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Reductive elimination of η^3-allyl(aryl)palladium complexes promoted by allyl halides

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Abstract

Comparison between the reactivity patterns of the reactions of η^3-allyl(aryl)palladium complexes with allyl chlorides and those with styrene, allylbenzene, methyl iodide and benzyl chloride suggested the dual role of allyl chloride in enhancing the reductive elimination of these complexes, namely coordination to Pd through the C=C bond and removal of the electron density via oxidative addition. The product distribution pattern in the reductive elimination of Pd(η^3-CH_2CHCH_2)(Ar)(EPh_3) (**1**) (E = P, As; Ar = $C_6H_3Cl_2$-2,5) accelerated by CH_2=$CMeCH_2Cl$ (reaction A) and that of Pd(η^3-CH_2CMeCH_2)(Ar)(EPh_3) (**2**) accelerated by CH_2=$CHCH_2Cl$ (reaction B) has been determined. For the reaction of the $AsPh_3$ complexes, both A and B carried out in toluene and dichloromethane afforded, at the early stages, only the coupling product (allylbenzene derivative) associated with the allyl unit of the original complex itself. At the later stages the product derived from the substrate chloride increased owing to facile ligand exchange (allyl-methallyl and/or aryl-Cl) between **1** and **2** and the η^3-allyl(chloro)palladium complex which is another product of the reductive elimination. Consistent with the oxidative addition of the allyl chlorides, the reaction of the PPh_3 complexes in dichloromethane and 1,2-dichloroethane gave a greater quantity of the product derived from the substrate chloride than that from the complex even at the early stages.

Introduction

Metal complex catalyzed C–C coupling between organometallic compounds and organic electrophiles (typically, alkyl halides) is thought to involve reductive elimination of diorganometallic complexes as a key step [1]. Although there was considerable progress in the mechanistic understanding of the reductive elimination step, most work utilized isolated diorganometallic intermediate models [2–4]. Some tried to gain insight into the role played by alkyl halides during the reductive elimination step [2b,3,5], but rather varying results have been obtained from these

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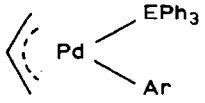
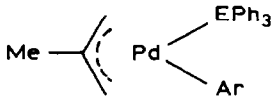
studies. Thus, for example, it was suggested that the reaction of dialkylpalladiums with methyl iodide or benzyl bromide proceeds via oxidative addition of the halide to form a palladium(IV) intermediate, followed by the C–C coupling step [3c,3d,5a]. On the other hand, the reductive elimination of diarylpalladium and aryl(methyl)palladium complexes in the presence of methyl iodide apparently involved no such palladium(IV) intermediates [3a]. The reaction of diorganonickel(II) and monoorganonickel(II) complexes with aryl iodide proceeded through single electron transfer from Ni to the iodide or oxidative addition of the iodide to an organonickel(I) intermediate [2b,5b].

We have shown before [6] that the reductive elimination of Pd(η^3-CH_2CHCH_2)($C_6H_3Cl_2$-2,5)(EPh_3) (**1a**: E = P; **1b**: E = As) is enhanced by some olefinic additives, e.g. dimethyl maleate and allyl halides. The initial step in this reaction for **1b** was thought to be coordination of the C=C bond of the olefinic additives, with $AsPh_3$ being released at the same time [6a,6b]. The step which follows in the case of the allylic electrophiles has not been fully elucidated, even though preliminary results utilizing the PPh_3 analog **1a** gave an indication of apparent involvement of a palladium(IV) intermediate [6c]. We wish to describe here studies aimed at gaining more insight into the role of allyl halides in enhancing the reductive elimination of the η^3-allyl(aryl)palladium complexes **1** and **2**.



