Alkylation of (π-Allyl)palladium Systems. Mechanism and Regiocontrol

Björn Åkermark,* Sverker Hansson, Bertil Krakenberger, Aldo Vitagliano,*[1] and Krister Zetterberg*

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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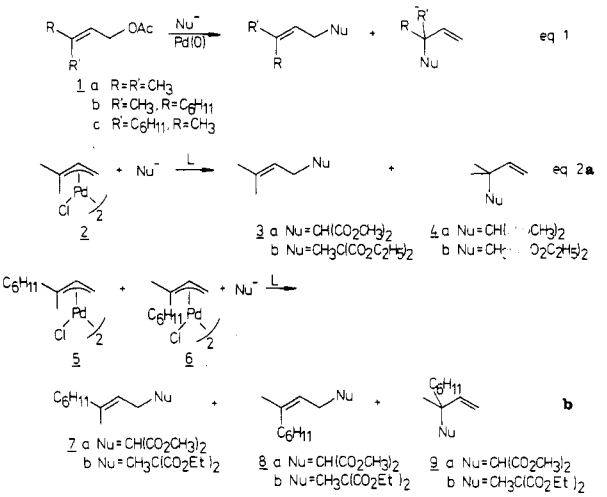
Palladium-catalyzed alkylation of 3-methyl-2-butenyl acetate with anions of dialkyl malonates gives the same product pattern as the stoichiometric alkylations of (η^3-3-methylbutenyl)palladium chloride and the corresponding cationic complex. Consequently a (π-allyl)palladium intermediate is probable in the catalytic reaction. According to NMR evidence the reactive intermediate is a η^3-allyl complex rather than a η^1-allyl complex. Acceptor ligands, even weak ones such as phosphines, have a strong electronic influence on the reaction and direct the attack toward the more substituted position. The formal charge of the complexes is important to the reactivity, but when phosphines are present as acceptor ligands, the formation of cationic intermediates may not be necessary.

Palladium-catalyzed nucleophilic substitution of allylic acetates has proved to be a useful and versatile reaction especially when the nucleophile is a stabilized carbanion, as developed by Trost and associates.[2]

The reaction has generally been assumed to proceed via cationic η^3-allyl intermediates.[3] A recent study using anions of dialkyl malonates as nucleophiles and chiral ligands suggests that η^1-allyl intermediates are important,[4] although this conclusion has been questioned.[5] In another recent study in this laboratory it was shown that cationic (η^3-allyl)palladium complexes and neutral (η^3-allyl)palladium complexes gave different regioisomers on amination.[6] The fact that the chloride complexes in the presence of excess triphenylphosphine reacted at the more substituted position was interpreted as an S_N2' type attack on a η^1-allyl species. These conflicting results led us to reexamine the evidence for a η^1-allyl intermediate and to study the factors that determine the regiochemistry of nucleophilic attack on η^3-allyl systems. We report here the results from a comparison of the product ratios from three different reactions: the catalytic alkylation of some allylic acetates (eq 1) (1, Nu^- = dialkyl malonate anions), the stoichiometric alkylation of the corresponding neutral (η^3-allyl)-palladium chloride species (eq 2) and finally the stoichiometric alkylation of the corresponding cationic (η^3-allyl)palladium tetrafluoroborate complexes.

3-Methyl-2-butenyl and geranyl/neryl were used as model allyl systems and the anions of dimethyl malonate and diethyl methylmalonate as nucleophiles, where the latter is an example of a moderately bulky nucleophile. Typical reaction conditions were room temperature in THF or toluene solutions for the reactions of the preformed η^3-allyl complexes and in refluxing THF for the catalytic reactions with allyl acetates.

The results are summarized in Tables I and II. At a first glance the tables seem featureless since the two possible regioisomers are generally formed. However, the following patterns are perceived. (1) The 3-methylbutenyl systems react predominantly at the more substituted position with dimethyl malonate. (2) Replacement of



dimethyl malonate by the slightly more bulky diethyl methylmalonate leads to predominant reaction at the less substituted position. (3) The product patterns from the 3-methylbutenyl system are similar in the catalytic reaction of the allyl acetate and the stoichiometric reactions of the corresponding neutral and cationic η^3-allyl complexes. (4) The cationic and the neutral η^3-allyl complexes give similar product patterns, which hold for the 3-methylbutenyl system as well as for the geranyl/neryl system. (5) The geranyl system, in contrast to the simple 3-methylbutenyl system, generally reacts preferentially at the less substituted position even with dimethyl malonate. (6) By the use of phase-transfer conditions and/or powerful acceptor ligands, the regiochemistry is sometimes altered.

