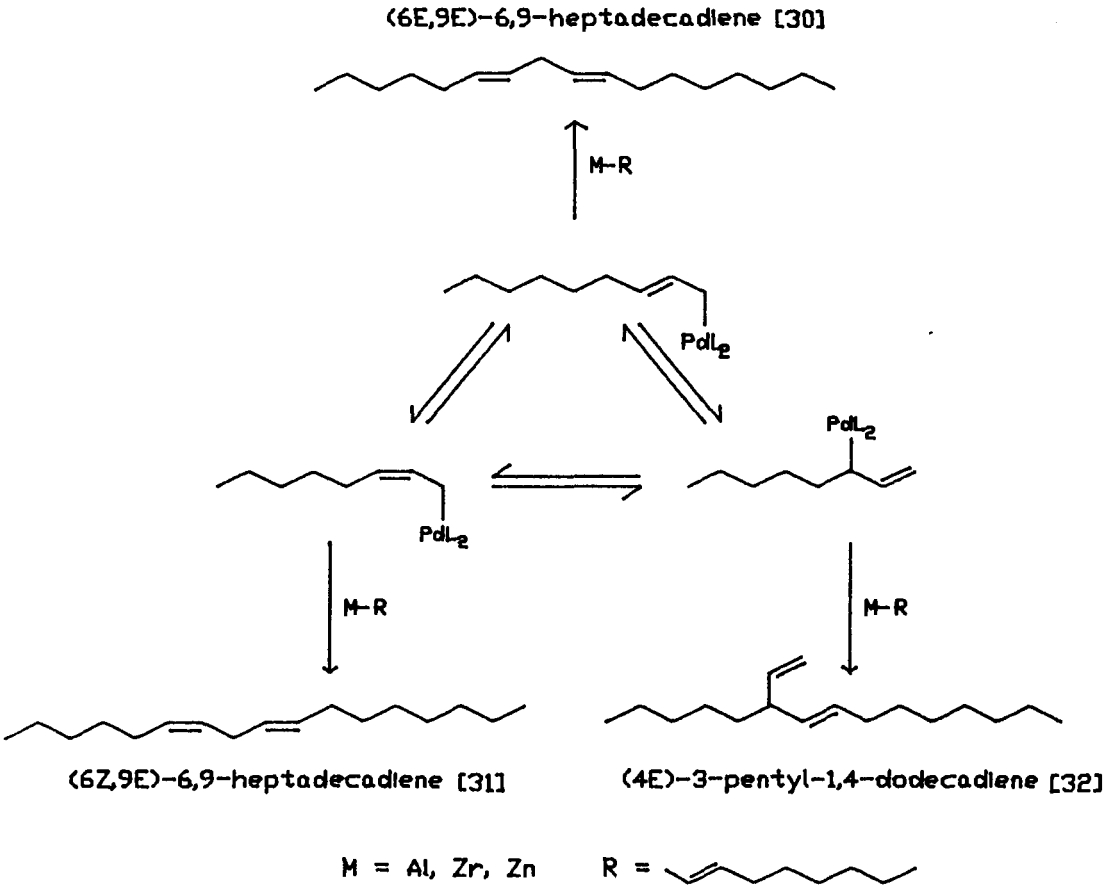


FIGURE 13: Processes giving rise to formation of diene isomers in palladium catalyzed cross coupling reactions

Table VI. $Pd(P\emptyset_3)_2$[a] catalyzed coupling of allylic chlorides[b] with (*E*)-vinyl organometallic reagents[c]

Entry	*E*-Metal[c]	Allylic chloride[b]	React. cond.	Regio-[d] isomer %(rel)	*E*,*E*[e] %(rel)	*Z*,*E*[f] %(rel)	Homo-[g] coupled (rel)
1	$Al(^iBu)_2$	*E*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	11(1)	64(5)	n.d.	trace
2		*Z*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	25(1)	58(2.3)	n.d.	trace
3	$Al(^iBu)_2Me]^-$	*E*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	6.8(1)	47(7)	n.d.	some(3)
4		*Z*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	16(1.5)	32(3)	n.d.	some(1)
5	HgOAC	*E*-Cl	C	n.d.	n.d.	n.d.	some
6		*Z*-Cl	C	n.d.	n.d.	n.d.	some
7	HgCl	*E*-Cl	C	n.d.	n.d.	n.d.	some
8		*Z*-Cl	C	n.d.	n.d.	n.d.	some
9	$ZrCp_2Cl$	*E*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	3.3(1)	11(3.2)	n.d.	some(34)
10		*Z*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	3(1)	13(4.4)	n.d.	some(47)
11	ZnCl	*E*-Cl	A	n.d.	n.d.	n.d.	some
			B	n.d.	2	n.d.	some
12		*Z*-Cl	A	n.d.	n.d.	n.d.	some
			B	2(1)	10(5)	n.d.	some(6)

[a] Prepared <u>in situ</u> by adding 2 equivalents of DIBAH to $PdCl_2(P\emptyset_3)_2$ in THF; [b] *E* or *Z*-1-chloro-2-octene; [c] Prepared according to reference 38; [d] (4*E*)-3-pentyl-1,4-dodecadiene; [e] (6*E*,9*E*)-6,9-heptadecadiene. [f] (6*Z*,9*E*)-6,9-heptadecadiene; [g] (8*E*,10*E*)-8,10-octadecadiene; [h] Yields and relative amounts of product isomers determined by g.c.; n.d.= not detected, < 2 % by g.c.; A = -78 °C/5 hr; B = -78 °C - RT/12 hr ; C = RT/24 hr.

The best regioselectivity was obtained when (*E*)-1-nonenyldiisobutylalane was the coupling partner (regioisomer:*E*,*E* = 1:5). Cross coupling reactions using mercuric acetate and mercuric chloride derived organometallics failed completely (entries 5-8; TABLE VI). Cross coupling using vinyl zinc organometals proved to be exceedingly tedious.

Due to the hygroscopic nature of $ZnCl_2$ all steps leading to the final product demanded rigorous exclusion of moisture. Although these results (entries 11,12; TABLE VI) are based on repeated experiments, contamination by water cannot be ruled out as the cause for poor yields in these cases.

An interesting side reaction observed in this series of experiments was the formation of the homocoupled product (8*E*,10*E*)-8,10-octadecadiene. The likely process is shown in Figure 14.

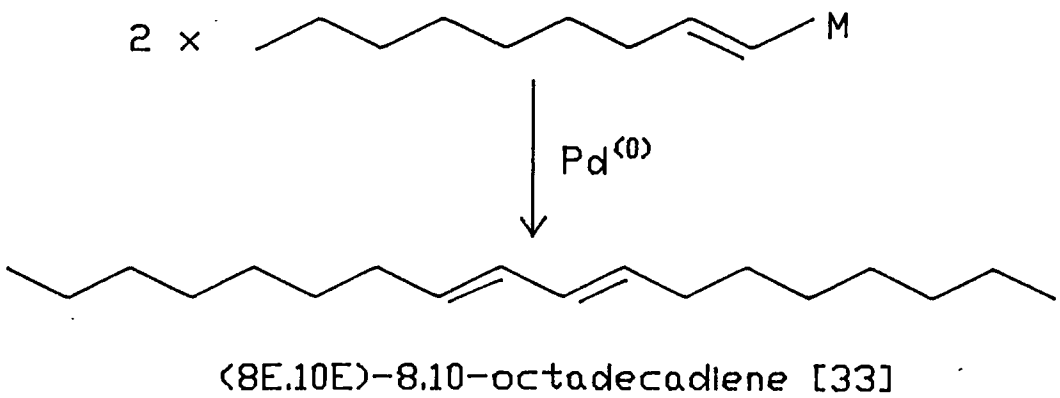


FIGURE 14: Homocoupling of vinyl organometallic reagents

This side reaction was of particular concern in cross coupling reactions employing the vinyl organozirconium reagent. The low yields in these instances may be attributed to rapid consumption of the starting organozirconium reagent to form the conjugated diene at the expense of 1,4-diene formation.

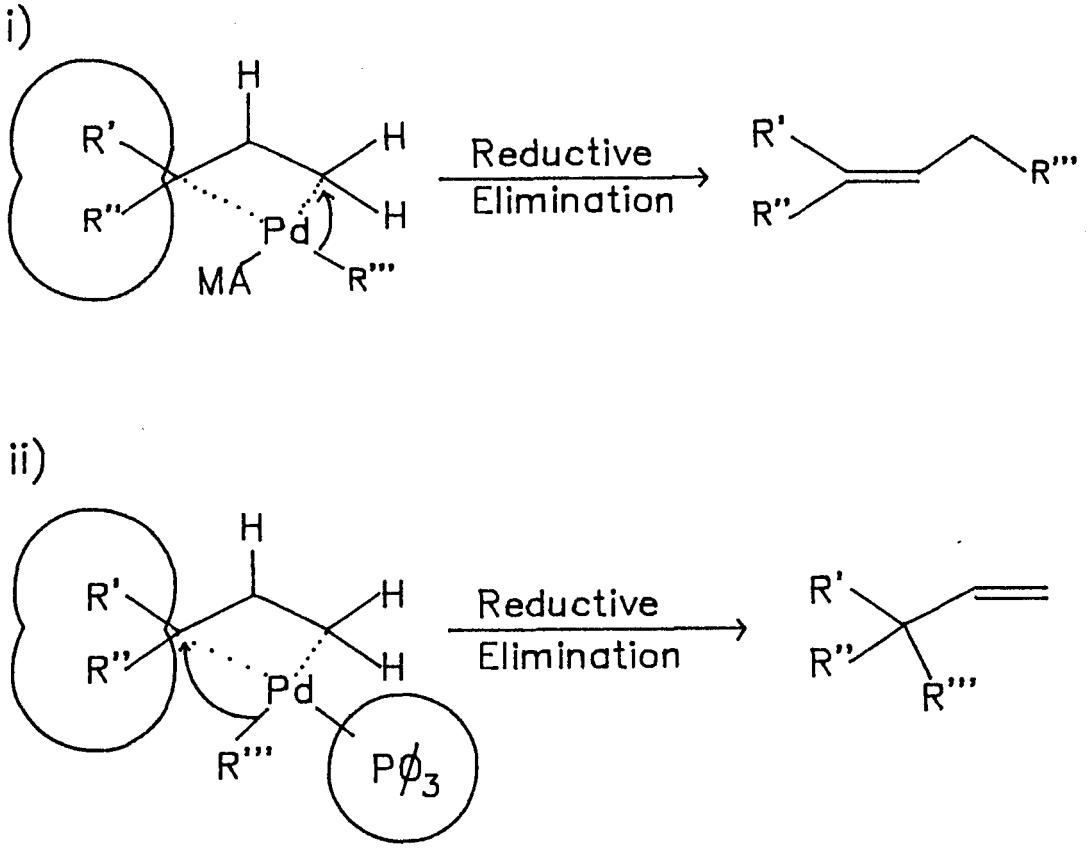
It should be pointed out that in all cases investigated, the linearly coupled 1,4-diene only contained *E* double bonds *regardless* of the starting geometry in the allylic chloride. This suggests that coupling

had occurred above -45 °C allowing the *Z* palladium adduct to isomerize to the more stable *E* isomer prior to coupling. A final attempt aimed at enhancing the reactivity of the vinyl organometal was based on reports that the reactivity of organometallics could be increased by forming the corresponding "ate" complexes[38]. It was reasoned that transmetallation with the cationic palladium intermediate might proceed more readily owing to the increased nucleophilicity of the attacking alkyl group in the negatively charged organometallic complexes. However, aside from a slight improvement in regioselectivity, yields were somewhat lower compared to reactions using the uncomplexed organoaluminum reagent (entries 3,4; TABLE VI).

ADDITION OF MALEIC ANHYDRIDE AND $P\emptyset_3$ TO $Pd(P\emptyset_3)_2$ CATALYZED CROSS COUPLING REACTIONS

In 1980 Schwartz and coworkers[23] made the observation that the regiochemistry in coupling reactions of allylpalladium complexes could be improved in favour of "head to head" coupling by the addition of electron withdrawing ligands such as maleic anhydride. It was also noted that addition of these ligands greatly facilitated coupling processes as was evidenced by shorter reaction times and milder reaction conditions. These observations are consistent with the view that reductive elimination is favoured by electron withdrawal from the metal in the diorganometallic intermediate[4d]. The marked improvement in regioselectivity observed when coupling reactions were carried out in the presence of maleic anhydride has been explained in terms of stereo-electronic effects. It has been suggested that in square planar allylpalladium complexes the metal atom

is disposed towards the sterically least congested allylic terminus. Electron withdrawing ligands are expected to bind preferentially to the most electron rich coordination sphere i.e. trans to the sterically least crowded allylic carbon. As a consequence, transmetallation gives rise to a diorganopalladium intermediate in which the transmetallated alkyl group



MA = maleic anhydride R = alkyl

Figure 15: Control of regioselectivity in cross coupling reactions by equilibrating allylpalladium complexes with extrinsic ligands

is *cis* to the least hindered allylic carbon. Reductive elimination from this intermediate yields the "head to head" coupled product (i; FIGURE 15). Conversely, equilibration of allylpalladium complexes with $P\emptyset_3$ favours coupling at the sterically *most* crowded allylic terminus. Due to the steric bulk of $P\emptyset_3$ combined with its weak electron *donating* properties, the geometry of this intermediate is opposite to that observed in allylpalladium complexes equilibrated with maleic anhydride. Reductive elimination in this case yields the branched isomer as a result of "head to tail" coupling (ii; FIGURE 15).

