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The mechanism of nucleophilic addition to η^3-allylpalladium complexes: the influence of ligands on rates and regiochemistry *

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Abstract

The influence of the ligands L in η^3-(3-methylbutenyl)palladium(L_2) complexes on the rates and regiochemistry of nucleophilic addition has been studied. Acceptor ligands such as phosphines and 1,5-cyclooctadiene have been found to increase the rate of addition as well as the preference for reaction at the more substituted allyl terminus. There is a good correlation between the rates and the ^{13}C NMR shifts of the more substituted η^3-allyl terminus, indiating that the NMR shifts can be used to predict acceptor properties of the ligands. There is a fair agreement between the rates and the regiochemistry of the palladium catalyzed nucleophilic displacement of allylic acetate from these complexes and those for the stoichiometric reactions involving η^3-allyl complexes.

Introduction

Nucleophilic addition to η^3-(allyl)palladium systems has proved to be a very useful reaction in selective organic synthesis [1,2]. Much attention has focused on regio-control. The usefulness of steric factors has been extensively demonstrated by Trost and coworkers, who have been able to achieve selective addition to the less substituted terminus of unsymmetrical η^3-allyl complexes by the use of sterically demanding, stabilized carbanions as nucleophiles [2,3].

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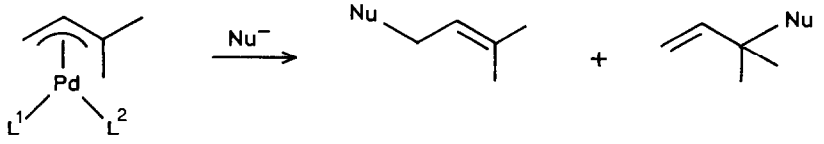
The sensitivity of η^3-(allyl)palladium systems to steric effects is also nicely demonstrated by the recent observation that trimethylamine adds exclusively to the less substituted terminus of η^3-(neryl)palladium(II) bis(triphenylphosphine) whereas dimethylamine reacts primarily at the more substituted terminus [4e]. Some recent studies indicate that the variation of the ligands and the central metal of η^3-allyl systems can be used to effect regio-control also through electronic factors [4,5]. In particular, it was noted that amination of η^3-(2-butenyl)palladium chloride with dimethylamine gave the product from reaction at the more substituted η^3-allyl terminus in the presence of triphenylphosphine and that from reaction at the less substituted terminus in its absence [4c]. Subsequent work, using the η^3-(geranyl)palladium system as a model, indicated that the product from reaction at the less substituted terminus may arise from isomerization of the other product, but also showed conclusively that electronic factors, in this case the donor–acceptor properties of the ligands, are important [4d,4e]. Thus phosphines and diethyl diazodicarboxylate, which are acceptors, were found to direct addition towards the more substituted terminus of an unsymmetrical η^3-allyl system, while dipyridine, which is mainly a donor, was found to direct it towards the less substituted terminus [4d,4e]. A rationale for this result is that, in analogy to acid catalyzed nucleophilic addition to simple olefins, the acceptor ligands induce positive charge preferentially at the more substituted η^3-allyl terminus (cf. ref. 5d). This leads to preference for reaction at this terminus as well as to a higher reaction rate in the presence of acceptor ligands. The study of the η^3-(geranyl) system also suggests that the ^{13}C shifts of the η^3-allyl termini are a good measure of the electronic influence of the ligands. This view is supported by the results of an extensive ^{13}C NMR study of η^3-(2-methylpropenyl)-, η^3-(2-butenyl)-, and η^3-(3-methyl-2-butenyl)-palladium complexes [6]. The present study was undertaken in order to see whether this correlation is confirmed by chemical reactivity and, in particular, by the regiochemistry of nucleophilic addition.

The η^3-(3-methylbutenyl)palladium system **1** was used as a model in this study. A mixture of the two products **2** and **3** was generally obtained in reactions with amines or with the anions from dialkyl malonates. These two classes of nucleophiles complement one another admirably, since their properties differ in some important respects. Firstly, the primary products from amination tend to isomerize during the reaction while those obtained from the reaction with malonate anion are stable [7 *]. Secondly, the progress of the amination reactions can generally be followed conveniently by simple NMR methods while the malonate reactions are frequently too rapid.



(1) (2) (3)

* This and other references marked with asterisks indicate notes occurring in the list of references.