If one looks at the reactions of the preformed η^3-allyl complexes, one finds that both possible regioisomers are generally formed, and only rarely is one obtained with selectivity. The preferential reaction of the 3-methylbutenyl system with dimethyl malonate anion at the more hindered position indicates that electronic effects direct the reaction to this position. On the other hand the importance of steric factors is evident in the preferential reaction of diethyl methylmalonate at the less hindered position of the same system. The sensitivity to steric effects in the catalytic reaction of allyl acetates has been noted by Trost and co-workers.[2] It was shown, for instance, that the replacement of dimethyl malonate by methyl benzenesulfonyl anion leads to an overwhelming preference for the less substituted position in the reaction of geranyl acetate. Rather subtle energetic effects clearly balance each other.

(1) Visiting Scholar, Royal Institute of Technology 1981/82. Permanent address: Istituto Chimico, Università di Napoli, 80134 Napoli, Italy.
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Table I. Alkylation of 3-Methylbutenyl Compounds

substrate	nucleophile Nu^-	ligand,[a] mol/Pd	solvent	yield of products, % 3	yield of products, % 4	product ratio 3:4
1a	$(CH_3O_2C)_2CH^-$	ca. 15	THF	15	47	0.3
2		4		26	70	0.4
10		1		21	43	0.5
2		4	toluene/water[b]	1	24	0.04
1a	$(C_2H_5O_2C)_2CCH_3^-$	ca. 15	THF	23	18	1.3
2		4		64	33	1.9
10		1		26	17	1.5
2		4	toluene/water[b]	23	28	0.8
10	$(CH_3O_2C)_2CH^-$	1[c]	THF	0.2	8	0.02

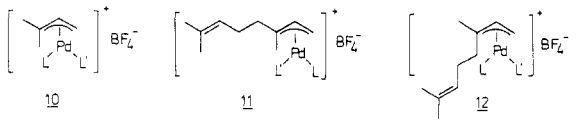
[a] The ligand was usually triphenylphosphine. [b] A phase-transfer reaction. [c] The ligand was diethyl azodicarboxylate.

Table II. Alkylation of Geranyl and Neryl Compounds

substrate	nucleophile Nu^-	Ph_3P, mol/Pd	solvent	yield of products, % 7	yield of products, % 8	yield of products, % 9
1b	$(CH_3O_2C)_2CH$	ca. 15	THF	48	1.5	12
5 + 6		4		45	12	39
11 + 12		1		39	2	19
5 + 6		4	toluene/water[a]	4	4	53
1b	$(C_2H_5O_2C)_2CCH_3$	ca. 15	THF	80	0	0
5 + 6		4		35	23	13
11 + 12		1		31	1	1
5 + 6		4	toluene/water[a]	45	12	9

[a] A phase-transfer reaction.

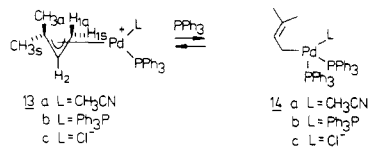
The similarity in the product patterns from the catalytic reaction of 3-methyl-2-butenyl acetate (**1a**) and the stoichiometric reactions of the cationic (fluoroborate, **10**) and



10 **11** **12**

neutral (chloride, **2**) (η^3-3-methylbutenyl)palladium complexes suggests that the three reactions proceed by similar intermediates. For the reasons to follow, these intermediates probably have a η^3-allyl structure, as suggested by some of the previous evidence.[5] Addition of more than 1 equiv of triphenylphosphine to the cationic η^3-3-methylbutenyl complex **10** does not induce dynamic π-σ(η^3–η^1) equilibration since the observed NMR spectrum is only compatible with a rigid η^3-allyl structure. Although this does not exclude the occurrence of a dynamic η^3–η^1 exchange, the concentration of η^1-species must be too low to be detectable even indirectly by NMR, and the exchange slow relative to the NMR time scale.