Table VII. Effect of added ligands on $Pd(P\emptyset_3)_2$[a] catalyzed coupling reactions of allylic chlorides[b] with (*E*)-1-nonenyldiisobutylalanate[c]

Entry	Ligand (equiv)	Allylic chloride[b]	React. cond.	Regio-[d] isomer %(rel)	*E*,*E*[e] %(rel)	*Z*,*E*[f] %(rel)	Homo-[g] coupled (rel)
1	M.A.(5)	*E*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	4.5(1)	7(1.5)	n.d.	n.d.
2		*Z*-Cl	A	n.d.	n.d.	n.d.	n.d.
			B	8(1)	20(2.5)	n.d.	n.d.
3	M.A.(50)	*E*-Cl	B	n.d.	n.d.	n.d.	n.d.
4		*Z*-Cl	B	n.d.	n.d.	n.d.	n.d.
5	$P\emptyset_3$(50)	*E*-Cl	B	n.d.	n.d.	n.d.	n.d.
6		*Z*-Cl	B	n.d.	n.d.	n.d.	n.d.

[a] Prepared <u>in situ</u> by adding 2 equivalents of DIBAH to $PdCl_2(P\emptyset_3)_2$ in THF; Stoichiometric amount of palladium used; [b] *E* or *Z*-1-chloro-2-octene; [c] Prepared according to reference 38; [d] (4*E*)-3-pentyl-1,4-dodecadiene; [e] (6*E*,9*E*)-6,9-heptadecadiene; [f] (6*Z*,9*E*)-6,9-heptadecadiene; [g] (8*E*,10*E*)-8,10-octadecadiene; [h] Yields and relative amounts of product isomers determined by g.c.; n.d.= not detected, < 2 % by g.c.; M.A.= maleic anhydride; $P\emptyset_3$ = triphenylphosphine; A = -78 °C/5 hr; B = -78 °C - RT/12 hr

Contrary to these observations, equilibration of allylpalladium complexes derived from the oxidative addition of τ-monosubstituted allylic chlorides to palladium neither improved the regioselectivity nor enhanced the reactivity in cross coupling reactions; warming to room temperature was necessary for coupling to take place (entries 1,5; TABLE VII). In separate experiments it was noted that oxidative addition was completely suppressed when ligands were added to Pd^0 prior to addition of the allylic chloride. This observation combined with the fact that equilibration with a large excess of maleic anhydride or $P\emptyset_3$ completely inhibited cross coupling emphasizes the importance of dissociative processes in these reactions.

CROSS COUPLING REACTIONS USING "LIGAND FREE" PALLADIUM CATALYSTS[a]

The studies outlined above led to the speculation that the reactivity of the palladium catalyst could be further increased by complete removal of the triphenylphosphine ligands. Methods for the preparation of "ligandless" palladium catalysts were therefore explored. ([a] The terms "ligandless" and "ligand free" imply in this context that $P\emptyset_3$ is not present in the reaction mixture, i.e. this ligand is not coordinated to the Pd^0 catalyst. The intermediate Pd^0 catalyst is presumably stabilized by coordination of solvent (THF) molecules prior to oxidative addition).

An initial approach involved the stripping of chloride ligands from Na_2PdCl_4 using 4 equivalents of DIBAH. Oxidative addition to the "naked" palladium catalyst was expected to be rapid and result in either formation of a bisallylpalladium adduct or an allylpalladium dimer (i; FIGURE 16). Unfortunately, allylic chlorides addition were reduced to the

corresponding alkane and alkene isomers (entries 1,2,5,6; TABLE VIII).

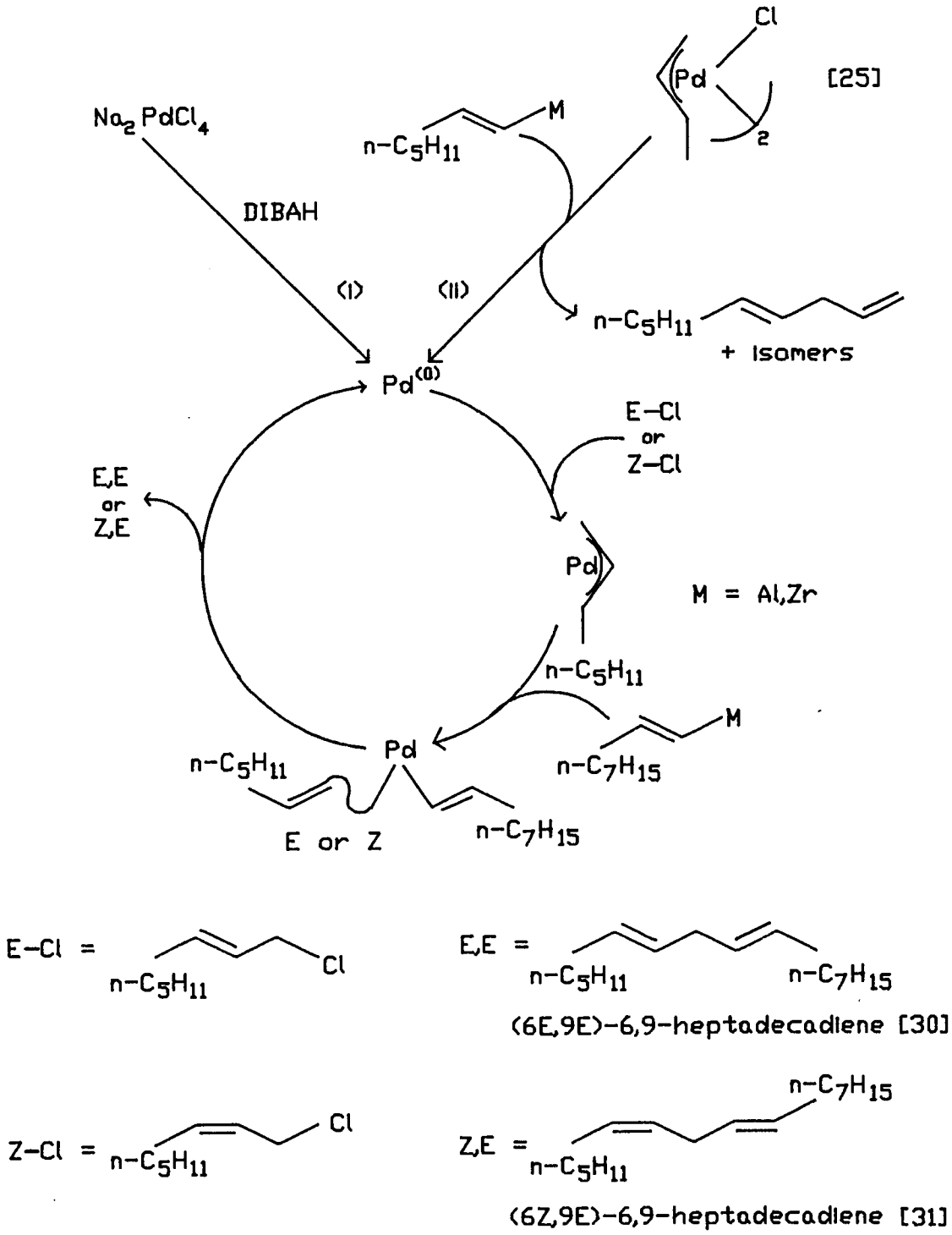


FIGURE 16: Cross coupling reactions using "ligand free" palladium catalysts

Table VIII. Use of a "ligand free" palladium catalyst[a] in cross coupling reactions of (*E*)-vinyl organometals[b] with allylic chloride[c].

Entry	*E*-Metal[c]	M.A. (eq.)	React. cond.	Regio-[d] isomer[h] %(rel)	*E*,*E*[e] %(rel)	*Z*,*E*[f] %(rel)	Homo-[g] coupled (rel)
1	$ZrCp_2Cl$	none	A	n.d.	n.d.	n.d.	n.d.
2		none	B	n.d.	n.d.	n.d.	n.d.
3		5	A	n.d.	n.d.	n.d.	some
4		5	B	2(1)	n.d.	7(3.5)	(11)
5	$Al(^iBu)_2$	none	A	n.d.	n.d.	n.d.	n.d.
6		none	B	n.d.	n.d.	n.d.	n.d.
7		5	A	1.7(1)	1.7(1)	2.6(1.5)	(2.7)
8		5	B	1.5(1)	2.9(2)	3.3(2.2)	(4.0)

[a] Prepared by reducing Na_2PdCl_4 with DIBAH; [b] Prepared by hydrometallation of 1-nonyne with DIBAH or $ZrCp_2HCl$; [c] *Z*-1-chloro-2-octene; [d] (4*E*)-3-pentyl-1,4-dodecadiene; [e] (6*E*,9*E*)-6,9-heptadecadiene; [f] (6*Z*,9*E*)-6,9-heptadecadiene; [g] (8*E*,10*E*)-8,10-octadecadiene; [h] Yields and relative amounts of product isomers determined by g.c.; n.d.= not detected, < 2 % by g.c.; M.A.= maleic anhydride; DIBAH = diisobutylaluminum hydride; A = -78 °C/3 hr.; B = -78°C - RT/12 hr

Reduction of allylic chlorides was presumed to be caused by a palladium hydride species formed during the removal of chloride with DIBAH. In order to ensure that reduction of allylic substrates was not simply due to unconsumed DIBAH, the experiment was repeated using two equivalents of DIBAH instead of four to generate the Pd^0 catalyst. As observed initially, a mixture of hydrocarbons was obtained which supports the view that palladium hydride is responsible for the reduction of allylic chlorides.

It was thought that in the absence of interfering $P\emptyset_3$ ligands it might be possible to successfully equilibrate allylpalladium complexes with maleic anhydride. Surprisingly, it was found that the presence of maleic anhydride completely suppressed the reduction of allylic chlorides. Unfortunately, the regioselectivity was poor in these cross

coupling reactions and yields were generally low (entries 4,7,8; TABLE VIII). It was noted, however, that cross coupling of (*Z*)-1-chloro-2-octene with the vinyl organozirconium reagent 21 was stereospecific; none of the coupled product containing the isomerized double bond was detected (entry 4; TABLE VIII). Two explanations for this observation seemed plausible: equilibration with maleic anhydride either induced cross coupling below the temperature of double bond isomerization (*vide supra*) or, alternatively, served to inhibit competing processes (palladium hydride reduction) thereby securing the supply of allylic chloride required for cross coupling. Based on these results it appeared that "ligand free" palladium was sufficiently reactive to catalyze cross coupling without isomerization of the allylic double bond. However, since the use of DIBAH in the preparation of this palladium catalyst interfered in the ensuing coupling steps an alternate method of preparing a "ligandless" palladium catalyst was investigated. The solution to this problem was found in the use of a bisallylpalladium dimer 25[40] which was reacted with a vinyl organometal to give the desired palladium species.

In the envisioned process, one mole equivalent of a vinyl organometallic reagent (based on palladium) reacts with the allylic ligand from the palladium dimer to generate the "ligandless" palladium catalyst. Oxidative addition of the allylic chloride, already present in solution, generates an allylpalladium intermediate which reacts with a second equivalent of the vinyl organometal to afford the 1,4 diene. This sequence is repeated until the supply of allylic chloride is exhausted (ii; FIGURE 16). The vinyl organozirconium reagent proved to be superior to the organometal based on aluminum as was manifested by higher yields,

Table IX. Palladium dimer[a] catalyzed cross coupling reactions of *E*-vinyl metals[b] with allylic chloride[c].

