Supplementary Material Available: Listings of the observed and calculated structure factors (Supplementary Table I) (4 pages). Ordering information is given on any current masthead page.

References and Notes

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Mercury in Organic Chemistry. 14.[1] A Convenient Regiospecific Synthesis of π-Allylpalladium Compounds via Vinylmercurials[2]

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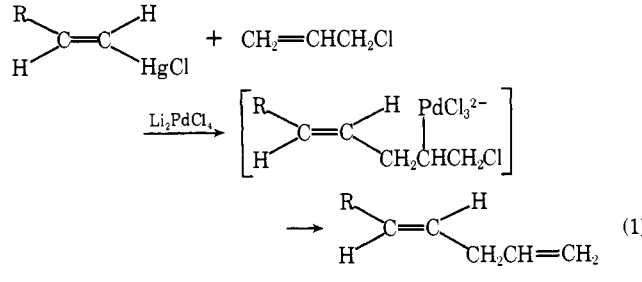
Abstract: Vinylmercuric chlorides readily react with palladium chloride, lithium chloride, and alkenes in tetrahydrofuran at 0 °C to give excellent yields of π-allylpalladium compounds. This reaction is especially valuable for the regiospecific synthesis of a wide range of functionally substituted π-allylpalladium compounds. The stereochemistry of these compounds is established by NMR spectral analysis. The mechanism of the reaction presumably involves the addition of a vinylpalladium species to the alkene, followed by a palladium hydride rearrangement to form the π-allylpalladium complex.

π-Allylpalladium compounds were first reported in 1957.[6] Since that time a number of procedures have been reported for the synthesis of these compounds.[7-10] At present the most useful general methods of preparing these compounds appear to be the direct allylic hydrogen substitution of alkenes by palladium salts,[11-15] the insertion of palladium(0) reagents into the carbon–halogen bond of allylic halides,[16-19] and the addition of aryl- and certain alkylmercurials to 1,3-dienes.[20] While the first method is certainly one of the most useful approaches to π-allylpalladium compounds because of the ready availability of alkenes, it sometimes suffers due to difficulties in predicting and controlling the regioselectivity of the palladation of unsymmetrical alkenes. Palladium insertion into allylic halides overcomes this disadvantage, but requires as starting materials allylic halides which are generally much more difficult to prepare and handle than alkenes. The palladium-promoted addition of organomercurials to 1,3-dienes also provides a reasonably general route to π-allylpalladium compounds, but is limited to only certain organomercurials and gives low yields. With rapidly increasing interest in the application of π-allylpalladium compounds in organic synthesis,[13-15] new methods of synthesis have become desirable. We wish at this time to report the details of our own novel, regiospecific route to π-allylpalladium compounds via vinylmercurials, which appears to have a number of advantages over previous methods.

Results and Discussion

Reaction Conditions. Our recent work has concentrated on the development of new synthetic organic procedures employing vinylmercurials. These studies have provided new routes to α,β-unsaturated acids,[21] esters,[21] and ketones,[22] as well as butenolides.[23] We have also developed methods for the convenient synthesis of symmetrical[24] and unsymmetrical[25] 1,3-dienes and 1,4-dienes.[26] The latter procedure utilizes the palladium-catalyzed coupling of vinylmercurials and allylic halides (eq 1). This reaction appears to involve the addition of



(1)

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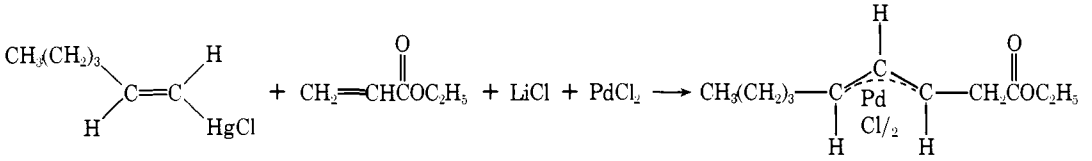
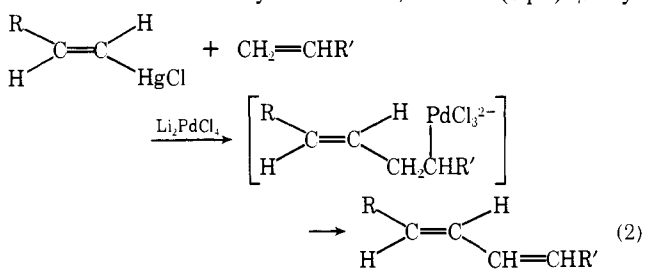
Table I. Reaction Conditions for the Synthesis of π-Allylpalladium Compounds[a]



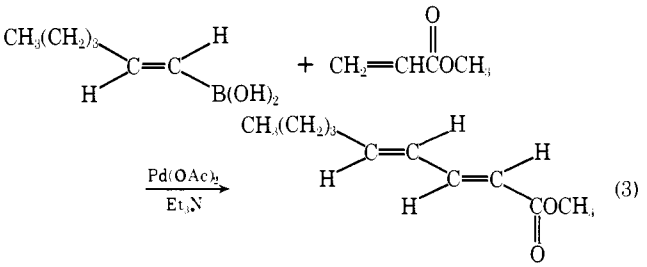
Solvent	Temp, °C	CH_2=$CHCO_2C_2H_5$, equiv	LiCl, equiv	Isolated crude yield of π-allylpalladium compound, %
Et_2O	0	10	2	41
CH_3CN				50
HMPA[b]				64
CH_2=$CHCO_2C_2H_5$		[c]		69[d]
THF[e]		10		66
	25			62
	−25			43
	−78			38
	0	2		34
		2	0	56

[a] 10 mmol of vinylmercurial, 10 mmol of $PdCl_2$, 100 ml of solvent. [b] HMPA = hexamethylphosphoramide. [c] 50 mL of neat ethyl acrylate used as a solvent. [d] Oily product. [e] THF = tetrahydrofuran.

