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SPECIFIC ALLYLIC–ALLYLIC COUPLING PROCEDURES EFFECTED BY LIGAND-INDUCED ELIMINATION FROM DI(ALLYLIC)PALLADIUM SPECIES

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Abstract— Bis(allylic)palladium complexes can be induced to undergo reductive elimination by replacement of phosphine ligands in the system with π-acidic ligands. The product 1,5-dienes, formed in high yield, are predominantly the 'head-to-head' coupled isomers. The bis(allylic)palladium intermediates may be formed by addition of an allylic Grignard or trialkyl(allylic)tin reagent to an (η^3-allyl)palladium chloride complex, or by 1,3-diene condensation. The latter process leads to cyclodimerization, 'unusual' for palladium catalysed reactions.

INTRODUCTION

Of the many new synthetic strategies which have evolved using transition metal-mediated processes for C—C bond formation, those based on organo-Pd intermediates have been among the most frequently and broadly utilized.[1–3] In this context, the chemistry of (η^3-allyl)Pd(II) systems has enjoyed an especially prominent role,[2,3] in part because of the ease of preparation of these materials from allylic alcohols, halides or even simple olefins. To a large extent, development of new synthetic organic procedures has been focused on routes involving attack by nucleophiles on the co-ordinated allylic ligand as the key bond-forming step.[2,4] A complementary process for C—C bond formation involves reductive elimination from a diorgano-substituted Pd complex, in which, commonly, an organo-Pd(II) halide or acetate reacts with another organometallic to give the key intermediate.[5–11] In this latter context, regiochemical control and adjustments in rates of reductive elimination can be accomplished by judicious choice of ligands for the metal.[9,11] Since Pd will bind selectively to one face of an allylic ligand (where stereochemical factors for the two faces are different), stereospecific reductive coupling reactions are possible and the broad scope of organometallic reagents which can transfer organic groups onto Pd(II), including Mg,[5] Hg,[6] Tl,[5] Zn,[7] Zr[9,10] and Sn,[11] makes these procedures especially appealing in concept. In most of them, however, phosphine ligands have been used in conjunction with either stoichiometrically or catalytically utilized Pd species, and we have found that the presence of such phosphine ligands actually suppresses the rate of reductive elimination from the diorgano-Pd intermediate and enables undesirable decomposition pathways to compete with it. In this paper we discuss our approach to the activation of (allylic)Pd complexes toward reductive elimination in the context of the development of methods to effect specific high yield allylic–allylic coupling.

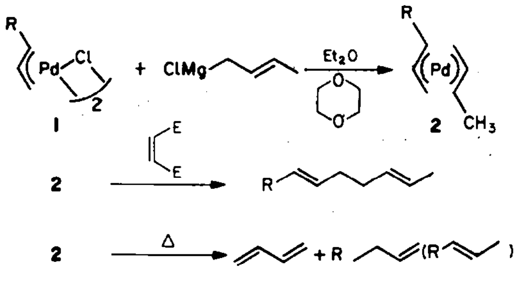
The problem of specific coupling of two different allylic units has been addressed repeatedly and from various perspectives due to the abundance of 1,5-dienes found in 'natural products'. Many coupling schemes which have been developed, however, result in loss of geometrical integrity of substituted allylic moieties, allylic transposition, and, especially, in scrambling of the different allylic units to give complex mixtures of homo- and cross-coupled products.[12]

Several approaches to the problem of effecting specific allylic cross-coupling have utilized transition metal reagents. Reaction between (η^3-allylic)Ni halides and allylic bromides, however, generally results in formation of mixtures of coupled products, attributed to rapid exchange between the allylic halide and the allyl ligand on Ni.[13] Pyrolysis of Ti alkoxides of allylic alcohols,[14] or the coupling of allylic halides promoted by low-valent metal species[15] have also been developed, but non-specific coupling results, likely due to formation of intermediary allylic radicals. Site-selective coupling has been observed in Pd(0)-catalysed coupling between allylic halides or acetates and allylic Sn species. This reaction occurs with allylic transposition of the Sn reagent which suggests that bond formation takes place by attack of the allylic Sn species directly upon the (η^3-allyl) ligand of the Pd(II) complex.[16] Unfortunately, as the allylic termini of the Sn reagent become more substituted, yields for this process fall. We and others[17] have found that terminally-substituted di(allyl)Pd(II) compounds do not thermally reductively eliminate as do their Ni analogs. Rather, β-hydride transfer reactions occur preferentially which result in formation of an olefin and a 1,3-diene. Reductive elimination can be induced from a variety of organometallic complexes; for example, oxidative methods have been demonstrated to accomplish this for several diorgano transition metal systems.[18] Temple *et al.*[3] have found that maleic anhydride or other π-acidic ligands will induce reductive elimination of a 1,4-diene from an (allylic)Pd(alkenyl) complex and we have now used this approach to prepare 1,5-dienes.

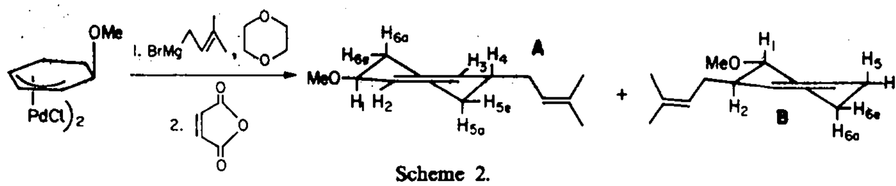
STOICHIOMETRIC CROSS-COUPLING OF ALLYLIC UNITS

Synthesis of Pd(*allyl*)(*allyl′*)

To accomplish selective allylic cross-coupling necessitates the preparation of an unsymmetrically-substituted di(allylic)Pd complex. Grignard reagents have been used in the preparation of *symmetrically-substituted* di(allyl) complexes of many transition



Scheme 1.



Scheme 2.

metals including Pd.[19] However, addition of an allylic Grignard reagent to an (η^3-allylic)Pd halide complex (**1**) results in formation of homocoupled 1,5-dienes as well as cross-coupled ones upon induced elimination (see below). Ligand metathesis must be possible, therefore, and scrambling of allylic units results.

Dioxane can be used to precipitate Mg and Li halide salts as adducts from ethereal solutions,[20] and we note that when several equivalents of dioxane are present in solution prior to addition of the Grignard or Li reagent, only the desired cross-coupling product results on induced reductive elimination. Unsymmetrically substituted di(allylic) complexes (**2**) may be isolated using this method as thermally sensitive solids which could be characterized by low temperature ^{1}H-NMR.† When reductive elimination from these isolated compounds is effected, the 1,5-diene is produced quantitatively.

Stoichiometric coupling procedures

Simply warming a solution of **2** results in formation of the 1,5-diene, but only in very low yield: β-hydride transfer occurs predominantly to form equal amounts of olefin and (non-coupled) 1,3-diene. However, when **2** is treated with a π-acidic ligand, successful coupling results[21] which also occurs regioselectively. Electron-deficient olefins, such as maleic anhydride or fumaronitrile, were found to be especially effective in this capacity, and benzoquinone was noted to be less so (Scheme 1).‡ The resulting distribution of 1,5-dienic products heavily favours coupling at the least hindered ends ('head-to-head') of both allylic units (Table 1). Given the facile *syn*/*anti* rearrangement of substituents in η^3-allylic units via corresponding η^1-allylic isomers,[22] the *E*, *Z* selectivity for the olefinic products formed is controlled by steric factors in **2**, and not by those of the starting materials. Significantly, we note that addition of phosphine ligands suppresses the coupling process.

