Palladium- or Nickel-Catalyzed Reactions of Alkenylmetals with Unsaturated Organic Halides as a Selective Route to Arylated Alkenes and Conjugated Dienes: Scope, Limitations, and Mechanism[†1,2]

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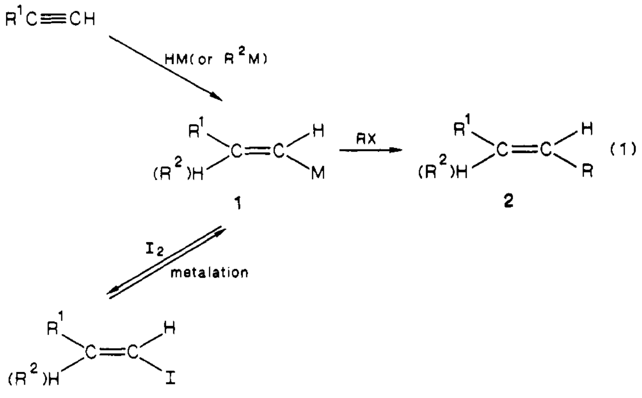
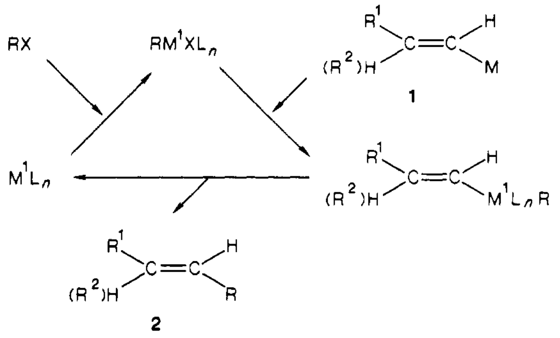
Abstract: Stereo- and regiodefined alkenylmetals containing Al, Zr, and Zn react with aryl and alkenyl iodides and bromides in the presence of catalytic amounts of Pd or Ni complexes containing phosphine ligands, such as PPh_3, to give the corresponding cross-coupled products. Palladium catalysts permit nearly 100% stereospecificity in both alkenyl–aryl and alkenyl–alkenyl coupling reactions, whereas nickel catalysts lead to partial stereochemical scrambling in the alkenyl–alkenyl coupling. Although many other metals including Li, Mg, Cd, Hg, B, Si, Sn, Ti, and Ce were also used, the results were inferior to those obtained with Al, Zr, and Zn under the conditions used in the present study. The turnover numbers for the palladium-catalyzed reactions of PhI with (*E*)-1-octenylmetals containing Al, Zr, and Zn were 2, 3, and >2000 mmol of (*E*)-1-octenylbenzene (**8**) per mmol of $Pd(PPh_3)_4$ per hour at room temperature, respectively. The stoichiometric reaction of $PhPd(PPh_3)_2I$ (**6**) with 1.2 equiv of (*E*)-1-octenylzinc chloride (**7**) in a 2:1 mixture of CD_2Cl_2 and THF was examined in detail. The reaction follows second-order kinetics (k_2 = 2.9 L/(mol·min) at 0 °C) to give **8** without the buildup of any intermediate. The results are consistent with a slow formation of **9** via transmetalation followed by its rapid reductive elimination to give **8** and "$Pd(PPh_3)_2$". Addition of PhI to the reaction mixture rapidly gives **6** in 98% yield, supporting the plausibility of the proposed oxidative addition step. These results are consistent with the proposed mechanism consisting of oxidative addition of Pd(0) complexes, rate-determining transmetalation involving Pd(II) complexes, and rapid decomposition of diorganopalladium(II) species to produce the coupling products in one or more subsequent steps. The rate-determining transmetalation step provides an explanation for the effect of metals in organometallic reagents used stoichiometrically.

Conversion of alkynes into stereo- and regio-defined alkenylmetals via hydrometallation or carbometallation followed by replacement of the carbon group is an attractive, efficient and selective route to alkenes (eq 1). Of particular interest among known hydrometalation reactions are those involving B,[3] Al,[4] and Zr,[5] since they normally involve essentially 100% cis addition. In addition, we have recently found that Al can also undergo an essentially 100% cis carbometalation that is catalyzed by Zr or Ti complexes.[6]



M = metal group; R, R^1, R^2 = carbon groups

Scheme I



M^{1}L$_n$ = nickel- or palladium-phosphine complex;
RX = aryl or alkenyl halide

The prime objective of this study is to devise selective procedures for converting alkenylmetals represented by **1** into **2**, where the R group is aryl or alkenyl. At the outset of this study, highly selective methods for synthesizing conjugated dienes via cross coupling were essentially unknown.[7] None of the known alkenylmetals containing the main group metals appeared to undergo satisfactorily a stereospecific substitution reaction at sp^2 hybridized carbon centers. Although a few reactions of alkenylcoppers with alkenyl halides were known,[7b] they were not selective and hence unsatisfactory from the synthetic viewpoint. And yet, selective synthesis of conjugated dienes was highly needed for synthesizing selectively a wide variety of organic molecules including caro-

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[†] This paper is dedicated to Professor Koji Nakanishi of Columbia University on the occasion of his 60th birthday.

[‡] Purdue University.

(1) Nickel- or Palladium-Catalyzed Cross Coupling. 31. Part 30. Negishi, E.; Akiyoshi, K., submitted for publication.

(2) Reported in part as preliminary communications. (a) Negishi, E.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976**, 596. (b) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729. (c) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (d) Okukado, N.; Van Horn, D. E.; Klima, W. E.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027.

(3) For a review, see: Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

(4) For a review, see: Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 1.

(5) For a review, see: Schwartz, J. *J. Organomet. Chem. Library* **1976**, *1*, 461.

(6) For a review, see: Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333.

(7) (a) The following organoboron methodologies were known, each probably representing the first highly selective method of some generality: *E,E*-dienes, Negishi, E.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1973**, 636; *E,Z*-dienes, Negishi, E.; Lew, G.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1973**, 874; *Z,Z*-dienes, Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1070**, *92*, 4068. (b) A very limited number of examples of copper-promoted alkenyl–alkenyl cross coupling were known. They were either low-yielding or nonselective: Posner, G. H. *Org. React.* **1975**, *22*, 253.

0002-7863/87/1509-2393$01.50/0

Table I. Nickel-Catalyzed Reaction of (*E*)-1-Alkenylalanes and (*E*)-1-Alkenylzirconium Derivatives with Aryl Halides[a]

(*E*)-$RAl(i\text{-}Bu)_2$ or (*E*)-$RZrCp_2Cl$(RM)						
R	metal	aryl halide (ArX)	RM[b]/ArX	$Ni(PPh_3)_4$, %	reaction time,[c] h	yield of RAr,[d] %
1-heptenyl	Al	iodobenzene	2	5	12	91 (85[e])
1-heptenyl	Al	bromobenzene	2	5	3[f]	89
1-heptenyl	Al	bromobenzene	2	g	24[h]	87
1-hexenyl	Al	*p*-bromotoluene	2	g	24	84
1-hexenyl	Al	*p*-chloroiodobenzene	1	5	6	90
1-hexenyl	Al	*p*-bromobenzonitrile	1	5	1	64
1-heptenyl	Al	1-bromonaphthalene	1	5	12	78
1-heptenyl	Al	1-bromonaphthalene	2	5	3	92
1-heptenyl	*i*	iodobenzene	2	5	12	21
1-heptenyl	Zr	iodobenzene	1.5	10	12–24	96
1-heptenyl	Zr	1-bromonaphthalene	1.5	10	12–24	70
β-ethoxyethenyl	Zr	1-iodobenzene	1.5	10	12–24	99 (76[e])
4-tetrahydropyranyloxyl-1-butenyl	Zr	1-iodobenzene	1.5	10	12–24	84
1-hexenyl	Zr	*p*-chloroiodobenzene	1.5	10	12–24	95
1-hexenyl	Zr	*p*-iodoanisole	1.5	10	12–24	80
1-hexenyl	Zr	*p*-bromobenzonitrile	1.5	10	12–24	92
1-hexenyl	Zr	methyl *p*-bromobenzoate	1.5	10	*j*	92

[a] Unless otherwise mentioned, the reaction was carried out at room temperature (22–25 °C). [b] The amount of RM is based on 1-alkyne used. [c] The indicated reaction time does not necessarily correspond to the time required for completion of reaction. [d] By GLC based on ArX. [e] Isolated yield. [f] At 50 °C. [g] $Pd(PPh_3)_4$ (5 mol %) was used in place of $Ni(PPh_3)_4$. [h] The reaction mixture was heated under reflux in THF–hexane. [i] M = $Al(i\text{-}Bu)_2(n\text{-}Bu)Li$. [j] 6 h at room temp and then 13 h at 50 °C.

tenoids, insect pheromones and hormones, and dienes for the Diels–Alder reaction.

We reasoned that one possible approach to solve the above problem would be to attempt to promote the reaction of alkenylmetals with alkenyl halides with appropriate transition-metal catalysts. We were attracted by the ability of Group VIII (8)[36] transition-metal complexes to interact readily with unsaturated organic halides and cleave the carbon–halogen bonds via oxidative addition.[8] Our attention was drawn to the nickel-catalyzed reaction of Grignard reagents with aryl and alkenyl halides reported in 1972.[9] The reaction was thought to proceed by (i) oxidative addition of an organic halide with a nickel–phosphine complex, (ii) transmetalation between an organonickel(II) halide intermediate and a Grignard reagent to form a diorganonickel(II) intermediate, and (iii) its decomposition with regeneration of the organonickel(II) halide. *If this mechanism is indeed correct, any organometallic reagents capable of undergoing transmetalation with the organonickel(ii) halide could, in principle, participate in this type of reaction.* We therefore decided to explore the feasibility of developing catalytic cross-coupling procedures that involved alkenylmetals containing various metals, especially B, Al, and Zr, according to Scheme I. Although proceeding stoichimetrically, the formation of $FC_6H_4Pd(PEt_3)_2X$, where X is a halogen, by oxidative addition of FC_6H_4X to $Pd(PEt_3)_4$, their reaction with PhMgBr and MeMgBr to form $FC_6H_4Pd(PEt_3)_2Ph$ and $FC_6H_4Pd(PEt_3)_2Me$, respectively, as isolable and characterizable species, and their decomposition via reductive elimination to produce FC_6H_4Ph and FC_6H_4Me, respectively, were reported in 1974.[10] Unfortunately, the formation of the organic products via reductive elimination in the above cases was extremely slow requiring weeks at room temperature, and no product yields were reported. Nonetheless, it was felt that, with suitable modifications of reaction conditions, cross-coupling catalyzed by Pd complexes might also be feasible.