Stoichiometric aminations

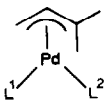
In the amination reactions an excess of amine (3 equiv.) was added to a 0.1 *M* solution of preformed η^3-allylpalladium complex in $CDCl_3$ or THF-d_8 in an NMR tube. The progress of the reaction was then monitored by NMR spectroscopy. The kinetic data obtained in this way are only semi-quantitative, but the differences in reported half lifes are significant and reproducible.

The examination of the results, Table 1, shows that, as suggested by the NMR shifts [6], the best acceptors induce the highest reactivity in the amination. Thus amine nucleophiles reacted rapidly with the triphenylphosphite and tris(4-chlorophenyl)phosphine complexes **1o** and **1n**, less rapidly with the trialkylphoshine complexes **1g** and **1h**, and very slowly with the methylamine and *N*,*N*-tetramethyldiaminoethane (TMEDA) complexes **1a** and **1b**.

The influence of ligands such as acetone and acetonitrile could not be determined since they are essentially quantitatively displaced by most amines even in the presence of an excess of the ligand. This behavior is, to some extent, true also for intermediate acceptor ligands such as triphenylphosphine sulfide and for 1,5-cyclooctadiene (COD). As by NMR spectroscopy both these ligands are completely displaced when the complexes **1e** and **1k** are treated with dimethylamine. In these cases, however, nucleophilic addition to the η^3-allyl unit does take place, although at

Table 1

Approximate rates for stoichiometric amination of η^3-(3-methyl-2-butenyl)palladium(II) complexes at 25 °C

Complex  (1)	C(3) shift (ppm)	Half life of nucleophile: $MeNH_2$	Me_2NH	Me_3N	Et_2NH	$PhCH_2NH_2$
1a $L_1 = L_2 = MeNH_2$	88	nr	nr	nr	nr	nr
1b $L_1 = L_2$ = TMEDA [a]	88	–	> 12 h	–	–	–
1c $L_1 = L_2 = (CH_3)_2CO$(excess)	94	nr	> 24 h	2 min	–	–
1d $L_1 = L_2 = CH_3CN$(excess)	99	–	> 24 h	> 2 h		
1e $L_1 = L_2 = Ph_3PS$	106	–	3 h	1 min		
1e (13 equiv.)			14 min			
1f L_1–$L_2 = PhS(CH_2)_2SPh$	108		5 min	14 min		
1g $L_1 = L_2 = Et_3P$	113	4.5 min	5 min	5 h	1 h	≈ 4 h
1h $L_1 = L_2 = Bu_3P$	113	3 min	4 min	3.5 h	50 min	2.5 h
1j $L_1 = L_2 = Cy_3P$	113	< 30 s	< 15 s	[b]	[b]	≤ 1 min
1k $L_1 = L_2$ = COD [c]	114	–	1.7 h	20 s	–	–
1k (8 equiv.)			25 min	< 15 s		
1k (8 equiv.) [d]			3 min			
1l $L_1 = L_2 = (CH_3O)_3P$	116	< 30 s	< 15 s	1 min	30 s	≈ 3 min
1m $L_1 = L_2 = Ph_3P$	119	< 15 s	< 15 s	30 s	25 s	≈ 2 min
1n $L_1 = L_2 = (4\text{-}ClPh)_3P$	121	< 15 s	< 15 s	< 15 s	< 15 s	–
1o $L_1 = L_2 = (PhO)_3P$	123	< 15 s	< 15 s	< 15 s	< 15 s	< 15 s

[a] TMEDA = tetramethylethylenediamine. [b] Only elimination products are formed. [c] COD = 1,5-cyclooctadiene. [d] The concentration of the nucleophile was decreased by one half.

a moderate rate. This indicates that the displacement is reversible and that low concentrations of the complexes **1e** and **1k** are present. Strong support for this assumption is provided by the observation that addition of an excess ($\approx$ 10 equiv.) of the ligand leads to a substantial rate increase for the triphenylphosphine sulfide complex **1e** (half life decreases from 3 h to 14 min) as well as for the COD complex **1k** (half life decreases from 1.7 h to 25 min). In one informative experiment with the COD complex, the increase in the ligand concentration was combined with a decrease by one half of the concentration of the dimethylamine nucleophile. This leads to a very large increase in the reaction rate (half life 3 min, Table 1). From these results it is safe to conclude that the complexes **1e** and **1k** are still present, and that their reactivities are in good agreement with the acceptor properties of the ligands as suggested by the ^{13}C NMR shifts (Table 1) [6].