Stereochemistry and mechanism

The stereochemical course of coupling was examined in two cases (Table 1, entries 6 and 8). In entry 6, the metal in the π-allyl complex has been demonstrated to co-ordinate only to the face of the allylic unit *trans* to the methoxy substituent.[23] Ligand-induced coupling procedures resulted in high yield formation of two products (**6a**–**6b**, 2.4:1). Both of these were shown to have *trans* geometries by ^{1}H-NMR decoupling and NOE experiments (Scheme 2). Irradiation of the methoxy group in **6a** showed nuclear Overhauser enhancement of signals for protons 1, 2, 4 and 6a. Since J_{1-6a} = 8.4 Hz, both ring substituents must occupy equatorial positions, *trans* to one another. Similarly, for **6b**, J_{1-6a} = 8.9 Hz and J_{1-2} = 8.4 Hz, clearly demonstrating axial locations and a *trans* relative configuration for the ring substituents. Transmetallation, followed by reductive elimination (net retention of configuration in the coupling step) can, therefore, account for the coupling sequence.

The stereochemical course of coupling was also probed utilizing steroidal complex (Table 1, entry 8) in which the metal is bound to the α-face. Overall retention of configuration was observed for the C-16 coupled product (C—C bond formation occurs on the α-face). This was proven by spectral comparison of hydrogenated product with the hydrogenated product of an authentic material[3] (Scheme 3). A small amount of C-20-coupled product was also isolated and was hydrogenated. Spectral analysis proved this to be identical with hydrogenated cholesterol which had been appropriately protected at C-3, demonstrating retention of configuration in the coupling step here too.

Regiochemical results for allylic–allylic coupling in the steroidal case stand in marked contrast to those noted for maleic anhydride-induced reductive elimination of a 1,4-diene from an (η^3-allylic)(η^1-alkenyl)Pd intermediate; in the latter case, preferential coupling at C-20 occurred. In fact, regiochemical results for allylic–allylic coupling in the steroidal case are even different from those noted for a 'model', monocyclic system in which coupling predominates at the 'exocyclic' C (Table 1, entry 3, **a**, **b**). It is known that di(η^3-allylic)-Pd(II) complexes are configurationally labile with regard to interconversion of *syn* and *anti* isomers. This interconversion could occur through intermediary (η^3-allylic)(η^1-allylic) isomers. In fact, phosphine adducts of di(allylic)Pd species show this ligand arrangement.[24] We have examined a series of unsymmetrically-substituted di(allylic)Pd complexes by ^{1}H-NMR which involve increased steric hindrance for one of the allylic ligands. We note that, as steric hindrance increases (and the steroidal case represents the upper limit for this phenomenon), signals in the ^{1}H-NMR spectrum, which can be attributed to an (η^3-allylic)(η^1-allylic)Pd complex, grow. Thus, it may be that 'head-to-head' coupling by reductive elimination, which predominates in small allyl ligand cases, derives from the the bis(η^3-allylic) material and that 'head-to-tail' coupling by reductive elimination predominates from the mixed allylic isomer. The possibility of

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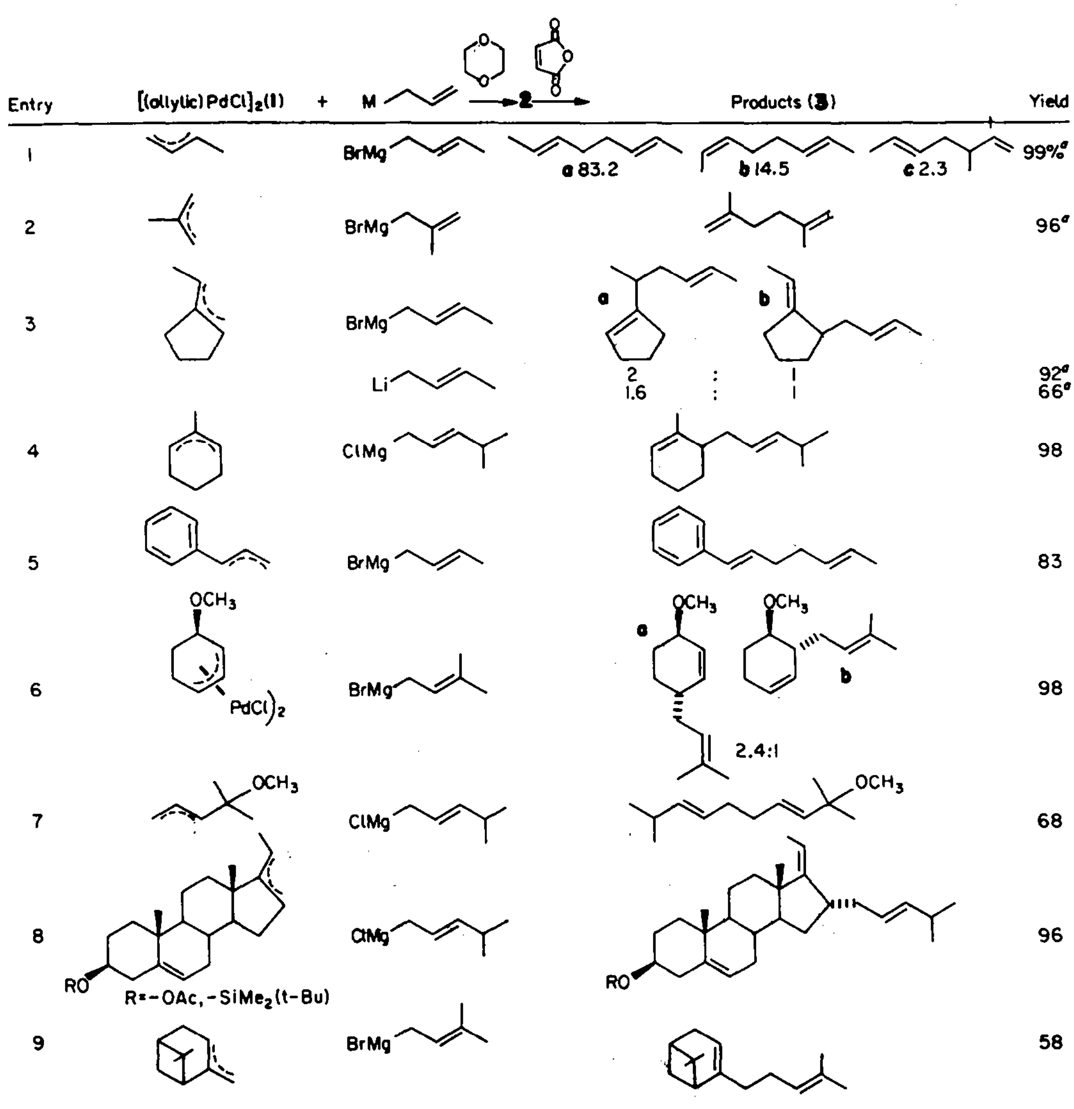
† A set of at least four isomers may be seen by ^{1}H-NMR.

‡ A carbon monoxide atmosphere also included the same selectivity in coupling but in low yields.

Table 1. Results of unsymmetrical allyl–allyl coupling



ᵃ Denotes GC yields; all others are isolated yields.

competing direct and conjugate elimination reactions varying as a function of increasing steric size of one of the allylic partners in a bis(allylic) complex, however, cannot be ruled out.