(**1a**: E = P ;
1b: E = As)

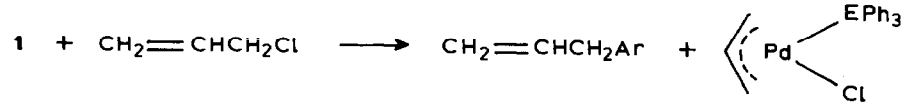


(**2a**: E = P ;
2b: E = As)

(Ar = $C_6H_3Cl_2$-2,5)

Results and discussion

The η^3-allyl(aryl)palladium complexes **1** underwent the facile reductive elimination in the presence of allyl chloride (eq. 1) at 0 °C under which condition the spontaneous reductive elimination of **1** proceeded much more slowly. The initial step in the reaction of eq. 1 for the $AsPh_3$ complex was demonstrated to be replacement of $AsPh_3$ by the C=C bond of CH_2=$CHCH_2Cl$ affording the intermediate **3** [6a,6b].



(1)

(Ar = $C_6H_3Cl_2$-2,5)

Although no kinetic analysis could be carried out on the analogous reaction of the PPh_3 complex in the presence of free PPh_3, a few observations are also consistent with the same ligand exchange pathway. Firstly, addition of PPh_3 or $AsPh_3$ in up to 2×10^{-3} *M* concentration to **1a** (0.02 *M*) and CH_2=$CHCH_2Cl$ (1 *M*) in dichloromethane at 0 °C completely inhibited the reductive elimination.

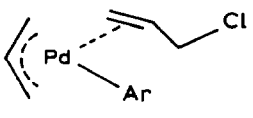
Table 1

Rates of reactions of η^3-allylpalladium complexes with allyl chlorides [a]

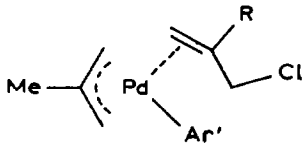
Complex	Allyl Chloride	Initial Rate (M h^{-1})
1a	CH_2=$CHCH_2Cl$	3.4×10^{-3}
1a	CH_2=$CMeCH_2Cl$	ca. 1×10^{-3}
2a	CH_2=$CHCH_2Cl$	ca. 3×10^{-3}
2a	CH_2=$CMeCH_2Cl$	2.0×10^{-4}
1b [b]	CH_2=$CHCH_2Cl$	1.4×10^{-3}
2b [b]	CH_2=$CHCH_2Cl$	ca. 2.8×10^{-4}

[a] In toluene at 0 °C. [Complex] = 0.02 M, [allyl chloride] = 1.0 M. [b] Triphenylarsine (1.25×10^{-3} M) was added. [Complex] = 0.008 M, [allyl chloride] = 1.23 M.

Secondly, the initial rate of the reductive elimination of **1a** or **2a** in the presence of CH_2=$CMeCH_2Cl$ was slower than that in the presence of CH_2=$CHCH_2Cl$, possibly reflecting the weaker coordination ability of the former olefin; Table 1 shows the relevant rate data. Thirdly, **1a** did not react with methyl iodide and benzyl chloride which normally have reactivities toward nucleophiles comparable to the allylic chlorides.



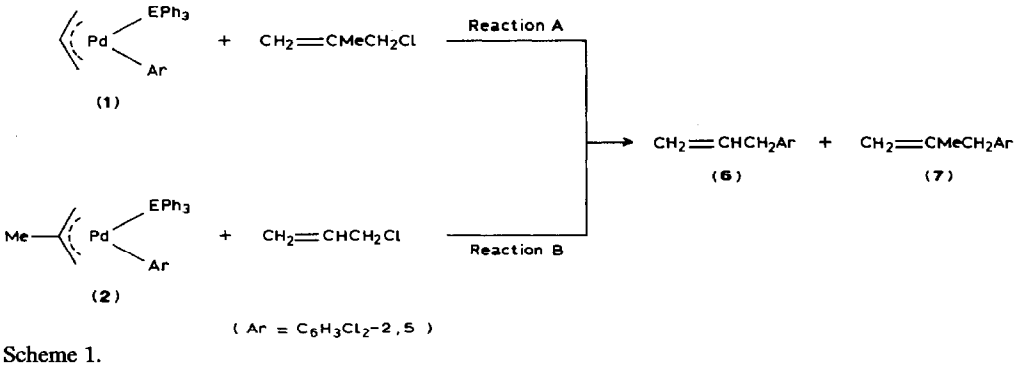
(3)