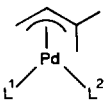
For the amination reactions with the η^3-(3-methylbutenyl)system **1**, isomerization of the primary products precludes any conclusions about the regiochemistry except when phosphines are present as ligands. In these cases, formation of the products **2** and **3** is rapid relative to isomerization, and it can be concluded that reaction of the more substituted terminus is favoured in accordance with the charge induction by these ligands indicated by the NMR data. More conclusive evidence is provided by the results from reaction with malonate anion, as described below.

Stoichiometric alkylation with malonate anions

The alkylations were performed by adding a slight excess of malonate anion, dissolved in 2 ml of THF, to 0.25 mmol of the appropriate η^3-(3-methylbutenyl)palladium complex in 2 ml THF at room temperature. In one experiment, dimethyl malonate was used with pyridine as the ligand. The product from reaction at the less substituted terminus was exclusively observed but the yield was low. Most of the experiments were carried out with diethyl methylmalonate as nucleophile. The results are summarized in Tables 2 and 3. The influence of the ligands on the regiochemistry, as shown by the ratio between the products **2** and **3** (Nu = diethyl methylmalonate anion), is remarkably consistent with the relative induced charge as indicated by the C(3) NMR shift and by the difference between the shifts at C(3) and C(1) for the two η^3-(allyl)termini (Table 2). For cationic symmetrical complexes **1**, the ratio **2/3** is small for the best acceptor ligands, e.g. 1.3 for triphenylphosphite and 2.7 for triphenylphosphine, demonstrating the electronic preference for the more substituted η^3-(allyl) terminus. The ratio increases as less potent acceptors are used as ligands; for example, 5–10 for triphenylarsine, 7 for COD, and 30 for methyl isocyanide. With donor ligands such as pyridine and TMEDA, only the product **2** from reaction at the less substituted η^3-(allyl) terminus is observed. For unsymmetrical complexes **1**, cationic as well as neutral there is a rough correlation between the relative charge suggested by the ^{13}C NMR data and the regiochemistry. Thus for the cationic mixed phosphine-pyridine complex **1x** the **2/3** ratio is 1.7, for the neutral phosphine-chloride complex **1u** 1.8, and for the phosphine-cyanide complex **1aa** 10 (Table 3). However, there is one striking exception, the phosphine-thiocyanate complex **1ab**, which according to the NMR data has a relatively high positive charge at the more substituted η^3-allyl terminus but which reacts exclusively at the less substituted terminus. The reason for this is not clear, but there could be a change in mechanism. This change may also be responsible for the formation of

Table 2

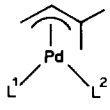
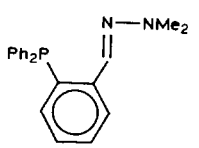
Stoichiometric addition of $Na^{+-}C(CH_3)(CO_2Et)_2$ to η^3-(3-methyl-2-butenyl)palladium(II) complexes, where $L_1 = L_2$

Complex  (1)	^{13}C NMR shift C(3) (ppm)	Shift difference C(3)–C(1) (ppm)	Yield (%) [a] 2+3	5	Ratio 2/3
1b $L_1 = L_2 =$ TMEDA	88	32	63	–	> 95
1q $L_1 = L_2 =$ Pyridine	92	37	15	–	> 95
1e $L_1 = L_2 = Ph_3PS$	106	46	36 [b]	–	3.8
1f $L_1–L_2 = PhS(CH_2)_2SPh$	108	45	95	5	19
1t $L_1–L_2$ = DIPHOS	109	48	90	≈10	12
1r $L_1 = L_2CH_3NC$	109	50	90	–	31
1h $L_1 = L_2 = Bu_3P$	113	56	95	–	4.8
1k $L_1 = L_2$ = COD	114	47	40 [b]	≈7	7
1l $L_1 = L_2 = (CH_3O)_3P$	116	57	89	–	11
1s $L_1 = L_2 = Ph_3As$	117	52	55	≈15	5–10
1m $L_1 = L_2 = Ph_3P$	119	54	74	≈15	2.7
1n $L_1 = L_2 = (4\text{-}ClPh)_3P$	121	54	87	–	3.4
1o $L_1 = L_2 = (PhO)_3P$	124	64	98	–	1.3

[a] Generally complete after 1 min. [b] Not complete after 1 min.