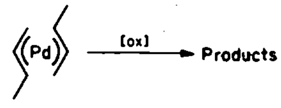
Attempts to induce coupling oxidatively

Methods other than co-ordination of electron-deficient olefins were examined to induce reductive coupling from di(allylic)Pd complexes. Cyclic voltametric analysis of bis(allyl)Pd and bis(crotyl)Pd displayed single *irreversible* oxidation waves at +0.85 and −1.25 V (vs SCE), respectively. However, preparative electrochemical procedures or the use of known single electron oxidizing agents in conjunction with di(allyl)Pd or a monophosphine adduct[24] resulted in only low coupling yields of products which displayed no regiochemical selectivity (Table 2). When Na_2IrCl_6 was used as the oxidant, substantial amounts of allylic chloride and (allylic)Pd chloride complex were obtained. Allylic radicals are known to react with iridium halides[25] to give allylic halides (Reaction 1).

$$CH_2{=}CH{-}\dot{C}H_2 + IrCl_6^{2-} \xrightarrow[S]{} CH_2{=}CHCH_2Cl + IrCl_5(S)^{2-} \quad (1)$$

Furthermore, oxidation with iridate under O_2 [bis(allyl)Pd is stable to O_2] produced 2-butene-2-ol and 2-butene-2-al; these are likely to result from decomposition of peroxide radicals[26] formed by rapid trapping of allylic radicals by O_2. Taken together these results suggest radical decomposition or competition between reductive elimination and radical decomposition of the singly oxidized Pd intermediate (Scheme 4). Similar oxidation-derived radical decomposition pathways have been suggested for

Table 2. Product distribution for oxidation of bis(η^3-crotyl)Pd

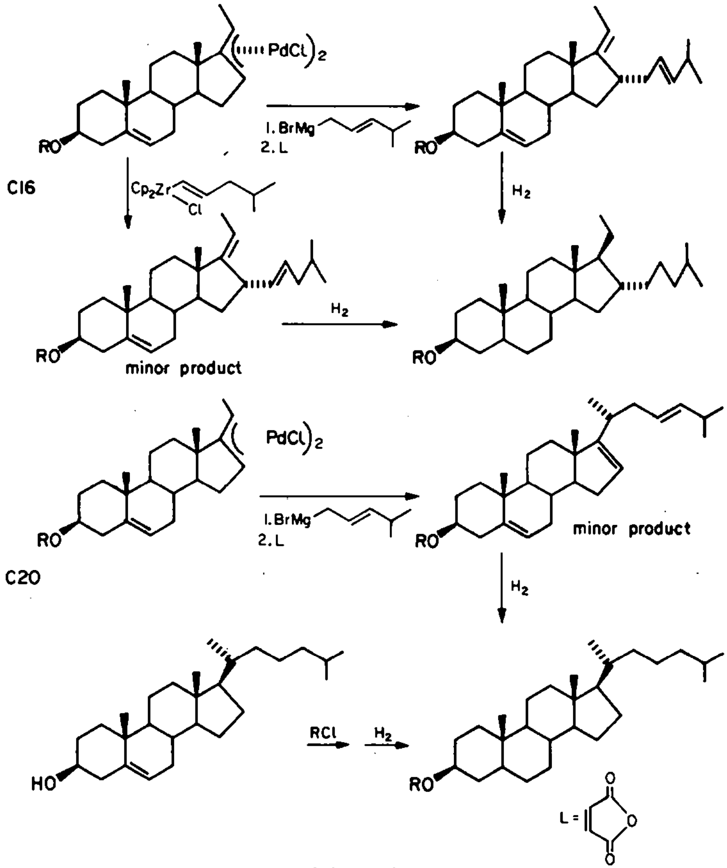


Oxidant				Other[a]	C_8 Yield %
Na_2IrCl_6[b]	38.1	15.1	29.4	27.2	42
$(NH_4)_2Ce(NO_3)_6$	33.7	17.2	31.2	17.6	35
$CuCl_2$	37.8	16.2	32.1	13.9	11
Electrolysis[c]	40.6	12.4	36.7	10.2	34

[a] Unidentified C_8 material.

[b] Oxidant added to MeCN solution of bis(allyl) at −30°.

[c] Ionic medium 0.1 M Bu_4NBF_4 in MeCN; reference electrode SCE; Pt working electrode; −30°.

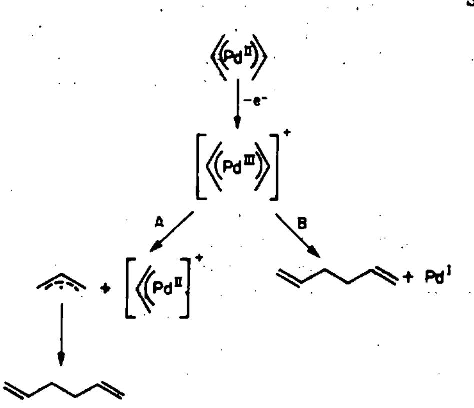


Scheme 3.

diorgano transition metal complexes of Fe,[27] Pt[28] and Ni.[29]

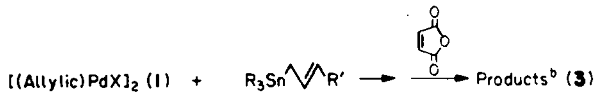
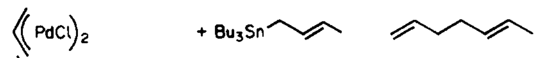
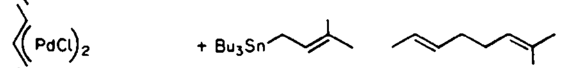
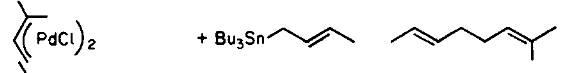
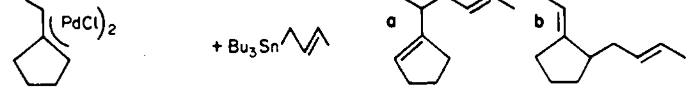
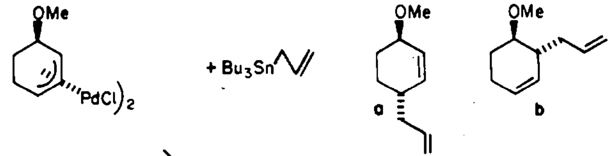
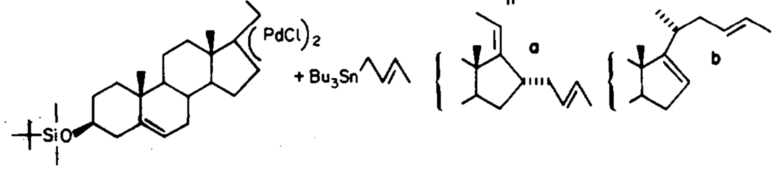
*Expansion in scope of the coupling reaction using organo-*Sn *reagents*

Organo-Sn reagents have been used in various Pd-catalysed cross-coupling reactions involving transfer of an organic group directly to the metal in a Pd(II) intermediate.[30] Organo-Sn compounds are tolerant of many functional groups and, thus, avoid limitations in use found for the more reactive Grignard reagents. Trialkyl(allyl)Sn compounds are easily prepared and have been found to transfer the allylic group exclusively to Pd(II) in the context of other types of coupling reactions.[30]



Scheme 4.

Table 3.

Entry		Yield (%)
1		49
2		47
3		42
4		55
5		54 (2.5:1)
6		78^a (3:1)
7		67^a (16:1)

^{a} Denotes isolated yields; all others were determined by vpc analysis.

When trialkyl(allyl)Sn reagents were stirred with (allyl)Pd chloride in ether at low temperature (−35°), followed by addition of maleic anhydride and gradual warming to room temperature, high C—C bond forming yields resulted (Table 3). Coupling occurs regiospecifically joining the least hindered termini of the allylic ligands, with selectivity that is identical to that obtained from preformed bis(allylic)Pd compounds prepared from Grignard reagents.† That functional group tolerance can exist under these conditions was also demonstrated (Table 3, entry 4, for example). Since triorgano-Sn halide residues of transmetallation are soluble in ether, some ligand metathesis occurred leading to homocoupled products. This could be suppressed somewhat by lowering the solubility of these halide residues using ether–pentane as solvent and triphenyl-Sn reagents. Stereochemistry of coupling at the allylic partner was demonstrated using a *trans*-(methoxy)cyclohexyl(η^3-allylic)Pd complex (Table 3, entry 6). Overall retention of configuration occurs at carbon,‡ substantiating the notion of a transmetallation–reductive elimination sequence.