(4 : R = Me ;
5 : R = H)

An attempt to generate and characterize an allyl chloride complex similar to **3**, namely Pd(η^3-CH_2CMeCH_2)(Ar′)(CH_2=$CMeCH_2Cl$) (**4**: Ar′ = C_6HCl_4-2,3,5,6) from [Pd(η^3-CH_2CMeCH_2)Cl]$_2$ and Ar'_3Tl in the presence of CH_2=$CMeCH_2Cl$ failed owing to quite a rapid formation of the coupling product, CH_2=$CMeCH_2Ar'$ even at −40 °C. In view of the ready formation of the fully characterizable styrene complex, Pd(η^3-CH_2CMeCH_2)(Ar′)(styrene) through the same method [6b], the above experiment most probably involves the initial generation of the methallyl chloride complex **4** whose reactivity, with respect to the reductive elimination, is much greater than that of the styrene complex. This is consistent with the much greater acceleration of the reductive elimination of **1a** by the addition of allyl chloride than that of styrene and allylbenzene.

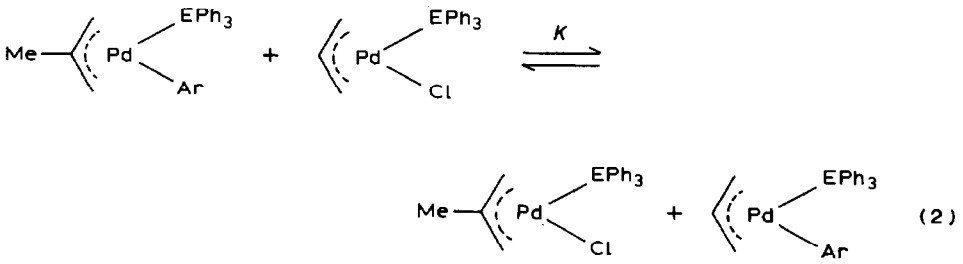
These results suggest the dual role of allyl chloride in enhancing the reductive elimination of **1**; one is to form the coordination bond to Pd via the C=C bond, and the other to reduce the electron density on the palladium atom through oxidative addition. The oxidative addition provides a possibility that the coupling product contains the allyl units of both the complex itself and the substrate chloride, as in the CD_3I-promoted reductive elimination of CH_3–Pd complexes [3c]. The reaction system composed of [Pd(η^3-CH_2CMeCH_2)Cl]$_2$, Ar'_3Tl and CH_2=$CHCH_2Cl$ gave a mixture of CH_2=$CHCH_2Ar'$ and CH_2=$CMeCH_2Ar'$. However, this result may not be regarded as evidence indicating participation of the CH_2=$CHCH_2$ group in the C–C bond-forming step of a palladium(IV) intermediate, for an intermolecular, net



Scheme 1.

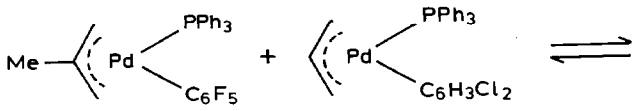
allyl ligand exchange between **5**, a plausible intermediate undergoing the reductive elimination, and $[Pd(\eta^3\text{-}CH_2CHCH_2)Cl]_2$, another product of the reductive elimination, is expected to be extremely fast (see below). A more detailed, time-resolved product analysis, such as was done in the reaction of the PPh_3 and $AsPh_3$ coordinated complexes (see below), could have been accomplished if the C–C bond-forming reaction had been much slower than the allyl ligand exchange.