Entry	*E*-Metal[b]	Pd[a]	React. cond.	Regio-[d] isomer [h] %(rel)	*E*,*E*[e] %(rel)	*Z*,*E*[f] %(rel)	Homo-[g] coupled (rel)
1	$Al(^iBu)_2$	1 eq	-78 °C/1.5hr	3.3(1)	6(1.8)	n.d.	some(20)
			B	5.3(1)	11(2)	n.d.	some(9)
2	$ZrCp_2Cl$	1 eq	A	14(1)	n.d.	37(2.7)	some(6.6)
			B	18(1)	n.d.	37(2.1)	some(7.7)
3		20 %	A	5.4(1)	n.d.	11(2)	some(3)
			B	5.8(1)	n.d.	12(3.1)	some(3.5)
4		10 %	A	2.2(1)	n.d.	7(3.1)	some(4.6)
			B	2.3(1)	n.d.	7(3.1)	some(4.6)

[a] Di-μ-di(π-crotyl)dipalladium. Amounts based on allylic chloride; [b] Prepared by hydrometallation of 1-nonyne with DIBAH or $ZrCp_2Cl$; [c] *Z*-1-chloro-2-octene; [d] (4*E*)-3-pentyl-1,4-dodecadiene; [e] (6*E*,9*E*)-6,9-heptadecadiene; [f] (6*Z*,9*E*)-6,9-heptadecadiene; [g] (8*E*,10*E*)-8,10-octadecadiene; [h] Yields and relative amounts of product isomers determined by g.c.; n.d.= not detected, < 2 % by g.c.; A = -78 °C/15 min; B = -78 °C - RT/12 hr

Table X. Palladium dimer[a] catalyzed cross coupling reactions of *E*-1-nonenylzirconium[b] with allylic chloride[c] in the presence of maleic anhydride[d].

Entry	Allylic chloride[c]	Reaction conditions	Regio-[e] isomer [i] %(rel)	*E*,*E*[f] %(rel)	*Z*,*E*[g] %(rel)	Homo-[h] coupled (rel)
1	*E*-Cl	A	3.4(1)	6.4(2)	n.d.	some(2.1)
		B	6.1(1)	59(9.6)	n.d.	some(2)
2	*Z*-Cl	A	3.9(1)	n.d.	4.3(1)	some(1.7)
		B	19(7.3)	n.d.	68(26)	some(1)

[a] Di-μ-di(π-crotyl)dipalladium, stoichiometric amount; [b] Prepared by hydrometallation of 1-nonyne with $ZrCp_2HCl$; [c] *Z*-1-chloro-2-octene; [d] 5 equivalents used based on palladium; [e] (4*E*)-3-pentyl-1,4-dodecadiene; [f] (6*E*,9*E*)-6,9-heptadecadiene; [g] (6*Z*,9*E*)-6,9-heptadecadiene; [h] (8*E*,10*E*)-8,10-octadecadiene; [i] Yields and relative amounts of product isomers determined by g.c.; n.d.= not detected, < 2 % by g.c.; A = -78 °C/15 min; B = -78 °C - RT/12 hr

greater regioselectivity and less homocoupling in cross coupling reactions (TABLE IX).

It is interesting to note that overall yields increased with the amount of palladium catalyst used. This suggests that the catalytic activity of palladium is destroyed after one or two coupling cycles (entries 2,3,4; TABLE IX). Equilibration of these intermediates with maleic anhydride resulted in a dramatic increase in yield and an improvement in regioselectivity (TABLE X). The extent of homocoupling was also markedly reduced.

PALLADIUM CATALYZED CROSS COUPLING OF ORGANOMETALS WITH AN ALLYLIC CHLORIDE CONTAINING A τ-TRIALKYLSILYL GROUP

Although conditions had been found in which the double bond geometry of the starting materials was retained in the coupled product, these reactions were accompanied by formation of appreciable amounts of the branched diene. Since it was known that coupling reactions with τ,τ-disubstituted allylic chlorides were stereospecific, it was proposed that a higher degree of selectivity in coupling reactions with τ-monosubstituted allylic chlorides might be achieved by increasing the steric crowding at the τ position. For this purpose a τ-hydrogen was substituted with a dimethyl(phenyl)silyl group since it fulfilled the steric requirements for stereospecific coupling and could be removed stereospecifically in the coupled product[42]. Synthesis of this allylic derivative was achieved by the bismetallation of the propargyl alcohol 5 with dimethyl(phenyl)silyl-diethylzinc, which was prepared by

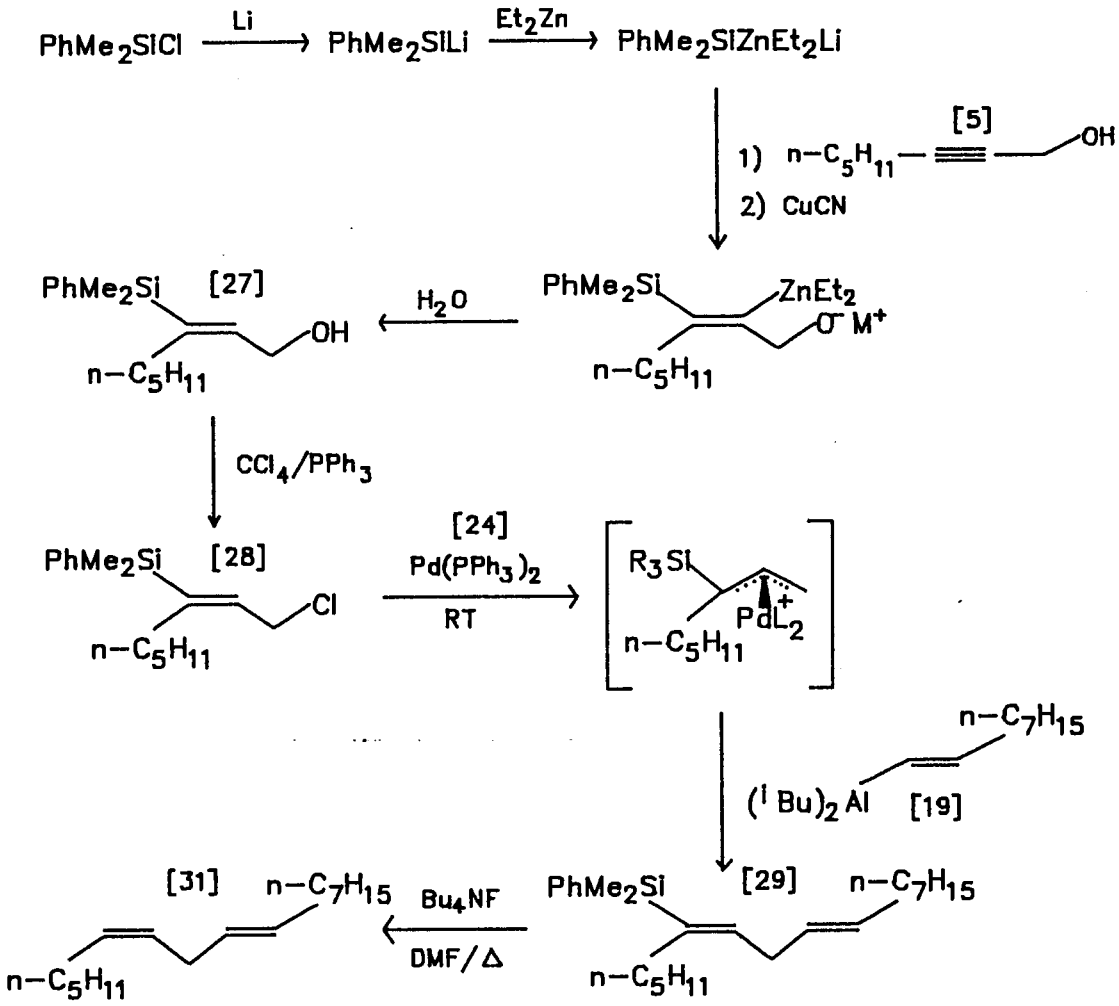


FIGURE 17: Stereospecific synthesis of (6*Z*,9*E*)-6,9-heptadecadiene

transmetallating dimethyl(phenyl)silyl-lithium with diethylzinc (FIGURE 17). Aqueous work up of the bismetallated adduct afforded the allylic alcohol 27 in 72% yield. Addition of the bismetal to the propargyl alcohol was regiospecific (100%). Treatment of 27 with $CCl_4/P\emptyset_3$ yielded the corresponding allylic chloride 28 (80%). This step was assumed to be stereospecific since analysis of the ^1H NMR spectra of the allylic chlorides 8 and 9 derived from the τ-monosubstituted allylic alcohols 6 and 7 revealed that double bond isomerization had not occurred. 28 was easily coupled with (*E*)-1-nonenyldiisobutylalane 19 to give the 1,4-diene 29 (88%) using the coordinatively unsaturated palladium catalyst 24.

Stereospecific replacement of silicon with hydrogen proved to be more challenging than anticipated. Treatment of 29 with HI or HF in various solvents (benzene, THF, acetonitrile) for prolonged periods at room temperature left the vinyl silane untouched. Refluxing these solutions resulted in the formation of unidentified decomposition products. It was thought that the the silyl group might be removed by enhancing the nucleophilicity of the fluoride ion using KF and a crown ether. However, this approach proved to be unsuccessful as well. Removal of the vinyl silane was finally accomplished by heating a solution of the 1,4-diene 29 and Bu_4NF in DMF for several hours. The "deprotected" (6*Z*,9*E*)-6,9-heptadecadiene 31 was obtained in 85% yield (by g.c.) without isomerization of the double bonds.

The silicon bearing diene 29 was found to isomerize to the corresponding conjugated diene over a period of two months at 4 °C. Removal of the trialkylsilyl group from the rearranged diene yielded (6*E*,8*E*)-6,8-heptadecadiene 34 and two other unidentified products.

CONCLUSION

Double bond isomerization of the allylic moiety in palladium intermediates derived from the oxidative addition of γ-monosubstituted allylic chlorides to palladium (0) catalysts is suppressed at low temperature. Experiments in which allylpalladium intermediates were captured with hydride revealed that isomerization occurs above -45 °C. The coordinatively unsaturated $Pd(P\emptyset_3)_2$ species was insufficiently reactive to achieve cross coupling below the isomerization temperature. Addition of $P\emptyset_3$ or maleic anhydride to these reactions inhibited cross coupling, presumably by blocking coordination sites and/or suppressing dissociative mechanisms involved in the coupling sequence. Cross coupling at temperatures below -45 °C necessitates the use of "ligand free" palladium catalysts.

Formation of a regioisomer resulting from "head to tail" coupling of allylpalladium species with vinyl organometals typically constituted 30% of total coupled products. In the best cases, a ratio of 5:1 was achieved in favour of coupling at C_1 over C_3 in the allylic fragment. The poor regioselectivity is due to similar rates of processes leading to carbon - carbon bond formation at C_1 and C_3. Substitution of a γ-hydrogen with a trialkylsilyl group in the γ-monosubstituted allylic chloride generates a rate difference to the extent that coupling occurs exclusively at C_1. Stereospecific removal of the vinyl silane in the coupled product afforded the unisomerized 1,4-diene.

EXPERIMENTAL

General

THF was freshly distilled under N_2 from Na containing benzophenone as an indicator. HMPA was distilled from CaH_2 and stored in the dark under N_2, over 3A and 10A molecular sieves. CH_3CN was distilled from CaH_2 and stored under N_2, over 4A molecular sieves. Air and moisture sensitive liquid reagents were stored under N_2 in vials or bottles sealed with rubber septa. Moisture was excluded from solid reagents by storing them in an evacuated descicator containing $CaCl_2$ as a drying agent. Chemicals obtained commercially were of analytical reagent quality.

Tetrakis(triphenylphosphine)palladium (0) [$Pd(P\emptyset_3)_4$] was stored under N_2 at -30 °C in a tinted glass vial (light sensitive). Bis(triphenylphosphine)palladium (II) chloride [$PdCl_2P\emptyset_3)_2$], Palladium (II) chloride [$PdCl_2$], Sodium tetrachloropalladate (II) [Na_2PdCl_4] and Di-μ-chloro-di-(π-crotyl)dipalladium were stored in a descicator at R.T. Palladium catalysts were handled under N_2.

Manipulations involving organometallic reagents were carried out under an atmosphere of argon or N_2. Addition of liquids without exposure to atmosphere was via syringe or transfer of reagents from one vessel to another under N_2 pressure through a double ended needle. Moisture sensitive solids were weighed and added in a glove bag containing an atmosphere of N_2 or argon. Reactions requiring moisture free conditions were carried out using either oven-dried (130 °C) or flamed glassware.

Flasks were stoppered with rubber septa and cooled to R.T. by flushing with N_2 directly prior to use. Syringes and needles were dried for at least 1 hr at 130^0C and cooled as assembled units by flushing with N_2.