Catalytic coupling interception of intermediates by maleic anhydride

The scope of allylic cross-coupling procedures could be broadened further by utilizing organo-Sn reagents: unlike Grignards these species do not react with maleic anhydride which, therefore, renders catalytic coupling schemes possible. Warming (60°) of allylic Sn reagents with allylic halides in THF in the presence of catalytic amounts of maleic anhydride and (η^3-allyl)Pd halide precatalyst resulted in regioselective cross-coupling between the Sn species and the halide. As shown in Table 4, coupling selectivity is identical to that obtained utilizing stoichiometric procedures (allylic halides and allylic Sn reagents have little propensity to react by themselves). In these coupling sequences, although turnovers based on the metal are high, some homocoupling is also noted, given the solubility of organo-Sn halide residues in the reaction medium.

The results described above offer an interesting contrast to the Pd-catalysed coupling reaction of allylic Sn species which occurs in the absence of maleic anhydride[16] and which apparently occurs by direct nucleophilic attack by the Sn reagent upon the (η^3-allylic) ligand of Pd(II) (and with presumed *anti*-stereochemistry). Since organo-Sn species can in fact transfer allylic units to Pd(II), this observation of products formed by *direct attack* may simply be due to the inability of a *reversibly* formed bis(allylic)Pd complex to reductively eliminate under the reaction conditions employed (Scheme 5). In the presence of maleic anhydride, attack by the π-acidic ligand upon

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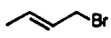
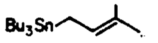
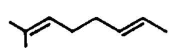
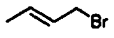
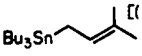
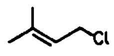
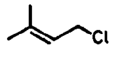
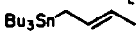
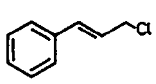
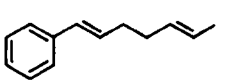
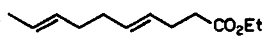
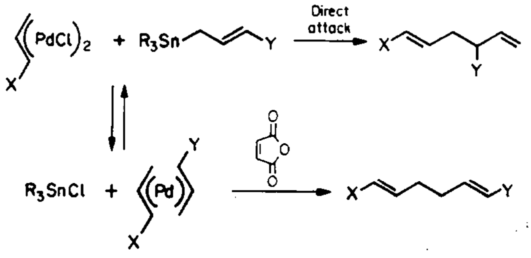
† Bis(allylic)zirconocene compounds[31] react in a manner similar to allylic Sn reagents with the (η^3-allyl)Pd halide complexes. The transmetallation from zirconium is, however, reversible resulting in diminished yields due to competitive homocoupling.

‡ The ^{1}H-NMR proof of *trans* products was identical to that for the Grignard coupling procedure.

Table 4.

Entry	Reagents[a]		Catalyst precursor (equiv.[b,c])	Conditions	Products[d]	Yield[e] (%)
1			None	THF, 50°		0.8
2			[(η^3-allyl)PdCl]$_2$, 1%	THF, 50°	"	40
3			None	THF, 25°	"	0.1
4			[(η^3-allyl)PdCl]$_2$, 2%	THF, 25°	"	38
5			[(η^3-allyl)PdCl]$_2$, 1%	THF, 50°		64
6			[(η^3-allyl)PdCl]$_2$, 1%	THF, 50°		35

[a] Halides used were a combination of both allylic transposition isomers.
[b] Based on the Sn reagent.
[c] Maleic anhydride added (5% equivalent) in all cases.
[d] > 90% E, E in all cases where appropriate.
[e] After 12 hr.



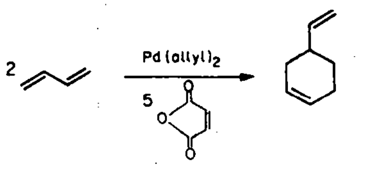
Scheme 5.

the di(allylic)Pd intermediate can occur to give 'head-to-head' coupled products by reductive elimination.[32]

Interception by maleic anhydride of bis(allylic) intermediates formed by butadiene dimerization

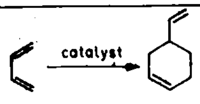
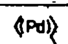
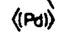
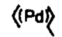
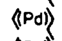
Coupling reactions derived from transition metal bis(allylic) species to give 1,5-dienes are best represented by the general class of oligomerization reactions of 1,3-dienes. For Ni-catalysed cyclo-oligomerization, elegant mechanistic elucidation[33] has demonstrated the presence of bis(allylic) intermediates; the distribution of reductive cyclization products can be controlled by the addition of various phosphines.[33] Many Pd-catalysed reactions of butadiene have also been well developed, including dimerization, teleomerization and carbonylation.[34] Palladium catalysts, however, have been thought to behave in a very different manner than Ni does. Classically, reactions involving Pd with butadiene result in the formation of only linear dimers and trimers, and an explanation usually offered to account for this difference in reactivity between Pd- and Ni-based procedures is based on the supposition that the larger size of Pd relative to Ni prevents ring closure of intermediary bis(allylic) complexes in the former case.

An alternative explanation can be formulated to explain this difference in reactivity of Ni complexes vs those of Pd which, in fact, invariably incorporate phosphine ligands. Not only might these phosphines stabilize Pd(0) intermediates, they might also inhibit the reductive elimination step necessary for the cyclization process to succeed. As we have already noted above, bis(allylic)Pd complexes are less prone to spontaneous reductive elimination than are Ni analogs; the former require the presence of π-acidic ligands to induce reductive elimination. In fact, we find that replacing phosphine ligands by maleic anhydride in Pd-catalysed reactions of butadiene completely changes the course of the reaction. When a THF solution of bis(allyl)Pd is added to a THF solution of butadiene and maleic anhydride at $-30°$, cyclodimerized product is formed exclusively; only a single product, vinylcyclohexene, is produced. Faster dimerization rates are noted at higher temperature; even under these conditions (Table 5) the predominant product is still vinylcyclohexene. A similar reaction course occurs in methanol, and cyclodimerization occurs as rapidly as does teleomerization (Table 5, entry 12). In contrast, utilizing 'conventional' phosphine-containing Pd complexes as catalysts,[35] teleomerization products are nearly exclusively produced. Isoprene can be cyclodimerized using phosphine-devoid Pd catalysts to give all four isomers of the dimers (Reaction 3).

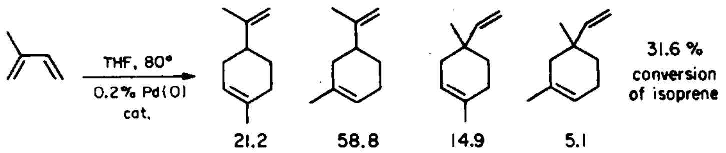


(2)

Table 5.