a vinylpalladium species to the carbon-carbon double bond of the allylic halide, followed by palladium chloride elimination. In examining analogous reactions with simple alkenes, we anticipated that similar addition reactions would occur, but that palladium hydride elimination would ensue, providing a useful new route to unsymmetrical 1,3-dienes (eq 2). β-Hydride elimination reactions of this sort are well established in organopalladium chemistry. Furthermore, Dieck and Heck had already reported an analogous coupling reaction of *trans*-1-hexenylboronic acid, palladium acetate, methyl acrylate, and triethylamine (eq 3).[27]

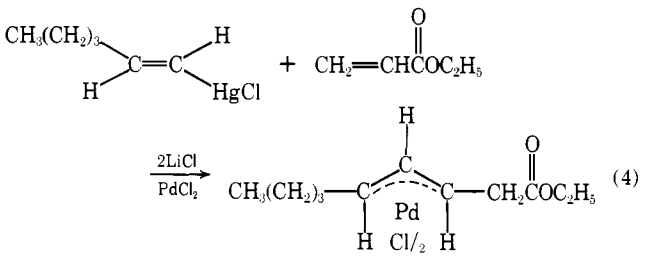


(2)



(3)

We ran the analogous reaction using *trans*-1-hexenylmercuric chloride, palladium chloride, lithium chloride, and ethyl acrylate, with no triethylamine present, and quite unexpectedly observed the formation of a π-allylpalladium compound instead (eq 4). This surprising result led us to further examine the reaction conditions so as to maximize the yield of π-allylpalladium compound. We have looked at the effect of various reagents, solvents, temperatures, and reagent ratios on the yield of π-allylpalladium compound in the above reaction. The results are summarized in Table I. Best results were obtained using a tenfold excess of alkene and 2 equiv of anhydrous lithium chloride in tetrahydrofuran (THF) solvent at 0 °C. Less polar solvents such as ether appeared less effective, as did lower reaction temperatures. The above conditions gave as high a yield of π-allylpalladium compound as using ethyl acrylate itself as the solvent.



(4)

Synthesis of π-Allylpalladium Compounds. Using our best reaction conditions and a wide variety of vinylmercurials and alkenes, we have examined the generality of this new approach to the synthesis of π-allylpalladium compounds (Table II). The reaction readily accommodates vinylmercurials derived from both terminal and internal alkynes.[28,29] A wide variety of functional groups, including esters, ketones, and nitriles, are readily incorporated in the alkene and should be readily accommodated by the mercurial as well. In fact, best results are generally obtained when these functional groups are directly attached to the carbon-carbon double bond of the alkene. The overall structure of the alkene is apparently more important than its functionality. Terminal unbranched alkenes such as ethylene (92%), 1-hexene (67%), ethyl acrylate (90%), acrylonitrile (89%), and methyl vinyl ketone (100%) all give excellent yields of π-allylpalladium compounds. Disubstituted terminal alkenes such as isobutylene (41%) and methyl methacrylate (29%) give significantly lower yields. Quite surprisingly *cis*-2-butene (59%) gives higher yields than either of these two compounds. Further substitution as in 2-methyl-2-butene (19%) once again sharply reduces the yield of π-allylpalladium compound. No tetrasubstituted alkenes were examined in these reactions.

NMR Spectral Analysis and Stereochemistry. Complete physical data have been obtained for all π-allylpalladium compounds. The melting points, infrared spectral data, and elemental analyses are reported in the Experimental Section. Since the NMR spectral data proved most informative and helped establish the stereochemistry of the products, they will be discussed in detail.

NMR data for a number of different π-allylpalladium compounds have been reported previously.[11,30-35] Our analysis of the NMR data for our compounds is entirely consistent with previous interpretations and is presented in Table III. For example, in compounds such as I where R and R′ contain no

Table II. Synthesis of π-Allylpalladium Compounds[a]

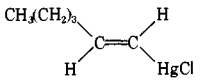
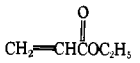
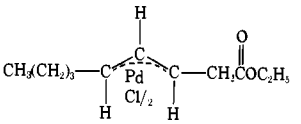
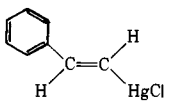
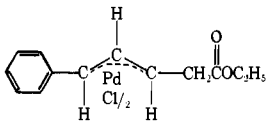
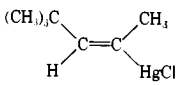
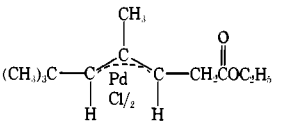
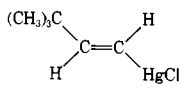
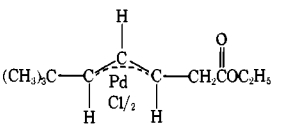
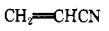
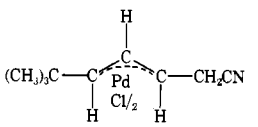
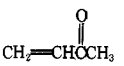
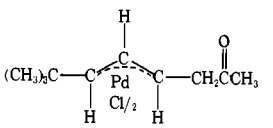
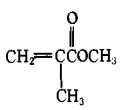
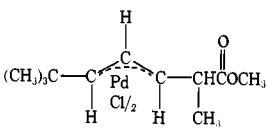
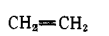
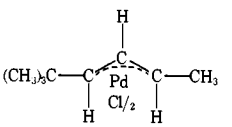
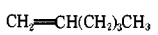
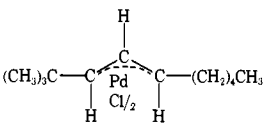
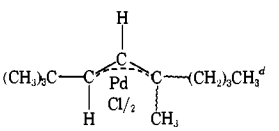
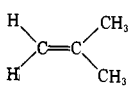
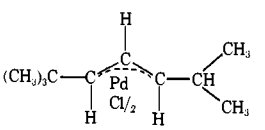
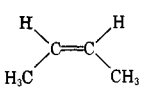
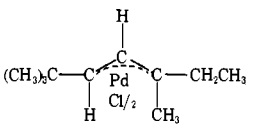
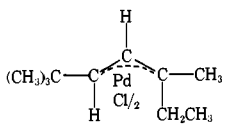
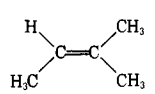
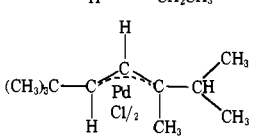
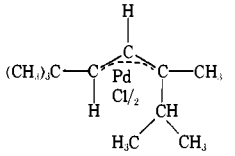
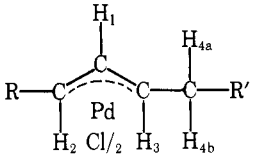
Entry	Vinylmercuric chloride	Alkene	π-Allylpalladium compd	% yield[b]
1				66
2				100 (58)
3				97 (83)
4				90 (82)
5				87 (71)
6				100 (67)
7				29 (22)
8				92
9a				67 (63)[c]
9b				
10				41 (21)
11a				59 (37)[e]
11b				
12a				19 (7)[f]