Results and Discussion

Nickel-Catalyzed Reactions of (*E*)-1-Alkenylalanes and (*E*)-1-Alkenylzirconium Derivatives with Aryl Halides. With the objective of developing nickel- or palladium-catalyzed reactions of alkenylmetals directly obtainable via hydrometalation of alkynes with unsaturated organic halides, (*E*)-1-alkenylmetals containing B, Al, and Zr were prepared by known hydrometalation reactions of 1-alkynes with disiamylborane,[3] diisobutylaluminum hydride[4] (DIBAH), and $HZrCp_2Cl$[5] ($Cp = \eta^5\text{-}C_5H_5$), respectively. These (*E*)-1-alkenylmetals were treated with aryl iodides and bromides in the THF–hexane or THF–benzene at room temperature in the presence of 5–10 mol% of $Ni(PPh_3)_4$, generated in situ by treating anhydrous $Ni(acac)_2$, where acac is acetylacetonato, with 1 molar equiv of DIBAH in THF in the presence of PPh_3 (4 equiv). Since the yields of (*E*)-1-alkenylmetals based on 1-alkynes were typically 80–100%, and since the desired cross-coupling reaction was expected to be very slow near the end of the reaction, a 50–100 mol% excess of an (*E*)-1-alkenylmetal relative to an aryl halide was used.

We have found that both (*E*)-1-alkenylalanes[2a] and (*E*)-1-alkenylzirconium derivatives[2c] readily react with aryl halides under these conditions to produce cleanly the desired arylated alkenes. These reactions represent the first examples of nickel-catalyzed cross coupling of organometals containing Al and Zr. Neither the corresponding (*E*)-1-alkenyldisiamylboranes nor their ate complexes obtained by their reaction with 1 equiv of *n*-BuLi gave the desired products in any more than 5% yields.[2a,11] The nickel-catalyzed reaction of (*E*)-1-heptenyldiisobutylalane with iodobenzene provided (*E*)-1-heptenylbenzene in 91% yield, and the corresponding reaction of lithium (*E*)-1-heptenyldiisobutyl(*n*-butyl)alanate gave the desired product only in 21% yield under comparable conditions. In no case did the cross-coupling reaction proceed in the absence of $Ni(PPh_3)_4$, indicating that these reactions were indeed catalyzed by $Ni(PPh_3)_4$. The experimental results are summarized in Table I. In cases where the yields of the desired products are ≥70%, the amounts of homocoupled byproducts, i.e., biaryls and conjugated dienes, are 0–5% each, the product region of the GLC traces of quenched reaction mixtures showing essentially one signal. The stereochemistry of each isolated pruduct determined by GLC, ^1H and ^{13}C NMR, and IR is ≥98%, indicating that the overall process is ≥98% stereoselective. There are no indications for regiochemical scrambling of the arene substituents. The chemoselectivity of the cross-coupling reactions

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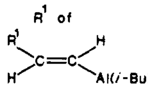
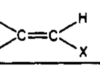
(8) For a review, see: Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(9) (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. (b) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144.

(10) Parshall, G. *J. Am. Chem. Soc.* **1974**, *96*, 2360.

(11) For successful palladium-catalyzed cross-coupling reactions of organoboron compounds, however, see the following papers. (a) Miyaura, N.; Suginome, H.; Suzuki, A. *Tetrahedron Lett.* **1981**, *22*, 127. (b) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. (c) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178 and references therein. (d) The first successful use of organoboron compounds in palladium-catalyzed cross coupling was reported at the ACS National Meeting, New Orleans, March, 1977. See, also: Negishi, E. In *Aspects of Mechanism and Organometallic Chemistry*; Brewster, J. H., Ed.; Plenum, New York, 1978; p 285. Also reported therein is a successful use of alkynylstannanes in palladium-catalyzed cross coupling.

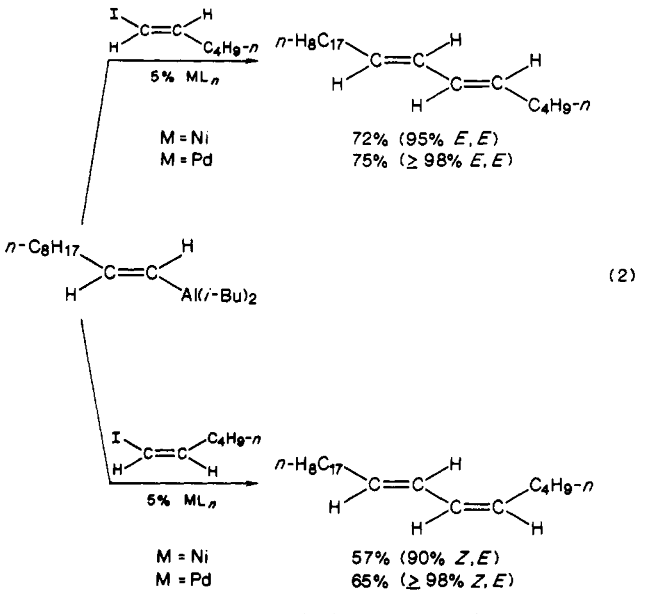
Table II. Palladium- or Nickel-Catalyzed Reaction of (*E*)-1-Alkenylalanes with Alkenyl Halides[a]

R^1 of 					cross-coupled product		
	R^2	R^3	X	M of $M(PPh_3)_n$[b]	yeild,[c] %	stereoismrc purity, %	homocoupled product[d] (yield %)
n-C_8H_{17}	n-C_4H_9	H	I	Pd	75 (65)	≥98	traces
n-C_8H_{17}	H	n-C_4H_9	I	Pd	65	≥98	n-C_{12} (3), n-C_{20} (traces)
n-C_4H_9	t-C_4H_9	H	I	Pd	82 (71)	≥98	traces
t-C_4H_9	H	n-C_4H_9	I	Pd	36	≥97	n-C_{12} (2), t-C_{12} (2)
n-C_4H_9	COOMe	CH_3	Br	Pd	75 (61)	≥97	traces
n-C_8H_{17}	n-C_4H_9	H	I	Ni	72	95	n-C_{12} (3), n-C_{20} (14)
n-C_8H_{17}	H	n-C_4H_9	I	Ni	57	90	n-C_{12} (5), n-C_{20} (traces)
n-C_4H_9	t-C_4H_9	H	I	Ni	48	93	n-C_{12} (6), t-C_{12} (8)
t-C_4H_9	n-C_4H_9	H	I	Ni	15	93	

[a] Unless otherwise mentioned, the reaction was carried out by using a 50 mol % excess of (*E*)-1-alkenylalanes in ether or THF at room temperature for 12–24 h in the presence of 5 mol % of a Pd or Ni catalyst. [b] Pd catalyst = $Cl_2Pd(PPh_3)_2$–DIBAH (1:2) Ni catalyst = $Ni(acac)_2$–DIBAH–PPh_3 (1:1:4). [c] By GLC. The numbers in parentheses are isolated yields. [d] n-C_{12} = $(n\text{-}C_4H_9CH{=}CH)_2$, n-C_{20} = $(n\text{-}C_8H_{17}CH{=}CH)_2$, t-C_{12} = $(t\text{-}C_4H_9CH{=}CH)_2$.

is indicated by the fact that various substituents in aryl halides, such as Me, MeO, Cl, CN, and COOMe, can be accommodated without any difficulty. The hydrozirconation–cross coupling sequence offers an advantage over that involving hydroalumination in that various etherial groups, such as EtO and tetrahydropyranyloxy (THPO), can be readily tolerated in hydrozirconation.

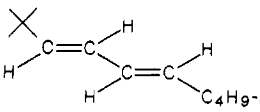
Palladium- or Nickel-Catalyzed Reactions of (*E*)-1-Alkenylalanes and (*E*)-1-Alkenylzirconium Derivatives with Alkenyl Halides. Stereospecific Alkenyl–Alkenyl Cross Coupling. The favorable results obtained above in the alkenyl–aryl coupling reactions prompted us to develop a related procedure for preparing conjugated dienes. To this end, we prepared (*E*)-1-decenyldiisobutylalane and reacted it with (*E*)- and (*Z*)-1-hexenyl iodides[4,12] in ether–hexane at room temperature in the presence of 5 mol% of $Ni(PPh_3)_4$, generated in situ as described earlier. The desired (*E*,*E*)- and (*Z*,*E*)-5,7-hexadecadienes were obtained in 72 and 57% yields, respectively (eq 2). Unfortunately, the *E*,*E* diene was contaminated with ca. 5% of the *Z*,*E* and/or *E*,*Z* isomers, and the stereoisomeric purity of the *Z*,*E* diene was ca. 90%, the major isomeric byproduct being the *E*,*E* isomer. In addition, the C_{12} and C_{20} homocoupled byproducts were also present to the extents of 2–15%.



(2)

In an attempt to improve the above stereoselectivity, we chose $Pd(PPh_3)_4$[13] and a palladium–phosphine complex we prepared in situ by treating $Cl_2Pd(PPh_3)_2$ with 2 molar equiv of DIBAH in THF at 25 °C and ran the two reactions shown in eq 2 in the presence of these palladium–phosphine complexes (5 mol%). The reactions run in the presence of $Cl_2Pd(PPh_3)_2$–DIBAH gave the desired *E*,*E* and *Z*,*E* dienes in 75 and 65% yields, respectively, within 12 h at room temperature.[2b] Only traces of homocoupled byproducts were formed. More importantly, the stereoisomeric purities of the two products were ≥98%. Although our initial results suggested that $Ph(PPh_3)_4$ was not an effective catalyst,[2b] more recent results have indicated that it is nearly as effective as $Cl_2Pd(PPh_3)_2$–DIBAH, as judged by the product yields. As in the cases of alkenyl–aryl coupling, no desired products were formed in the absence of Pd or Ni complexes, indicating that these reactions are catalyzed by these transition-metal complexes.