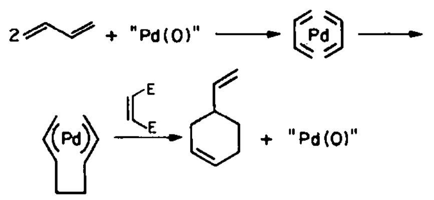
Entry	 Catalyst, mmol	Temp (°C)	Time (hr)	Solvent	Add'n^a of MAH	% conv of C_4H_6	Product yields (mmol) 4-VCH^b	 1,3,7-OT^c	 1,3,6,11-DT^{d,7}	 Other^e
1	 0.13	85	14	THF	yes^x	68.4	26.7		2.2	
2	 0.20	40	14	THF	yes^x	41.9	21.6		0.7	
3	 0.20	−10	24	THF	yes^y	9.1^f	2.2			
4	 0.25	60	14	THF	no	8.0	1.9		0.3	
5	 0.20	90	14	THF	no	3.1	0.4		0.5	
6	 0.13	40	68	THF	no	6.8	0.29		1.4	
7	none	95	14	THF	no	0.32	0.44			
8	none	60	14	THF	no	0.10	0.52			
9	none	25	30	THF	no	0.06	0.08			
10	$Pd(PPh_3)_4$ 0.25	60	14	THF	no	1.83	0.23	0.16		0.10^1
11	$Pd(PPh_3)_4$ 0.20	95	14	i-propanol	no	16.4	2.3	5.6		
12	 0.20	50	14	CH_3OH	yes^x	44.0	3.1			3.9^2

[a] MAH, Maleic anhydride; *x*, five equivalent added; *y*, 1.1 equivalent added.
[b] 4-Vinylcyclohexene.
[c] 1,3,7-Octatriene.
[d] 1,3,6,11-Dodecatetriene.
[e] 1 = Unidentified C_8 material (MW 108); 2 = includes *cis/trans* combination of 1-methoxy-2,7-octadiene and a very small amount of 3-methoxy compound.
[f] Reaction at low temperature; still in progress.



(3)

We believe that the mechanism for phosphine-devoid Pd-based butadiene cyclodimerization parallels the Ni-based route and involves initial formation of a bis(allylic) intermediate, followed by reductive elimination. It is interesting to note that, whereas



(4)

bis(allyl)Pd requires the presence of maleic anhydride (to induce reductive elimination of the diene) in order to form a good cyclodimerization catalyst, *alkyl-substituted allylic* Pd *species* do not require this added π-acidic ligand. These latter compounds, however, can decompose to Pd(0) at low temperature by the hydride transfer based procedures described above. In light of these results, there is reason to doubt the commonly held supposition that the catalytically active species derived from thermolysis of bis(allyl)Pd[36] is in fact a zero-valent metallic species: although the mechanism for thermal decomposition of bis(η^3-allyl)Pd is as yet unknown, it is likely not reductive elimination. Linear oligomerization using phosphine ligand-substituted Pd(0) catalysts may result from an inhibition of reductive elimination steps by these phosphines. (It has been reported† that PCl_3-substituted Pd complexes can be used to prepare vinylcyclohexene from butadiene. In this case it may simply be that this weakly donating ligand may not stabilize the intermediary bis(allylic)Pd complex against reductive elimination and, therefore, *indirectly* allows that process to occur.)

CONCLUSION

We have described observations which show that C—C bond formation by ligand-induced reductive elimination from di(allyl)-substituted Pd(II) complexes is a powerful technique for accomplishing stereospecific coupling of allylic units with regiochemical control. We have found that the critical bis(allylic)Pd intermediates can be prepared in a variety of ways: they are readily available from Grignard reagents or from triorgano(allylic)Sn species and can be generated by condensation reactions of dienes. In general and in the last case specifically, our results show that commonly held conceptions concerning the ability of bis(allylic)Pd species to undergo facile reductive elimination are not entirely accurate: whereas these species do not undergo *spontaneous* reductive elimination readily, they can be made to do so by the simple expedient of replacing phosphine ligands by π-acidic ones. Perhaps it is due to the historical use of

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† The oligomerization of butadiene catalyzed by species derived from thermolysis of bis(allyl)Pd has been found to give only linear trimers.[36] These catalysts were prepared by thermal decomposition of bis(allyl)Pd and similar observations have been noted in Table 5 (entries 4 and 5).

phosphine-based organo-Pd complexes that the reactions described herein had not been discovered earlier; we anticipate, therefore, that other processes for forming C—C bonds by reductive elimination from organometallic intermediates which have been developed from a phosphine ligand-based historical perspective can be rendered more efficient through judicious consideration of the removal of these ligands or of their replacement by others more conducive toward the critical C—C reductive elimination step.

EXPERIMENTAL

General details. All expts, unless aq. conditions were employed, were performed under an atmosphere of purified N_2. Solvents were distilled just prior to use under N_2 from an appropriate drying reagent (THF and Et_2O from sodium benzophenone, and CH_2Cl_2 and acetonitrile from CaH_2).

Allylic halides. 3-Chloro-1-propene, 1-chloro-2-butene, 1-bromo-2-butene, 4-chloro-2-methyl-2-butene, 3-chloro-2-methyl-1-propene and (3-chloro-1-propenyl)benzene were commercially available as combinations of allylic isomers. Each was filtered through basic alumina and distilled prior to use. 1-Chloro-4-methyl-2-pentene was prepared as a mixture of isomers according to the lit.[37]

*General procedures for preparation of π-allyl*Pd *chloride dimers.* (*A*) *From allylic chlorides.* An adaption of a lit.[38] procedure was used. The allylic chloride (0.040 mol) was added to $PdCl_2$ (315 g, 0.020 mol) in 20 ml $CHCl_3$ and 60 ml H_2O. The reaction was stirred vigorously while being gently refluxed for 15 hr. The aq. layer was separated and further extracted with $CHCl_3$. The combined organic layers were dried ($MgSO_4$) and the vol. was reduced. LC (silica gel, $CHCl_3$–hexanes) was used to purify the complex as a yellow crystalline solid. (*B*) *From activation of allylic hydrogen.* In a general procedure, Na_2CO_3 (2.0 g, 17.6 mmol), NaCl (2.0 g, 32 mmol), 15-crown-5-ether (400 μl) and the respective olefin (10.0 mmol) were stirred in 80 ml of CH_2Cl_2 for 30 min. Bis(acetonitrile)dichloroPd (2.8 g, 11.4 mmol) was added over 30 min and the reaction was then stirred for a further 15 hr. The mixture was filtered through Celite and the solvent vol. was reduced. LC (silica gel, $CHCl_3$–hexanes) was used to purify product. (*C*) *From* 1,3-*dienes.* A published procedure was used.[22]

The following π-allylPd complexes prepared by the indicated method have identical properties with those previously reported. Bis[(1-3-η^3-propenyl)Pd chloride][39] (method A), bis[(1-3-η^3-butenyl)Pd chloride][39] (A), bis[(2-methyl-1-3-η^3-propenyl)Pd chloride][39] (A), bis[(4-methoxy-1-3-η^3-cyclohexenyl)Pd chloride][23] (C), bis[(2-methyl-1-3-η^3-cyclohexenyl)Pd chloride][40] (B), bis[(3-methyl-1-3-η^3-butenyl)Pd chloride][39] (A) and bis{[6,6-dimethyl-2,3,10-η^3-2-methylenebicyclo(3.1.1)heptyl]Pd chloride}[40] (B, from β-pinene). *Bis*[(1-*phenyl*-1-3-η^3-*propenyl*)Pd *chloride*] (A). ^{1}H-NMR ($CDCl_3$): δ 7.38 (m, 5), 5.72 (m, 1), 4.52 (d, 1), 3.87 (d, 1), 2.96 (d, 1). *Bis*[(1-*methyl*-2,3-*trimethylene*-1-3-η^3-*propenyl*)Pd *chloride*] (B, from ethylene cyclopentane prepared by standard Wittig olefination[41] of cyclopentanone). ^{1}H-NMR ($CDCl_3$): δ 3.84 (m, 2), 2.7–1.7 (m, 5), 1.30 (m, 1), 1.22 (d, 3). *Bis*{[(4-*methoxy*-4-*methyl*)-1-3-η^3-*pentenyl*]Pd *chloride*} (C). ^{1}H-NMR ($CDCl_3$): δ 5.4 (m, 1), 3.95 (d, 1), 3.71 (d, 1), 3.26 (s, 3), 2.96 (d, 1), 1.39 (s, 6).