Table II (*Continued*)

Entry	Vinylmercuric chloride	Alkene	π-Allylpalladium compd	% yield[b]
12b				

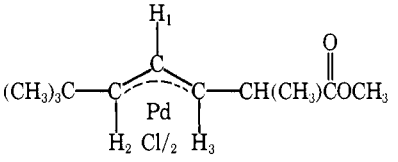
[a] 10 mmol of vinylmercuric chloride, 10 mmol of $PdCl_2$, 20 mmol of LiCl, 100 mmol of alkene, 100 mL of THF, 0 °C. [b] Crude yield (recrystallized yield). [c] Approximate ratio **9a**:**9b** is 5:1 by NMR spectral analysis. [d] Presumed to be a mixture of syn and anti isomers. [e] Approximate ratio of stereoisomers **11a**:**11b** is 6:4 by NMR spectral analysis after one recrystallization, with **11a** presumed to be the major isomer. [f] Approximate ratio of stereoisomers **12a**:**12b** is 7:3 by NMR spectral analysis after three recrystallizations, with **12a** presumed to be the major isomer.



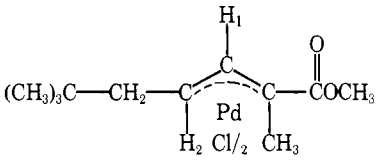
I

hydrogens adjacent to the rest of the system, H_1, which appears furthest downfield at δ 5–6, shows up as a triplet due to coupling with magnetically equivalent H_2 and H_3. The anti hydrogen H_2 appears as a doublet with J = 11–12 Hz due to coupling with H_1. Our π-allylpalladium compounds with R = *tert*-butyl and phenyl exhibit a similar pattern. The signal for H_3 appears as a doublet due to coupling with H_1 (J = 11–12 Hz) which is further split by the H_4 hydrogens, the extent of splitting depending upon the number of H_4 hydrogens and their magnetic equivalence or nonequivalence.

Using the above reasoning the position of the π-allyl system in our compounds is readily determined. Consider, for example, entry **7** in Table II. Two possible π-allylpalladium compounds, II and III, can be envisioned as arising from this reaction (see

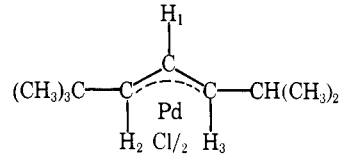


II

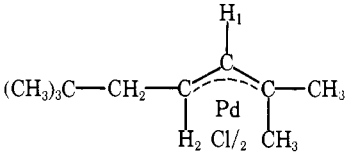


III

the latter mechanistic discussion). The proton H_1, which shows up at δ 5.13, is clearly seen as a triplet, consistent with structure II and ruling out structure III. A similar argument can be used to differentiate between structures IV and V for the π-allyl

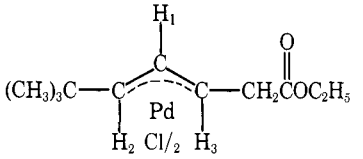


IV

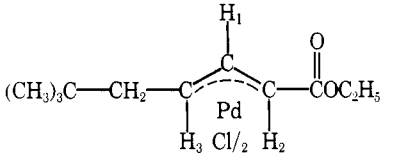


V

product of entry **10** in Table II. The products arising from the reactions of terminal monosubstituted alkenes are less easily distinguished, however. Consider, for example, the possible products VI and VII which might arise from entry **4** in Table

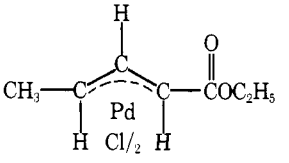


VI



VII

II. Although H_1 should appear as a triplet and H_2 as a doublet in either compound, the structures can be differentiated by examining the relative chemical shifts of H_2 and H_3. As seen in compound VIII,[11] a π-allyl hydrogen flanked by an ester is



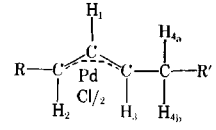
δ 4.22 δ 3.44

VIII

shifted upfield by approximately δ 0.8 relative to a π-allyl hydrogen flanked by an alkyl group. In the product of entry **4**, H_2 appears at δ 3.76 while H_3 appears further upfield at δ 3.47–3.68. This is inconsistent with structure VII and suggests that compound VI is the product.

The question of the syn or anti stereochemistry of the products must also be addressed. In general the more bulky alkyl or functional groups tend to prefer the syn arrangement (cis to H_1). Since hydrogens anti to H_1 are easily distinguished from hydrogens syn to H_1 due to the large difference in coupling constants ($J_{anti} \simeq 12$ and $J_{syn} \simeq 7$ Hz), the two possible stereoisomers are usually readily distinguished. Large anti coupling constants of J = 11–12 Hz are seen in the mercurial-derived portion of the π-allylpalladium compounds prepared from styrylmercuric chloride, *trans*-1-hexenylmercuric chloride, and *trans*-3,3-dimethyl-1-butenylmercuric chloride. In all but one case, terminal alkenes give rise to π-allylpalladium products in which coupling has occurred between the vinyl portion of the mercurial and the terminal carbon of the alkene, and the products show large anti hydrogen–hydrogen coupling constants consistent with a syn-arrangement of the organic group.