The experimental results of the palladium- or nickel-catalyzed reactions of (*E*)-1-alkenylalanes with alkenyl halides are summarized in Table II. The palladium-catalyzed reaction in each case is highly stereospecific (≥97%) and proceeds with overall retention of the alkenyl stereochemistry. Although mechanisms involving double inversions or other processes that are totally different from Scheme I, such as addition–elimination, cannot be rigorously ruled out at this point, the results are nevertheless consistent with Scheme I, in which all steps proceed with retention. The stereochemistry of the diene products was determined by GLC, ^1H and ^{13}C NMR, and IR. For example, the *E*,*E*, *E*,*Z*, and *Z*,*E*[14] isomers of 2,2-dimethyl-3,5-decadiene (**3**–**5**) were



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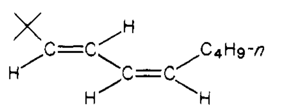

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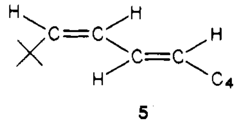

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distinguishable by GLC (SE-30) by using a $^1/_8$ in. × 6 ft column, although capillary GLC was necessary for isomer distinction in most of the other cases. The ^{13}C NMR spectra of **3**–**5** showed the following distinct olefinic carbon signals: ^{13}C NMR ($CDCl_3$, Me_4Si) δ *E*,*E* isomer, 125.7, 131.4, 132.7, and 143.3 ppm; *E*,*Z* isomer, 120.3, 129.0, 130.1, and 145.4 ppm; *Z*,*E* isomer, 127.0, 127.6, 135.7, and 139.7 ppm. Their ^1H NMR spectra showed singlets for the *tert*-butyl protons at δ 1.02, 1.04, and 1.16 ppm, respectively. In general, capillary GLC and ^{13}C NMR spectroscopy appear to be reliable and applicable tools for distinguishing stereoisomers of conjugated dienes. The data summarized in Table II reveal one noteworthy effect of bulky substituents. Whereas the *tert*-butyl group in an alkenylalane leads to a low product yield, e.g., the preparation of **3** using a Ni catalyst, its presence in an alkenyl iodide leads to much more favorable results.

The palladium-catalyzed alkenyl–alkenyl coupling reaction described above provided, for the first time, a highly stereospecific

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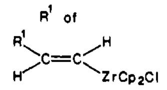
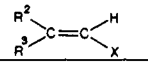
(12) Alexakis, A.; Cahiez, G.; Normant, J. F. *Org. Synth.* **1984**, *62*, 1.
(13) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(14) The *Z*,*E* isomer **5** was prepared by the method reported in ref 7a.

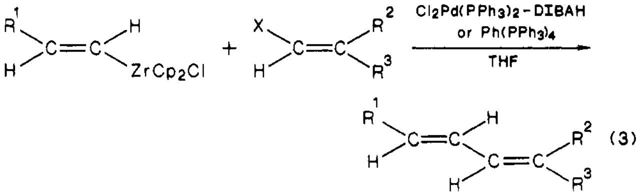
Table III. Palladium-Catalyzed Reaction of (*E*)-1-Alkenylzirconium Derivatives with Alkenyl Halides[a]

R^1 of 						cross-coupled product	
	R^2	R^3	X	Pd Catalyst[b]	time, h	yield,[c] %	stereoismrc purity, %
n-pentyl	*n*-butyl	H	I	I	1	91	≥98
n-hexyl	*n*-butyl	H	I	I	1	93	≥98
n-butyl	COOMe	CH_3	Br	II	3	75	≥98
$THPOCH_2$[d]	COOMe	CH_3	Br	II	12	70	≥98
$THPOCH_2$	H	H	Br[e]	I	12	77	≥99
n-butyl	3-bromo-2-cyclohexenone			II	3	60	≥99

[a] Unless otherwise mentioned, the reaction was carried out by using a 50 mol % excess of an alkenylzirconium derivative in THF at room temperature. [b] I = $Pd(PPh_3)_4$. II = $Cl_2Pd(PPh_3)_2$ + DIBAH. [c] By GLC. [d] THP = tetrahydropyranyl. [e] The ratio of $R^1C{\equiv}CH$ to $CH_2{=}CHBr$ was 1/5.

cross-coupling method for preparing doubly stereodefined conjugated dienes. Together with the palladium-catalyzed reaction of alkynylsodiums with organic halides,[15] which was published during our investigation, the results presented above show some distinct advantages for palladium-catalyzed cross coupling over that involving Ni. Although advantages of Pd catalysis were not apparent, a stoichiometric reaction of organopalladium derivatives with organolithiums and a few examples of its catalytic version involving MeMgI and $CH_2{=}CHMgBr$ reported in 1975[16] are also worth mentioning.

As expected, the reaction of (*E*)-1-alkenylzirconium derivatives, prepared as above, with alkenyl halides at room temperature in THF in the presence of 5 mol% of $Cl_2Pd(PPh_3)_2$–DIBAH or $Pd(PPh_3)_4$ produced the desired dienes in satisfactory yields[2d] (eq 3). The experimental results are summarized in Table III. The stereoisomeric purity of each product was ≥97%.



(3)

Scope of Palladium-Catalyzed Alkenyl–Alkenyl Cross Coupling with Respect to Metals in Alkenylmetals. Our finding that both alkenylalanes and alkenylzirconium derivatives readily participate in the palladium- or nickel-catalyzed cross coupling prompted us to explore the scope of the palladium- or nickel-catalyzed cross coupling with respect to metals in the organometallic reagents used stoichiometrically. To this end, we chose the palladium-catalyzed reaction of (*E*)-1-octenylmetals containing various metals (1.5 equiv) with (*E*)-1-hexenyl iodide by using 5 mol% of $Pd(PPh_3)_4$ as a catalyst. (*E*)-1-Octenyllithium was prepared by treating the corresponding iodide with 2 equiv of *t*-BuLi in ether (−78 °C to room temperature). (*E*)-1-Octenylmetals containing MgCl, ZnCl, CdCl, Hg, $SiMe_3$, $SnBu_3$, $TiCp_2$, and $CeCl_2$ were prepared by treating (*E*)-1-octenyllithium with 1 equiv of the corresponding chlorides except in the Hg and Ti cases in which 1 equiv of $HgCl_2$ or Cl_2TiCp_2 was used. The preparation of the alkenylmetals containing B, Al, and Zr was performed as described earlier. The alkenyl–alkenyl coupling reaction was, in most cases, carried out in THF at room temperature (21–23 °C) at an initial halide concentration of 0.5 M, and the reaction mixture was analyzed by GLC after quenching with aqueous HCl.

The experimental results are summarized in Table IV. Under the above-described conditions, (*E*)-1-alkenylmetals containing Zn, Cd, Al, and Zr give the desired cross-coupled product in ≥70% yields within 6 h, while Li, Mg, Hg, B, Si, Sn, Ti, and Ce do not. Although the yield of the desired product observed with Cd is satisfactory, a significant amount (17%) of 7,9-hexadecadiene is also formed along with 8% of 5,7-dodecadiene.

Subsequent to our initial study, the palladium-catalyzed cross-coupling reactions of B,[11] Sn,[17,18] Cu,[19] and Hg[17c] as well as additional results with Li[20] and Mg[20,21] have been reported, and some of them have been applied to the synthesis of natural products.

Table IV. Palladium-Catalyzed Reaction of (*E*)-1-Octenylmetals with (*E*)-1-Hexenyl Iodide[a]

metal	time, h	unreacted iodide,[b] %	yield of dienes A–C,[b,j] %		
			A[c]	B[d]	C[c]
Li[e]	1	0	40	25	16
MgCl[e]	1	51	31	5	7
MgCl[e]	3	46	32	7	8
ZnCl[e]	1	trace	95	3	3
CdCl[e]	1	trace	86	17	8
Hg[f]	1	57	40	80	3
$B(Sia)_2(n\text{-}Bu)$[g,h]	1	69	12	0	0
$B(Sia)_2$[g–i]	1	5	65	5	1
$Al(i\text{-}Bu)_2$[g]	1	51	41	2	3
$Al(i\text{-}Bu)_2$[g]	3	9	71	6	6
$Al(i\text{-}Bu)_2$[g]	6	3	75	7	6
$SiMe_3$[e]	3	100	0	0	0
$Sn(i\text{-}Bu)_3$[e]	3	66	2	trace	4
$TiCp_2$[f]	1	73	trace	21	0
$ZrCp_2Cl$[g]	1	7	93	trace	trace
$CeCl_2$[e]	1	0	42	33	26

[a] Unless otherwise stated, the reaction was run at room temperature (21–23 °C) in THF in the presence of 5 mol % of $Pd(PPh_3)_4$ by using an (*E*)-1-octenylmetal derived from 1.5 equiv of 1-octyne or (*E*)-1-octenyl iodide relative to (*E*)-1-hexenyl iodide. [b] GLC yield. [c] Based on (*E*)-1-hexenyl iodide. [d] Based on the amount of 1-octyne or (*E*)-1-octenyl iodide. [e] Prepared from 1.5 equiv of (*E*)-1-octenyl iodide. [f] Prepared from 3 equiv of (*E*)-1-octenyl iodide. [g] Prepared from 1.5 equiv of 1-octyne. [h] Sia = 3-methyl-2-butyl. [i] The reaction was carried out in benzene in the presence of 5 mol % of $Pd(PPh_3)_4$ and 2 equiv of sodium ethoxide in ethanol.[11a] [j] $n\text{-hex}(CH{=}CH)_2Bu\text{-}n$ = A. $n\text{-hex}(CH{=}CH)_2\text{hex-}n$ = B. $n\text{-Bu}(CH{=}CH)_2Bu\text{-}n$ = C.

The use of Li in the alkenyl–alkenyl coupling reaction discussed here is seriously complicated by competitive lithium–halogen exchange. Although our own results obtained with Mg were disappointing, those obtained by other workers[21] under somewhat different conditions are much more promising. The use of tetraorganoborates, which led to satisfactory results in the case of 1-alkynyltrialkylborates,[11d] gave only a 12% yield of the desired product. On the other hand, the corresponding reaction of (*E*)-1-octenyldisiamylborane in the presence of NaOEt (2 equiv) in benzene–ethanol[11a] led to a reasonable yield of 65%. In our hands, the reaction of (*E*)-1-octenyltri(*n*-butyl)stannane with (*E*)-1-hexenyl iodide gave no more than 2% of the desired product,

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(17) (a) Kosugi, M.; Sasazawa, K.; Shimizu, I.; Migita, T. *Chem. Lett.* **1977**, 301. (b) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (c) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551 and references therein.

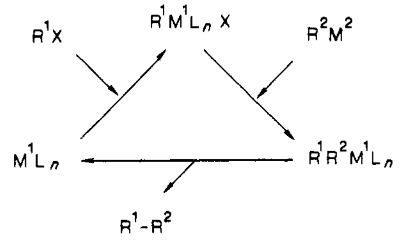
(18) For the palladium-catalyzed reaction of alkenyltins with alkenyl triflates, see: Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.