Allylic Grignard reagents. These were prepared by an adaption of a published procedure.[42] Mg filings (9.7 g, 0.40 mol) were covered with 100 ml Et_2O. The allylic halide (0.04 mol) dissolved in 10 ml Et_2O was added over 1 hr at −30°. The reaction was stirred for a further 1 hr before raising the temp to ambient. After stirring for a further 3 hr, the reaction was permitted to settle, and the clear soln was removed by a cannula and titrated (H_2O vs CCl_4). Most Grignard reagents used were dried to yield a solid and were redissolved just prior to use. Allylic Li reagents were prepared from the corresponding triphenyl-Sn compound.[43]

Preparation of 17-*ethyleneandrost*-5-*en*-3β-*ol.* Ethyltriphenylphosphonium bromide (20.2 g, 53.6 mmol) and dehydro-iso-androsterone (Aldrich, 510 g, 17.3 mmol) were stirred in 80 ml of THF, while *t*-BuOK was added as a slurry (65 mmol, 30 ml THF). After refluxing for 12 hr the mixture was added to iced H_2O and the aqueous layer was further extracted with Et_2O (3 × 20 ml). The combined organic layers were dried ($MgSO_4$), filtered and the solvent was removed. LC purification gave the product (4.2 g, 83%); NMR analysis showed that a small amount of the *E* isomer was present.

Preparation of 17-*ethyleneandrost*-5-*en*-3β-*dimethyl*, t-*butylsiloxyl.* In 60 ml of DMF were dissolved *t*-butyldimethylsilyl chloride (113 g, 8.6 mmol), imidazole (1.2 g, 17.3 mmol) and 17-ethyleneandrost-5-en-3-ol (210 g, 6.9 mmol). After stirring overnight, the reaction was hydrolysed and extracted with Et_2O. The organic layer was washed sequentially with H_2O and sat. NaCl, then dried ($MgSO_4$) and filtered through silica gel (2% Et_2O in hexane) (98% yield). ^{1}H-NMR ($CDCl_3$): δ 5.24 (m, 1), 5.08 (q of t, 1), 3.40 (m, 1), 1.57 (d, 3), 1.00 (s, 3), 0.86 (s, 12), 0.10 (s, 6).

Preparation of bis{[16,17,20 - η^3 - 3 - (*dimethyl* - t - *butylsiloxyl*) - 17 - *ethyleneandrost* - 5 - *en*]Pd *chloride*}. This compound was prepared by procedure B. Purification was accomplished by LC (silica gel, Et_2O–hexanes) (1.82 g, 88%). A trace of *anti* isomer was removed by repeated LC. ^{1}H-NMR ($CDCl_3$): δ 5.24 (br, 1), 3.62 (m, 2), 3.41 (m, 1), 2.4–0.90 (m, 17), 1.22 (d, 3), 1.00 (s, 3), 0.86 (s, 12), 0.10 (s, 6).

General procedure for the preparation of Pd-(η^3-*allyl*)(η^3-*allyl′*). The π-allylPd chloride dimer (4 mmol) was suspended in 10 ml Et_2O containing dioxane (120 μl, 13.5 mmol) at −35°. The allylic Grignard (4.2 mmol) was slowly injected which resulted in much white ppt. There was a gradual loss of the bright yellow color of the dimer (3–4 hr) while the mixture was stirred at −30°. The Et_2O was pumped off and the residue was extracted with cold pentane (3 × 20 ml). The pentane was filtered through Celite within a closed, cold system. The pentane was removed (−35°) yielding a light golden-yellow crystalline solid (80%). Low temp ^{1}H-NMR displayed a set of at least four distinguishable isomers. The general shifts for (1 - methyl - 2,3 - trimethylene - 1 - 3 - η^3 - propenyl)(1 - 3 - η^3 - butenyl)Pd are: for the crotyl ligand set ^{1}H-NMR ($CDCl_3$): δ 4.8 (m, 1), 3.6 (d, 1), 3.3 (d, 1), 2.5 (d, 1), 1.8 (d, 3); and for other unit δ 3.4 (m, 1), 3.2 (m, 2), 2.2 (br, 4), 2.0 (d, 3), 1.8 (m, 2).

*General procedure for selective coupling of π-allyl*Pd *chloride dimer and allylic Grignards.* To a Schlenk flask containing π-allylPd chloride dimer (2.0 mmol) was added 10 ml Et_2O and dioxane (6.6 mmol). Allylic Grignard was slowly injected at −30°. Upon stirring for 2 hr, maleic anhydride (sublimed, 980 mg, 10 mmol) dissolved in Et_2O was added. After stirring for a further 1 hr, the temp was permitted to rise to room temp resulting in the gradual formation of a black ppt.

If the coupling products were volatile, they were recovered by low pressure distillation. If the products were not sufficiently volatile, the reaction mixture was gel filtered through alumina to remove metal residues. Reactions were analysed by GC (and TLC). Analytically pure samples were isolated by preparative GC or liquid chromatography (silica gel) and were identified by the reported data: *E,E*-1,5-*heptadienylbenzene*[44] (preparative GC).

1-(1-*Methyl*-3-*pentenyl*)*cyclopentene* (*preparative GC*). ^{1}H-NMR ($CDCl_3$) δ 5.34 (m, 3), 2.09 (br, 6), 2.92 (m, 1), 1.78 (m, 2), 1.62 (m, 3), 0.98 (d, 3). MS *m/z* (rel. int.): 150 (5), 95 (100), 32 (88), 67 (57), 41 (38), 39 (30).

2-(2-*Butenyl*)*ethylidene cyclopentane* (*preparative GC*). ^{1}H-NMR ($CDCl_3$): δ 5.38 (m, 2), 5.17 (q of d, 1), 2.88 (m, 1), 2.19 (br, 4), 1.86 (m, 4), 1.55 (m, 6). MS *m/z* (rel. int.): 150 (4), 32 (100), 95 (41), 67 (32), 41 (18), 44 (18), 39 (17).

1-*Methyl*-6-(4-*methyl*-2-*pentenyl*)*cyclohexene* (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.35 (m, 3), 2.16 (m, 1), 1.93 (br, 5), 1.66 (s, 3), 1.53 (br, 4), 0.97 (d, 6). MS *m/z* (rel. int.): 178 (1.8), 95 (100), 41 (29), 67 (23), 55 (22), 94 (15), 39 (14).

2,9-*Dimethyl*-2-*methoxy*-3,7-*decadiene* (*preparative GC*). ^{1}H-NMR ($CDCl_3$): δ 5.33 (m, 4), 3.12 (s, 3), 2.18 (m, 1), 2.07 (m, 4), 1.22 (s, 6), 0.94 (d, 6, $J = 6.5$ Hz). Irradiate at δ 2.1; see collapse of signals at δ 5.3 to two AB patterns, $J_{AB} = 16$ Hz.

6,6-*Dimethyl-2-(3-pentenyl)bicyclo*(3.1.1)-2-*heptene* (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.58 (m, 2), 5.34 (br, 1), 2.48 (m, 1), 2.37 (m, 2), 2.18 (br, 5), 1.78 (m, 3), 1.44 (s, 3), 1.27 (m, 2), 1.02 (s, 3).

16-(3-*Methyl*-2-*butenyl*)-17(Z)-*ethylideneandrost*-5-*en*-3β-(t-*butyldimethylsiloxyl*) (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.26 (br, s, 1), 5.14 (q, 1, J = 7), 5.07 (t, 1, J = 7.5), 3.41 (m, 1), 2.5–0.8 (v br, 20), 1.65 (s, 3), 1.62 (d, 3), 1.53 (s, 3), 0.96 (s, 3), 0.85 (s, 3), 0.83 (s, 9), 0.02 (s, 6). Irradiate at δ 5.14, doublet at δ 1.63 collapses to doublet with $J \leqslant 1$ Hz.