The cationic complex **10** therefore most probably reacts in the η^3-allyl form. The addition of phosphine to the neutral η^3-3-methylbutenyl complex **2**, by contrast, does lead to dynamic η^3–η^1 interconversion in agreement with results reported earlier.[7] However, examination of the NMR spectra shows that, within experimental error, all shifts and coupling constants of the dynamic system are the average of the syn and anti forms of the neutral η^3-complex.[8] Again the concentration of the η^1-complex **14** must be low and less than 2% of the η^3-allyl concentration. If the η^1-complex were to compete, its reactivity would have to be at least 100-fold higher than that of the η^3-complex. This seems unlikely, and the neutral chloride complex probably reacts via the η^3-allyl form. This is clear from the product distribution, which is similar for the cationic and neutral π-allyl complexes (Table I).



13 a L = CH_3CN, b L = Ph_3P, c L = Cl **14** a L = CH_3CN, b L = Ph_3P, c L = Cl

The interpretation of the parallel results from the geranyl system is less straightforward. From Table II it is seen that the product ratios for the three reaction types are quite different. A recent report by Trost and Verhoeven shows that geranyl (**1b**) and neryl acetate (**1c**) give different regioisomers on alkylation.[9] Neryl acetate reacts preferentially at the more substituted position in analogy with the simple 1-acetoxy-3-methyl-2-butene (**1a**), while geranyl acetate undergoes preferential attack at the less substituted position (Table II).[10] The η^3-allyl complex prepared from geranyl chloride is an approximately equal mixture of (η^3-geranyl)- (**5**) and (η^3-neryl)palladium chloride. It is not surprizing that this mixture gives a product distribution substantially different from that from the catalytic reaction of the pure geranyl acetate (Table II). A detailed study of the geranyl/neryl system will appear.[10] The results from this study, as well as those from 3-methylbutenyl system, suggest that η^1-allyl species are generally not intermediates in the alkylation of allylpalladium species.

The mechanistic question that remains is whether cationic intermediates are involved as suggested by Trost and this group.[3] Conductivity studies,[6] as well as NMR (this

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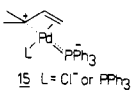
(8) In contrast, the mixture of (η^3-butenyl)palladium chloride and 2 equiv of triphenylphosphine in chloroform or dichloromethane is clearly in equilibrium at room temperature with the cationic complex. ^1H NMR (at room temperature) 5.23 (1 H, t, J = 10.0 Hz, H_2), 2.82 (2 H, d, J = 10.0 Hz, H_{1a} + H_{1s}), 1.86 (3 H, s, CH_{3a}), 1.44 (3 H, s, CH_{3s}). Interestingly, as the temperature is lowered, the relative concentration of the cationic complex increases. At −83 °C, the ^1H NMR spectrum is quite similar to that of the cationic complex: 5.54 (1 H, dd, H_2), 3.71 (1 H, s, H_{1s}), 2.87 (1 H, t, H_{1a}), 1.16 (6 H, s, CH_3). All peaks are broad.

(9) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(10) Åkermark, B.; Vitagliano, A., unpublished results.

study), show that addition of triphenylphosphine, a common ligand in the catalytic alkylation of allylic acetates, to the chloride complex **2** in THF solution produces no appreciable concentration of cationic species.[8] Furthermore, it has been shown that an isolable phosphine complex of (η^3-allyl)palladium acetate does not produce detectable amounts of cations even in acetone, which is a far better ionizing solvent than THF.[12] However, since NMR experiments show that in THF solution, and in the presence of 2.3 equiv of triphenylphosphine, the cationic complex **10** reacts more than 100 times faster with dimethylamine than the neutral complex **2**,[11] a low concentration of cationic species may be formed as the reactive intermediate from both the chloride and acetate complexes. The formal charge of the η^3-allyl complex may thus have an influence on the reactivity, but it is possible that the added ligands are even more important. This is suggested by an extensive study of the ^{13}C NMR spectra and of the reactivity of cationic η^3-allylpalladium complexes.[11] This study indicates that the intermediate and most probably the transition state have considerable carbonium ion character, e.g., **15**, with the trans phosphine ligand