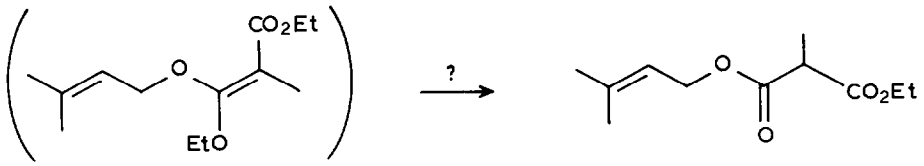
Table 3

Stoichiometric addition of $Na^{+-}C(CH_3)(CO_2Et)_2$ to η^3-(3-methyl-2-butenyl)palladium complexes where $L_1 \neq L_2$

Complex (solvent)  (1)	^{13}C NMR shift C(3) (ppm)	Shift difference C(3)–C(1) (ppm)	Yield 2+3	Ratio 2/3
1u $L_1 = Ph_3P$, L_2 = Cl (THF)	116	64	100	1.8
1u (CH_3CN)	116	64	45	1.5
1u (Pyridine)	116	64	80	1.2
1u (THF) [a]	116	64	100	1.1
1v $L_1 = Ph_3P$, $L_2 = CH_3CN(CH_3CN)$	123	72	59	2.5
1x $L_1 = Ph_3P$, L_2 = Pyr (pyridine)	116	66	52	1.7
1z $L_1 = Ch_3NC$, L_2 = Cl (THF)	109	59	98	16
1aa $L_1 = Ph_3P$, L_2 = CN (THF)	107	50	54	10
1ab $L_1 = Ph_3P$, L_2 = SCN (THF)	115	59	69	> 95
1p $L_1–L_2$ = 	123	78	55	3.3

[a] 1 PPh_3 added.

3-methyl-2-butenyl(ethyl)methylmalonate (**5**) in some reactions (Table 2), perhaps via the *O*-alkylated intermediate **4**.



(**4**) (**5**)

For some of the unsymmetrical complexes with one acceptor and one donor ligand, where the NMR data indicates an extreme polarization, the regioselectivity is disappointingly low. For example the NMR data indicate that reaction at the more substituted η^3-(allyl) terminus of the complex **1p** should be very favorable, but the ratio **2/3** is only 3.3 (Table 3). The fact that the isomeric complex, in which the acceptor activates the less substituted η^3-(allyl) terminus is present, is probably only a partial explanation. Another factor, ligand exchange and formation of η^3-(allyl)palladium(II)(malonate) complexes, perhaps also contributes, but this has only been conclusively confirmed in the reaction between the triphenylphosphine sulfide complex **1e** and malonate. The complications have to be studied further, but they do not impair the conclusions regarding charge effects.

Since charge is clearly important in the malonate reactions, the influence of solvents and counter ions on regiochemistry was also briefly studied. It had previously been observed that the counter ion had a strong effect in η^3-allyl reactions involving enolate as nucleophile [8]. The η^3-(3-methylbutenyl)palladium complex **1u** was therefore treated with the sodium, potassium, and lithium salts of diethyl methylmalonate (Table 4). The ratio **2/3** was low, about 1.5, with the sodium and potassium salts but considerably higher with the lithium salt (4.5). An attractive explanation is that the lithium salt is dimeric or oligomeric and has a higher preference for the less substituted η^3-(allyl) terminus for steric reasons. Some support for this view may be derived from the observed decrease to about 3.2 of the **2/3** ratio on addition of a crown ether that forms good Li complexes, no such changes being observed for the sodium salt when a suitable crown ether is added.

Finally, a small solvent effect may be noted. The **2/3** ratio in the reaction of the anion of diethyl methylmalonate with the phosphine-chloride complex **1u** decreases from 1.8 in THF to 1.5 in acetonitrile and 1.2 in pyridine (Table 3). This suggests

Table 4

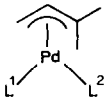
The effect of the counterion on stoichiometric addition of $M^+ {}^- C(CH_3)(CO_2Et)_2$ to (triphenylphosphine)(η^3-3-methyl-2-butenyl)palladium chloride

Counterion	Yield **2**+**3**	Ratio **2/3**
Na^+	100	1.8
K^+	100	1.4
Li^+	100	4.5
Li^+ [a]	100	3.2

[a] 14-crown-6 added.