Low temperature reactions were conducted by immersing reaction flasks in dewars containing the cryogen. In order to minimize fluctuations in reaction temperature during addition of reagents, solutions (at R.T.) were transferred by touching the tip of the double ended needle to the neck of the flask causing the added solution to flow down the sides of the reaction vessel. This method allowed rapid cooling of substrates before mixing with the palladium catalyst. Progression of reactions was monitored by gas chromatography by analyzing aliquots withdrawn from the reaction mixture at regular time intervals. Samples taken from reactions involving organometallic reagents were prepared for g.c. analysis by quenching with HCl (3 N) followed by extraction with n-pentane. The organic layer was then filtered through a bed of $MgSO_4$/celite (1:1) and analyzed immediately.

Heat stable compounds were purified by distillation at reduced pressure using a short path distillation apparatus. Smaller quantities (typically 100 mg) were purified using a kugelrohr distillation apparatus. Isolation of labile compounds was accomplished by flash chromatography using SiO_2 (230-400 mesh) or Al_2O_3 (80-200 mesh) as stationary phases. The N_2 pressure was adjusted to maintain a solvent flow of approximately 5 mL/min Column fractions were collected and analyzed by thin layer chromatography (T.L.C.). Spots were made visible

by charring developed plates sprayed with a solution of ceric sulfate (1 %), molybdic acid (1.4 %) in H_2SO_4 (10 %). Purification of dienes was achieved by preparative T.L.C. using SiO_2 powder impregnated with $AgNO_3$ (20 %) as the stationary phase. Freshly prepared plates were dried in the dark at R.T. overnight and activated at 150 °C for 2 hr directly prior to use. Crude diene extracts were diluted to 50 % in diethyl ether and these solutions streaked onto the bottom of T.L.C. plates using a syringe applicator. Plates were developed in hexane and allowed to air dry for several minutes before spraying with a solution of Rhodamine 6G (1 % in acetone). Bands were detected under U.V. light. The desired sections were then removed with a spatula and extracted exhaustively with diethyl ether by suction filtration. Removal of solvent on a rotary evaporator at reduced pressure afforded the pure diene (typically > 90 %). Purified dienes were stored under N_2 at 4 °C since they were found to slowly decompose at R.T.

Gas chromatographic analyses were carried out using a Hewlett Packard Model 5890A chromatograph equipped with a F.I.D. and a DB-1 capillary column (length: 15 m, film thickness: 0.25 μm, id: 0.25 mm). Peak integration was carried out on a Hewlett Packard Model 3392A integrator. Mass spectral analyses were performed on a Hewlett Packard Model 5985B GC/MS/DS using electron impact as the method of ionization (70 eV). Gas phase I.R. spectra were obtained using a Bruker GC/FT/IR Model IFS85. ^1H and ^{13}C NMR spectra were analyzed on a Bruker Model WM400 NMR spectrometer. Values are reported relative to δ TMS (= 0). ^{13}C NMR data are proton noise decoupled. ^1H NMR data are reported in the following

abbreviated form: number of protons (xH), proton position within the molecule (C_x), peak multiplicity and coupling constants where appropriate. Proton assignments are made by using a C and a subscript to denote the location within the molecule. Elemental analyses were performed by M.K.Yang of Simon Fraser University. Boiling points are uncorrected.

Preparation of octene isomers

1-Octene (1)[38] To a stirred aliquot of 1-octyne (0.5 g, 45 mmol) under N_2 was added dropwise by syringe 46 mL of DIBAH (1 M in hexanes, 46 mmol) at 0 °C. Stirring was continued for an additional 10 min at 0 °C before heating to 75 °C for 2.5 hr. The reaction was then cooled to R.T., placed under high vacuum (0.2 mmHg) and stirred for several minutes in order to remove any unreacted 1-octyne. The flask was flushed with N_2 and n-pentane (10 mL) was added to the stirred solution. This sequence was repeated twice and the solution then quenched at 0 °C by addition of brine (10 mL) followed by HCl (3 N, 5 mL). The organic layer was separated, washed with brine (3 x 50 mL) and filtered through a bed of anhyd $MgSO_4$. Solvent was removed to give an orange oil. Bulb to bulb distillation at 25 °C (0.25 mmHg) lit. bp: 121.3 °C (760 mmHg)[32] gave 1 (0.31 g, 61 %) as a colourless liquid. FT/IR (vapour) 3084(w), 2935(s), 2870(m), 1643(w), 1462(w), 995(w), 914(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.8 (1 H, C_2, ddt, J_{trans} = 17 Hz, J_{cis} = 10 Hz, $J_{2,3}$ = 7 Hz), 5.0 (1 H, $C_{1\ (c)}$, ddt, J_{trans} = 17 Hz, J_{gem} = 2 Hz, $J_{1,3}$ = 2 Hz), 4.9 (1 H,

$C_{1(t)}$, ddt, J_{cis} = 10 Hz, J_{gem} = 2 Hz, $J_{1,3}$ = 1.5 Hz), 2.1 (2 H, C_3, dtt, J = 7 Hz, $J_{1,3}$ = 1.5 Hz), 1.37 (2 H, C_4, quint, J = 7 Hz) 1.37-1.2 (6 H, $C_{5,6,7}$, m) 0.9 (3 H, C_9, 0.9 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 112(16, M^+), 97(8), 84(35), 83(60), 82(14), 70(100), 69(55), 56(43), 55(60), 43(25), 42(17), 41(29).

2-Octyne (2) To a stirred solution (-20 °C, under N_2) of 1-heptyne (8.8 g, 92 mmol) in diethyl ether (100 mL) was added dropwise by syringe 40 mL of n-BuLi (2.4 M in hexane, 94 mmol). After 10 min MeI (6 mL, 97 mmol) was added dropwise by syringe followed by slow addition of HMPA (20 mL). The solution was stirred for an additional 5 min at -20 °C and then warmed to R.T. over a period of 1 hr. The solution was washed with brine (3 x 50 mL) and the organic layer filtered through a bed of anhyd $MgSO_4$. Solvent was removed leaving a yellow oil which distilled at 135 °C (760 mmHg) lit. bp: 138 °C (760 mmHg)[32] to give 2 (7.81 g, 77 %) as a colourless liquid. FT/IR (vapour) 2939(s), 2878(m), 1466(w), 1381(w), 1335(w), 640(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.1 (2 H, C_4, tquart, $J_{4,5}$ = 7 Hz, $J_{1,4}$ = 2.5 Hz), 1.5 (3 H, C_1, t, J = 2.5 Hz), 1.3 (2 H, C_5, quint, J = 7 Hz) 1.4-1.25 (4 H, $C_{6,7}$, m) 0.8 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 110(5, M^+), 95(62), 81(100), 67(63), 54(35), 53(34), 41(36).

(*E*)-2-Octene (3) To a cooled flask (-78 °C) containing liquid NH_3 under N_2 was added Na (0.3g, 13 mmol) and alkyne 2 (0.5 g, 4.5 mmol). After refluxing at -33 °C for 2.5 hr 10 mL of water was added dropwise by pipette followed by addition of n-pentane (50 mL). The solution was

warmed to R.T. and the organic layer separated and washed with brine (2 x 10 mL). The organic fraction was filtered through a bed of anhyd $MgSO_4$ and solvent removed to give a clear liquid. Bulb to bulb distillation at 23 °C (0.25 mmHg) lit. bp: 125.0 °C (760 mmHg)[32] gave 3 (0.32 g, 73 %) as a colourless liquid. FT/IR (vapour) 2934(s), 2869(m), 1464(w), 1383(w), 966(w), 766(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.55-5.35 (1 H, C_2, dqt, $J_{2,3}$ = 15.5 Hz, $J_{1,2}$ = 5.5 Hz, $J_{2,4}$ = 1.5 Hz; 1H, C_3, dtq, $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 5.5 Hz, $J_{1,3}$ = 1.5 Hz), 1.96-1.93 (2 H, C_4, bm), 1.69-1.51 (3 H, C_1, m), 1.36-1.18 (6 H, $C_{5,6,7}$, bm), 0.9 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 112(72, M^+), 97(5), 83(45), 70(91), 69(51), 67(10), 57(19), 56(48), 55(100), 42(10), 41(34).

(*Z*)-2-Octene (4)[38] To a stirred aliquot of alkyne 2 (0.5 g, 45 mmol) under N_2 was added dropwise by syringe 46 mL DIBAH (1 M in hexane, 46 mmol) at 0 °C. Stirring was continued for 10 min at 0 °C before heating to 75 °C for 3 hr. The solution was then cooled to 0 °C and quenched with brine (10 mL) followed by slow addition of HCl (3 N, 5 mL). The organic layer was separated, washed with brine (3 x 50 mL) and filtered through a bed of anhyd $MgSO_4$. Solvent was removed to give a yellow oil. Bulb to bulb distillation at 25 °C (0.25 mmHg) lit. bp: 125.6 °C (760 mmHg)[32] gave 4 (0.32 g, 71 %) as a colourless liquid. FT/IR (vapour) 3024(m), 2937(s), 1840(w), 1664(w), 1464(w), 982(w), 924(w), 856(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.5 (1 H, C_2, dqt, $J_{2,3}$ = 11 Hz, $J_{1,2}$ = 6.5 Hz, $J_{2,3}$ = 1.5 Hz), 5.4 (1 H, C_3, dtq, $J_{2,3}$ = 11 Hz, $J_{3,4}$ = 6.5 Hz, $J_{1,3}$ = 1.5 Hz), 2.0 (2 H, C_4, dt, J = 7 Hz), 1.6 (3 H, C_1, ddt, $J_{1,2}$ = 6 Hz, $J_{1,3}$ = 1.5 Hz, $J_{1,4}$ = 1 Hz), 1.4-1.2 (6 H, $C_{5,6,7}$, m), 0.8 (3 H, C_8, t, J = 7 Hz);

mass spectrum, m/e (relative intensity) 112(100, M^+), 97(6), 84(25), 83(54), 70(87), 69(52), 67(12), 56(39), 55(78), 53(10), 41(33).

Preparation of allylic substrates

2-Octyn-1-ol (5)[18] To a stirred solution of 1-heptyne (25 g, 240 mmol) in THF (250 mL) at 0 °C was added under N_2 by syringe 100 mL of n-BuLi (2.4 M in hexanes, 240 mmol). After stirring for 15 min at 0 °C paraformaldehyde (10.5 g, 350 mmol) was added and the solution refluxed for 3.5 hr. The cooled reaction mixture was then quenched with 200 mL of ice water, the aqueous layer was separated and extracted with diethyl ether (4 x 50 mL). The combined organic fractions were filtered through a bed of anhyd $MgSO_4$ and concentrated to give a crude yellow oil. The oil was distilled at 55 °C (0.35 mmHg) lit. bp: 91 °C (12 mmHg)[30] to give 5 (2.7 g, 83 %) as a colourless liquid. FT/IR (vapour): 3670(w), 2941(s), 2880(m), 2222(w), 1389(m), 1138(w), 1013(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.30 (1 H, OH, s), 4.25 (2 H, H_2, dt, $J_{1,2}$ = 6 Hz, $J_{2,3}$ = 2.5 Hz), 2.28 (2 H, C_3, tt, $J_{3,4}$ = 7 Hz, $J_{2,3}$ = 2.5 Hz), 1.48 (2 H, C_4, J = 7 Hz), 1.42-1.25 (4 H, $C_{5,6}$, m), 0.88 (3 H, C_7, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 125(1, M^+), 111(10), 95(55), 93(63), 83(61), 70(76), 69(57), 67(87), 55(100), 41(97).

(*E*)-2-Octen-1-ol (6)[20] To an unquenched solution of propargyl alcohol 5 prepared as above, was added at 0 °C $LiAlH_4$ (9.5 g, 260 mmol). The solution was stirred for 10 min at 0 °C and warmed to R.T. before heating

to reflux for 45 min. The solution was then cooled to 0 °C and quenched by slow addition HCl (3 N, 50 mL) followed by brine (100 mL). After stirring at R.T. for 10 min the aqueous layer was separated and extracted with n-pentane (4 x 50 mL). These extracts were combined with the organic layer and filtered through a bed of anhyd $MgSO_4$. Removal of solvent gave a yellow oil which was distilled at 51 °C (0.2 mmHg) lit. bp: 94-95 °C (13 mmHg)[29] to give 6 (22.8 g, 65.8 %) as a colourless liquid. FT/IR (vapour) 3659(w), 3479(m), 2935(s), 2872(m), 1460(w), 1385(w), 1207(w), 1086(w), 1001(m), 974(m), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.68 (1 H, C_4, dtt, $J_{3,4}$ = 15.5 Hz, $J_{4,5}$ = 6.5 Hz, $J_{2,4}$ = 1 Hz), 5.61 (1 H, C_3, dtt, $J_{3,4}$ = 15.5 Hz, $J_{2,3}$ = 6.5 Hz, $J_{3,5}$ = 1 Hz), 4.07 (2 H, C_2, dd, $J_{2,3}$ = 5.5 Hz, $J_{2,4}$ = 1 Hz), 2.03 (2 H, C_5, dt, J = 7 Hz), 1.83 (1 H, C_1, s), 1.37 (2 H, C_6, quint, J = 7 Hz), 1.33-1.22 (4 H, $C_{7,8}$, m), 0.89 (3 H, H_9, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 110(4, M^+ -H_2O), 99(2), 95(9), 81(25), 67(26), 57(100), 55(40), 43(38), 41(76).