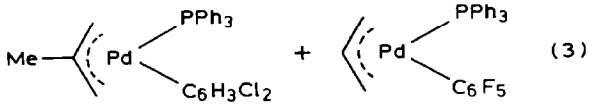
We then analyzed the product ratio in the reaction of **1** with CH_2=$CMeCH_2Cl$ (Scheme 1, reaction A) and that of $Pd(\eta^3\text{-}CH_2CMeCH_2)(C_6H_3Cl_2\text{-}2,5)(EPh_3)$ (**2a**: E = P; **2b**: E = As) with CH_2=$CHCH_2Cl$ (reaction B). We found that the ratio of the two products shown in Scheme 1 is a somewhat complex function of several factors including the reaction time, the nature of EPh_3 and the solvent. Firstly, it should be pointed out that quite a rapid ligand exchange (eq. 2) which has been confirmed separately (see below) critically affects the product ratio, since the η^3-allyl(aryl)palladium species becomes a mixture of **1** and **2** in the course of both reactions A and B through participation of η^3-allyl(chloro)palladium species, another product of the reductive elimination, as in eq. 2.



Ligand exchange. The reaction of eq. 2 was followed by ^1H NMR spectroscopy in CD_2Cl_2 at 0 °C. For both PPh_3 and $AsPh_3$ complexes the equilibrium stage was almost attained within 3 min on starting from both sides of the reaction; the equilibrium constant K was close to unity ($K = 1.5$ for E = P, and 1.1 for E = As). The reaction might have proceeded through either allyl-methallyl or aryl-chloride exchange or both, but we have no clue at the moment to distinguish between them. However, the observation that an analogous ligand exchange between $Pd(\eta^3\text{-}CH_2CHCH_2)(C_6H_3Cl_2\text{-}2,5)(PPh_3)$ and $Pd(\eta^3\text{-}CH_2CMeCH_2)(C_6F_5)(PPh_3)$ (eq. 3)

required a much longer reaction time (more than 10 min at 25 °C) suggests an important role of the chloride ligand in the reaction of eq. 2.





(3)

Triphenylarsine complex. The distribution of the two products in reactions A and B of the $AsPh_3$ complexes **1b** and **2b** in dichloromethane is shown in Table 2. Similar results were obtained in toluene solutions. In the case of reaction A, the product from the allyl unit of the chloride **7** was not detected at the early stages of the reaction, but its formation at the later stages was considerable. We suggest that the formation of a considerable amount of **7** at the late stages is due to accumulation of the η^3-methallyl(aryl) complex **2b** in the course of the reductive elimination of **1b** via eq. 2.

No doubt **2b** must have been produced from the very early stage of the reaction, because $Pd(\eta^3\text{-}CH_2CMeCH_2)(Cl)(AsPh_3)$ is generated each time **1b** undergoes reductive elimination forming **6** in the presence of $CH_2{=}CMeCH_2Cl$ and this chloride complex is immediately subjected to the ligand exchange of eq. 2. However, it should be noted that the reactivity of **2b** is considerably lower than that of **1b**; e.g. the initial rate of the reaction of **2b** with $CH_2{=}CHCH_2Cl$ is ca. 1/5 of that of **1b** with $CH_2{=}CHCH_2Cl$ under identical conditions (see Table 1). Therefore, the formation of **7** in an amount detectable by the GLC technique would not have occurred until a considerable proportion of the arylpalladium moiety was converted from **1b** to **2b**.

Presumably, the formation of the greater quantity of **6** than **7**, at the late stage of reaction B is also due to the increasing degree of accumulation of **1b** and the higher reactivity of **1b** than of **2b**. However, at first sight it seems somewhat difficult to determine whether the detection of **6** even at relatively early stages (Table 2) is ascribed to the same secondary reaction course (i.e. eq. 2) or to an intrinsic, primary process of the reductive elimination. We attribute the origin of this result again to the secondary reaction on the basis of the following considerations.

Firstly, the yields of the product **6** at the reaction times 1 h and 2 h are well within the range calculated (0.6 and 2.5%, respectively) by assuming that (i) the equilibrium of eq. 2 is fast, (ii) the ratio of the reactivity of **1b** vs. **2b** is ca. five (for details, see Appendix). Secondly, the reaction of **2b** with $CH_2{=}CHCH_2Cl$ was carried out in the presence of an excess of $Pd(\eta^3\text{-}CH_2CMeCH_2)(Cl)(AsPh_3)$ (ca. 4.5 times as much as **2b**) in dichloromethane. Then we could not observe, within the GLC detection limit, any formation of **6** up to ca. 9% conversion (Table 2). After this conversion the amount of **6** increased gradually, the final amount being 25%. This amount is less than that obtained in the absence of $Pd(\eta^3\text{-}CH_2CMeCH_2)(Cl)(AsPh_3)$ (45%). Quite similar results were obtained in toluene solution containing a saturated concentration (ca. 0.02 *M*) of $Pd(\eta^3\text{-}CH_2CMeCH_2)(Cl)(PPh_3)$ ([**2b**] 7.7×10^{-3} *M*). The role of the η^3-