Table 5

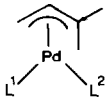
Catalytic reaction between 3-methyl-2-butenyl acetate and $Na^+ {}^- C(CH_3)(CO_2Et)_2$

Catalyst  (1)	Time (h)	Yield (%)		Ratio
		2+3	5	2/3
$L_1 = L_2 = Ph_3PO$	0.5	15	22	> 95
$L_1 = L_2 = Ph_3PS$	0.5	2.5	54	> 95
$L_1-L_2 = PhS(CH_2)_2SPh$	0.5	12	40	> 95
L_1-L_2 = DIPHOS	0.5	88	–	8.5
$L_1 = L_2 = Et_3P$	0.5	100	–	3.9
$L_1 = L_2 = Bu_2P$	0.5	100	–	3.1
$L_1 = L_2 = Cy_3P$	0.5	18	25	> 95
$L_1 = L_2 = (CH_3O)_3P$	1	93	–	4.4
$L_1 = L_2 = Ph_3P$	0.5	82	–	1.9
$L_1 = L_2 = (4\text{-}ClPh)_3P$	1	5	46.5	> 95
$L_1 = L_2 = (PhO)_3P$	1	90	–	4.8

[a] THF at reflux as solvent.

Table 6

Catalytic reactions between 3-methyl-2-butenyl acetate and $Na^+ {}^- C(CH_3)(CO_2Et)_2$ using excess of ligand and 15–20 h reaction time

Catalyst  (1)	Added ligand (10 equiv.)	Solvent (temperature, °C)	Yield (%)		Ratio
			2+3	5	2/3
$L_1 = Bu_3P$, $L_2 = Cl$	Bu_3P	THF (66)	100	–	8
$L_1 = Ph_3As$, $L_2 = Cl$	Ph_3As	THF (66)	78	≈ 2	3.5
$L_1 = (2\text{-}CH_3Ph)_3P$, $L_2 = Cl$	$(2\text{-}CH_3Ph)_3P$	THF (66)	58	≈ 10	7
$L_1 = [2,4,6\text{-}(CH_3)_3Ph]_3P$, $L_2 = Cl$	$[2,4,6\text{-}(CH_3)_3Ph]_3P$	THF (66)	91	–	7
$L_1 = Ph_3P$, $L_2 = Cl$	Ph_3P [a]	THF (66)	100	–	1.9
$L_1 = (PhO)_3P$, $L_2 = Cl$	$(PhO)_3P$	THF (66)	90	–	6
$L_1 = L_2 = Ph_3P$	Ph_3P	THF (66)	90	–	1.7
$L_1 = L_2 = Ph_3P$	Ph_3P	Toluene (80)	100	–	1.5
$L_1 = Ph_3P$, $L_2 = CH_3CN$	Ph_3P	CH_3CN (60)	45	15	2
$L_1 = Ph_3P$, $L_2 = Pyr$	Ph_3P	Pyridine (60)	93	–	2
$L_1 = L_2 = Ph_3P$	Ph_3P	EtOH (80)	29	–	1.9
$L_1 = L_2 = Ph_3P$	Ph_3P	DMSO (80)	100	–	1.6
$L_1 = Ph_3P$, $L_2 = CN$	–	THF (50), (60 h)	55	–	3
$L_1 = Ph_3P$, $L_2 = SCN$	–	THF (66)	44	–	> 95
$L_1 = Ph_3P$, $L_2 = SCN$	Ph_3P [b]	THF (66)	76	22	> 95

[a] 2 equiv. [b] 4 equiv., KSCN added.

that the polarity of the solvent may have an influence but that the coordinating power is more important.

Catalytic alkylation reactions

In all the catalytic reactions, 3-methyl-2-butenyl acetate was used as substrate and most of the reactions were performed in refluxing THF, although a few other solvents and temperatures were also used. The nucleophile was generally the sodium salt of diethyl methylmalonate, and between 1 and 2% of a number of different η^3-(3-methylbutenyl) complexes were added as catalysts. In one set of experiments, an excess of the appropriate ligand was also added. The results are summarized in Tables 5 and 6.