(*Z*)-2-Octen-1-ol (7)[19] A solution of $NaBH_4$ (approximately 1 M) was prepared by dissolving $NaBH_4$ (4.0 g) in a solution of absolute EtOH (95 mL) and NaOH (2 N, 5 mL). The solution was stirred for 30 min and the small amount of undissolved material removed by suction filtration through a sintered glass filter. An oxygen free solution of nickel(II) acetate was prepared by sparging a vigorously stirred solution of $Ni(OAc)_2 \cdot 4H_2O$ (124 g, 5 mmol) in 95 % EtOH (40 mL) with N_2 at R.T. for 5 min To this mixture was then added in one portion 5 mL of a freshly prepared solution of $NaBH_4$ which caused the immediate formation of a black suspension. After hydrogen evolution had ceased (approx. 5 min)

ethylene diamine (0.66 mL, 10 mmol) was added and stirred for several minutes before adding propargyl alcohol **5** (10 g, 80 mmol). Reduction was achieved by continuous sparging of the stirred solution with H_2 at R.T. for 4 hr. Then n-pentane (50 mL) was added and stirring continued for several minutes before the solution was filtered through a bed of anhyd $MgSO_4$. Solvent was removed to give a green oil which was distilled at 50 °C (0.25 mmHg) lit. bp: 90 °C (8-10 mmHg)[31] to give **7** (7.57 g, 74 %); FT/IR (vapour) 3655(w), 3022(w), 2966(s), 2935(s), 2878(m), 1657(w), 1464(w), 1373(w), 1024(m), 725(w), cm^{-1}; ^1H NMR (400 M Hz, $CDCl_3$) δ 5.58 (2 H, C_3, dtt, $J_{3,4}$ = 11 Hz, $J_{2,3}$ = 6.5 Hz, $J_{3,5}$ = 1.5 Hz), 4.18 (2 H, C_2, ddt, $J_{2,3}$ = 6 Hz, $J_{2,4}$ = 1 Hz, $J_{2,5}$ = 0.5 Hz), 2.05 (2 H, C_5, dt, J = 7 Hz), 1.38 (2 H, C_6, quint, J = 7 Hz) 1.33-1.22 (4 H, $C_{7,8}$, m) 0.9 (3 H, C_9, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 128(< 0.5, M^+), 110(11), 95(9), 82(20), 81(31), 69(27), 68(31), 67(34), 57(100), 55(47), 54(34), 43(39), 41(88).

(*E*)-1-Chloro-2-Octene (**8**)[21] To a stirred solution of allylic alcohol **6** (2.4 g, 18.8 mmol) in CCl_4 (10 mL) at R.T. was added $P\emptyset_3$ (6 g, 22.9 mmol). After 5 min CH_3CN (10 mL) was added to the solution which caused the temperature to rise to approx. 40 °C. Gas chromatographic analysis of an aliquot (pentane extract) revealed that conversion to the allylic chloride was complete after 30 min; n-Pentane (20 mL) was then added and stirring continued for 10 min The mixture was washed with brine (2 x 50 mL) and $P\emptyset_3$ as well as $\emptyset_3PO$ were separated from the organic layer by crystallization at 4 °C for several hours followed by filtration through a bed of anhyd $MgSO_4$. The solvent was removed to give a colourless liquid

which was distilled at 24 °C (0.035 mmHg) to yield **8** (2.2 g, 80.4 %). FT/IR (vapour) 2968(s), 2937(s), 2870(m), 1666(w), 1452(w), 1254(w), 964(m), 694(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (1 H, C_2, dtt, $J_{2,3}$ = 15.5 Hz, $J_{1,2}$ = 6.5 Hz, $J_{2,4}$ = 1 Hz), 5.61 (1 H, C_3, dtt, $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 7 Hz, $J_{1,3}$ = 1.5 Hz), 4.04 (2 H, C_1, ddt, $J_{1,2}$ = 6.5 Hz, $J_{1,3}$ = 1.5 Hz, $J_{1,4}$ = 0.5 Hz), 2.06 (2 H, C_4, dt, J = 7 Hz), 1.38 (2 H, C_5, quint, J = 7 Hz), 1.37-1.22 (4 H, $C_{6,7}$, m), 0.88 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 146(4, M^+), 118(2), 110(3), 106(3), 104(8), 81(15), 69(38), 55(61), 41(100).

(*Z*)-1-Chloro-2-Octene (**9**)[21] Synthesis of **9** was carried out in a fashion analogous to the preparation of allylic chloride **8** starting with allylic alcohol **7**: bp 24 °C (0.035 mmHg); yield, (2.10 g, 78 %). FT/IR (vapour) 3032(w), 2968(s), 2937(s), 2871(m), 1651(w), 1460(w), 1256(w), 768(m), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.63 (2 H, $C_{2,3}$, m, $J_{2,4} = J_{1,3}$ = 6.5 Hz, $J_{2,3}$ = 11 Hz), 4.11 (2 H, C_1, bd, $J_{1,2}$ = 7 Hz, $J_{1,4}$<0.5 Hz), 2.43 (2 H, C_4, dt, J = 7 Hz), 1.36 (2 H, C_5, quint, J = 7 Hz), 1.37-1.23 (4 H, $C_{6,7}$, m, J = 7 Hz) 0.85 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 146(3, M^+), 118(1), 111(2),110(4), 104(6), 95(4), 81(20), 70(37), 69(35), 68(24), 67(24), 55(64), 54(51), 53(31), 41(100).

(*E*)-1-acetoxy-2-octene (**10**) To the allylic alcohol **6** (5 g, 39 mmol) was added acetic anhydride (4.5 g, 44 mmol) followed by dropwise addition of pyridine (3.5 g, 44 mmol) at R.T. The reaction is exothermic as evidenced by a rise in temperature of the reaction mixture during addition of pyridine. After 40 min, excess reagents were removed on a

rotary evaporator at reduced pressure. The residue was distilled to yield **10** (6.1 g, 92 %). Bp: 41 °C (0.025 mmHg). FT/IR (vapour) 2966(m), 2935(m), 2868(w), 1763(s), 1456(w), 1367(w), 1231(s), 1024(w), 968(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (1 H, C_2, dtt, J_{trans} = 15.5 Hz, J_{1-2} = 6.5 Hz, J_{2-4} = 1.3 Hz), 5.57 (1 H, C_3, dtt, J_{trans} = 15.5 Hz, J_{3-4} = 6.5 Hz, J_{1-3} = 1.3 Hz), 4.52 (2 H, C_1, dd, J_{1-2} = 6.5 Hz, J_{1-3} = 1 Hz), 2.08 (3 H, $CH_{3\ acetate}$, s), 2.05 (2 H, C_4, quart, J = 6 Hz), 1.33-1.2 (4 H, $C_{6,7}$, m), 0.88 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 170(< 0.5, M^+), 128(6), 110(9), 81(24), 69(16), 68(18), 67(23), 57(10), 55(18), 54(30), 43(100), 41(36).

(*Z*)-1-acetoxy-2-octene (**11**) This compound was prepared (6.11 g, 92 %) in an analogous manner to allylic acetate **10** starting with allylic alcohol **7**: bp 42 °C (0.075 mmHg); FT/IR (vapour) 3032(w), 2968(m), 2935(m), 2870(w), 1761(s), 1462(w), 1377(w), 1231(s), 1028(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.65 (1 H, C_2, dtt, J_{cis} = 11 Hz, J_{1-2} = 7 Hz, J_{2-4} = 1.5 Hz), 5.53 (1 H, C_3, dtt, J_{cis} = 11 Hz, J_{3-4} = 7 Hz, J_{1-3} = 1.5 Hz), 4.62 (2 H, C_1, dd, J_{1-2} = 7 Hz, J_{1-3} = 1.5 Hz), 2.08 (2 H, C_4, quart, J = 6 Hz), 2.05 (3 H, CH_3 acetate, s), 1.35 (2 H, C_5, quint, J = 6 Hz), 1.33-1.23 (4 H, $C_{6,7}$, m), 0.85 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 170(< 0.5, M^+) 128(5), 110(8), 100(3), 99(4), 95(7), 82(14), 81(24), 69(14), 68(19), 67(24), 55(17), 54(31), 43(100), 41(36).

(*E*)-1-bromo-2-octene (**12**)[33] To a 250 mL flask equipped with a stirbar and charged with THF (50 mL) was added, under N_2, $ZnBr_2$ (2.64 g, 11.7

mmol) followed by $P\emptyset_3$ (9.3 g, 35.5 mmol). After the solids dissolved allylic alcohol **6** (1.5 g, 11.7 mmol) was added followed by dropwise addition of diethyl azodicarboxylate (5.54 mL, 35.2 mmol). The solution was stirred at R.T. for 30 min and chilled at 4 °C overnight. The resultant crystals were removed by centrifugation (1000 rpm, 2 min) and washed with cold (-78 °C) THF (3 x 20 mL). The organic fractions were combined and THF removed on a rotary evaporator under reduced pressure at 30 °C. Purification of the crude oil by flash chromatography (id: 3 cm, column length: 15 cm, eluant: 1 % EtOAc in hexane) yielded **12** as the pale yellow liquid (1.9 g, 85 %); FT/IR (vapour) 2968(s), 2935(s), 2868(m), 1663(w), 1448(w), 1385(w), 1207(m), 962(m), 733(w), cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.58 (1 H, C_2, dtt, J_{2-3} = 10.5 Hz, J_{1-2} = 1.5 Hz, J_{2-4} = 2 Hz), 5.34 (1 H, C_3, dt, J_{2-3} = 10.5 Hz, J_{3-4} = 8 Hz), 3.85 (2 H, C_1, d, J = 8.5 Hz), 1.88 (2 H, C_4, dt, J_{3-4} = 8 Hz, J_{4-5} = 7 Hz), 1.25 (6 H, C_{5-7}, bm), 0.98 (3 H, C_8, s, J = 7 Hz); mass spectrum, m/e (relative intensity) 190/192(47, M^+), 165(2), 148/150(10), 147/149(9), 135/137(75), 111(27), 69(100), 55(24), 41(18).

(*Z*)-1-bromo-2-octene (13)[33] This compound was prepared (1.5 g, 67 %) from allylic alcohol **7** following the same procedure for the synthesis of allylic bromide **12**; FT/IR (vapour) 3034(w), 2968(s), 3935(s), 2872(m), 1460(w), 1391(w), 1209(m), 748(w), 665(w), cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.5 (1 H, C_2, dtt, J_{2-3} = 15 Hz, J_{1-2} = 7 Hz, J_{2-4} = 1.2 Hz), 5.37 (1 H, C_3, dtt, J_{2-3} = 15 Hz, J_{3-4} = 7 Hz, J_{1-3} = 1 Hz), 3.59 (2 H, C_1, dd, J_{1-2} = 7 Hz, J_{1-3} = 1 Hz), 1.82 (2 H, C_4, dt, J = 7 Hz), 1.18 (6 H, C_{5-7}, bm), 0.91 (3 H, C_8, t, J = 7 Hz); mass spectrum, m/e (relative intensity)

190/192(60, M^+), 148/150(20), 133/135(35), 121(22), 111(22), 69(100), 55(23), 41(18).

Preparation of (*E*)-vinyl organometallic reagents

(*E*)-1-nonenyl-1,3,2-benzodioxaborole (14)[34] To a solution of 1-nonyne (13.1 g, 25 mmol) in THF (50 mL) was added under N_2 catecholborane (3 g, 25 mmol). The solution was stirred at 80 - 90 °C for 2 hr and allowed to cool to R.T. This solution was distilled directly (no work up) to afford a clear transparent liquid 14 (4.9 g, 80 %); bp 105 - 108 °C (0.05 mmHg); ^{1}H NMR (400 MHz, C_6D_6) δ 7.13 (1 H, C_2, dt, J_{trans} = 17.5 Hz, J_{2-3} = 6.5 Hz), 7.13-7.07 (2 H, benzene, m), 6.88-6.81 (2 H, benzene, m), 5.88 (1 H, C_1, dt, J_{trans} = 17.5 Hz), 2.03 (2 H, C_3, dquart, $J_{(2,4-3)}$ = 6.5 Hz, J_{1-3}-1.5 Hz), 1.35-1.2 (4 H, $C_{4,5}$, bm), 1.2-1.08 (6 H, C_{6-8}, bm), 0.85 (3 H, C_9, t, J = 7 Hz).