(19) (a) Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 959. (b) Normant, J. F.; Alexakis, A. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed., Pergamon: Oxford, 1982; p 291.

(20) Murahashi, S. I.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408.

(21) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, 191.

Scheme II



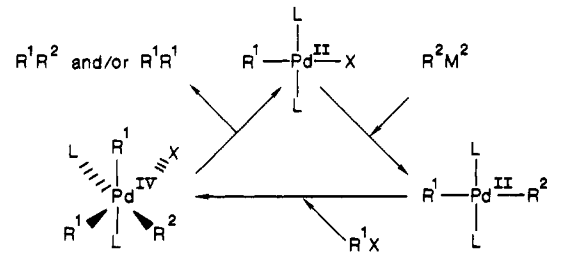
Scheme III

$$ArNi^{I}L_n + ArX \rightarrow Ar_2Ni^{III}L_nX$$

$$Ar_2Ni^{III}L_nX + ArNi^{II}L_nMe \rightarrow ArNi^{II}L_nX + Ar_2Ni^{III}L_nMe$$

$$Ar_2Ni^{III}L_nMe \rightarrow ArMe + ArNi^{I}L_n$$

Scheme IV



although the corresponding reaction of vinyltri(n-butyl)stannane gave (E)-1,3-nonadiene in 21%. Thus, recent results in the literature[18] obtained with alkenyl triflates are much superior to those obtained with alkenyl halides in this study. The reaction of bis[(E)-1-octenyl]mercury with (E)-1-hexenyl iodide gave the cross-coupled diene in 40% yield along with 7,9-hexadecadiene (80%, i.e., 12 mmol from 15 mmol of the dialkenylmercury reagent) and 5,7-dodecadiene (5%) in 1 h. No further change in the yields of these dienes took place. The reaction of dialkenylmercuries to produce conjugated dienes and metallic mercury catalyzed by $Pd(PPh_3)_4$ is a known reaction.[22] Also known is a stoichiometric reaction of alkenylmercuric chlorides with $^1/_2$ molar equiv of Li_2PdCl_4 to give conjugated dienes, $HgCl_2$, LiCl, and Pd.[23]

On the basis of the above survey of metals in alkenylmetals we selected Zn, Zr, and Al as three highly satisfactory metals for the palladium-catalyzed cross-coupling reactions of alkenylmetals. To further compare their relative reactivity and efficiency, the catalytic turnover number was determined for these three metals. The turnover numbers [mmol PhI consumed or (E)-1-octenylbenzene formed per mmol $Pd(PPh_3)_4$ per hour] for the reactions of (E)-1-octenylmetals containing $Al(i\text{-}Bu)_2$, $ZrCp_2Cl$, and ZnCl with PhI in the presence of a catalytic amount of $Pd(PPh_3)_4$ in THF at room temperature were 2 (Al), 3 (Zr), and at least 2000 (Zn). Specifically, the reaction of (E)-1-octenylzinc chloride (1.5 equiv) with PhI in THF with 0.05 mol% of $Pd(PPh_3)_4$ was complete in 1 h at room temperature, and it produced (E)-1-octenylbenzene in essentially quantitative yield. The turnover numbers for Al and Zn at 50 °C were 25 and 30, respectively. These results clearly indicate that the alkenylzinc reagent is far more effective than those containing Al or Zr.

Mechanism of the Palladium-Catalyzed Cross-Coupling Reaction. The synthetic study described above has been carried out on the assumption that the desired palladium- or nickel-catalyzed alkenyl–alkenyl and alkenyl–aryl coupling reactions may proceed according to Scheme I involving oxidative addition, transmetalation, and reductive elimination, which can be generalized as shown in Scheme II. The feasibility of each of these three steps has previously been demonstrated under stoichiometric conditions.[10] For some nickel-catalyzed aryl–methyl[24] and alkenyl–aryl[25] coupling reactions, however, a mechanism involving Ni(I) and Ni(III) species appears plausible (Scheme III). On the other hand, the palladium-catalyzed methyl–benzyl and other related coupling reactions have been reported to proceed via Pd(IV) intermediates[26] (Scheme IV). And yet, the reported results of the palladium-catalyzed methyl–styryl coupling reaction[27] do not appear to require Pd(IV) intermediates, and they can be accommodated by the mechanism represented by Scheme II or a minor modification of it. In all of the previous studies mentioned above, diorganonickel(II) or diorganopalladium(II) species were generated as isolable and/or detectable species by transmetalation reactions that are faster than their decomposition via reductive elimination. On the other hand, the strong dependency on metals in the organometallic reagents observed in our study suggested that, in some or all of the reactions herein described, the transmetalation step might well be rate-determining. We therefore undertook to probe mechanistic details of some representative reactions described above. One of our specific goals was to clarify the origin of the above-mentioned metal dependency.

Table V. Reaction of Iodo(phenyl)bis(triphenylphosphine)palladium with (E)-1-Octenylzinc Chloride at 0 °C[a]

time, min	**6**, %	**7**, %	**8**, %	total Ph **6** + **8**, %	total 1-octenyl **7** + **8**, %
0[b]	85	118	2	87	120
3	32	61	64	96	125
7	15	29	84	99	113
12	3	17	95	98	112
17	2	17	87	89	104

[a] The reaction was run in a 2:1 mixture of CD_2Cl_2 and THF. The amounts of compounds are all relative to the initial amount of **6**. [b] The reactants were mixed in an NMR tube at 0 °C, and its ^1H NMR spectrum was taken immediately after mixing.

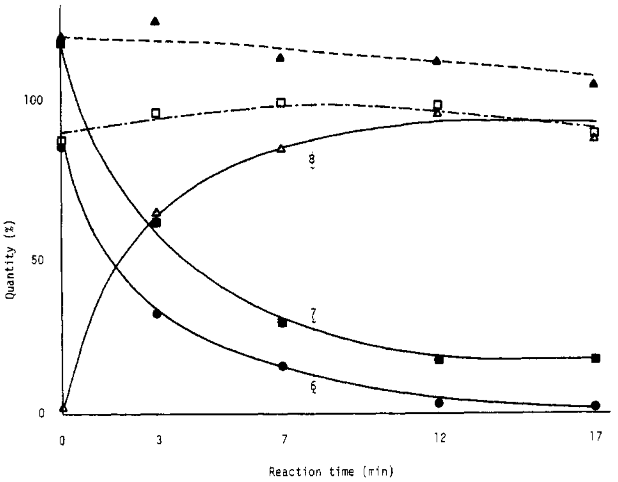


Figure 1. Reaction of Iodo(phenyl)bis(triphenylphosphine)palladium with (E)-1-octenylzinc chloride at 0 °C. The dashed line (—▲—) represents the sum of **7** and **8**. The line (—□—) represents the sum of **6** and **8**.

We chose the palladium-catalyzed alkenyl–aryl coupling reaction for our mechanistic investigation partly because spectroscopic investigation of alkenyl–aryl coupling was expected to be less complicated and yet more informative than that of the alkenyl–alkenyl coupling and also because the corresponding nickel-catalyzed alkenyl-aryl coupling reaction has previously been

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(22) Vedejs, E.; Weeks, P. D. *Tetrahedron Lett.* **1974**, 3207.

(23) Larock, R. C. *J. Org. Chem.* **1976**, *41*, 2241.

(24) Smith, G.; Kochi, J. K. *J. Organomet. Chem.* **1980**, *198*, 199. See, also: Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.

(25) (a) Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3976. (b) Dayrit, F. M.; Schwartz, J. *Ibid.* **1981**, *103*, 4466.

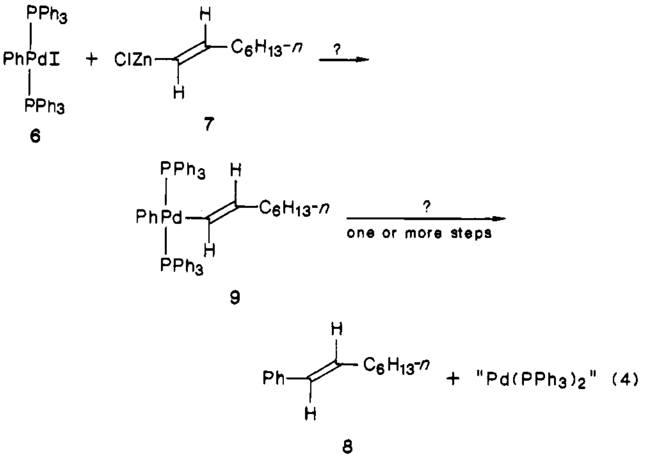
(26) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981. (b) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (c) Moravskiy, A.; Stille, J. K. *Ibid.* **1981**, *103*, 4182.

(27) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

subjected to a mechanistic investigation,[25] which would serve for comparison.

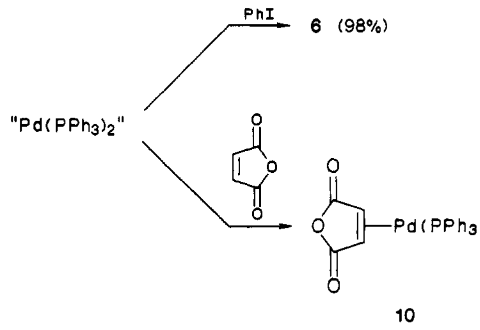
To probe the plausibility of each microstep in the mechanism shown in Scheme I under stoichiometric conditions, $PhPd(PPh_3)_2I$ (**6**) was prepared in 90% yield by the reaction of 1 equiv each of PhI and $Pd(PPh_3)_4$ by the literature method.[28] The reaction of **6** with 1.2 equiv of (*E*)-1-octenylzinc chloride (**7**) in a 2:1 mixture of CD_2Cl_2 and THF (0.1 M in **6**) was monitored by ^1H NMR at 0 °C. It was necessary to add CD_2Cl_2 to THF in the above-indicated ratio to dissolve **6**. Fortunately, the ^1H NMR signals for the phenyl protons of **6**, the alkenyl protons of **7**, and the alkenyl protons of (*E*)-1-octenylbenzene (**8**) were seen in three discrete regions, which permitted quantitative determination of their amounts. The experimental results are summarized in Table V and Figure 1.