The majority of the η^3-(3-methylbutenyl) complexes with phosphines as ligands give high yields of the expected products **2** and **3** and also ratios between these two products which correspond fairly well to those obtained from the stoichiometric reactions. Only for the triphenylphosphite complex **10** is the ratio a little high (4.8).

In contrast, the η^3-allyl catalysts which have tricyclohexylphosphine and tris(4-chlorophenyl)phosphine, as well as triphenylphosphine oxide, triphenylphosphine sulfide, and 1,2-bis(phenylthio)ethane as ligands, all give low yields of **2** and **3**. In addition, the **2**/**3** ratio is much higher (> 95) in the catalytic than in the stoichiometric reactions and substantial amounts of the mixed allyl-ethyl ester **5** are formed, indicating a change in mechanism, perhaps due to initial ligand displacement and alkylation on palladium.

The effects of solvents and ionic ligands appear to be smaller in the catalytic reactions than in the stoichiometric reactions but the unsymmetrical phosphine-thiocyanate complex **1ab** retains the high preference for reaction at the less substituted terminus.

Conclusions

The rates and the regiochemistry in the stoichiometric addition of nucleophiles to the η^3-(3-methyl-butenyl)palladium(II) system appear to be proportional to the total and relative positive charge of the η^3-allyl unit. It also appears that the influence of added ligands on the charge can be estimated fairly simply from ^{13}C NMR data. Thus acceptor ligands produce reactive complexes which react preferentially at the more substituted η^3-allyl terminus and display large downfield ^{13}C NMR shifts for this terminus.

Donor ligands give less reactive complexes which react preferentially at the less substituted terminus. The ^{13}C downfield shifts for these complexes are small, as is also true for the shift difference between the two η^3-allyl termini.

In the catalytic reactions, donor ligands are less useful for electronic control since palladium(0) tends to precipitate out, terminating the reaction at an early stage. However, the combination of an ionic ligand, thiocyanate, and triphenylphosphine produces an active catalyst that directs the reaction towards the less substituted terminus. Use of this system thus complements the use of steric control.

Also for the acceptor ligands there are some limitations in their usefulness for electronic control in the catalytic reactions. In the amination reactions the problem is isomerization of the primary products, and in the alkylation reactions it appears

to be ligand displacement. The second problem, which is perhaps the most serious, is related to the ability of the ligands to coordinate to the η^3-allyl catalyst. If the ligands are very efficient acceptors they will generally be expected to be more readily displaced from the catalyst, leading to inefficient electronic control. However, there is a clear trend towards higher relative reactivity at the more substituted position as the acceptor character of the ligands increases. With small nucleophiles, such as methylamine, dimethylamine, and the anion of dimethyl malonate [4d,4e], it is even possible to obtain predominant reaction at the more substituted terminus by the use of acceptor ligands such as phosphines.

Experimental

General data. The NMR spectra were recorded on a Bruker WP 200, spectrometer operating at 200 MHz for ^1H and at 50.3 MHz for ^{13}C. The solvent was $CDCl_3$ and the shifts are reported as δ values in ppm relative to Me_4Si as internal standard. GC analyses of amines were performed on alkalized Chromosorb W, with 10% Apiezon E as stationary phase and those of the malonate derivatives on Chromosorb W with 5% SE-30 as stationary phase.

Materials. The preparations and NMR spectra of the compounds have been described previously [6]. Tetrahydrofuran-d_8 (THF-d_8) (Stohler Isotope Chemicals), was used as received, chloroform-*d* (J.T. Baker chemicals, min 99.8%0 was dried over 4Å molecular sieves prior to use, as were dichloromethane (Merck P.A.), toluene (Merck P.A.), and pyridine (Merck P.A.). Acetonitrile (Merck P.A.) was distilled from calcium chloride, and dimethylsulfoxide (Merck P.A.) was distilled from calcium hydride at reduced pressure (0.1 mmHg); both solvents were then stored over 4Å molecular sieves.

Approximate determination of amination rates. The appropriate complex (0.1 mmol) was dissolved in 1 ml $CDCl_3$ in an NMR tube at 20 °C and 0.3 mmol of the amine was added from a syringe. The progress of the reaction was monitored by ^1H NMR spectroscopy. The total and relative yields of the products **2** and **3** were determined from the NMR spectra, but the results were checked by GC and in a number of cases by isolation of the products. The results are summarized in Table 1. In low temperature experiments the same procedure was used except that the solution of the complex in $CDCl_3$ was cooled to −50 °C before addition of the amine.