Table 2

Product distribution in reactions of η^3-allylpalladium complexes with allyl chlorides [a]

EPh_3	Reaction [b]	Solvent	Time (h)	Yield (%)	
				CH_2=$CHCH_2Ar$ (6)	CH_2=$CMeCH_2Ar$ (7)
$AsPh_3$	A	CH_2Cl_2	0.33	6	0
			0.67	10	0
			1.33	22	2
			24	55	20
$AsPh_3$	B [c]	CH_2Cl_2	1	1(0)	5(4)
			2	3(0)	9(9)
			3	7(1)	14(13)
			24	45(25)	35(65)
PPh_3	A	Toluene	0.5	4	0
			1	6	0
			2	10	0
			4	15	0
			96	62	12
		CH_2Cl_2	0.5	3	6
			1	7	8
			2.5	20	14
			4	28	18
			26	42	34
		CH_2ClCH_2Cl	0.5	3	5
			1.5	11	8
			3	23	10
PPh_3	B	Toluene	0.25	2	5
			0.5	5	10
			1	10	15
			2.5	23	27
			4.5	37	34
			24	58	43
		CH_2Cl_2	0.125	9	2
			0.25	16	3
			0.5	28	7
			1.25	37	12
			24	60	31
		CH_2ClCH_2Cl	0.5	8	1
			1	16	3
			3	38	15
			48	64	32

[a] All reactions were run at 0 °C; [Complex] = 0.02 *M*, [CH_2=$CHCH_2Cl$] = 1.23 *M*, [CH_2=$CMeCH_2Cl$] = 1.0 *M*. [b] For notation, see Scheme 1. [c] Triphenylarsine (6.3×10^{-4} *M*) was added. [Complex] = 0.024 *M*. The data for the reaction carried out by adding Pd(η^3-CH_2CMeCH_2)(Cl)($AsPh_3$) (0.085 *M*) to **2b** (0.019 *M*) are shown in parentheses.

methallyl(chloro)palladium complex added in these experiments is most probably to suppress the accumulation of a significant amount of **1b** for a certain period at the initial stages by enforcing the backward reaction of the equilibrium shown in eq. 2. From these observations we conclude that there was no intrinsic incorporation of the allyl halide unit in the C–C coupling product of eq. 1 (E = As).

Triphenylphosphine complex. As shown in Table 2, the course of reaction A for the PPh_3 complex **1a** in toluene was almost the same as that for the $AsPh_3$ complex

1b described above. The reaction of **2a** with CH_2=$CHCH_2Cl$ (reaction B) in toluene also gave the greater quantity of **7** at the early stages (Table 2). However, the amounts of **6** formed at these stages appear somewhat higher than those estimated by assuming only the contribution of eq. 2, as was pointed out above in the case of reaction B for **2b**. Unfortunately, an experiment to determine the product ratio in reaction B in the presence of added $Pd(\eta^3\text{-}CH_2CMeCH_2)(Cl)(PPh_3)$ could not be carried out owing to the poor solubility of this complex in toluene.

A clearer case of the intrinsic contribution of the substrate chloride to the coupling product was observed in the reactions A and B (E = P) carried out in dichloromethane and 1,2-dichloroethane (Table 2). Thus, for example, the product **7** was formed even from the early stages of reaction A in amounts greater than those of **6**. In view of a supposedly minor accumulation of **2a** at these stages and the greater reactivity of **1a** than **2a**, it is hard to attribute the higher yield formation of **7** than **6** only to the secondary effect associated with eq. 2.