15 L = Cl^- or PPh_3

acting as an electron acceptor. In analogy to the acid-catalyzed Markovnikov addition of nucleophiles to olefins, positive charge should be preferentially stabilized at the more substituted position. By promoting trans carbonium ion character, acceptor ligands can direct the reaction to the more substituted position. The counterion, such as BF_4^- and Cl^-, certainly has an influence on the reactivity, and it is possible that the formation of truly cationic intermediates[3] is necessary when only donor ligands such as amines are present. However, it is felt that the presence of acceptor ligands is sufficient for reactivity, and even a simple olefin is probably a fair acceptor.[10]

Although the yields are low due to side reactions, exploratory experiments with the more powerful acceptor ligand diethyl azodicarboxylate (Table I) show that even higher selectivity for the more substituted position is obtained as suggested by the model presented above. Interestingly, a similar directive effect is also observed when phase-transfer conditions are used. This result is difficult to rationalize. One possibility is that water molecules help to stabilize an intermediate such as **15** by solvation. Another is that this reaction actually goes via the σ-complex,[6] and a third is selective destruction of **3**.

The present results support the idea that palladium-catalyzed alkylation of allylic acetates goes via (η^3-allyl)-palladium complexes. Alkylations of preformed (η^3-allyl)palladium(II) complexes indicate that the formation of cationic complexes may not be necessary provided an acceptor ligand such as triphenylphosphine is present. Finally, the product distribution provides evidence that η^1-allyl complexes are not of general importance. The exploratory experiments show that auxiliary acceptor ligands such as triphenylphosphine, diethyl azodicarboxylate, and even olefins may have a profound influence of the regiochemistry of the addition. The directive effect, which is probably electronic, promotes addition to the more substituted position and thus complements the effect of steric crowding, which directs reaction to the less substituted position. Proper use of these effects offers a potential way of controlling the regiochemistry of alkylation of π-allyl systems equally efficiently as during amination.[6] The scope of this electronic control is under investigation in our laboratories.

Experimental Section

The NMR spectra were recorded at 60 MHz on a Varian Model EM-360 and at 200 MHz on a Bruker Model WP 200 spectrometer. The shifts are expressed as δ relative to Me_4Si. GLC was performed on a Pye-Unicam GCD using 5% SE-30 on Chromosorb W as the stationary phase. The yields were determined with a Hewlett-Packard Model 3380 A integrator using undecane, tridecane, hexadecane, or heptadecane as internal standards. Flash chromatography was accomplished on Merck silica gel 60 (230–400 mesh) and TLC on Merck silica gel 60 (F 254). Light petroleum (bp 40–60 °C) was distilled. Tetrahydrofuran (THF) was refluxed over potassium/benzophenone and distilled immediately prior to use. The phase-transfer reagent Adogen 464 (mainly tridecylmethylammonium chloride) was donated by Bofors-Synecon AB, Stockholm.

(η^3-3-Methylbutenyl)palladium Chloride (2). A modification of a literature procedure[13] was used. An excess of crude 1-chloro-3-methyl-2-butene[14] (1.2 g, ca. 12 mmol) was added to disodium tetrachloropalladate (1.0 g, 3.4 mmol) in 30 mL of methanol (1% H_2O). Carbon monoxide (ca. 60 mL/min) was bubbled through the solution. During the first few minutes the color changed from dark brown to light yellow, and then a yellow-orange precipitate formed. After 30 minutes, 50 mL of water was added and the product extracted four times with 30 mL of chloroform. Evaporation of the solvent gave essentially pure (η^3-3-methylbutenyl)palladium chloride (0.70 g, 98% based on Pd).[13,15]