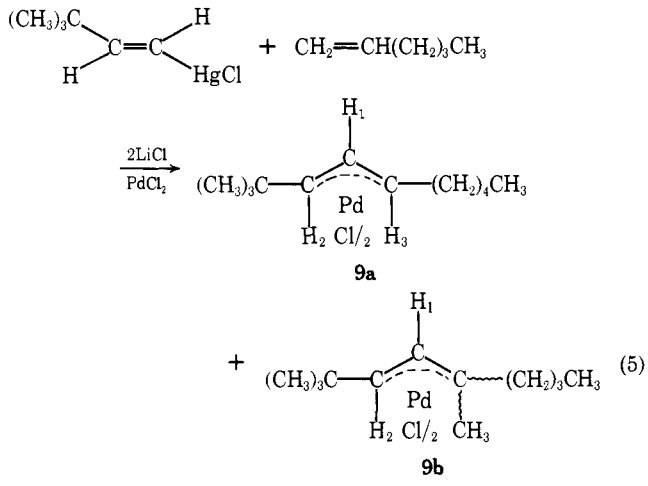
Table III. NMR Spectra Data[a]



Entry[b]	R	H_1	H_2	H_3	H_{4a}	H_{4b}	R'
1	0.8–1.9 (m, 9 H, $CH_3(CH_2)_3$)	5.18 (t, J = 11)	------3.50–4.00(m)----------		2.48 (dd, J = 9 and 17)	2.78 (dd, J = 5 and 17)	1.20 (t, 3 H, J = 7, CH_3) 4.12 (q, 2 H, J = 7, OCH_2)
2	7.1–7.6 (m, 5 H, C_6H_5)	5.75 (t, J = 11)	4.59 (d, J = 11)	3.7–4.1(m)	2.56 (dd, J = 9 and 17)	2.82 (dd, J = 5 and 17)	1.24 (t, 3 H, J = 7, CH_3) 4.44 (q, 2 H, J = 7, OCH_2)
3	1.24 (s, 9 H, $(CH_3)_3C$)	2.13 (s, 3 H, CH_3)	3.42 (s)	3.46 (dd, J = 6 and 8)	2.52 (dd, J = 8 and 17)	2.79 (dd, J = 6 and 17)	1.24 (t, 3 H, J = 7, CH_3) 4.15 (q, 2 H, J = 7, OCH_2)
4	1.10 (s, 9 H, $(CH_3)_3C$)	5.14 (t, J = 11)	3.76 (d, J = 11)	3.47–3.68 (m)	2.48 (dd, J = 9 and 17)	2.76 (dd, J = 5 and 17)	1.20 (t, 3 H, J = 7, CH_3) 4.09 (q, 2 H, J = 7, OCH_2)
5	1.17 (s, 9 H, $(CH_3)_3C$)	5.38 (t, J = 11)	3.92 (d, J = 11)	3.41 (dt, J = 5 and 11)[c]	----------2.69 (d, J = 5)----------		
6	1.17 (s, 9 H, $(CH_3)_3C$)	5.13 (t, J = 11)	3.84 (d, J = 11)	3.5–3.8 (m)	2.62 (dd, J = 8 and 18)	2.99 (dd, J = 4 and 18)	2.21 (s, 3 H, CH_3)
7	1.15 (s, 9 H, $(CH_3)_3C$)	5.18 (t, J = 11)	3.80 (d, J = 11)[d]	3.80 (dd, J = 5 and 11)[d]	1.38 (d, 3 H, J = 7, CH_3)	2.83 (m)	3.68 (s, 3 H, OCH_3)
8	1.14 (s, 9 H, $(CH_3)_3C$)	5.09 (t, J = 11)	3.63 (d, J = 11)	3.69 (dq, J = 5 and 11)[e]	----------1.23 (d, 3 H, J = 7, CH_3)----------		
9a[f]	1.18 (s, 9 H, $(CH_3)_3C$)	5.00 (t, J = 11)	3.56 (d, J = 11)	3.4–3.7 (m)	----------0.80–1.60 (m, 11 H, $CH_3(CH_2)_4$)----------		
9b[f,g]		4.85 (d, J = 11)	3.89 (d, J = 11)				
10	1.16 (s, 9 H, $(CH_3)_3C$)	5.11 (t, J = 11)	3.65 (d, J = 11)	3.70 (dd, J = 5 and 11)	1.55–2.2 (m)	------ 1.0–1.2 (underneath δ 1.16, $C(CH_3)_2$)-------	
11a[h]	1.14 (s, 9 H, $(CH_3)_3C$)	4.92 (d, J = 12)	3.98 (d, J = 11)	1.30 (s, 3 H, CH_3)	----------0.9–1.9 (m 5 H, CH_2CH_3)----------		
11b[h]		4.88 (d, J = 12)	3.92 (d, J = 11)				
12a[i]	1.16 (s, 9 H, $(CH_3)_3C$)	4.87 (d, J = 12)	4.00 (d, J = 12)	1.22 (s, 3 H, CH_3)[j]	2.00 (septet, J = 6)[k]----------	1.15 (d, 6 H, J = 6, $C(CH_3)_2$)[j]----------	
12b[i]		4.85 (d, J = 12)	3.90 (d, J = 12)				

[a] All spectra recorded on a 100-MHz Varian HA-100 spectrometer; $DCCl_3$ used as solvent except where noted; chemical shifts reported as δ values downfield from tetramethylsilane; coupling constants reported in hertz. [b] Entry number corresponds to entry number in Table II. [c] The inside two peaks overlap resulting in a five-line pattern. [d] These signals partially obscured by OCH_3, but assigned due to similarity to entry 10. [e] Only four peaks are visible; the others are obscured by the signal at δ 3.63. [f] Approximate ratio 9a:9b is 5:1. [g] Spectrum run in CCl_4; assumed to be a syn, anti mixture with the compound containing the syn butyl group predominating; most of the peaks are obscured by the presence of 9a; note the similarity of the assignments to those of entry 11. [h] Approximate ratio 11a:11b is 6:4 after one recrystallization, with 11a presumed to be the major isomer. [i] Approximate ratio 12a:12b is 7:3 after three recrystallizations, with 12a presumed to be the major isomer. [j] Signal appears as a side peak on the signal at δ 1.16. [k] Two peaks are obscured; five are clearly visible.