16α-(4-*Methyl*-2-*pentane*)-17(Z)-*ethylideneandrost*-5-*en*-3β-(t-*butyldimethylsiloxyl*) (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.28 (br, 3), 5.10 (q, 1), 3.41 (m, 1), 1.64 (d, 3, J = 7.1 Hz), 0.96 (d, 3, J = 6.4 Hz), 2.5–0.8 (br, 21), 0.83 (s, 9), 0.02 (s, 6). MS *m/z* (rel. int.): 496 (6.6), 439 (100), 440 (36), 381 (23), 463 (10), 441 (9), 355 (8), 497 (2.2).

trans-1-*Methoxy*-4-(3-*methyl*-2-*butenyl*)-2-*cyclohexane* (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.67 (t, 2), 5.1 (t, 1), 3.76 (m, 1), 3.32 (s, 3), 1.75–2.20 (m, 5), 1.55 (s, 3), 1.66 (s, 3), 1.42 (m, 1), 1.18 (m, 1). Irradiate δ 3.76 see collapse of δ 1.42 proton (J = 8.7 Hz). NOE difference collection affects δ 1.4, 2.1, 3.8 and 5.17. Irradiate at δ 1.96, see collapse at δ 1.20 and 3.76 (to a doublet, J = 8.4 Hz).

trans-1-*Methoxy*-2-(3-*methyl*-2-*butenyl*)-3-*cyclohexene* (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.62 (d, 1), 5.48 (d, 1), 5.11 (m, 1), 3.33 (s, 3), 3.08 (m, 1), 2.22–1.85 (br, 6), 1.68 (s, 3), 1.59 (s, 3), 1.51 (m, 1). Irradiate δ 3.08, see collapse at δ 1.51. Irradiate at δ 1.51, see collapse at δ 3.08 to a doublet (J = 8.9 Hz).

Studies on steroidal coupling stereochemistry (*Scheme* 3). The Grignard coupling reaction followed the above general procedure. The small amount of C-20 coupled product was isolated by preparative GC. (A) *Coupling with alkenylzirconium.* The steroidal π-allylPd chloride dimer (300 mg, 0.54 mmol) was dissolved in 5 ml THF and the zirconocene (4-methyl-2-pentyl)chloride[45] (1.08 mmol) dissolved in THF was injected. The reaction turned black within a few seconds, but the mixture was allowed to stir for 15 hr. After silica gel filtration, GC analysis showed a 78% yield of combined olefins and 22% C-16 coupled product was produced. The product mixture was hydrogenated. (B) *General hydrogenation procedure.* Pd–C catalyst in 1 ml EtOH was stirred for 1 hr under 1 atm H_2 in a Fischer–Porter bottle. The substrate dissolved in EtOAc, was added and the system was pressurized with H_2 to 80 psi for 2 hr. The reaction mixture was filtered through Celite and was concentrated for preparative GC. (C) *Protection of the cholesterol* 3-*hydroxy group.* Cholesterol (1.0 g, 2.6 mmol), *t*-butyldimethylsilyl chloride (480 mg, 3.2 mmol) and imidazole (440 mg, 6.5 mmol) were stirred in DMF for 24 hr. After partitioning between H_2O–Et_2O, the organic layer was washed with H_2O and sat NaCl and dried ($MgSO_4$). The product was purified by LC (silica gel, Et_2O–hexanes, quantitative yield) and hydrogenated according to the above procedure.

17-*Ethyl*-16α-(4-*methylpentyl*)*androstan*-3β-(t-*butyldimethylsiloxyl*). ^{1}H-NMR (C_6D_6): δ 3.67 (m, 1), 1.25–0.80 (br, 31), 1.08 (s, 9), 1.07 (t, 3), 0.98 (s, 3), 0.95 (s, 3), 0.74 (d, 6), 0.18 (s, 6). ^{13}C-NMR: δ 72.5, 60.1, 55.1, 54.7, 45.4, 43.9, 43.4, 39.8, 39.4, 38.1, 37.6, 35.9, 35.7, 32.7, 32.6, 32.4, 30.2, 29.3, 28.4, 27.2, 26.2, 23.6, 22.9, 22.7, 21.5, 18.4, 14.7, 13.7, 12.5. MS *m/z* (rel. int.): 502 (0.4), 445 (100), 446 (37), 447 (9), 369 (6), 355 (2), 370 (2).

17-[(1,5)-*dimethylhexyl*]-*androstan*-3β-(t-*butyldimethylsiloxyl*). ^{1}H-NMR (C_6D_6): δ 3.67 (m, 1), 1.24–0.8 (br, 31), 1.08 (s, 9), 1.07 (d, 3), 0.98 (s, 3), 0.96 (s, 3), 0.74 (d, 6, J = 15.3 Hz), 0.18 (s, 6). ^{13}C-NMR (C_6D_6): δ 72.4, 56.9, 56.8, 54.9, 45.3, 43.0, 40.6, 40.0, 39.4, 37.5, 36.7, 36.2, 35.9, 35.8, 32.6, 29.2, 28.7, 28.4, 26.2, 24.6, 24.4, 23.0, 22.8, 21.7, 19.1, 18.4, 12.5, 12.4, 1.4. MS *m/z* (rel. int.): 502 (0.4), 445 (100), 446 (37), 447 (9), 369 (6), 443 (4.0), 370 (2), 335 (2), 487 (2), 331 (1).

Electrochemical expts. Electrochemical analyses were performed using a Princeton Applied Research model 174/175 potentiostat/galvanostat. The working electrode was a 10 mm Pt fan; the counter electrode was a Pt wire in a chamber containing $(Cp_2Fe)PF_6$ connected to the cell by a ceramic frit. The reference electrode was sat calomel (SCE). The supporting electrolyte, tetra-*n*-butylammonium perchlorate was recrystallized from EtOAc and was dried *in vacuo* at 150° for 12 hr. Cell preparation was done in a dry box and expts were performed with an N_2 purge. CV analysis was performed in quiet solns. Typically, 0.1 M TBAP solns were used and expts were performed at −30° using a cryocool. After preparative electrolysis, CV analysis showed that the original oxidation wave had gone. Reaction solns were distilled at reduced pressure and analysed by GC. Monophosphine adducts of bis(allylic)Pd complexes were prepared by a lit. method.[24]

Oxidation of bis(π-*allyl*)Pd *complexes by electron transfer oxidants.* These reactions were typically performed in THF or acetonitrile at −30°. The solid oxidants were added (0.50 mmol) to a stirred soln of the bis(allyl)Pd complex (0.50 mmol) at −30°. After 15 min, the temp was permitted to rise to ambient and the mixture was stirred for 12 hr. Volatiles were distilled at reduced pressure and analysed by GC. Reverse order of addition yielded similar results.

The bis(crotyl)Pd complex was found to be relatively stable under O_2; coupling reactions proceeded in an identical fashion to that noted under N_2. In a radical trapping expt,[46] Na_2IrCl_6 (170 mg, 0.3 mmol) was dissolved in 5 ml THF under O_2 and the temp was lowered to −40°. Bis(η^3-crotyl)Pd (0.30 mM) was added dropwise by a syringe. When addition was complete, the temp was permitted to rise to 25° and the reaction was stirred for 4 hr. Volatiles were distilled under reduced pressure and analysed by GC/MS to indicate the presence of 2-buten-1-ol and 2-butenal[47] as well as crotyl chloride and 1,5-diene products.

General procedure for cross-coupling utilizing (η^3-*allyl*)Pd *chloride dimer and bis*(*allylic*)*zirconocene reagents.* Bis(allyl)- and bis(crotyl)zirconocene were prepared from zirconocene dichloride by lit. methods.[31] Bis(allyl)zirconocene (2.0 mmol) dissolved in 4 ml Et_2O was added to (η^3-allyl)Pd chloride dimer (1.0 mmol) suspended in cold Et_2O (−30°). After 20 min, maleic anhydride dissolved in Et_2O was added and the reaction was stirred for 12 hr at room temp. Reaction work-up was similar to that used in Grignard coupling procedures.