The reaction follows second-order kinetics, first order in **6** and **7**, and the second-order rate constant (k_2) was 2.9 L/mol·min at 0 °C. One critically important feature of the reaction is that the sum of **6** and **8** as well as that of **7** and **8** remained more or less constant within experimental errors at near 100 and 120% (based on the initial amount of **6**), respectively. There is no indication for the buildup of any other species over the entire period. Unless **6** and **7** directly give **8** in a single step, which is highly unlikely, the reaction must produce first an intermediate, such as **9**, in the rate-determining step, which then decomposes rapidly in one or more subsequent steps to give **8**. In any event, the overall transformation demands that $Pd(PPh_3)_2$ or its derivative, tentatively represented as "$Pd(PPh_3)_2$", be the second product (eq 4).



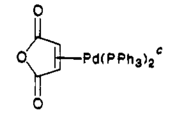
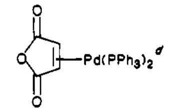
(4)

Addition of 1.5 equiv of PhI to the above reaction mixture at the 17-min reaction time gives **6** in 98% yield within 5 min at 35 °C. Therefore, not only the formation of "$Pd(PPh_3)_2$" but also the proposed oxidative addition reaction of PhI and "$Pd(PPh_3)_2$" in the reaction of **7** with PhI catalyzed by $Pd(PPh_3)_4$ is likely. The formation of "$Pd(PPh_3)_2$" is further supported by the formation of **10**[29] upon addition of maleic anhydride to the cross-coupling reaction mixture[30] (eq 5). The results presented above indicate that, if the presumed transmetalation reaction between **6** and **7** occurs as shown in eq 4, it is distinctly slower than the presumed reductive elimination step.



(5)

Table VI. Examination by ^{31}P NMR of the Reaction of Iodo(phenyl)bis(triphenylphosphine)palladium with (*E*)-1-Octenylzinc Chloride

compd	compd no.	chem shift,[a] ppm
$PhPdI(PPh_3)_2$	**6**	23.57 (s)
"$Ph(PPh_3)_2$"[b]		20.37 (br)
	**10**	27.75 (s)
	**10**	27.70 (s)

[a] Relative to 85% H_3PO_4. [b] By examination of the reaction mixture after completion of the reaction. [c] Generated in situ by addition of maleic anhydride to the above reaction mixture. [d] Prepared by a literature method.[29]

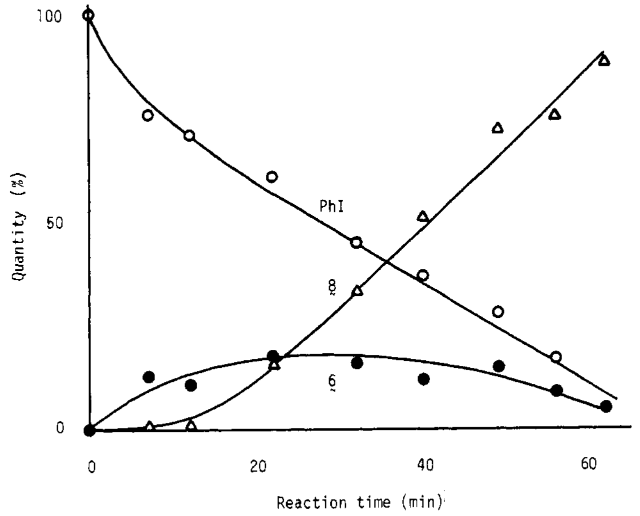


Figure 2. Reaction of (*E*)-1-octenylzinc chloride with phenyl iodide in the presence of 0.5 equiv of tetrakis(triphenylphosphine)palladium at −10 °C.

To establish whether or not the transmetalation step of the reaction of **7** with PhI in the presence of $Pd(PPh_3)_4$ is rate-determining even under catalytic conditions, **7** was treated with PhI in a 1:1 ratio in the presence of 0.5 equiv of $Pd(PPh_3)_4$ at −10 °C in a 2:1 mixture of CD_2Cl_2 and THF, and the reaction was directly monitored by ^1H NMR. The experimental results summarized in Figure 2 clearly show that there is an initial buildup of the oxidative addition product **6**. After 22 min its amount reaches 0.18 equiv corresponding to 36% of the maximum possible amount of 0.50 equiv and then gradually decreases. Taken together with the results of the stoichiometric reaction of preformed **6** with **7**, it now appears certain that the transmetalation reaction is indeed the slowest step of the reaction.

Further mechanistic investigation of the cross-coupling reaction promoted by Pd–PPh_3 complexes, especially that run under catalytic conditions, is severely hampered by the highly labile nature of the organopalladium intermediates other than **6**. Nonetheless, our finding that the transmetalation reaction is most likely the rate-determining step at least in some cases provides an explanation for the effect of the metal counter cations in the organometallic reagents used stoichiometrically.

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(28) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem Commun.* **1968**, 6.

(29) Takahashi, S.; Hagihara, N. *Nippon Kagaku Zasshi* **1967**, *88*, 1306.

(30) We have recently found that "$Pd(PPh_3)_2$" obtained by treatment of $Cl_2Pd(PPh_3)_2$ with 2 equiv of an organolithium in THF under N_2 is either $LiClPd(PPh_3)_2$ or $Li_2Cl_2Pd(PPh_3)_2$ [Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338]. It is therefore likely that "$Pd(PPh_3)_2$" generated in the present study is also complexes with metal salts, such as those containing Al and Zn.

Experimental Section

General Methods. All organometallic reactions were run under an inert atmosphere of nitrogen. Unless otherwise stated, chemicals obtained from commercial sources were used without further purification. Tetrahydrofuran (THF) and ether were dried over sodium and benzophenone. Zinc chloride was flame-dried in vacuo. Diisobutylaluminum hydride (DIBAH) was obtained in a cylinder from Ethyl Corporation. Gas-liquid chromatographic analyses (GLC) were performed on SE-30 columns by using appropriate linear and saturated hydrocarbons as internal standards. NMR spectra were obtained by using Perkin-Elmer R32, Varian CFT-20, and Varian XL-200 spectrometers. Dichlorobis(triethylphosphine)palladium was prepared by the reaction of PEt_3 with a suspension of anhydrous palladium chloride in benzene at 60 °C.[31] Dichlorobis(triphenylphosphine)palladium was prepared by reaction of triphenylphosphine with sodium tetrachloropalladate in ethanol.[31] Tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] was prepared by a literature procedure.[13] Tetrakis(triphenylphosphine)nickel was generated in situ by the reaction of anhydrous $Ni(acac)_2$ with 1 equiv of DIBAH in the presence of 4 equiv of PPh_3 in THF.[2a] (*E*)-1-Octenyl iodide, (*E*)-1-hexenyl iodide, and (*E*)-3,3-dimethyl-1-butenyl iodide were prepared from the corresponding alkynes via hydroalumination–iodinolysis.[32] (*Z*)-1-Hexenyl iodide was prepared from *n*-BuLi and acetylene via carbocupration–iodinolysis.[12] Methyl (*E*)-3-bromo-2-methylpropenoate (>99% E) was prepared in 85% yield from methyl methacrylate via bromination–dehydrobromination.[33] 3-Bromo-2-cyclohexen-1-one was prepared as described in the literature.[34] Disiamylborane [$(Me_2CHMeCh)_2BH$][3] and $HZrCp_2Cl$[5] were also prepared as described in the literature.

Nickel-Catalyzed Reaction of (*E*)-1-Alkenyldiisobutylalanes and (*E*)-1-Alkenylzirconocene Chlorides with Aryl Halides. Representative Procedures. The following two procedures are representative of the reactions of aryl halides with (*E*)-1-alkenylalanes and (*E*)-alkenylzirconium derivatives, respectively.

(a) (*E*)-1-Heptenylbenzene. To $Ni(PPh_3)_4$ prepared by the reaction of anhydrous $Ni(acac)_2$ (0.066 g, 0.25 mmol) with DIBAH (0.05 mL, 0.25 mmol) in the presence of 0.262 g (1.0 mmol) of triphenylphosphine in 5 mL of THF[2a] were sequentially added (*E*)-1-heptenyldiisobutylalane *prepared by the treatment of* 1-heptyne (0.96 g, 10 mmol) *with* DIBAH (1.84 mL, 10 mmol) in 5 mL of hexane at 50–55 °C for 2 h[4] and iodobenzene (1.02 g, 5.0 mmol) at room temperature. Aliquots were periodically quenched with 3 N HCl and examined by GLC (SE-30). *After* 12 h *at room temperature the yield of the title compound reached* 91% and did not increase further. The reaction mixture was quenched with 3 N HCl and extracted with petroleum ether. The organic layer was washed with water, aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Column chromatography (neutral alumina, pentane) provided 0.74 g (85% yield) of (*E*)-1-heptenylbenzene: IR(neat) 3000 (w), 2900 (s), 1710 (w), 1600 (w), 1490 (m), 1465 (m), 1450 (m), 965 (s), 745 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.87 (t, J = 7 Hz, 3 H), 1.1–1.8 (m, 6 H), 2.0–2.45 (m, 2 H), 5.9–6.6 (m, 2 H), 7.05–7.55 (m, 5 H). Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.32; H, 10.56.

In the absence of $Ni(PPh_3)_4$ the reaction run under otherwise the same conditions did not produce the desired product.

(b) (*E*)-8-Ethoxystyrene. To a light-shielded slurry of 3.87 g (15 mmol) of $HZrCp_2Cl$ in 20 mL of benzene was added 1.32 mL (15 mmol) of freshly distilled ethoxyacetylene at room temperature under nitrogen. After 2 h at this temperature the reaction mixture was evaporated under reduced pressure to give a brownish yellow solid. To this was added a solution of $Ni(PPh_3)_4$ (1 mmol) in 15 mL of THF prepared as described earlier. After a homogeneous solution had been obtained, 2.04 g (10 mmol) of phenyl iodide was added at room temperature, and the mixture was stirred for 16 h. Examination by GLC of a quenched aliquot indicated the formation of the title compound in essentially quantitative yield. The reaction mixture was quenched with 1 mL of water. After addition of 40 mL of petroleum ether (30–60 °C) and subsequent stirring for 10 min, the resultant mixture was filtered through anhydrous $MgSO_4$, and the filter cake was rinsed thoroughly with ethyl ether. The organic extract was dried over $MgSO_4$ and distilled to give 1.13 g (76%) of the title compound of >98% stereoisomeric purity: bp 67–68 °C (1–1.5 mmHg); IR (neat) 3000 (w), 2940 (w), 2860 (w), 1630 (s), 1230 (s), 1220 (s), 1160 (s), 1150 (s), 1120 (m), 1110 (m), 932 (m), 924 (m), 750 (s), 694 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.27 (t, J = 7 Hz, 3 H), 3.80 (q, J = 7 Hz, 2 H), 5.83 (d, J = 13 Hz, 1 H), 6.97 (d, J = 13 Hz, 1 H), 7.23 (br s, 5 H). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.79; H, 8.02.