If the temperature was raised after the low temperature reactions were complete, rapid isomerizations were frequently observed if the primary products were those of addition to the more substituted η^3-allyl terminus. The products from reaction at the least substituted terminus are thus the thermodynamically stable species.

*Amination of bis(triphenylphosphine)[(1,2,3-η)-3-methyl-2-butenyl]palladium(II) tetrafluoroborate (**1m**).* The complex **1m** (0.1 mmol) was dissolved in 1 ml of dichloromethane and the solution was cooled to −60 °C. A solution of triphenylphosphine (100 mg, ca. 0.4 mmol) in 1 ml of dichloromethane was then added, followed by an excess (ca. 0.4 mmol) of dimethylamine, added as a gas by syringe. A yellow precipitate of $(Ph_3P)_4Pd$ rapidly formed and after 6 min the precipitate was removed by filtration at −60 °C. An excess of trifluoroacetic acid (100 μl) was then added and the mixture was shaken with 2 ml of water. The aqueous phase was separated made alkaline with sodium hydroxide and then extracted with 0.6 ml of

$CDCl_3$ to give a solution for NMR analysis. For isolation of the product, the product solution was extracted with ether, and the ether was then evaporated off through a Vigreux column. The yield of a 1/9 mixture of the amines **2** and **3** ($Nu = Me_2N$) was essentially quantitative.

Stoichiometric alkylations with diethyl methylmalonate anion. The appropriate (1,2,3-η)-(3-methyl-2-butenyl)palladium complex (0.25 mmol) was dissolved in 2 ml of THF and diethyl methylmalonate anion, prepared at 0 °C in 2 ml of THF from sodium hydride (or in a few experiments, from potassium hydride or lithium hydride), was added at 20 °C. After 20 min, 10 ml of water was added, and the solution was extracted with three 5 ml portions of ether. Tridecane was added as internal standard, and relative and absolute yields of the products **2** and **3** ($Nu = (EtO_2C)_2C(CH_3)$) were determined by GLC. The results are presented in Tables 2, 3 and 4.

Catalytic alkylations with the anion of diethyl methylmalonate. 3-Methyl-2-butenyl acetate (2 mmol) and the appropriate catalyst (0.02 mmol) were dissolved in 2 ml THF. When appropriate, ca. 0.2 mmol of the auxiliary ligand was added, followed by 8 mmol of the anion of diethyl methylmalonate, dissolved in 10 ml THF (or other solvent). The solution was then held at the chosen reaction temperature for 15–20 h, and the yields of the products **2**, **3**, and **5** were determined by GLC. The results are presented in Tables 5 and 6.

References

1 J. Tsuji, Organic Synthesis by means of Transition Metal Complexes. A Systematic Approach, Springer-Verlag, New York, 1975.

2 B.M. Trost and T.R. Verhoeven, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, Oxford, 1982.

3 (a) B.M. Trost, and T.R. Verhoeven, J. Am. Chem. Soc., 98 (1976) 630; (b) 102 (1980) 4730.

4 (a) Y. Hayashi, M. Riediker, J.S. Temple and J. Schwartz, Tetrahedron Lett., (1981) 2629; (b) J.S. Temple, M. Riediker, and J. Schwartz, J. Am. Chem. Soc., 104 (1982) 1310; (c) B. Åkermark, G. Åkermark, L.S. Hegedus, and K. Zetterberg, J. Am. Chem. Soc., 103 (1981) 3037; (d) B. Åkermark, K. Zetterberg, S. Hansson, B. Krakenberger, and A. Vitagliano, Organometallics, 3 (1984) 679; (e) B. Åkermark, and A. Vitagliano, ibid., 4 (1985) 1275.

5 (a) B.M. Trost, and M. Lautens, J. Am. Chem. Soc., 104 (1982) 3543; (b) 105 (1983) 3343; (c) B.M. Trost, and M.-H. Hung., 105 (1983) 7757; (d) 106 (1984) 6837.

6 B. Åkermark, S. Hansson, B. Krakenberger, and A. Vitagliano, Organometallics, 6 (1987) 620.

7 In some cases, the ratios between products **2** and **3** (Nu = malonate) were observed to change slowly with time after the reactions were complete. Further work is necessary to elucidate the reason for this change.

8 B. Åkermark, and A. Jutand, unpublished results.