(*E*)-1-iodo-1-nonene (15)[35] To a cooled solution of bronic ester 14 was added 25 mL of water and this mixture stirred at R.T. for 2 hr to effect the hydrolysis of the boronic ester. The white gel thus formed was filtered and rinsed with ice-cold water. The solid material was then dissolved in diethyl ether (50 mL) followed by sequential addition of NaOH (3 N, 50 mL) and I_2 (60 mL, 0.5 M in diethyl ether, 30 mmol) at 0 °C. After 30 min the solution was warmed to R.T. and excess I_2 removed by addition of $Na_2S_2O_8$. The organic layer was separated, washed with brine (2 x 50 mL) and the solvent removed on a rotary evaporator. The crude oil was purified by distillation at reduced pressure to yield 15 (3.9 g, 62 %

based on 1-nonyne [13.1 g, 25 mmol]); bp 42 - 44 °C (0.02 mmHg); FT/IR (vapour) 3057(w), 2935(s), 2866(m), 1607(w), 1458(w), 1354(w), 1211(w), 714(w), 660(w), cm^{-1}; ^1H NMR (400 M Hz, C_6D_6) δ 6.36 (1 H, C_2, dt, J_{1-2} = 14.5 Hz, J_{2-3} = 7.5 Hz), 5.74 (1 H, C_1, dt, J_{1-2} = 14.5 Hz, J_{1-3} = 1.5 Hz), 1.68 (2 H, C_3, dquart, $J_{(2,4)-3}$ = 7.5 Hz, J_{1-3} = 1.5 Hz), 1.29 (2 H, C_5, quint, J = 7 Hz), 1.25-1.07 (8 H, C_{5-8}, m), 0.97 (3 H, C_9, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 250(98, M^+), 211(5), 196(3), 183(11), 167(73), 154(52), 141(2), 127(20), 109(3), 97(3), 83(49), 69(100), 55(76), 41(36).

(*E*)-1-nonenylmercuric acetate (16)[36] To a cooled solution containing $Hg(OAc)_2$ (0.045 g, 0.14 mmol) in THF (5 mL) was added under N_2 in one portion boronic ester 14 (0.035 g, 0.14 mmol). After stirring at 0 °C for 5 min the $Hg(OAc)_2$ had disappeared indicating that the formation of 16 was complete. Nonenylmercuric acetate 16 was used directly in cross coupling reactions by transferring the solution using a double ended needle.

(*E*)-1-nonenylmercuric chloride (17)[36] Prepared by pouring a solution of 16 into 100 mL of cold water saturated with NaCl. A precipitate formed immediately which was collected by suction filtration and subsequently rinsed with small portions of ice cold water. The white crystals were dried under high vacuum and stored under N_2. Yield: (1.3 g, 89 % based on 1 g 14)

(*E*)-1-nonenylzinc chloride (18)[37] To a cooled solution (-78 °C) of

vinyl iodide 15 (0.04 g, 0.163 mmol) in dry Et_2O (10 mL) was added dropwise under N_2 0.068 mL n-BuLi (2.4 M in hexane, 0.163 mmol). Gas chromatographic analysis of the reaction mixture after 30 min at -78 °C revealed the only organic products of the reaction to be iodobutane, 1-nonene and a trace of unreacted 15. Prolonged reaction times did not increase yields of the vinyl lithium intermediate. To this mixture was then added dropwise via double ended needle 2.3 mL of an anhyd solution of $ZnCl_2$ (0.73 M in Et_2O, 20.169 mmol) and allowed to warm to R.T. over a 15 min period. Anhyd $ZnCl_2$ was prepared by melting $ZnCl_2$ under high vacuum and dissolving the cooled solid in dry ether under N_2. The reaction was accompanied by formation of a yellow-white coloured precipitate which was presumed to be LiCl. This solution was used directly in cross coupling reactions by transferring with a double ended needle.

(*E*)-(1-nonenyl)diisobutylalane (19)[38] To a 25 mL round bottom flask equipped with a stirbar and a reflux condenser was added under N_2 1-nonyne (1 g, 8 mmol) followed by dropwise addition of 8 mL diisobutylaluminum hydride (1 M in hexane, 8 mmol) over a period of several minutes. The stirred solution was then refluxed for 2 hr while ensuring that the temperature did not exceed 50 °C (significant amounts of dialuminum adduct formation at higher temperatures!). Gas chromatographic analysis of a hydrolyzed aliquot (3 N HCl) revealed the presence of 10 % nonane (hydrolysis of the di-adduct), ca. 85 % 1-nonene (hydrolysis of the mono-adduct) and a small amount of unreacted 1-nonyne. This solution was used directly without purification since the by-

products were found to be unreactive towards π-allylpalladium complexes in cross coupling reactions. Solutions were transferred under N_2 using a double ended needle.

Lithium-(*E*)-(1-nonenyl)diisobutylmethylalanate (20)[38] To a stirred solution of vinylalane **19** at 0 °C was added dropwise under, N_2, 5.3 mL MeLi (1.5 M in Et_2O, 8 mmol). The reaction mixture was warmed to R.T. and used directly in cross coupling reactions by transferring the solution under N_2 using a double ended needle.

(*E*)-1-nonenylchlorobis (η^5-cyclopentadienyl) zirconium (21)[39] To a solution of $ZrCp_2HCl$ (0.2 g, 0.78 mmol) in dry benzene (10 mL) was added under N_2 1-nonyne (0.1 g, 0.78 mmol) and the whole stirred at R.T. for 2.5 hr. The initial pale yellow colour changed to deep orange during this period. Gas chromatographic analysis of a worked up aliquot revealed that most of the alkyne had reacted to form **21** as the sole product. **21** was used directly in cross coupling reactions by transferring the solution under N_2 using a double ended needle.

Alternate approach to the synthesis of 21 To the vinyl lithium intermediate (0.15 g, 0.6 mmol) prepared as in the synthesis of vinylzinc chloride **18** was added at -78 °C, under N_2, a solution of $ZrCp_2Cl_2$ (0.17 g, 0.6 mmol in 5 mL THF). The reaction was allowed to warm to R.T. overnight and used directly in cross coupling reactions by transferring with a double ended needle.

Attempted preparation of (*Z*)-vinyl organometallic reagents

1-iodo-1-nonyne (22) To a stirred solution of 1-nonyne (2.48 g, 20 mmol) in THF (50 mL) was added at -78 °C, under N_2, 8.5 mL n-BuLi (2.5 M in hexane, 22 mmol) dropwise by syringe. After 15 min a solution of I_2 (6 g, 24 mmol) in THF (20 mL) was slowly added and stirring continued for 30 min at -78 °C. The reaction mixture was then warmed to R.T. and unreacted I_2 removed by addition of aqueous $Na_2S_2O_8$. n-Pentane (50 mL) was then added and the solution stirred for an additional 5 min. The organic layer was separated, washed with brine (2 x 50 mL) and the solvent removed at reduced pressure on a rotary evaporator. The resultant crude oil was distilled at 51 - 55 °C (0.075 mmHg) to give a clear transparent liquid 22 (4.5 g, 90 %) and stored at -20 °C. FT/IR (vapour) 2939(s), 2868(m), 1464(w), 1329(w), 731(w), cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 2.09(3H, C_3, t, J = 7 Hz), 1.35-1.05(10H, C_{4-8}, m), 0.96(3H, C_9, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 250(23, M^+), 207(23), 193(24), 180(78), 165(23), 81(100), 67(48), 55(27).

(*Z*)-1-iodo-1-nonene (23) To a neat sample of alkynyl iodide 22 (4 g, 16 mmol) was added at R.T., under N_2, 16 mL DIBAH (1M in hexane, 16 mmol). After the exothermic reaction (30-40 °C) had subsided the solution was stirred at R.T. for 1 hr. Gas chromatographic analysis revealed that most of the alkynyl iodide had been converted to a mixture of 1-nonyne, 1-nonene and nonane. Other unidentified decomposition products were formed in smaller amounts.

Palladium catalysts

Preparation of $Pd(P\emptyset_3)_2$ (24)[26] The following procedure is representative: To a stirred solution of $PdCl_2(P\emptyset_3)_2$ (0.2 g, 0.28 mmol) was added at R.T., under N_2, 0.57 mL DIBAH (1M in THF, 0.57 mmol = 2 equiv.) dropwise by syringe. Formation of the black $Pd(P\emptyset_3)_2$ was rapid and only a few yellow $PdCl_2(P\emptyset_3)_2$ crystals remained after stirring at R.T. for 10 min. The solution was then cooled to the desired temperature by immersing the reaction flask in a cooling bath.

Di-μ-chloro-di-(π-crotyl)dipalladium (25)[40] A solution containing $PdCl_2$ (1 g, 5.6 mmol), NaCl (0.66 g, 11.4 mmol), H_2O (1.5 g, 83 mmol) and crotyl chloride (2.3 g, 25 mmol) in methanol (30 mL) was sparged with CO (2.5 mL/hr., 1 atm.) at R.T. for 3 hr. During the course of the reaction the solution changed colour from brown-red to yellow. The mixture was then poured into 300 mL of water and extracted with CH_3Cl (4 x 50 mL). The organic fractions were combined and the solvent removed on a rotary evaporator under reduced pressure. The resultant black residue was dissolved in a minimum of warm benzene (ca.40 °C) and purified by flash chromatography (alumina absorption Fisher A-540 AL_2O_3 80-200 mesh, id: 1.5 cm, column length: 20 cm, eluant: benzene). The combined column fractions were evaporated to dryness on a rotary evaporator and the remaining yellow-green crystals washed with small portions of cold n-pentane. Yield: (1 g, 90 % based on $PdCl_2$[1 g, 5.6 mmol]); mp: 137.5 - 138.5 °C, lit. mp: 136 - 137 °C[40]; IR (solution in $CHCl_3$) 3683(w),

3622(w), 3019(s), 2967(m), 2895(w), 2431(w), 2400(m), 1523(m), 1475(m), 1423(m), 1390(w), 1333(w), 1046(m), 1031(m), 929(m), 877(w), 849(w), 668(s), 627(m), 496(w), 361(s), cm^{-1}.

Hydride reduction of π-allylpalladium complexes

A stirred solution of Pd^0 (0.1 g, 0.14 mmol), under N_2, in THF (20 mL) was cooled to the desired temperature by immersing the reaction flask in a cooling bath. After the temperature had equilibrated (10 min), (*E*) or (*Z*)-1-chloro-2-octene (0.02 g, in 2 mL THF, 0.14 mmol) was slowly added to the main reaction chamber by carefully pressurizing the addition tube with N_2[a]. Gas chromatographic analysis of samples taken from the reaction mixture revealed that the allylic chloride was no longer present after stirring at -78 °C for 10 min, indicating that oxidative addition to Pd^0 was complete. 5 equivalents of reducing agent were then introduced into the addition tube and the temperature allowed to equilibrate for 15 min Addition to the mother liquor was achieved as before by carefully pressurizing the addition tube with N_2. Reactions were monitored by gas chromatography at 10 min intervals. Octene peaks (G.C. trace) were identified by G.C./M.S. and by coinjection of authentic samples. Yields were calculated using n-decane as an internal standard.

[a] The apparatus for low temperature additions is depicted in appendix 1. This technique allowed a more rigorous control over addition temperatures than other methods employed in which reducing agents (at R.T.) were slowly added to precooled solutions containing the π-allylpalladium complex.

Hydride reduction of allylic chlorides in the absence of palladium

The following procedure is representative: To (*Z*)-allylic chloride 9 (0.02 g, 0.14 mmol) in THF (10 mL) was added at R.T., under N_2, 0.7 mL DIBAH (1 M in THF, 0.7 mmol = 5 equiv.) and the reaction stirred at R.T. for 12 hr. Reductions with $LiBEt_3D$ were conducted in an analogous fashion. LAH and $NaBH_4$ reducing agents were added as solids in one portion with brief exposure to the atmosphere. 5 equivalents of reducing agent were used in each case. Products were identified and yields determined by gas chromatography (*vide supra*).