The reaction of 1-hexene and *trans*-3,3-dimethyl-1-butenylmercuric chloride (entry **9,** Table II) proved to be an exception. This reaction appears to give products of addition at both ends of the carbon-carbon double bond (eq 5). The ap-

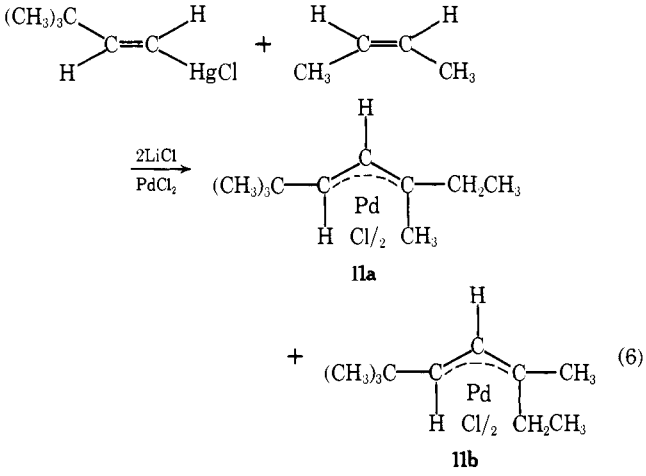


(5)

9a **9b**

proximate ratio **9a**:**9b** is 5:1 as determined by integration of the appropriate NMR peaks. The product **9a** is readily recognized by its characteristic downfield triplet due to the central π-allyl proton H_1. Although compound **9b** is presumed to be a syn-anti mixture, only one peak, a doublet, due to the central π-allyl proton H_1, is evident in the proper region of the NMR spectrum. However, what appear to be three doublets due to the terminal π-allyl protons H_2 in the mixture of **9a** and **9b** are evident in the region δ 3.56–3.89 and these may be due to the three possible π-allylpalladium compounds **9a** and *syn*- and *anti*-**9b.**

In the reactions of internal alkenes, syn and anti isomers are also to be expected and they have indeed been observed. The reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride and *cis*-2-butene (entry **11,** Table II) gives rise to two compounds, present in a 6:4 ratio, easily recognized by the presence of two different sets of doublets in the regions δ 3.92–3.98 and 4.88–4.92 of the NMR spectrum (eq 6). Although it is not

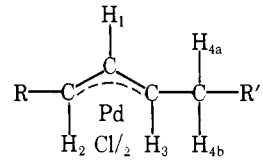


(6)

11a **11b**

obvious which peaks are due to what product, it is assumed that the major product contains the more bulky ethyl group in the syn position. Similar results are evident in the reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride and 2-methyl-2-butene where overlapping sets of doublets are observed at approximately δ 4.85 and 4.87, and δ 3.90 and 4.00. The observed isomer ratio from NMR spectral analysis is approximately 7:3. Once again we assume that the predominant isomer is the one containing the more bulky isopropyl group syn to the central π-allyl proton.

Several other interesting observations were made during a close examination of the NMR spectra of these π-allylpalladium compounds. Our data show that when R′ in IX contains

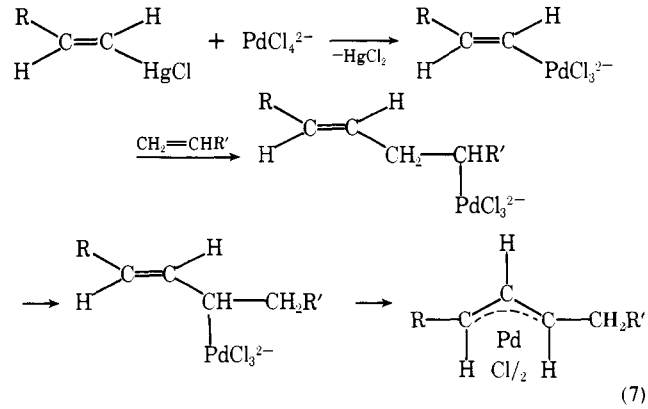


IX

a carbonyl group, either a ketone or an ester, adjacent to the carbon bearing H_4, the protons H_4 become magnetically nonequivalent. For example, the reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride and methyl vinyl ketone (entry **6,** Table II) gives a π-allylpalladium compound in which each of the H_4 protons appears as a doublet of doublets (J = 8 and 18 and J = 4 and 18 Hz). The proton H_3 is coupled to three different types of protons and appears as a multiplet. The spectra obtained from the π-allylpalladium compounds derived from α,β-unsaturated esters can be interpreted in a similar fashion with only minor variations in the coupling constants. Interesting enough, the NMR spectrum of the analogous π-allylpalladium compound derived from acrylonitrile (entry 5, Table II) shows no such coupling of the H_4 protons and they appear as a simple doublet.

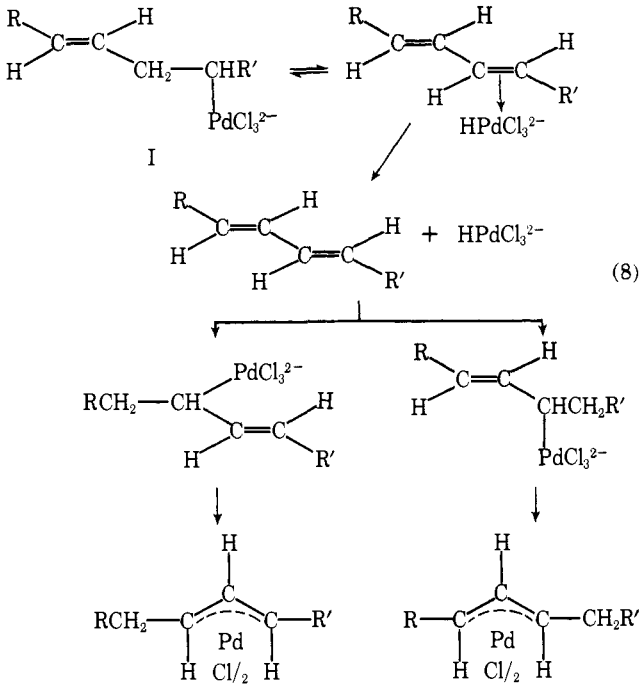
We feel that the magnetic nonequivalence of the H_4 protons arises from restricted carbon-carbon bond rotation. This could conceivably arise due to either coordination of the carbonyl group to the palladium or steric hindrance to bond rotation. Since no shift in the carbonyl absorption is evident in the infrared spectra of these compounds relative to normal saturated ketones and esters, we prefer the latter explanation. Upon examination of molecular models, it appears that a significant degree of steric hindrance exists between the palladium-chlorine bridges of these compounds and the groups bonded to the remote end of the carbonyl group (OC_2H_5, CH_3), this interaction presumably restricting carbon-carbon bond rotation. The linear cyano group presents no such difficulties.