Mixture (1:1) of (η^3-Geranyl)- (5) and (η^3-Neryl)palladium Chloride (6). A modification of a published general procedure[13] was used. Commercial geraniol was purified by adding 500 g of anhydrous calcium chloride to a solution of 100 mL of geraniol (ca. 70%) in 1 L of light petroleum and stirring for 2 h.[16] The geraniol–calcium chloride complex was collected by filtration, washed with 500 mL of light petroleum, and dissolved in 1.5 L of water. Extraction twice with 750 mL each of light petroleum and evaporation of the solvent at aspirator pressure gave 30 mL of ca. 96% pure geraniol. This was converted to geranyl chloride.[17] Geranyl chloride (ca. 90% pure, 7.9 g, 46 mmol) was added to a solution of 5.0 g (17 mmol) of disodium tetrachloropalladate in 150 mL of methanol (1% H_2O). Carbon monoxide was bubbled through the solution until it turned yellow (ca. 30 min). The dissolved carbon monoxide was removed at aspirator pressure, and the solution was neutralized by the addition of aqueous bicarbonate (ca. 5%). The solution was concentrated to ca. 50 mL, 100 mL of water was added, and the mixture was extracted three times with 50 mL of dichloromethane. The solvent was evaporated in a rotary evaporator and the product was purified by flash chromatography using ether–light petroleum (1:9). A ca. 1:1 mixture of (η^3-geranyl)- (5) and (η^3-neryl)palladium chloride (6) was obtained (4.3 g, 91% based on palladium). The mixture slowly (2 weeks) crystallized from ethanol at −20 °C.

Catalytic Alkylation of the Acetates. These reactions were performed as reported earlier for geranyl acetate.[9] Geranyl acetate gave essentially the reported isomer distribution in the reaction with dimethyl malonate (Table II).[9] With diethyl methylmalonate the only product was ethyl (*E*)-2-(ethoxycarbonyl)-2,5,9-tri-

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(13) Dent W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.
(14) A mixture of methylbutenyl chlorides was prepared by shaking 2-methyl-3-buten-2-ol (10 mL) with 10 mL of concentrated hydrochloric acid for 3 min in a separatory funnel and then washing the organic phase with sodium bicarbonate solution. The crude product contained 1-chloro-3-methyl-2-butene (70%), 3-chloro-3-methyl-1-butene (20%), and unreacted starting material (10%): Baeckström, P., personal communication.
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methyldeca-4,8-dienoate (**7b**). ^{1}H NMR ($CDCl_3$) 1.25 (6 H, t, J = 7.1 Hz), 1.37 (3 H, s), 1.59 (3 H, s), 1.61 (3 H, s), 1.68 (3 H, s), 2.03 (4 H, m), 2.59 (2 H, d, J = 7.6 Hz), 4.18 (4 H, q, J = 7.1), 4.96–5.20 (2 H, m); ^{13}C NMR ($CDCl_3$) 172.0, 138.0, 131.4, 124.2, 118.3, 61.0, 53.0, 39.9, 34.0, 26.6, 25.6, 19.6, 17.6, 16.2, 14.0.

1-Acetoxy-3-methyl-2-butene. With dimethyl malonate a mixture of the two products **3a** and **4a** was obtained (Table I). Separation by flash chromatography using ether–light petroleum (1:9) gave the two nearly pure isomers methyl 2-(methoxycarbonyl)-5-methyl-4-hexenoate (**3a**, 15%); ^{1}H NMR ($CDCl_3$) 1.63 (3 H, s), 1.68 (3 H, d, J = 1 Hz), 2.60 (2 H, t, J = 8 Hz) and methyl 2-(methoxycarbonyl)-3,3-dimethyl-4-pentenoate (**4a**, 47%); ^{1}H NMR ($CDCl_3$) 1.24 (6 H, s), 3.38 (1 H, s), 3.70 (6 H, s), 5.05 (1 H, d, J = 11.5 Hz), 5.06 (1 H, d, J = 17 Hz), 6.04 (1 H, dd, J = 11.5, 17 Hz). The reaction with diethyl methylmalonate gave a mixture (1:1) of **3b** and **4b** (Table I). Separation by flash chromatography gave ethyl 2-(ethoxycarbonyl)-2,5-dimethyl-4-hexenoate (**3b**, 25%). ^{1}H NMR ($CDCl_3$) 1.25 (6 H, t, J = 7.1 Hz), 1.37 (3 H, s), 1.62 (3 H, s), 1.62 (3 H, s), 1.70 (3 H, d, J = 1 Hz), 2.58 (2 H, d, J = 7.6 Hz), 4.18 (4 H, 1, J = 7 Hz), 5.02 (1 H, superficial t, J = ca. 7.6 Hz). Further elution then afforded ethyl 2-(ethoxycarbonyl)-2,3,3-trimethylpent-4-enoate (**4b**, 18%). ^{1}H NMR ($CDCl_3$) 1.23 (6 H, s), 1.25 (6 H, t, J = 7.2 Hz), 1.41 (3 H, s), 4.17 (4 H, q, J = 7 Hz), 5.02 (1 H, d, J = 17 Hz), 5.03 (1 H, d, J = 12 Hz), 6.22 (1 H, dd, J = 17, 12 Hz).