The experimental results of the nickel-catalyzed alkenyl–aryl coupling reactions are summarized in Table I, and the products have yielded the following data.

(c) (*E*)-*p*-1-Hexenyltoluene: bp 76–78 °C (0.7 mmHg); IR (neat) 3000 (m), 2900 (s), 1520 (m), 960 (s), 800 (s), 740 (m), 690 (s) cm^{-1}; ^1H NMR (CCl_4, Me_4Si) δ 0.90 (t, J = 7 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.9–2.4 (m with a peak at 2.27, 5 H), 6.0–7.5 (m, 6 H).

(d) (*E*)-*p*-1-Hexenylchlorobenzene: bp 67–68 °C (0.1 mmHg); IR (neat) 3000 (w), 2900 (s), 1655 (w), 1600 (w), 1490 (s), 1095 (s), 1015 (s), 965 (s), 850 (s), 805 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 7 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.9–2.4 (m, 2 H), 5.8–6.5 (m, 2 H), 7.25 (s, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.96, 22.38, 31.54, 32.77, 127.14, 128.60, 128.70, 131.80, 132.37, 136.56. Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.03; H, 7.77. Found: C, 74.18; H, 7.59.

(e) (*E*)-*p*-1-Hexenylcyanobenzene: bp 110–111 °C (0.8 mmHg); IR (neat) 2970 (w), 2880 (s), 2210 (s), 1635 (m), 1595 (s), 1170 (m), 966 (s), 856 (s), 810 (m), cm^{-1}; ^1H NMR (CCl_4, Me_4Si) δ 0.90 (t, J = 7 Hz, 3 He, 1.1–1.8 (m, 4 H), 1.9–2.5 (m, 2 H), 6.3–6.5 (m, 2 H), 7.2–7.7 (m, 4 H).

(f) (*E*)-1-(1-Heptenyl)naphthalene: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.6–1.8 (m, 9 H), 2.0–2.6 (m, 2 H), 6.13 (dt, J = 16 and 7 Hz, 1 H), 7.07 (d, J = 16 Hz, 1 H), 7.1–8.2 (m, 7 H).

(g) (*E*)-4-(Tetrahydropyranyloxy)-1-phenyl-1-butene: IR (neat) 3020 (w), 2920 (s), 1200 (m), 1138 (s), 1120 (s), 1078 (s), 1032 (s), 968 (s), 744 (s), 694 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.2–2.2 (m, 6 H), 2.25–2.8 (m, 2 H), 3.25–4.3 (m, 4 H), 4.6–4.9 (s, 1 H), 6.1–7.8 (m, 7 H).

(h) (*E*)-*p*-1-Hexenylanisole: bp 88 °C (0.4 mmHg); IR (neat) 3000 (w), 2920 (s), 1620 (s), 1515 (s), 1465 (m), 1246 (s), 1177 (s), 1040 (s), 968 (s), 846 (m), 808 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 7 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.9–2.4 (m, 2 H), 3.73 (s, 3 H), 5.7–6.5 (m, 2 H), 7.1–7.45 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.00, 22.40, 31.86, 32.83, 55.05, 113.96, 127.07, 128.79, 129.34, 130.94, 158.82. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.23; H, 9.45.

(i) Methyl (*E*)-*p*-1-Hexenylbenzoate: bp 95 °C (0.5 mmHg); IR (neat) 2980 (w), 2900 (s), 1720 (s), 1600 (s), 1430 (s), 1270 (s), 1175 (s), 1105 (s), 968 (s), 758 (s), 698 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 7 Hz, 3 H), 1.2–1.6 (m, 4 H), 1.9–2.4 (m, 2 H), 3.90 (s, 3 H), 6.3–6.5 (m, 2 H), 7.37 (d, J = 9 Hz, 2 H), 8.00 (d, J = 9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.96, 22.41, 31.42, 32.91, 51.78, 125.81, 128.44, 129.19, 129.95, 133.99, 142.52, 166.74. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.67; H, 8.19.

Reaction of Lithium (*E*)-1-Heptenyldiisobutyl-*n*-butylaluminate with Iodobenzene in the Presence of $Ni(PPh_3)_4$. This reaction was carried out according to the representative procedure described above except that lithium (*E*)-1-heptenyldiisobutyl-*n*-butylaluminate, prepared by treatment of (*E*)-1-heptenyldiisobutylalane with 1 equiv of *n*-BuLi, was used as the organometallic reagent. After 12 h, the yield of (*E*)-1-heptenylbenzene was 21%.

Reaction of (*E*)-1-Heptenyldisiamylborane or Lithium (*E*)-1-Heptenyl-(*n*-butyl)disiamylborate with Iodobenzene in the Presence of $Ni(PPh_3)_4$. (*E*)-1-Heptenyldisiamylborane and lithium (*E*)-1-heptenyl-(*n*-butyl)disiamylborate were prepared as described in the literature. The cross-coupling reaction was carried out according to the representative procedure except that either (*E*)-1-heptenyldisiamylborane or lithium (*E*)-1-heptenyl-(*n*-butyl)disiamylborate was used in place of (*E*)-1-heptenyldiisobutylalane. After 24 h at room temperature, the yield of (*E*)-1-heptenylbenzene was less than 5% in either case.

Palladium- or Nickel-Catalyzed Reaction of (*E*)-1-Alkenylalanes with Alkenyl Halides. (a) (3*E*,5*E*)-2,2-Dimethyl-3,5-decadiene: Representative Procedure. To 0.74 g (1 mmol) of $Cl_2Pd(PPh_3)_2$[31] suspended in 20 mL of THF were sequentially added 0.37 mL (2 mmol) of neat DIBAH (25 °C, 10 min), (*E*)-1-hexenyldiisobutylalane,[4] prepared in a separate flask from 2.46 g (30 mmol) of 1-hexyne dissolved in 20 mL of hexane and DIBAH (5.52 mL, 30 mmol), and 4.20 g (20 mmol) of (*E*)-3,3-dimethyl-1-butenyl iodide[32] (25 °C). After the reaction mixture had been stirred overnight at room temperature, it was treated with 3 N HCl and extracted with ethyl ether. The organic layer was washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and distilled to provide 2.36 g (71%) of the title compound of ≥98% stereoisomeric purity: bp 60–62 °C (4 mmHg); IR (neat) 2930 (s), 1460 (m), 1360 (m), 990 (s) cm^{-1}; ^1H NMR (CCl_4, Me_4Si) δ 0.7–1.2 (m with a singlet at 1.02, 12 H), 1.2–1.7 (m, 4 H), 1.7–2.3 (m, 2 H), 5.2–6.2 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.22, 22.57, 29.94, 31.99, 32.67, 33.22, 125.69, 131.41, 132.67, 143.31. Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.75; H, 13.18.

Examination of an aliquot of the reaction mixture, after quenching, indicated the formation of the title compound in 82% yield. Only traces,

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(31) (a) Booth, G. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 1. (b) Jenkins, J. M.; Verkade, J. G. *Inorg. Synth.* **1968**, *11*, 108.

(32) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.

(33) Caubere, P. *Bull. Soc. Chem. Fr.* **1964**, 144.

(34) Piers, E.; Nagakura, I. *Synth. Commun.* **1975**, *5*, 193.

if any, of the homocoupled products were present.

The experimental results are summarized in Table II, and the cross-coupled products have yielded the following data.

(b) (3*E*,5*Z*)-2,2-Dimethyl-3,5-decadiene: IR (neat) 2900 (s), 1460 (s), 1355 (s), 1265 (m), 985 (s), 950 (s), 920 (w), 850 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.2 (m with a peak at 1.04, 12 H), 1.2–1.6 (m, 4 H), 1.8–2.4 (m, 2 H), 5.0–6.6 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.90, 22.26, 27.35, 29.56, 31.87, 33.20, 120.29, 128.95, 130.13, 145.40.

(c) (3*Z*,5*E*)-2,2-Dimethyl-3,5-decadiene:[14] IR (neat) 2950 (s), 1460 (s), 1360 (s), 1210 (m), 985 (s), 950 (s), 730 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.2 (m with a peak 1.16, 12 H), 1.2–1.6 (m, 4 H), 1.6–2.4 (m, 2 H), 5.1–6.8 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.1, 22.4, 31.8, 32.7, 33.8, 127.0, 127.6, 135.7, 139.7.

(d) (5*E*,7*E*)-5,7-Hexadecadiene: IR (neat) 1370 (m), 982 (s), 722 (m) cm^{-1}; ^{1}H NMR (CCl_4, Me_4Si) δ 0.89 (t, $J = 6$ Hz, 6 H), 1.15–1.7 (m, 16 H), 1.8–2.2 (m, 4 H), 5.2–6.15 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.93, 14.06, 22.34, 22.76, 29.40, 26.62, 31.16, 31.78, 32.03, 32.37, 32.72, 130.59, 132.19, 132.26; high resolution MS calcd for $C_{16}H_{30}$ 222.2347, found 222.2325.

(e) (5*Z*,7*E*)-5,7-Hexadecadiene: IR (neat) 1630 (m), 1370 (m), 978 (s), 943 (s), 720 (m) cm^{-1}; ^{1}H NMR (CCl_4, Me_4Si) δ 0.90 (t, $J = 6$ Hz, 6 H), 1.15–1.5 (m, 16 H), 1.9–2.3 (m, 4 H), 5.15 (dt, $J = 10$ and 8 Hz, 1 H), 5.61 (dt, $J = 14$ and 7 Hz, 1 H), 5.92 (dd, $J = 10$ and 11 Hz, 1 H), 6.30 (dd, $J = 11$ and 14 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.97, 14.10, 22.40, 22.75, 27.48, 29.38, 29.58, 32.04, 32.97, 125.81, 128.84, 129.96, 134.61.