The initial product ratio **6**/**7** in reaction B (E = P) in dichloromethane and 1,2-dichloroethane is likewise considerably larger than unity. However, this ratio in reaction B as well as the ratio **7**/**6** in reaction A became smaller as the reaction proceeded. This is somewhat unexpected, since the amount of product derived from the allyl unit of the substrate chloride relative to that from the complex usually increases with the progress of the reaction (see above). The data in Table 2 show that in dichloromethane and 1,2-dichloroethane the absolute amount of product associated with the allyl unit of the complex appears to increase a little too abruptly at the early stages. This behavior might bear some relation to the non-first-order dependency of the rate on the concentration of **1a** in the reaction of **1a** with CH_2=$CHCH_2Cl$, which was observed only in these chlorocarbon solvents *. That is, a conventional pseudo-first-order plot always gave a curvature in which the rate increased gradually as the reaction proceeded. We have no explanation for this kinetic behavior.

A similar involvement of the allyl unit of CH_2=$CHCH_2Br$ in the coupling product was also observed at the early stages of the reaction between **2a** and this bromide in dichloromethane. On the other hand, the reaction of **2a** with CH_2=$CHCH_2OPh$ in both dichloromethane and toluene did not give any **6** at the early stages.

Concluding remarks. The present work stressed the need for careful analysis of the product ratio in those experiments which are undertaken for the purpose of confirming the involvement of substrate alkyl halides in the product-forming step of the reductive elimination accelerated by the halides. It was revealed here that although the allyl halides accelerate the reductive elimination of η^3-allyl(aryl)palladiums via oxidative addition, the allyl unit of the halides is not always incorporated into the coupling product during the C–C bond forming step. It is known that the oxidative addition of allyl halides affords several types of product, e.g. η^3-allyl

* In toluene the rate of the reaction of **1a** with the allylic electrophiles obeyed pseudo-first-order kinetics [6c], even though the rate constants were found to depend on the initial concentration of **1a**, unlike the clean kinetic behavior of **1b** under similar conditions [6b]. It was also found recently that the reported first-order dependence of the rate on the concentration of the allylic electrophiles [6c] contained the greater errors, especially for allyl acetate, if the initial concentration of the complex was kept rigorously constant.

(neutral and cationic) and η^1-allyl (from S_N2 and S_N2' pathways), depending upon the reaction conditions, e.g. the nature of the solvent, a metal moiety including ligand frameworks and the structure of the allyl unit [7]. We propose that structures of a palladium(IV) intermediate * formed by oxidative addition of allyl chloride in the complex of the type **3** differ between the reactions of the PPh_3 coordinated complexes carried out in CH_2Cl_2 and related solvents and the other cases; structure(s) in the former case may be suited to the C–C coupling between Ar and the incoming allyl unit, and structure(s) in the latter case to the coupling between Ar and the originally metal-bound allyl unit. Unfortunately, the available evidence provides no clue for specifying each structure. Further studies are in progress to clarify this problem.

Experimental

Materials. Complex **2b** was prepared in a manner similar to that for **1a**, **1b** and **2a** described previously [6]: it had no definite m.p. but decomposed above 105 °C. (Found: C, 54.90; H, 4.17%. $C_{28}H_{25}Cl_2AsPd$ calcd.: C, 54.80; H, 4.11%). ^1H NMR ($CDCl_3$): δ 1.90 (s, 3H), 2.66 (s, 1H), 2.87 (s, 1H), 3.66 (br, 1H), 3.76 (br, 1H). Complex, $Pd(\eta^3\text{-}CH_2CMeCH_2)(C_6F_5)(PPh_3)$ was prepared in a manner similar to that for the allyl analog [9]: m.p. 159 °C(dec.). (Found: C, 57.09; H, 3.49%. $C_{28}H_{22}F_5PPd$ calcd.: C, 56.92; H, 3.75%). ^1H NMR ($CDCl_3$): δ 1.89 (s, 3H), 2.65 (s, 1H), 2.88 (d, $J_P = 10$ Hz, 1H), 3.66 (br, 1H), 3.89 (v br, 1H).