Mechanism. The mechanism of the formation of the π-allylpalladium compounds presumably involves the generation and subsequent addition of a vinylpalladium species (either a vinylpalladium chloride or more likely a vinylpalladium trichloride dianion) to the carbon-carbon double bond of the alkene to form a σ-bonded homoallylic palladium complex, which subsequently undergoes palladium hydride rearrangement to the π-allylpalladium compound (eq 7). Since only one



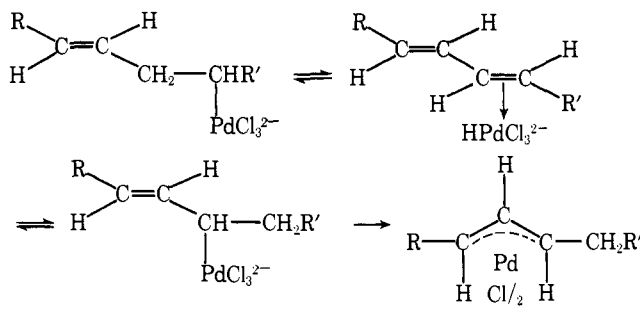
(7)

regioisomer is generally observed in these reactions, it would appear that the palladium hydride rearrangement does not proceed by complete elimination of a palladium hydride species and subsequent readdition in the opposite direction as shown below (eq 8). Such palladium hydride readdition might also



(8)

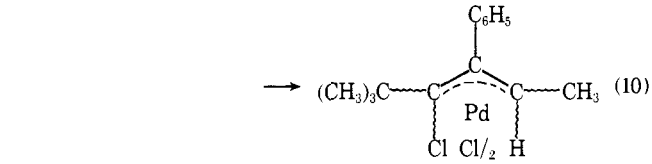
be expected to occur at the opposite end of the 1,3-diene system resulting in a mixture of π-allylpalladium compounds. Since that does not occur, we may assume that the rearrangement proceeds via elimination only as far as an alkene π complex and that subsequent readdition either affords a σ-allyl species which immediately collapses to the more stable π-allyl species, or generates the π-allyl species directly (eq 9).



(9)

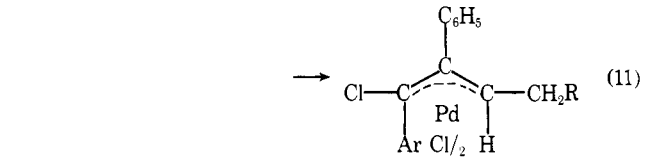
The reaction of 1-hexene (entry **9**, Table II) provides some additional valuable information. In this case palladium hydride elimination might also be expected to occur toward carbon number 3 of the original alkene. This might in fact be occurring since the yield in this reaction (67%) is somewhat lower than in the reaction of most other terminal alkenes. However, the majority of the product is still the π-allylpalladium compound indicating that either the vinyl group present in the initial homoallylic palladium complex is able to direct elimination in the desired direction or that the elimination-addition reactions are completely reversible and continue until the more stable π-allylpalladium complexes are formed. Among all of the reactions of terminal alkenes, the reaction of 1-hexene stands alone in giving products of addition of the original vinyl group of the mercurial to the internal carbon of the alkene. However, this mode of addition has also been observed in the addition of arylpalladium acetates to 1-hexene.[36] In fact, the ratio of terminal to internal addition of approximately 5:1 is not too far from the ratio of 3:1 observed with the arylpalladium compounds.

It is interesting to compare several earlier reported literature preparations of π-allylpalladium compounds with our own reaction. In 1969 it was reported that *tert*-butylphenylacetylene reacts with $[(C_2H_4)PdCl_2]_2$ to give a π-allylpalladium compound of undetermined stereochemistry (eq 10).[37] In



(10)

similar fashion diarylacetylenes, alkenes, and dichlorobis(benzonitrile)palladium(II) react to give π-allylpalladium compounds (eq 11).[38] The reaction of vinylsilanes and -germanes and dichlorobis(benzonitrile)palladium(II) also reportedly yields π-allylpalladium compounds (eq 12).[39] All of



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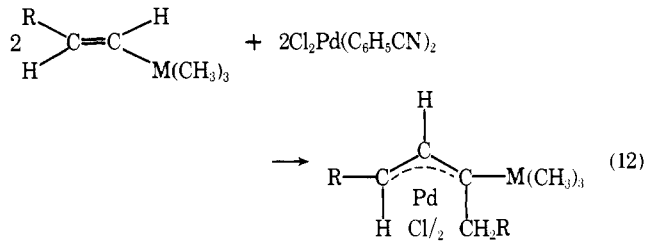
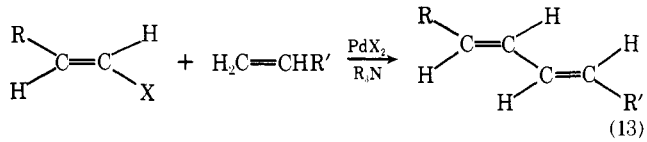


(12)

these reactions also appear to involve the generation of vinylpalladium species, in the first two cases through palladium chloride addition to diarylacetylenes and in the latter example via transmetalation reactions. The vinylpalladium species then presumably react further as suggested by eq 7 and 9.