(f) Methyl (2*E*,4*E*)-2-Methyl-2,4-nonadienoate: bp 78–79 °C (1 mmHg); IR (neat) 1715 (s), 1645 (s), 1620 (w), 1245 (s), 1105 (s), 975 (s), 750 (s) cm^{-1}; ^{1}H NMR (CCl_4, Me_4Si) δ 0.90 (t, $J = 6$ Hz, 3 H), 1.1–1.6 (m, 4 H), 1.90 (s, 3 H), 2.0–2.5 (m, 2 H), 3.67 (s, 3 H), 5.7–6.6 (m, 2 H), 7.10 (d, $J = 10$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 11.8, 13.3, 21.9, 30.7, 32.6, 51.1, 124.3, 125.6, 138.3, 142.6, 168.3. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.57; H, 9.82.

Palladium-Catalyzed Reaction of (*E*)-1-Alkenylzirconocene Chlorides with Alkenyl Halides. (a) Methyl (2*E*,4*E*)-2-Methyl-6-(tetrahydropyranyloxy)-2,4-hexadienoate: Representative Procedure. To $HZrCp_2Cl$ prepared from 14.6 g (50 mmol) of Cl_2ZrCp_2 and 25 mmol of $NaAlH_2(OCH_2CH_2OCH_3)_2$ as reported in the literature[5] were added 50 mL of benzene and 6.39 mL (48 mmol) of 2-propynyl tetrahydropyranyl ether at room temperature. After 2 h, the solvent was evaporated. To this were added sequentially a Pd catalyst, prepared from $Cl_2Pd(PPh_3)_2$ (2 mmol) and DIBAH (4 mmol) in 50 mL of THF, and 6.36 g (40 mmol) of methyl (*E*)-β-bromomethacrylate at room temperature. After the reaction mixture had been stirred overnight at room temperature, it was treated with 4 mL of water and 80 mL of petroleum ether. The resultant mixture was filtered, and the filter cake was thoroughly rinsed with ethyl ether. The combined organic extracts were dried over $MgSO_4$, concentrated, chromatographed (neutral alumina, ethyl ether), and distilled at 0.01 mmHg to give 6.25 g (65%) of the title compound which was stereoisomerically $\geq$98% pure: IR (neat) 2850 (s), 1690 (s), 1425 (s), 1275 (s), 1215 (s), 1100 (s), 1020 (s), 965 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.3–1.8 (m, 6 H), 1.93 (br s, 3 H), 3.3–4.1 (m, 2 H), 3.73 (s, 3 H), 4.20 (t, $J = 6$ Hz, 2 H), 4.5–4.8 (m, 1 H), 5.9–7.4 (m, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.65, 19.48, 25.67, 30.70, 51.64, 61.96, 66.95, 98.09, 126.66, 127.12, 137.89, 138.28, 168.50. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.69; H, 8.37.

The experimental results are summarized in Table III, and the other products have yielded the following data.

(b) (5*E*,7*E*)-5,7-Tridecadiene: IR (neat) 2900 (s), 1460 (s), 1375 (m), 985 (s), 727 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, $J = 6$ Hz, 6 H), 1.1–1.7 (m, 10 H), 1.8–2.4 (m, 4 H), 5.2–6.7 (m, 4 H).

(c) (5*E*,7*E*)-5,7-Tetradecadiene:[11b] IR (neat) 2900 (s), 1460 (s), 1375 (s), 727 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, $J = 6$ Hz, 6 H), 1.1–1.7 (m, 12 H), 1.8–2.4 (m, 4 H), 5.2–6.7 (m, 4 H).

(d) (3*E*)-5-(Tetrahydropyranyloxy)-1,3-pentadiene: bp 65–66 °C (1–2 mmHg); IR (neat) 1600 (w), 1130 (s), 1110 (s), 1070 (s), 1030 (s), 1020 (s), 1000 (s), 950 (m), 900 (s), 870 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.3–2.0 (m, 6 H), 3.3–4.5 (m, 4 H), 4.60 (br s, 1 H), 4.8–5.5 (m, 2 H), 5.5–6.7 (m, 3 H).

(e) (*E*)-3-(1-Hexenyl)-2-cyclohexen-1-one: IR (neat) 1660 (s), 1630 (s), 1580 (w), 960 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, $J = 6$ Hz, 3 H), 1.1–2.6 (m, 12 H), 5.70 (s, 1 H), 6.0–6.2 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.62, 26.13, 26.24, 28.71, 34.89, 36.68, 41.50, 130.42, 135.41, 141.87, 159.94, 198.05. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.92; H, 10.25.

Reactions of Various (*E*)-1-Octenylmetals of Vinylmetals with (*E*)-1-Hexenyl, (*E*)-1-Heptenyl, or (*E*)-1-Octenyl Iodide in the Presence of $Pd(PPh_3)_4$. (a) Reaction of (*E*)-1-Octenylzinc Chloride with (*E*)-1-Hexenyl Iodide: Representative Procedure. To a mixture of 1.85 g (7.5 mmol) of (*E*)-1-octenyl iodide and 2 mL of ether was added 8.5 mL (1.76 M, 15 mmol) of *tert*-butyllithium at −78 °C. The mixture was stirred for 1 h at −78 °C and then for 1 h at room temperature. The reaction mixture was evaporated, and the residue was dissolved in 5 mL of THF. This solution of (*E*)-1-octenyllithium was added to 1.02 g (7.5 mmol) of dry zinc chloride and 5 mL of THF. The mixture was stirred for 2 h at room temperature. This solution, in turn, was added to a mixture of 289 mg (0.25 mmol) of tetrakis(triphenylphosphine)palladium, 1.05 g (5 mmol) of (*E*)-1-hexenyl iodide, and 1 mL of THF. Additional THF was added to make the total volume 10 mL (0.5 M in (*E*)-1-hexenyl iodide). The mixture was stirred at room temperature for 1 h, quenched with 1 N HCl, and analyzed by GLC by using undecane as an internal standard. (5*E*,7*E*)-5,7-Tetradecadiene, which was identified by co-injection with an authentic sample, was formed in 95% yield. Homocoupled hexadecadiene and dodecadiene were formed in 3% yield each.

Unless otherwise mentioned, the following experiments were carried out according to the above representative procedure, and the results are summarized in Table IV.

(b) Reaction of (*E*)-1-Octenyllithium with (*E*)-1-Hexenyl Iodide. (5*E*,7*E*)-5,7-Tetradecadiene, hexadecadiene, and dodecadiene were formed in 40, 25, and 16% yields, respectively. (*E*)-1-Hexenyl iodide was completely consumed.

(c) Reaction of (*E*)-1-Octenylmagnesium Chloride with (*E*)-1-Hexenyl Iodide. (5*E*,7*E*)-5,7-Tetradecadiene was formed in 31% yield (GLC). Hexadecadiene and dodecadiene were also obtained in 5 and 7% yields, respectively, with 51% of (*E*)-1-hexenyl iodide remaining unreacted. The yield did not increase after stirring the reaction mixture for 2 additional hours.

(d) Reaction of Vinylmagnesium Bromide with (*E*)-1-Octenyl Iodide.[21] To a mixture of 0.48 g (2 mmol) of (*E*)-1-octenyl iodide, 116 mg (0.1 mmol) of tetrakis(triphenylphosphine) palladium, and 0.1 mL of THF was added 3.6 mL (0.84 M, 3 mmol) of vinylmagnesium bromide. Additional THF was added to the mixture to make the total volume 4 mL (0.5 M in (*E*)-1-octenyl iodide). The mixture was stirred for 1 h at room temperature and quenched with 1 N HCl. GLC analysis using undecane as internal standard indicated that (*E*)-1,3-decadiene was formed in 83% yield along with a 5% yield of hexadecadiene. Only a trace amount of (*E*)-1-octenyl iodide remained unreacted.

(e) Reaction of (*E*)-1-Octenylcadmium Chloride with (*E*)-1-Hexenyl Iodide. (5*E*,7*E*)-5,7-Tetradecadiene was formed in 86% yield (GLC). Hexadecadiene and dodecadiene were also obtained in 17 and 8% yields, respectively. A trace amount of (*E*)-1-hexenyl iodide remained unreacted.

(f) Reaction of (*E*)-Bis(1-octenyl)mercury with (*E*)-1-Hexenyl Iodide. (*E*)-Bis(1-octenyl)mercury was prepared according to a literature method[35] by using 0.815 g (3 mmol) of mercuric chloride, 3 mL of THF, and 15.6 mL (0.45 M, 7 mmol) of (*E*)-1-octenyllithium. The cross-coupling reaction was carried out in the same manner as the reaction of (*E*)-1-octenylzinc chloride mentioned above by using 0.42 g (2 mmol) of (*E*)-1-hexenyl iodide, 116 mg (0.1 mmol) of tetrakis(triphenylphosphine)palladium, and 4 mL of THF. After stirring the reaction mixture for 1 h at room temperature, the mixture was quenched with 1 N HCl. The formation of metallic mercury was observed. GLC analysis using undecane as an internal standard indicated that (5*E*,7*E*)-5,7-tetradecadiene was formed in 46% yield with 57% of (*E*)-1-hexenyl iodide remaining unreacted. Hexadecadiene and dodecadiene were also formed in 90 and 3%, respectively. The yield of (5*E*,7*E*)-5,7-tetradecadiene did not increase after stirring the reaction for an additional 2 h.

(g) Reaction of Lithium (*E*)-1-Octenylbutyldisiamylborate with (*E*)-1-Hexenyl Iodide. A solution of (*E*)-1-octenyldisiamylborane (1.22 M, 6.15 mL, 7.5 mmol) prepared according to a literature method[3] was evaporated to remove Me_2S and redissolved in 5 mL of THF. To this was added 3.49 mL (2.15 M, 7.5 mmol) of *n*-butyllithium at −78 °C. The cross-coupling reaction was carried out following the representative procedure. (5*E*,7*E*)-5,7-Tetradecadiene was formed in 12% yield, with 69% of (*E*)-1-hexenyl iodide remaining unreacted.

(h) Reaction of (*E*)-1-Octenyldisiamylborane with (*E*)-1-Hexenyl Iodide in the Presence of Sodium Ethoxide. This reaction was carried out in a manner similar to that reported in the literature.[11a] A solution of (*E*)-1-octenyldisiamylborane (1.22 M, 6.15 mL, 7.5 mmol) prepared by a literature method[3] was evaporated and dissolved in 3 mL of benzene.

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(35) Makarova, L. G.; Nesmeyanov, A. N. *The Organic Compounds of Mercury*; North-Holland: Amsterdam, 1967, p 32.