Coupling reactions catalyzed by $Pd(P\emptyset_3)_4$

(4*E*)-1,4-undecadiene (26) To a solution (R.T.) of $Pd(P\emptyset_3)_4$ (0.33 g, 10 % b.o. allylbromide) in THF (30 mL) was added, under N_2, allylbromide (0.3 g, 2.8 mmol in 1 mL THF) followed by vinylalane 19 (10 % excess). Gas chromatographic analysis of the reaction mixture revealed that coupling had not occurred after stirring at R.T. for 12 hr. Conversion to 26 was achieved by refluxing the solution at 80 °C for 30 min. Work up and purification (*vide infra*) afforded diene 26 (0.32 g, 75 %). FT/IR (vapour) 3084(w), 2934(s), 2864(m), 1639(w), 1458(w), 1350(w), 968(w), 914(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.83 (1 H, C_2, ddt, J_{trans} = 17 Hz, J_{cis} = 10 Hz, J_{2-3} = 6 Hz), 5.40 (1 H, C_4, dt, J_{trans} = 17Hz, J_{3-4} =

6 Hz), 5.03 (1 H, $C_{1(cis)}$, ddt, J_{trans} = 17 Hz, J_{gem} = 2.5 Hz, J_{1-3} = 2 Hz), 4.81 (1 H, $C_{1(trans)}$, ddt, J_{cis} = 10 Hz, J_{gem} = 2.5 Hz, J_{1-3} = 1.5 Hz), 2.74 (2 H, C_3, t, J = 6 Hz), 2.00 (2 H, C_6, dt, J_{5-6} = 6 Hz, J_{6-7} = 7 Hz), 1.40-1.20 (8 H, C_{7-10}, m), 0.89 (3 H, C_{11}, s, J = 7 Hz); mass spectrum, m/e (relative intensity) 166(19, M^+), 138(12), 124(10), 123(6), 110(12), 109(18), 96(41), 95(40), 83(26), 82(66), 81(100), 79(60), 69(45), 68(68), 67(92), 55(31), 54(36), 43(14), 41(34).

Coupling reactions catalyzed by $Pd(P\emptyset_3)_2$

Alternate preparation of diene 26 To a cooled (0 °C) solution of $Pd(P\emptyset_3)_2$ 24 (10 % b.o. allylbromide) in THF (30 mL) was added dropwise, under N_2, a solution of allylbromide (0.34 g, 2.8 mmol in 1 mL THF). After stirring at 0 °C for 5 min vinylalane 19 (10 % excess) was added dropwise, under N_2, using a double ended needle. Gas chromatographic analysis of aliquots taken at various time intervals indicated that the coupling reaction was sluggish at 0 °C (4 % conversion after 3 hr) but was essentially complete upon warming to R.T. over a 1 hr period. The solution was then quenched with HCl (3 N) in order to destroy unreacted vinylalane and solubilize aluminum hydroxide salts. The organic layer was separated, concentrated on a rotary evaporator and subsequently filtered through a bed of $MgSO_4$/celite (1:1) to effect the removal of palladium salts. n-Pentane was used for rinsing in these steps since palladium salts were found to be insoluble in this solvent. Purification by preparative T.L.C. (SiO_2 impregnated with 20 % $AgNO_3$) afforded 26 as a

pale yellow liquid (0.38 g, 90 %).

(6*E*,9*E*)-6,9-heptadecadiene (30) Synthesized on a preparative scale as follows: To a solution of $Pd(P\emptyset_3)_2$ 24 (10 % b.o. allylic chloride) in THF (30 mL) was added at R.T, under N_2, a solution of (*E*)-allylic chloride 8 (0.3 g, 2.1 mmol in 2 mL THF) followed by vinylalane 19 (10 % excess). Analysis by gas chromatography revealed that the reaction was complete after stirring at R.T. for 1 hr. The diene 30 and the regioisomer 32 were formed in a ratio of 5.5 to 1. Standard work up and purification by preparative T.L.C. (SiO_2/20 % $AgNO_3$) gave 30 as a pale yellow liquid (0.32 g, 72 %). FT/IR (vapour) 2966(m), 2934(s), 2864(w), 1462(w), 1350(w), 1090(w), 968(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.48-5.34 (4 H, vinyl, m), 2.68 (2 H, C_8, t, J = 5 Hz), 1.96 (4 H, $C_{5,11}$, td, $J_{4-5} = J_{11-12} = 7$ Hz, $J_{5-6} = J_{10-11} = 5$ Hz), 1.40-1.18 (16 H, $C_{2-4;\ 12-16}$, m), 0.88 (6 H, $C_{1,17}$, s); ^{13}C NMR, alkene-C, δ 131.16 ($C_{7,9}$), 128.73 ($C_{6,10}$), methyl and methylene-C, δ 35.56, 32 49, 31.81, 31.37, 29.50, 29.18, 29.10, 29.09, 22.57, 22.45, 13.39; mass spectrum, m/e (relative intensity) 236(38, M^+), 165(2), 152(5), 151(4), 138(16), 137(11), 124(29), 123(18), 110(40), 109(43), 96(72), 95(85), 83(24), 82(79), 81(100), 79(47), 69(27), 68(30), 67(95), 55(26), 54(18), 43(15), 41(28).

Low temperature coupling reactions The following procedure is representative: To a cooled solution (-78 °C) of $Pd(P\emptyset_3)_2$ 19 (10 % b.o. allylic substrate) in THF (10 mL) was added a solution of (*Z*)-allylic chloride 9 (0.02 g, 0.14 mmol in 1 mL THF). Stirring was continued for 10 min and a 10 % excess of a vinyl metal then added. Addition of reagents

was carried out using a double ended needle. Special precaution was taken not to upset the temperature equilibrium during the course of addition (*vide supra*).

Coupling reactions using Na_2PdCl_4

To a cooled (-78 °C) solution of Na_2PdCl_4 (0.04 g, 0.14 mmol) in THF (20 mL) was added, under N_2, (*Z*)-allylic chloride 9 (0.02 g, 0.14 mmol in 1 mL THF) followed by 0.57 mL DIBAH (1 M in THF, 0.57 mmol = 4 eq. b.o. Pd). The solution immediately changed colour from rusty red to black indicating that a Pd^0 species had formed. To this mixture was then added dropwise, under N_2, vinylalane 19 or vinylzirconene 21 (10 % excess) and the solution allowed to warm to R.T. overnight. In a second series of experiments the palladium catalyst was equilibrated with maleic anhydride by adding 5 equivalents to Na_2PdCl_4 prior to reduction with DIBAH.

Coupling reactions using di-μ-chloro-di(π-crotyl)dipalladium 25

The palladium dimer (0.56 g, 0.14 mmol) was dissolved in THF (20 mL) by stirring at R.T., under N_2, for 5 min. The solution was then cooled to -78 °C and an allylic substrate 8,9,12 or 13 (0.14 mmol in 1 mL THF) added, followed by either vinylalane 19 or vinylzirconene 21 (excess). Solutions were warmed to R.T. overnight. Equilibration of π-allylpalladium complexes with maleic anhydride was achieved by adding

this ligand (dissolved in THF) by syringe, under N_2, to cooled solutions (-78 °C) of the allylpalladium dimer. Reaction mixtures were stirred at -78 °C for a minimum of 30 min prior to addition of the vinyl organometal.

Preparation and coupling of (*Z*)-allylic chloride containing a τ-dimethyl(phenyl)silyl substituent

(*E*)-3-dimethyl(phenyl)silyl-2-octene-1-ol (27)[41] To a solution of finely cut lithium wire (0.83 g, 120 mmol) suspended in dry THF (50 mL) was added under argon at R.T. dimethyl(phenyl)silylchloride (4.1 g, 24 mmol). After stirring at R.T. for 24 hr the metallic brown solution was transferred under argon to a cold ethereal solution (0 °C, 20mL) of diethylzinc (2.45 mL, 24 mmol) using a double ended needle. Formation of the silyl-zinc bismetal is presumed to be instantaneous under these reaction conditions since it was observed that the brown colouration of the dimethyl(phenyl)silyl lithium solution disappeared as it was being added to diethyl zinc. After stirring at 0 °C for 30 min CuCN (0.048 g, 0.5 mmol) and propargyl alcohol 5 (1 g, 8 mmol) were added and the whole stirred for 30 min at 0 °C followed by 30 min at R.T. The cooled (0 °C) solution was then quenched by slow addition of a saturated NH_4Cl solution and the resultant slurry filtered through a bed of celite. The aqueous phase was extracted with diethyl ether (2 x 50 mL) and solvent removed under reduced pressure on a rotary evaporator. The crude product was purified by flash chromatography (id: 3 cm, column length: 30 cm, eluant: dichloromethane/EtOAc (9:1) to give 27 as a colourless liquid (1.5 g, 72

%). **27** was stored at 4 °C under N_2 since it was found to gradually decompose to a milky solution when kept at R.T. FT/IR (vapour) 3061(m), 2937(s), 2868(m), 2361(m), 2336(w), 1425(w), 1375(w), 1256(m), 1195(w), 1109(m), 1026(m), 820(s), 773(m), 730(m), 700(m), cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.4 (5 H, benzene, dm), 6.09 (1 H, C_2, t, J_{1-2} = 6 Hz), 3.96 (2 H, C_1, quart, J = 6 Hz), 2.12 (2 H, C_4, t, J = 7 Hz), 1.18 (6 H, C_{5-7}, m), 0.98 (3 H, C_8, t, J = 7 Hz), 0.24 (6 H, $SiMe_2$, s); mass spectrum, m/e (relative intensity) 262(< 0.5, M^+), 247(3), 244(2), 229(1), 205(1), 185(2), 173(2), 152(3), 137(100), 136(11), 121(11), 105(10), 91(6), 81(7), 75(33), 67(9), 54(4), 43(6), 41(4). Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.27; H, 9.91. Found: C, 73.60; H, 10.19.

(*E*)-3-dimethyl(phenyl)silyl-1-chloro-2-octene (28) Allylic alcohol 27 (0.35 g, 1.3 mmol) was converted to **28** according to the same procedure outlined in the synthesis of allylic chloride **8**[21]. The solution was concentrated on a rotary evaporator at reduced pressure and purified by flash chromatography (id: 3 cm, column length: 10 cm, eluant: hexanes). Column fractions were combined and solvent removed under reduced pressure to afford **28** as a clear liquid. The product was prepared for analysis by placing the purified compound under high vacuum for 12 hr at R.T. (0.3 g, 80 %). **28** was stored at 4 °C since it readily decomposed at R.T. FT/IR (vapour) 3200(w), 3065(m), 2964(s), 2937(s), 2887(m), 2361(w), 1256(s), 1105(m), 818(s), 777(m), 700(m), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (5 H, benzene, dm), 5.97 (1 H, C_2, tt, J_{1-2} = 7.5 Hz, J_{2-4} = 1 Hz), 4.13 (2 H, C_1, dt, J_{1-2} = 7.5 Hz, J_{1-4}<0.5 Hz), 2.15 (2 H, C_4, bt, J = 7 Hz), 1.27 (4 H, $C_{5,6}$, m), 1.18 (2 H, C_7, m), 0.9 (3 H, C_8, t, J = 7 Hz); mass

spectrum, m/e (relative intensity) 280(< 0.5, M^+), 265(5), 245(1), 224(3), 209(2), 196(4), 187(3), 173(4), 170(4), 157(24), 155(62), 145(5), 135(100), 121(18), 105(17), 93(29), 81(2), 67(26), 54(12), 43(9). Anal. Calcd. for $C_{16}H_{25}ClSi$: C, 68.57; H, 8.93. Found: C, 68.82; H, 8.90.

(6*E*,9*E*)-6-dimethyl(phenyl)silyl-6,9-heptadecadiene (29) To a solution of $Pd(P\emptyset_3)_2$ (*vide supra*) (10 %, based on **28**) in dry THF (30 mL) at R.T. was transferred a solution of **28** (0.5 g, 1.8 mmol, in 2 mL THF) using a double ended needle. After stirring at R.T. for 10 min a 5 fold excess of vinylalane **19** (9 mmol in hexanes) was added over a period of 10 min and stirring continued for for 30 min thereafter. The solution was then quenched by slow addition of HCl (3 N), the organic layer separated and subsequently concentrated on a rotary evaporator at reduced pressure. The remaining liquid was combined with the organic extracts of the aqueous phase (n-pentane, 2 x 50 mL) and filtered by suction through a bed of celite/$MgSO_4$ to effect the removal of palladium(0) and its salts. The filtrate was concentrated to yield a crude oil which was purified by flash chromatography (id: 3 cm, column length: 20 cm, eluant: hexanes) to afford pure **29** (0.58 g, 88 %). FT/IR (vapour) 2964(m), 2934(s), 2864(m), 1460(w), 1355(w), 966(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57-7.30 (5 H, benzene, dm), 5.82 (1 H, C_7, t, J = 7 Hz), 5.47 (1 H, C_{10}, dt, J_{trans} = 15 Hz, J_{10-11} = 6 Hz), 5.38 (1 H, C_9, dt, J_{trans} = 15 Hz, J_{8-9} = 5 Hz), 2.84 (2 H, C_8, dd, J_{7-8} = 7 Hz, J_{8-9} = 5 Hz), 2.15-2.03 (2 H, C_5, m), 2.03-1.97 (2 H, C_{11}, m), 1.28-1.12 (16 H, $C_{2-4,\ 12-16}$, m), 0.90 (3 H, C_1, t, J = 7 Hz), 0.85 (3 H, C_{17}, t J = 7 Hz), 0.37 (6 H, $SiMe_2$, s); mass spectrum, m/e (relative intensity) 370(1, M^+), 292(1), 271(2), 234(12),

208(1), 194(1), 173(1), 159(1), 152(2), 145(2), 137(8), 136(21), 135(100), 121(16), 107(6), 91(3), 79(3), 59(3), 43(6). Anal. Calcd for $C_{25}H_{42}Si$: C, 81.15; H, 11.35. Found: C, 80.83; H, 11.60.