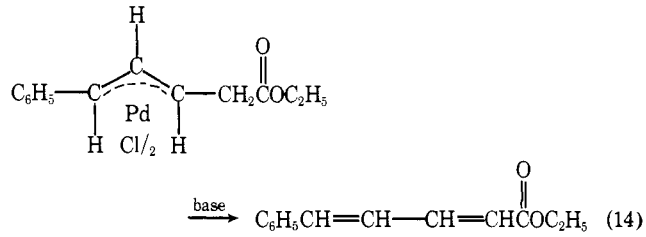
During the early stages of our work, Dieck and Heck also reported some reactions very closely related to our π-allylpalladium reactions.[27] They reported that vinyl halides and palladium catalysts, as well as vinylboronic acids and palladium acetate, react with alkenes in the presence of organic bases to give 1,3-dienes (eq 13). They suggested that some of



(13)

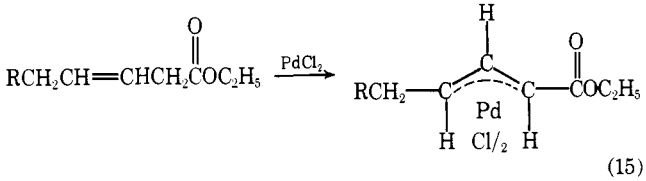
the isomerization products produced in their reactions might be arising via intermediate π-allylpalladium compounds formed from palladium hydride elimination-readdition reactions similar to ours, but that the majority of the product probably arises via immediate β-hydride elimination. We have examined the reaction of some of our π-allylpalladium compounds with various bases (Et_3N, k_2CO_3, NaOH, etc.) and observed that those compounds possessing neighboring electron-withdrawing groups such as esters, ketones, and cyano groups readily undergo elimination at room temperature to provide 1,3-dienes, thus supporting Heck's suggestion (eq 14). It is not clear, however, whether this is only a side reaction in Heck's work or in fact all of his dienes arise in this manner.

Advantages. Our procedure for the preparation of π-allylpalladium compounds offers a number of advantages over previous methods employed in the preparation of these compounds. It proceeds under very mild reaction conditions (0 °C to room temperature overnight), tolerates considerable organic



functionability (esters, ketones, nitriles), and employs very simple starting materials (alkenes and vinylmercurials readily prepared directly from alkynes[28,29]). It utilizes carbon–carbon bond forming reactions to rapidly build up complex carbon structures, thus avoiding the need to prepare more complicated alkenes or difficultly handled allylic halides as starting materials.

Although the regioselectivity of the direct palladation of alkenes is often high, it is sometimes difficult to predict and control. Our procedure allows one to predictably control the position of the π-allyl moiety, while also generating regioisomers not previously available via direct palladation. Compare, for example, the following two π-allylpalladium syntheses (eq 15, 16).



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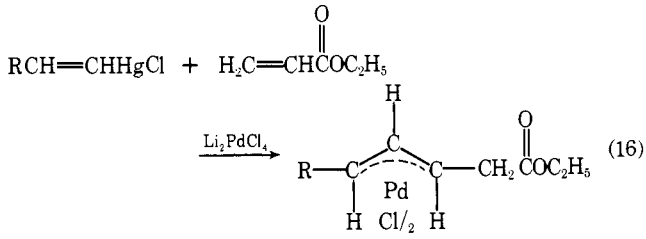
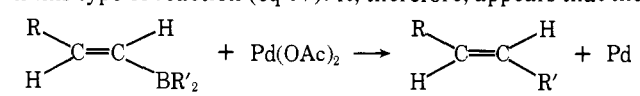


(16)

The vinylmercurial reactions also allow the synthesis of a wider variety of π-allylpalladium structures than the aryl- and alkylmercurial 1,3-diene addition reactions,[20] which also give substantially lower yields.

In an effort to further simplify our π-allylpalladium synthesis, we have examined the direct reaction of vinyldialkylboranes (the intermediates in our vinylmercurial syntheses) with palladium salts and alkenes. It does not appear that *trans*-1-hexenyldicyclohexylborane gives any appreciable reaction with dilithium tetrachloropalladate and ethyl acrylate after 36 h at room temperature in THF. Upon workup a large amount of unreacted palladium salt was extracted upon washing with saturated aqueous ammonium chloride, and only a very pale yellow ether solution was obtained, much paler than the usual intense yellow solution obtained from the vinylmercurial reactions. Evaporation gave a light yellow-brown, gummy substance which failed to crystallize upon addition of pentane and cooling in the freezer. Attempted hexane–ethanol recrystallization gave only an oil. While palladium acetate reacted much more readily with the organoborane than the chloride, as evidenced by the formation of a palladium mirror on the sides of the flask, identical results were again obtained. We and others[40] have observed the formation of coupled olefin in this type of reaction (eq 17). It, therefore, appears that the



(17)

vinylmercurials provide a much cleaner route to the π-allylpalladium compounds than the organoboranes.

With ever-increasing interest in the application of π-allylpalladium compounds in organic synthesis due in large part to the ease with which these compounds undergo facile stereocontrolled carbon–carbon bond formation,[13-15] this novel new approach to π-allylpalladium compounds should prove of real synthetic value. This approach also holds promise as a possible route to many other π-allyl transition metal complexes, a proposition we are presently examining.

Experimental Section

Reagents. All chemicals were used directly as obtained commercially unless otherwise indicated. All vinylmercuric chlorides were prepared by hydroboration-mercuration of the appropriate alkyne.[28,29] Diethyl ether, THF, and HMPA were distilled from lithium aluminum hydride prior to use. Infrared spectra were recorded on a Beckman IR-4250 spectrophotometer and NMR spectra on a Varian HA-100 spectrometer. All NMR data were obtained in $DCCl_3$ solutions except where noted and can be found in Table III. Elemental analyses were performed by Galbraith Laboratories, Inc.

Reaction Conditions. The best reaction conditions for the formation of π-allylpalladium compounds were determined by employing the following general procedure. The appropriate amounts of anhydrous lithium chloride and 10 mmol of palladium chloride (1.78 g) were weighed into a well-dried round-bottom flask containing a nitrogen inlet tube and septum inlet. After flushing with nitrogen, 100 mL of the appropriate solvent and 100 mmol of ethyl acrylate (10.0 g) were added by syringe. After the temperature of the flask was adjusted accordingly, 100 mmol of *trans*-1-hexenylmercuric chloride (3.19 g) was added while back-flushing with nitrogen. The well-stirred reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Ether and activated carbon were added to the reaction mixture which was filtered and washed with saturated aqueous ammonium chloride. The combined washings were reextracted with ether and the combined ether extractions dried over anhydrous sodium sulfate. Removal of the solvent provided the crude yields of π-allylpalladium compound, di-μ-chloro-di(1-carboethoxyoct-2-enyl)-dipalladium(II), indicated in Table I.