Reactions of (η^3-Allyl)palladium Chloride Complexes. The appropriate complex, either the mixed (η^3-geranyl/η^3-neryl)-palladium chloride or (η^3-3-methylbutenyl)palladium chloride (0.25 mmol) was dissolved in 2 mL of THF under nitrogen. Triphenylphosphine (1 mmol) in 2 mL of THF was added, followed immediately by sodium dialkyl malonate (0.3 mmol) in 2 mL of THF. A yellow precipitate, consisting mainly of $(Ph_3P)_4Pd(0)$ immediately formed. After stirring for 20 min, 20 mL of water was added and the mixture extracted four times with 5 mL of ether. The majority of $(Ph_3P)_4Pd$ remained undissolved. The yields were determined by GLC and the pure products were isolated, after evaporation of the ether at aspirator pressure, by flash chromatography. The yields are reported in Tables I and II. The mixed geranyl/neryl complex gave a mixture of the three possible products, **7–9**, with both nucleophiles. The products from diethyl methylmalonate were only obtained as mixtures enriched in one isomer, but the structures could be unambiguously assigned by NMR. The mixture included **7b** and as a second product ethyl (*Z*)-2-(ethoxycarbonyl)-2,5,9-trimethyl-deca-4,8-dienoate (**8b**). ^{1}H NMR ($CDCl_3$) 1.25 (6 H, t, J = 7.1 Hz), 1.37 (3 H, s), 1.57 (3 H, s), 1.61 (3 H, s), 1.68 (3 H, s), 2.03 (4 H, m), 2.59 (2 H, d, J = 7.6 Hz), 4.18 (4 H, q, J = 7.1 Hz), 4.96–5.20 (2 H, m). The ^{13}C NMR ($CDCl_3$) is in the mixture indistinguishable from the *E* isomer except that the methyl group on the 4-double bond appears at δ 23.5 for the *Z* isomer and at δ 16.2 for the *E* isomer and that the 6-methylene group appears at δ 32.0 for the *Z* isomer and at δ 39.9 for the *E* isomer. These shifts define the stereochemistry of the two isomers.[10,17,18] The third product is ethyl 2-(ethoxycarbonyl)-3-ethenyl-2,3,7-trimethyl-6-octenoate (**9b**); ^{1}H NMR ($CDCl_3$) 1.18 (3 H, s), 1.25 (6 H, t, J = 7.1 Hz), 1.42 (3 H, s), 1.61 (3 H, s), 1.68 (3 H, s), 2.03 (4 H, m), 4.18 (4 H, q, J = 7.1 Hz), 4.96–5.20 (3 H, m), 6.1 (1 H, dd, J = 16.5, 11 Hz).

Reactions of (η^3-Allyl)palladium Tetrafluoroborate Complexes in the Presence of Triphenylphosphine. The fluoroborate complexes were prepared from the chloride complexes (0.25 mmol) by dissolving them in THF (2 mL) and then adding a solution of silver tetrafluroborate (0.25 mmol) in THF (1 mL), stirring for 5 min, and removing the precipitated silver chloride by filtration. Under nitrogen atmosphere, triphenylphosphine (0.25 mmol) in THF (2 mL) was added at room temperature to the solution of the fluoroborate complex, immediately followed by a THF solution (2 mL) containing the appropriate dialkyl sodiomalonate. Immediate precipitation of palladium metal followed. After 20 min, water (10 mL) was added and the mixture extracted four times with 5 mL of ether. The yields were determined by GLC of the ether solution. After evaporation of the solvent, the products were purified by flash chromatography. The yields are reported in Tables I and II.

Reactions of (η^3-Allyl)palladium Tetrafluoroborate Complexes in the Presence of Diethyl Azodicarboxylate. These reactions were performed as above except that azodicarboxylate replaced triphenylphosphine.