(6*Z*,9*E*)-6,9-heptadecadiene (31) To a solution of freshly prepared diene 29 (0.02 g, 0.05 mmol) in DMF (10 mL) was added, under N_2, 0.1 mL Bu_4NF (1 M in THF, 0.1 mmol). The mixture was refluxed for 4 hr, and n-pentane (5 mL) then added to the cooled solution. Gas chromatographic analysis revealed that the diene 31 had formed in 85 % yield. This solution was extracted with brine (3 x 50 mL) and the aqueous fractions back - extracted with n-pentane. The organic fractions were combined and solvent removed at reduced pressure on a rotary evaporator. An analytical sample was prepared by purification of the crude diene by preparative thin layer chromatography (*vide supra*). Desilylation of a sample of 29 stored at 4 °C for several months yielded 34 as the major product. Presumably, 29 had isomerized to the corresponding conjugated diene during this period. FT/IR (vapour) 3018(w), 2966(m), 2934(s), 2866(m), 1460(w), 1385(w), 1350(w), 966(w), 714(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.47-5.31 (4 H, vinyl, m), 2.72 (2 H, C_8, t,J = 6 Hz), 2.01 (4 H, $C_{5,11}$, quart, J = 7 Hz), 1.39-1.16 (16 H, $C_{2-4,12-16}$, bm), 0.87 (6 H, $C_{1,17}$, t, J = 7 Hz); ^{13}C NMR, alkene-C, δ 130.94 (C_9), 130.56 (C_7), 128.42 (C_{10}), 127.86 (C_6), methyl and methylene-C, δ 32.49, 31.80, 31.50, 30.76, 30.39, 29.64, 29.51, 29.28, 29.10, 27.04, 22.47, 22.26, 13.92; mass spectrum, m/e (relative intensity) 236(15, M^+), 152(4), 151(3), 138(10), 137(7), 124(21), 123(14), 110(40), 109(34), 96(57), 95(67),

83(21), 81(95), 79(39), 69(28), 18(37), 67(100), 55(34), 54(26), 43(17), 41(34).

(4*E*)-3-pentyl-1,4-undecadiene (32) FT/IR (vapour) 3084(w), 2966(m), 2934(s), 2866(m), 1637(w), 1556(w), 1464(w), 1352(w), 968(w), 914(w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.64 (1 H, C_2, ddd, J_{trans} = 17 Hz, J_{cis} = 10 Hz, J_{2-3} = 7.5 Hz), 5.33 (1 H, C_5,dt, J_{trans} = 15.5 Hz, J_{5-6} = 6 Hz), 5.20 (1 H, C_4, ddt, J_{trans} = 15.5 Hz, J_{3-4} = 7.5 Hz, J_{4-6} = 1.5 Hz), 4.92 (1 H, $C_{1(cis)}$, ddt, J_{trans} = 17 Hz, J_{gem} = 2 Hz, $J_{1(cis)-3}$ = 1 Hz), 4.87 (1 H, $C_{1(trans)}$, ddt, J_{cis} = 10 Hz, J_{gem} = 2 Hz, $J_{1(trans)-3}$ = 1.5 Hz), 2.54 (1 H, C_3, br quint, J = 7 Hz), 1.96 (2 H, C_6, quart, J = 7 Hz), 1.32-1.12 (18 H, C_{7-11} + CH_2-pentyl, m), 0.81(6H, C_{12} + CH_3-pentyl), t, J = 7 Hz); ^{13}C NMR, alkene-C, δ 142.64 (C_2), 132.98 (C_4), 130.48 (C_5), 113.20 (C_1), methyl and methylene-C, δ 46.68, 34.86, 32.54, 29.09, 29.04, 27.05, 26.73, 22.56, 22.52, 22.47, 13.92; mass spectrum, m/e (relative intensity) 236(3, M^+), 207(8), 165(16), 138(7), 137(29), 124(13), 123(27), 110(27), 109(61), 96(24), 95(88), 83(18), 82(27), 81(89), 79(39), 69(23), 68(37), 67(100), 55(21), 43(18), 41(23).

(8*E*,10*E*)-8,10-octadecadiene (33) ^1H NMR (400 MHz, $CDCl_3$), δ 6.05-5.95 (2 H, vinyl, m), 5.63-5.50 (2 H, vinyl, m), 2.05 (4 H,C_{5-10}, quart, J = 7 Hz), 1.42-1.18 (20 H, $C_{2-6,\ 13-17}$, two br s), 0.88 (6 H, $C_{1,18}$, t, J = 7 Hz); ^{13}C NMR, alkene-C, δ 132.48, 130.46, methyl and methylene-C, δ 32.54, 31.78, 29.63, 29.40, 29.12, 22.58, 13.96; mass spectrum, m/e (relative intensity), 250(10, M^+), 152(7), 138(5), 137(5), 124(35), 123(17), 110(23), 109(33), 96(48), 95(59), 83(24), 82(90), 81(86),

79(36), 69(23), 68(24), 67(100), 55(23), 54(17), 43(14), 41(19).

(6*E*,8*E*)-6,8-heptadecadiene (34) FT/IR (vapour) 3171(w), 2934(s), 2864(m), 1462(w), 1352(w), 984(w), cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), δ 6.05-5.95 (2 H, vinyl, m), 5.63-5.50 (2 H, vinyl, m), 2.05 (4 H,C_{5-10}, quart, J = 7 Hz), 1.42-1.18 (18 H, $C_{2-4,\ 11-16}$, two br s), 0.88 (6 H, $C_{1,17}$, t, J = 7 Hz); ^{13}C NMR, alkene-C, δ 132.46, 130.48, methyl and methylene-C, δ 32.53, 31.77, 31.69, 29.63, 29.40, 29.36, 29.11, 28.82, 22.57, 22.52, 13.94; mass spectrum, m/e (relative intensity) 236(33, M^+), 165(3), 152(4), 151(5), 138(14), 137(8), 124(25), 123(17), 110(46), 109(42), 96(54), 95(69), 83(19), 82(68), 81(85), 79(44), 69(19), 68(25), 67(100), 55(17), 54(12), 43(13), 41(18).

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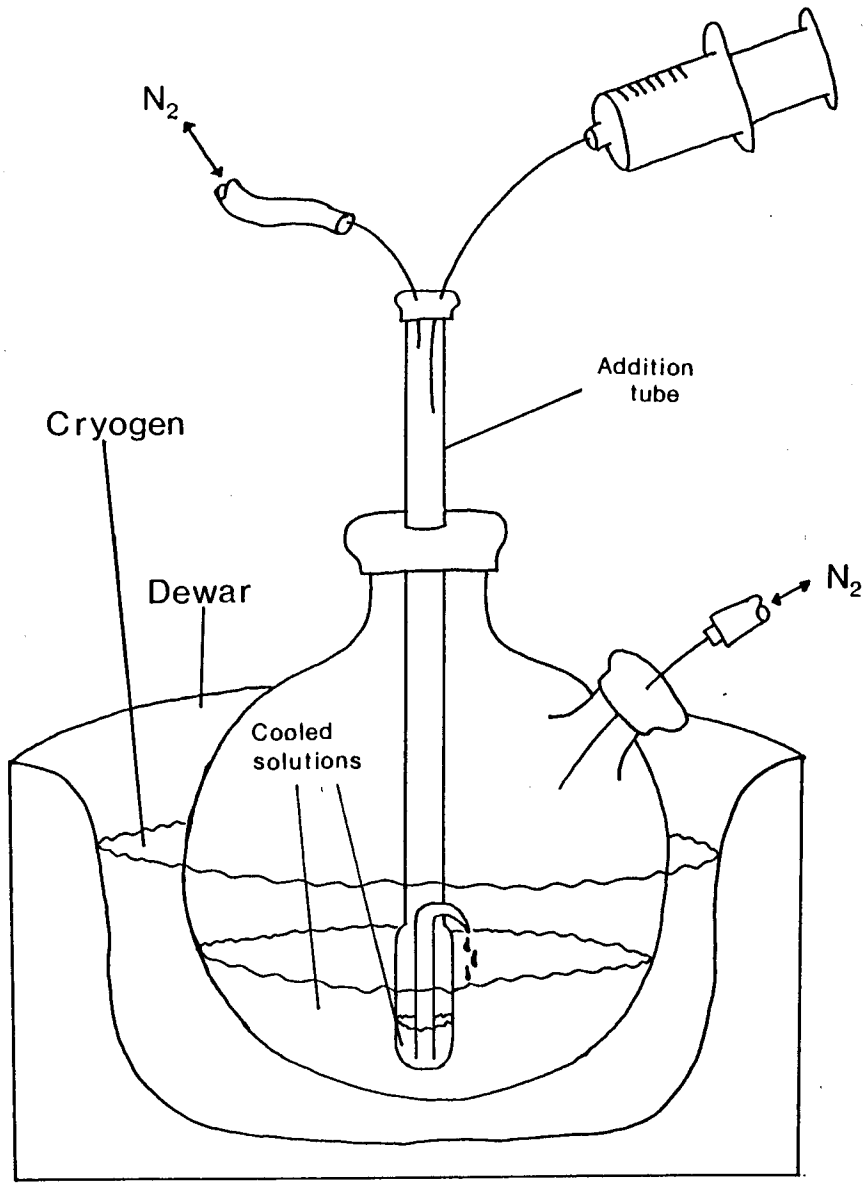
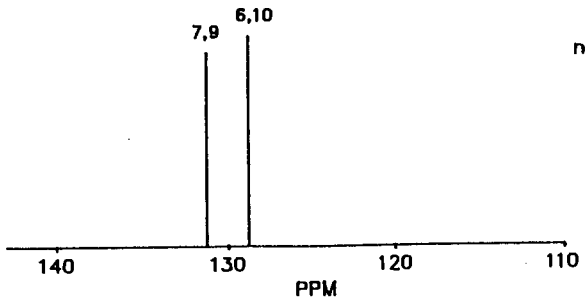
APPENDIX 1

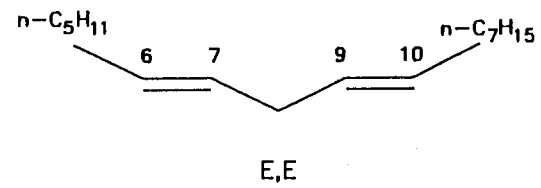


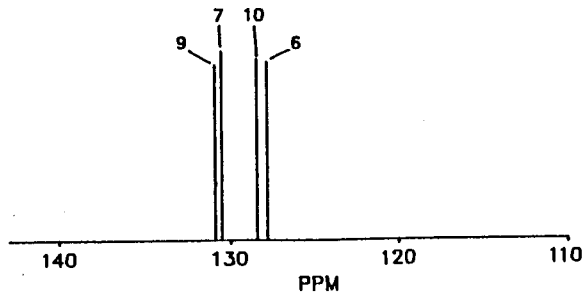
Apparatus for reductions of allylpalladium complexes at low temperatures

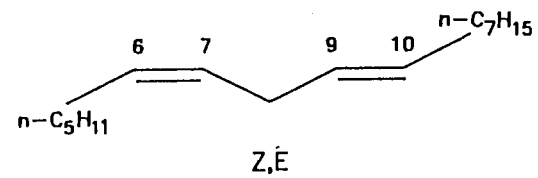
APPENDIX 2

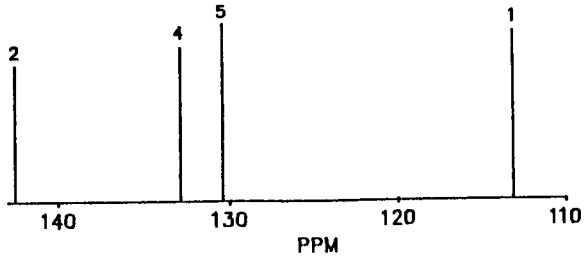
^{13}C NMR SPECTRA OF UNSATURATED
REGIONS IN 1,4-DIENES

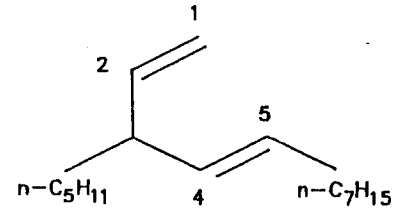












Regioisomer