Sn *reagents.* Tributylallyl-Sn, tributylcrotyl-Sn and tributylprenyl-Sn were prepared according to the lit.[48] The Sn reagents were distilled to give predominantly one allylic isomer. The 6-(trimethyl-Sn)-4-hexenoate, ethyl ester was prepared as follows. Ethyl 3,5-hexadienoate[49] (3.4 g, 24 mmol) was added to trimethyl Sn hydride (25 mmol) dissolved in 10 ml THF. AIBN (54 mg, 0.3 mmol) was added and the reaction was refluxed for 15 hr.[50] The solvent was removed at 60 mm and the diene was removed at 0.5 mm. Kugelrohr distillation (125°, 15 mm) gave a clear liquid. ^{1}H-NMR (C_6D_6): δ 5.85 (m, 2), 3.93 (q, 2), 2.91 (d, 2), 2.20 (m, 4), 0.92 (t, 3), 0.22 (s, 9). MS *m/z* (rel. int.), considering only the largest isotope of the Sn pattern: 306 (1.7), 165 (100), 135 (34), 237 (14), 150 (14), 291 (9), 209 (7), 261 (3).

General procedure for selective cross-coupling using (η^3-*allyl*)Pd *chloride and allyl* Sn *reagents.* Into a Schlenk flask containing (η^3-allyl)Pd chloride dimer (1.0 mmol) suspended in 10 ml Et_2O at −30° was injected the trialkylallyl-Sn reagent (112 mmol). After stirring for 5 hr, maleic anhydride dissolved in Et_2O was added. After stirring for a further 12 hr, the temp was permitted to rise to room temp at which time black Pd material began to ppt. If coupling products were sufficiently volatile, reaction mixtures were vacuum distilled and products were analysed by GC. If products were not sufficiently volatile, metallic residues were removed by gel filtration (Florisil). Products were then analysed by GC or were isolated by LC. Analytically pure samples of coupled products were isolated by either preparative GC or LC (silica gel).

(E)2-*Methyl-2,6-octadiene*[44] (*preparative LC*) *and ethyl* 4,8-*decadienoate* (*preparative GC*). ^{1}H-NMR ($CDCl_3$): δ 5.40 (m, 4), 4.09 (q, 2), 2.31 (br s, 4), 1.99 (br s, 4), 1.61 (d, 3), 1.22 (t, 3). MS *m/z* (rel. int.): 196 (2.3), 55 (100), 71 (94), 67 (77), 41 (51), 39 (43), 99 (42), 43 (28), 68 (28), 53 (25).

16-(2-*Butenyl*)-17(Z)-*ethylideneandrost*-5-*en*-3β-(t-*butyldimethylsiloxyl*) (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.28 (m, 3), 5.10 (q of d, 1), 3.40 (m, 1), 2.5–0.9 (br, 23), 1.6 (d of d, 3, J = 7.2, 2.0 Hz), 0.6 (s, 3), 0.88 (s, 3), 0.80 (s, 9), 0.02 (s, 6). The C-20 coupled product is indicated by a doublet at δ 1.0 and a triplet at δ 5.2.

trans-*Methoxy-4-(2-propenyl)-2-cyclohexene* (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.71 (m, 3), 4.98 (m, 2), 3.77 (m, 1), 3.36 (s, 3), 1.80–2.25 (br, 5), 1.51 (m, 1), 1.20 (m, 1). Irradiate at δ 2.08, see collapse of δ 3.77 to a doublet (J = 7.3 Hz).

trans-1-*Methoxy-2-(2-propenyl)-3-cyclohexene* (*LC*). ^{1}H-NMR ($CDCl_3$): δ 5.59 (m, 3), 4.98 (m, 2), 3.34 (s, 3), 3.08 (m, 1), 2.3–1.8 (br, 6), 1.48 (m, 1).

General procedure for the catalytic coupling of allylic halides and allyl-Sn *reagents*. Trialkylallyl-Sn (2 mmol), allylic halide (2.4 mmol) and (η^3-allyl)Pd chloride (0.02 mmol) were dissolved in 5 ml of THF. The temp was lowered to $-30°$ and maleic anhydride (10 mg, 0.10 mmol) dissolved in THF was added. After 15 min the reaction was placed in a preheated oil bath at 55°. After 12 hr, the mixture was either distilled at reduced pressure or was filtered through Florisil if products were non-volatile. Products were analysed by GC or isolated by preparative LC.

*Preparation of bis(η^3-allyl)*Pd *using tributylallyl*-Sn. (η^3-Allyl)Pd chloride dimer (200 mg, 1.1 mmol) was suspended in 1 ml of Et_2O at $-30°$. Tributylallyl-Sn (1.3 mmol) was added and the reaction mixture was stirred for 14 hr. When the reaction mixture was warmed to 0°, a small amount of insoluble material was noted after 2 hr. The Et_2O was slowly removed at $-35°$ leaving the product as a yellow–orange solid which was washed with cold pentane. The solid was pumped dry ($-35°$) and was filtered into an NMR tube; the low temp ^{1}H-NMR spectrum clearly demonstrated the presence of bis(η^3-allyl)Pd.[19]

General procedure for butadiene cyclodimerization. Maleic anhydride (98 mg, 1.0 mmol) was dissolved in 2 ml of THF under N_2 in a Fischer–Porter bottle. A cold bath ($-78°$) was applied and precondensed butadiene (9 ml, 108 mmol, dried over 4 Å molecular sieves) was transferred into the flask via a cannula by slightly warming the butadiene-containing flask. The bis(allyl)Pd catalyst precursor (0.2 mmol) dissolved in 0.5 ml THF was injected. After stirring for 20 min the cold bath was replaced by a preheated oil bath (80°). The reaction was run for 14 hr at that pressure which was created by warming the system (42 psi). After cooling the mixture excess butadiene was vented. A Pd mirror had formed. A sample of the remaining liquid was filtered through alumina, GC analysis demonstrated nearly complete, selective formation of 4-vinylcyclohexene. Solvent was removed by evacuation at 0°.

The same procedure applied to isoprene resulted in four coupling products as indicated by GC/MS analyses. They were isolated by preparative GC and were identified by comparison of NMR data with reported values.[51]

Butadiene linear trimerization. Precondensed butadiene (10.0 ml, 120 mmol, dried over 4 Å molecular sieves) was transferred via a cannula into a Fischer–Porter bottle containing 3 ml THF at $-78°$ under N_2. The bis(allyl)Pd catalyst precursor (0.20 mmol) dissolved in 0.5 ml THF was injected. After stirring for 20 min the cold bath was replaced with a preheated oil bath (40°) and was permitted to stir for 68 hr. After cooling, the excess butadiene was vented and a GC reference was added. A sample was filtered through alumina and analysed by GC (Table 5, entry 6). A combination of dodecatriene isomers identified by GC/MS was collected by preparative GC; hydrogenation produced only *n*-dodecane. The major isomer (42%) was further isolated and its structure confirmed by the spectral data as 1,3,6,11-dodecatriene. ^{1}H-NMR ($CDCl_3$): δ 6.45–4.82 (m, 10), 2.78 (br t, 2), 2.02 (br s, 4), 1.60 (br, 2). MS *m/z* (rel. int.): 162 (2.1), 79 (100), 41 (62), 91 (57), 39 (54), 27 (48), 29 (40), 55 (34).

Teleomerization. The above procedure was repeated except that the THF was replaced by 6 ml of MeOH (distilled from NaOMe). Products were isolated by preparative GC and were proven to be vincyclohexene and *E*, *E* and *E*, *Z* isomers of 1-methoxy-2,7-octadiene.[52]

For the linear dimerization of butadiene, the lit.[52] procedure was followed. Properties of products isolated by preparative GC agreed with the reported data.

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