(36) In this paper the periodic group notation in parentheses in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

To a mixture of 289 mg (0.25 mmol) of tetrakis(triphenylphosphine)palladium, 1.05 g (5 mmol) of (*E*)-1-hexenyl iodide, and 1 mL of benzene were added (*E*)-1-octenyldisiamylborane in benzene obtained above and 4 mL (2.5 M, 10 mmol) of sodium ethoxide in ethanol. Additional benzene was added to make the total volume 10 mL (0.5 M in (*E*)-1-hexenyl iodide). The mixture was stirred at room temperature for 1 h and oxidized with 2 mL each of 3 M solution of sodium hydroxide and 30% hydrogen peroxide for 2 h at room temperature. Analysis by GLC using undecane as an internal standard indicated the formation of (5*E*,7*E*)-5,7-tetradecadiene in 65% yield which was confirmed by coinjection with an authentic sample and the recovery of unreacted (*E*)-1-hexenyl iodide (5%). Homocoupled dienes, 7,9-hexadecadiene and 5,7-dodecadiene, were also formed in 5% and 1% yields, respectively.

(i) Reaction of (*E*)-1-Octenyldiisobutylalane with (*E*)-1-Hexenyl Iodide. After 1, 3, and 6 h of reaction time, (5*E*,7*E*)-5,7-tetradecadiene was obtained in 41, 71, and 75% yields, respectively. The corresponding amounts of the unreacted iodide were 51, 9, and 3%, respectively. The amounts of homocoupled products are also summarized in Table IV.

(j) Reaction of (*E*)-1-Octenyltrimethylsilane with (*E*)-1-Hexenyl Iodide. The reaction did not produce any dienes, with essentially 100% of (*E*)-1-hexenyl iodide remaining unreacted.

(k) Reaction of (*E*)-1-Octenyltributyltin with (*E*)-1-Hexenyl Iodide. Only a trace amount of (5*E*,7*E*)-5,7-tetradecadiene was formed in 1 h at room temperature with 66% of (*E*)-1-hexenyl iodide remaining unreacted. The yield did not increase thereafter.

(l) Reaction of Vinyltributyltin with (*E*)-1-Heptenyl Iodide. To a 0.976 g (3 mmol) of tributyltin chloride in 1 mL of THF was added 1.60 mL (1.88 M, 3 mmol) of vinyllithium in THF. The mixture was stirred for 24 h at room temperature. This vinyltributyltin solution was added to a mixture of 0.448 g (2 mmol) of (*E*)-1-heptenyl iodide, 116 mg (0.1 mmol) of tetrakis(triphenylphosphine)palladium, and 0.4 mL of THF. After having been stirred for 1 h at room temperature, the mixture was quenched with 1 N HCl. GLC analysis using decane as an internal standard indicated that (*E*)-1,3-nonadiene, which was identified by coinjection with an authentic sample, was formed in 17% yield with 36% of (*E*)-1-heptenyl iodide remaining unreacted. The yield was not improved after stirring for additional 2 h.

(m) Reaction of (*E*)-Bis(1-octenyl)titanocene with (*E*)-1-Hexenyl Iodide. To a mixture of 0.747 g (3 mmol) of titanocene dichloride and 3 mL of THF was added 7.32 mL (0.82 M, 6 mmol) of (*E*)-1-octenyllithium. The mixture was stirred for 2 h at room temperature and then concentrated to a volume of 3 mL. This was added to a mixture of 116 mg (0.1 mmol) of tetrakis(triphenylphosphine)palladium, 0.418 g (2 mmol) of (*E*)-1-hexenyl iodide, and 0.4 mL of THF. An additional amount of THF was added to the mixture to make the total volume 4 mL. The mixture was stirred for 1 h at room temperature and quenched with 1 N HCl. GLC analysis using undecane as an internal standard indicated the formation of only a trace amount of (5*E*,7*E*)-5,7-tetradecadiene with 73% of (*E*)-1-hexenyl iodide remaining unreacted. Hexadecadiene was formed in 21% yield. The yield of (5*E*,7*E*)-5,7-tetradecadiene did not increase after stirring for an additional 2 h.

(n) Reaction of (*E*)-1-Octenylzirconocene Chloride with (*E*)-1-Hexenyl Iodide. (5*E*,7*E*)-5,7-Tetradecadiene was obtained in 93% yield in 1 h with 7% of (*E*)-1-hexenyl iodide remaining unreacted. No more than traces of the homocoupled products were formed.

(o) Reaction of (*E*)-1-Octenylcerium Dichloride with (*E*)-1-Hexenyl Iodide. After 1 h, (5*E*,7*E*)-5,7-tetradecadiene was produced in 42% yield along with 7,9-hexadecadiene and 5,7-dodecadiene formed in 33 and 26% yields, respectively.

Catalytic Turnover Numbers in the Reaction of Iodobenzene with (*E*)-1-Octenylmetals Containing Al, Zr, or Zn in the Presence of Pd(PPh_3)$_4$. (a) (*E*)-1-Octenyldiisobutylalane. To a mixture of 0.82 g (4 mmol) of PhI, 5 mL of THF, and 0.23 g (5 mol%) of $Pd(PPh_3)_4$ was added (*E*)-1-octenyldiisobutylbutylalane (0.81 M, 7.4 mL, 6 mmol). After stirring the reaction mixture for 1 h at 22 °C, GLC analysis indicated that (*E*)-1-octenylbenzene was formed in 8% yield with 89% of iodobenzene remaining unreacted. A similar experiment run at 50 °C by using 1 mol% of $Pd(PPh_3)_4$ produced in 1 h a 25% yield of (*E*)-1-octenylbenzene with 80% of iodobenzene remaining unreacted. The turnover numbers at 22 and 50 °C are 2 and 25 per h, respectively.

(b) (*E*)-1-Octenylzirconocene Chloride. This experiment was carried out analogously by using (*E*)-1-octenylzirconocene chloride. The turnover numbers at 22 and 50 °C are 3 and 30 per h, respectively.

(c) (*E*)-1-Octenylzinc Chloride. This experiment was carried out analogously by using (*E*)-1-octenylzinc chloride and 0.05 mol% of $Pd(PPh_3)_4$. The yield of (*E*)-1-octenylbenzene was >95% at 1 h at 22 °C. The turnover number is therefore >2000 per h.

***trans*-Iodo(phenyl)bis(triphenylphosphine)palladium.**[28] To a mixture of 2.32 g (2 mmol) of tetrakis(triphenylphosphine)palladium and 15 mL of benzene was added 0.224 mL (2 mmol) of iodobenzene at room temperature. When the reaction mixture was stirred, it immediately turned into a dark homogeneous solution, from which white precipitates were formed. After stirring the reaction mixture for 10 h, the white precipitates were filtered, washed with hexane, and dried in vacuo. Recrystallization from CH_2Cl_2/hexane gave 1.50 g (90% yield) of pale yellow crystals of *trans*-$PhPdI(PPh_3)_2$: mp 75–78 °C (dec); IR (Nujol) 3060 (w), 1560 (w), 1480 (m), 1445 (m), 1190 (w), 1100 (s), 1070 (w), 1655 (w), 1030 (w), 1020 (w), 1000 (w), 895 (w), 750 (s), 730 (s), 700 (s), 690 (s); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.1–6.4 (m, 2 H), 6.5–6.8 (m, 2 H), 6.9–7.1 (m, 1 H), 7.1–7.4 (m, 18 H), 7.4–7.7 (m, 12 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 121.91, 127.57, 127.58, 128.97, 129.73, 136.66, 134.95, 135.25, 136.12; ^{31}P NMR (CH_2Cl_2/THF (2:1), 85% H_3PO_4) δ 23.68.

^{1}H NMR Examination of the Reaction of Iodo(phenyl)bis(triphenylphosphine)palladium with (*E*)-1-Octenylzinc Chloride. To 42 mg (0.05 mmol) of $PhPd(PPh_3)_2I$, 0.34 mL of CD_2Cl_2, and 0.07 mL of THF in a 5-mm NMR tube was added 0.075 mL (0.8 M, 0.06 mmol) of (*E*)-octenylzinc chloride at −78 °C. It was necessary to add CD_2Cl_2 to dissolve $PhPd(PPh_3)_2I$. The mixture was warmed to 0 °C, and the reaction was followed by ^{1}H NMR at 0 °C. The results are summarized in Table V and Figure 1. At δ 6.05–6.6 ppm were observed the signals corresponding to the olefinic protons of free (*E*)-1-octenylbenzene uncoordinated with palladium. No signals assignable to (*E*)-1-octenyl(phenyl)bis(triphenylphosphine)palladium were observed. The ^{31}P NMR spectrum of this reaction mixture shows a broad singlet at 20.37 ppm. This reaction follows second-order kinetics, and the rate constant at 0 °C was 2.9 L/mol min.

Addition of Phenyl Iodide to the Mixture Obtained by the Reaction of Iodo(phenyl)bis(triphenylphosphine)palladium with (*E*)-1-Octenylzinc Chloride. To the reaction mixture obtained in the preceding experiment was added 8.4 μL (0.075 mmol) of phenyl iodide at room temperature. The reaction was followed by ^{1}H NMR and ^{31}P NMR. Iodo(phenyl)bis(triphenylphosphine)palladium was regenerated in 98% yield by ^{1}H NMR. Its ^{31}P NMR spectrum showed a singlet at 23.68 ppm. No other signals were discernible.

Addition of Maleic Anhydride to the Mixture Obtained by the Reaction of Iodo(phenyl)bis(triphenylphosphine)palladium with (*E*)-1-Octenylzinc Chloride. To the reaction mixture prepared as described above was added 7 mg (0.07 mmol) of maleic anhydride. Examination by ^{31}P NMR indicated that a broad singlet at 20.37 ppm was rapidly replaced by a new singlet at 27.75 ppm. Addition of an authentic sample of the $Pd(PPh_3)_2$–maleic anhydride complex prepared as described in the literature[29] did not show any sign of splitting. No other ^{31}P NMR signals were discernible.

^{1}H NMR Examination of the Reaction of (*E*)-1-Octenylzinc Chloride with Phenyl Iodide in the Presence of Tetrakis(triphenylphosphine)palladium. To a mixture of 58 mg (0.05 mmol) of $Pd(PPh_3)_4$ and 0.32 mL of CD_2Cl_2 were added 0.161 mL (0.62 M, 0.1 mmol) of (*E*)-1-octenylzinc chloride and 11 μL (0.1 mmol) of phenyl iodide at −78 °C. The mixture was warmed to −10 °C and then monitored by ^{1}H NMR at −10 °C. The results are summarized in Figure 2.

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