Allyl chloride, methallyl chloride, and all the solvents were distilled prior to use.

Ligand exchange. Ligand exchange shown in eqs. 2 and 3 was followed by ^1H NMR spectroscopy in CD_2Cl_2 taking the initial concentrations of the complexes as ca. 0.1 M. In the case of eq. 2, it took at least 3 min after mixing the reactants at 0 °C for spectra to be run, when the reaction had reached completion.

Reductive elimination. The methods of sample preparation and product analysis (GLC, SE-30, 3 mm × 2 m) for the reactions of **1** and **2** with allylic chlorides were the same as those described before [6b]. Initial rates of these reactions (up to ca. 10% total conversion) are shown in Table 1. The reaction of **1a** (0.02 *M*) with MeI, $PhCH_2Cl$, styrene and allylbenzene (each ca. 1.0 *M*) in toluene at 0 °C afforded **6** in only a trace amount after 10 h. The reaction of $[Pd(\eta^3\text{-}CH_2CMeCH_2)Cl]_2$ with Ar'_3Tl ($Ar' = C_6HCl_4$-2,3,5,6) in the presence of allylic chlorides was also carried out in a manner similar to that reported [6b].

GLC analyses were done on a Hitachi 164 chromatograph, and ^1H NMR spectra were run on a JEOL PS-100 spectrometer.

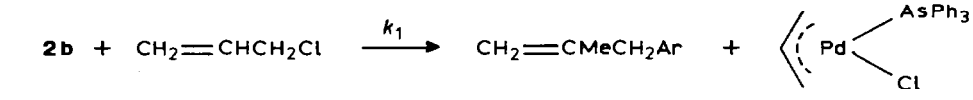
Acknowledgment

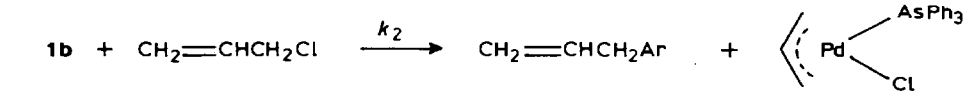
Partial support of this work by a grant-in-aid for Scientific Research, Ministry of Education, Science and Culture (62550630) is acknowledged.

* Recent reports described isolation and structure determination of well-characterizable trimethylpalladium(IV) complexes [8].

Appendix

Firstly we assume that in the early stages almost all the Pd(η^3-CH_2CHCH_2)(Cl)($AsPh_3$) generated in eq. 4 and 5 is converted to **1b** rapidly via eq.





2 because **2b** participating in eq. 2 is more abundant by far than the other species. Then we get

$$d[\mathbf{1b}]/dt = R_4$$

where R_4 is the rate of eq. 4. Since R_4 may well be almost constant at the early stages, we can assume

$$[\mathbf{1b}] = R_4 t$$

Hence, $d[\mathbf{6}]/dt = k_2[CH_2{=}CHCH_2Cl][\mathbf{1b}] = k_2 R_4[CH_2{=}CHCH_2Cl]t$ and $[\mathbf{6}] = 1/2\{k_2[CH_2{=}CHCH_2Cl]R_4 t^2\}$

Here we make another assumption that $k_2 = 5k_1$ (see text), thus giving rise to

$$[\mathbf{6}] = 5/2\{k_1[CH_2{=}CHCH_2Cl]R_4 t^2\}$$

Since the initial rate of eq. 4 is also given by

$$R_4 = k_1[CH_2{=}CHCH_2Cl][\mathbf{2b}]_0$$

we finally obtain the amount of **6** as

$$[\mathbf{6}] = 5/2\{R_4^2/[\mathbf{2b}]_0\} \times t^2$$

Taking the observed initial rate of eq. 4 as 1.2×10^{-3} M h^{-1} (see Table 2) and $[\mathbf{2b}]_0 = 2.4 \times 10^{-2}$ M, gives the calculated amount of **6** as 1.5×10^{-4} M (0.63%) at 1 h and 6.0×10^{-4} M (2.5%) at 2 h.

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