Synthesis of π-Allylpalladium Compounds. The following procedure for the preparation of di-μ-chloro-di(1-carboethoxy-5,5-dimethylhex-2-enyl)dipalladium(II) (entry **4**, Table II) is representative. Twenty millimoles of anhydrous lithium chloride (0.85 g) and 10 mmol of palladium chloride (1.78 g) were added to a well-dried round-bottom flask containing a nitrogen inlet tube and septum inlet. After flushing with nitrogen, 100 mL of THF and 100 mmol of ethyl acrylate (10.0 g) were added by syringe. After cooling to 0 °C, 10 mmol of *trans*-3,3-dimethyl-1-butenylmercuric chloride (3.19 g) was added while back-flushing with nitrogen. The well-stirred reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Ether and activated carbon were added to the reaction mixture which was filtered and washed with saturated aqueous ammonium chloride. The combined washings were reextracted with ether and the combined ether extractions dried over anhydrous sodium sulfate. Removal of the solvent provided 2.92 g (90% yield) of bright yellow π-allylpalladium compound. Recrystallization of the π-allylpalladium compounds proved tedious. A universal solvent could not be found and some compounds could not withstand hot or warm filtration (procedure A). The recrystallization procedure for heat-sensitive compounds (procedure B) consisted of dissolving the sample in an excess of the recrystallization solvent, followed by filtration at room temperature and removal of the solvent until precipitation just began to occur. The flask was then cooled (−15 °C) in a freezer to provoke further precipitation. Crude yields and recrystallized yields are shown in Table II. Recrystallization of the above compound using procedure A (4:1 hexane–ethanol) provided an 82% overall yield: mp 125 °C dec; IR (KBr) 1730 cm^{-1}. Anal. Calcd for $C_{11}H_{19}ClO_2Pd$: C, 40.64; H, 5.89. Found: C, 40.50; H, 5.80.

All other π-allylpalladium compounds were prepared in a similar fashion with only a few requiring slight procedural modifications. Entries **2, 5,** and **6** (Table II) were not completely soluble in the ether solution and required additional tetrahydrofuran to solubilize the product before workup.

The following compounds from Table II were prepared according to the above general procedure and modifications. Di-μ-chloro-di-(1-carboethoxyoct-2-enyl)dipalladium(II) (entry 1): mp 116–117 °C dec (procedure A, hexane–ethanol); IR (KBr) 1728 cm^{-1}. Anal.

Calcd for $C_{11}H_{19}ClO_2Pd$: C, 40.64; H, 5.89. Found: C, 40.28; H, 5.67. Di-μ-chloro-di(1-carboethoxy-4-phenylbut-2-enyl)dipalladium(II) (entry **2**): mp 179–180 °C dec (procedure A, $CHCl_3$); IR (KBr) 1725 cm^{-1}. Anal. Calcd for $C_{13}H_{15}ClO_2Pd$: C, 45.20; H, 4.38. Found: C, 45.39; H, 4.32. Di-μ-chloro-di(1-carboethoxy-3,5,5-trimethylhex-2-enyl)dipalladium(II) (entry **3**): mp 168–168.5 °C dec (procedure A, hexane-$CHCl_3$); IR (KBr) 1732 cm^{-1}. Anal. Calcd for $C_{12}H_{21}ClO_2Pd$: C, 42.46; H, 6.24. Found: C, 42.39; H, 6.24. Di-μ-chloro-di(1-cyano-5,5-dimethylhex-2-enyl)dipalladium(II) (entry **5**): mp 201–205 °C dec (procedure B, $CHCl_3$); IR (KBr) 2240 cm^{-1}. Anal. Calcd for $C_9H_{14}ClNPd$: C, 38.87; H, 5.07. Found: C, 38.62; H, 4.74. Di-μ-chloro-di(7,7-dimethyl-2-oxooct-4-enyl)dipalladium(II) (entry **6**): mp 180–183 °C dec (procedure B, $CHCl_3$); IR (KBr) 1722 cm^{-1}. Anal. Calcd for $C_{10}H_{17}ClOPd$: C, 40.90; H, 5.79. Found: C, 40.73; H, 5.78. Di-μ-chloro-di(2-carbomethoxy-6,6-dimethylhept-3-enyl)dipalladium(II) (entry **7**): mp 177–180 °C dec (procedure B, ethanol); IR (KBr) 1740 cm^{-1}. Anal. Calcd for $C_{11}H_{19}ClO_2Pd$: C, 40.64; H, 5.89. Found: C, 40.31; H, 5.69. Di-μ-chloro-di(5,5-dimethylhex-2-enyl)dipalladium(II) (entry **8**): mp 158–159 °C dec (procedure B, 4:1 hexane-ethanol). Anal. Calcd for $C_8H_{13}ClPd$: C, 37.97; H, 5.97. Found: C, 37.95; H, 5.98. Di-μ-chloro-di(2,2-dimethyldec-3-enyl)dipalladium(II) (entry **9a**): mp 98–100 °C (procedure B, hexane); NMR spectra taken in CCl_4. Anal. Calcd for $C_{12}H_{23}ClPd$: C, 46.62; H, 7.50. Found: C, 46.18; H, 7.54. Di-μ-chloro-di(2,2,6-trimethylhept-3-enyl)dipalladium(II) (entry **10**): mp 159–161 °C dec (procedure B, ethanol). Anal. Calcd for $C_{10}H_{19}ClPd$: C, 42.73; H, 6.81. Found: C, 42.77; H, 6.89. Di-μ-chloro-di(2,2,5-trimethylhept-3-enyl)dipalladium(II) (entry 11): mp 152–154 °C dec (procedure B, ethanol). Anal. Calcd for $C_{10}H_{19}ClPd$: C, 42.73; H, 6.81. Found: C, 42.62; H, 6.74. Di-μ-chloro-di(2,2,5,6-tetramethylhept-3-enyl)dipalladium(II) (entry **12**): mp 154–156 °C dec (procedure B, $CHCl_3$). Anal. Calcd for $C_{11}H_{21}ClPd$: C, 44.77; H, 7.17. Found: C, 44.73; H, 7.25.

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