Alkylation Using Phase-Transfer Conditions. The appropriate (η^3-allyl)palladium chloride (0.25 mmol) in 2 mL of toluene was added to a mixture of Adogen 464 (0.025 mmol) and dialkyl malonate (1 mmol) in 2 mL of toluene. Triphenylphosphine (1 mmol) in 2 mL of toluene and a sodium hydroxide solution (100 mmol in 4 mL of water) were then quickly added, and the resulting two-phase system was stirred vigorously for 12 h under a nitrogen atmosphere. The product was extracted three times with 4 mL of ether, and the yields were determined by GLC (Tables I and II).

NMR Data. (η^3-3-Methylbutenyl)(triphenylphosphine)(acetonitrile)palladium tetrafluoroborate (**13a**): ^{1}H NMR ($CDCl_3$) 5.39 (1 H, dd, J_{1a-2} = 12.3, J_{1s-2} = 7.9 Hz, H_2), 3.26 (1 H, dd, J_{1s-2} = 7.4, J_{1s-P} = 3.0 Hz, H_{1s}), 2.80 (1 H, dd, J_{1a-2} = 12.6, J_{1a-P} = 2.8 Hz, H_{1a}), 2.01 (3 H, d, $J_{CH_{3s}-P}$ = 9.6 Hz, CH_{3s}), 1.60 (3 H, d, $J_{CH_{3a}-P}$ = 5.2 Hz, CH_{3a}).

(η^3-3-Methylbutenyl)bis(triphenylphosphine)palladium tetrafluoroborate (**13b**): ^{1}H NMR ($CDCl_3$) 5.68 (1 H, dd, J_{1a-2} = 13.4, J_{1s-2} = 8.0 Hz, H_2), 3.66 (1 H, qd, J_{1s-2} = 7.8, $J_{1s-P_{trans}}$ = 9.0, $J_{1s-P_{cis}}$ = 2.4 Hz, H_{1s}), 2.89 (1 H, qd, J_{1a-2} = 13.8, $J_{1a-P_{trans}}$ = 9.6, $J_{1a-P_{cis}}$ = 2.2 Hz, H_{1a}), 1.16 (6 H, m, CH_3). The spectrum remains unchanged on addition of triphenylphosphine, except that the phosphine slowly adds as a nucleophile to the η^3-allyl system.

(η^3-3-Methylbutenyl)(triphenylphosphine)palladium chloride: ^{1}H NMR (THF-d_8) (a) At room temperature: 5.16 (1 H, t, J_{1-2} = 10.0 Hz), 2.77 (2 H, broad s, H_{1a} + H_{1s}), 1.86 (3 H, d, $J_{CH_{3a}-P}$ = 9.0 Hz, CH_{3s}), 1.40 (3 H, d, $J_{CH_{3a}-P}$ = 5.8 Hz, CH_{3a}). (b) At −50 °C: 5.20 (1 H, dd, J_{1a-2} = 7.4, J_{1s-2}), 2.87 (1 H, dd, $J_{H_{1s}-P}$ = 2.4, J_{1s-2} = 12.6 Hz, H_{1s}), 2.66 (1 H, dd, J_{1a-P} = 2.3, J_{1a-2} = 7.3 Hz, H_{1a}), 1.86 (3 H, d, $J_{CH_{3a}-P}$ = 8.8 Hz, CH_{3s}), 1.39 (3 H, d, $J_{CH_{3a}-P}$ = 5.6 Hz, CH_{3a}). Average values 5.20 (J_{1-2} = 9.8 Hz, H_2), 2.76 (J_{1-2} = 9.9 Hz, H_{1a} + H_{1s}), 1.86 (CH_{3s}), 1.39 (CH_{3a}). (c) At −60 °C, after addition of 2 equiv of triphenylphosphine: 5.20 (1 H, t, J_{1-2} = 9.7 Hz, H_2), 2.76 (2 H, d, J_{1-2} = 9.8 Hz, H_{1a} + H_{1s}), 1.84 (s, CH_{3s}), 1.38 (s, CH_{3a}). At −77 °C all peaks begin to broaden to become humps at −104 °C.

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