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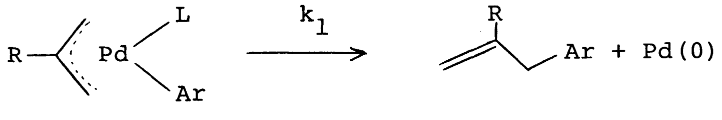
NON-DISSOCIATIVE LIGAND CONTROL OVER THE REDUCTIVE ELIMINATION OF η^3-ALLYL COMPLEXES OF Pd(II)

Hideo KUROSAWA* and Mitsuhiro EMOTO
Department of Applied Chemistry, Osaka University, Suita, Osaka 565

Kinetic studies on reductive elimination of η^3-allyl(aryl)-palladium(II) complexes suggest lack of ligand dissociation prior to the C-C coupling. On the contrary, the fourth ligand which remains coordinated plays an important role, by virtue of its electronic effect, in determining the barrier to the C-C coupling.

Mechanistic studies on reductive elimination of square-planar Pd(II) complexes containing η^1-bound organic ligands (class I) have seen great progress in recent years.1) It seems of particular importance to know to which extent the basic knowledges gained in these studies can be applied to the reductive elimination of η^3-allylpalladium(II) complexes (class II), because this is a key step in some catalytic and stoichiometric transformations of growing synthetic value.2-4) Scattering informations suggest some similarities between the reactions of two classes, e.g. concerted nature of cis C-C coupling,1,5a) or rate enhancement by the action of organic halides.1a,5b) We wish to report on a very significant difference; namely initial ligand dissociation to make the fourth coordination site vacant, which is one of the most remarkable features in the reaction of class I complexes,1) is not required in class II complexes.

We have examined details of kinetic aspects6) in reductive elimination of complexes **1**7) and **2** (Eq. 1) in the presence of large excess amounts of L.8) The rate was first-order with respect to [**1**] or [**2**] up to more than two half-lives.



(1)

(Ar= $C_6H_3Cl_2$-2,5)

1 R= H, L= $P(C_6H_4Y\text{-}4)_3$ (Y= H **a**; Cl **b**; Me **c**; OMe **d**), $P(OPh)_3$ (**e**), $AsPh_3$ (**f**)
2 R= Me, L= PPh_3

Notably, the first-order rate constants for Eq. 1, including the initial rate data,[8)] were independent of the amount of L added (up to 0.26 M) (Table 1). This is in marked contrast to retardation of the reductive elimination of cis-$PdMe_2(PR_3)_2$ by added PR_3,[1a,b)] and denies reversible ligand dissociation prior to the C-C coupling.

Table 1. First-Order Rate Constants for Eq. 1 in the Presence of L [a)]

Complex	L	Conc. / M	$k_1 \times 10$ / h^{-1}
1a	PPh_3	0.057	2.12[b)]
		0.12	2.11
		0.20	2.01
1e	$P(OPh)_3$	0.13	10.3
		0.26	10.0
1f	$AsPh_3$	0.080	0.38[b)]
		0.20	0.44

a) In toluene at 30 °C. Initial concentrations of the complexes were 0.020 M. b) Initial rate.

A rate-determining dissociation of L in **1** and **2**, which is not inconsistent with the results in Table 1, may also be excluded in view of the $\Delta S^{\ddagger}$ values observed and little solvent effect on Eq. 1 (Table 2). This lack of significant solvent effect is again quite different from the trend in the decomposition of the dimethyl complex.[1a)] The slower rate of the reaction of **2** than **1a** (Table 2) is also hard to rationalize in terms of the rate-determining ligand dissociation. Such dissociation of L in **2** would not be expected to be more difficult than in **1a**.

We propose that the ligand (L) in **1** and **2** is kept coordinated during the spontaneous reductive elimination. A possibility that a η^1-allyl species participates in the C-C coupling reaction has previously been suggested to be highly unlikely.[5b)]

Comparison of the rate data for **1a**-**d** (Table 2) shows the lower barrier to the C-C coupling in the less donating ligand complex, in agreement with the theoretical

Table 2. Kinetic Data[a)] for Eq. 1

Complex	Solvent	$k_1 \times 10$ / h^{-1}	$\Delta H^{\ddagger}$ [b)] / kJ mol^{-1}	$\Delta S^{\ddagger}$ [b)] / J K^{-1} mol^{-1}
1a	Toluene	2.1 ± 0.1	94 ± 2	-16 ± 4
	$ClCH_2CH_2Cl$	1.2 ± 0.1	99 ± 2	-4 ± 7
	MeCN/THF (5/3)	0.97 ± 0.03	99 ± 2	-6 ± 2
1b	Toluene	4.1 ± 0.1	92 ± 5	-17 ± 15
1c	"	0.83 ± 0.19	101 ± 2	-1 ± 5
1d	"	0.73 ± 0.23	102 ± 2	2 ± 6
1e	"	10.1 ± 0.1	93 ± 2	6 ± 4
1f	"	0.41 ± 0.02	103 ± 2	0 ± 2
2	"	0.26 ± 0.01	102 ± 2	-7 ± 7

a) At 30 °C. b) Obtained by k_1 values at 15 - 50 °C.

prediction.[1c)] However, the electron-donating ability of the ligand alone is not sufficient to explain the relative reactivity of **1f** vs. **1a**-**e**, since $AsPh_3$ apparently is a less basic ligand than the phosphines and phosphites (cf. Ref. 7). We propose that another electronic factor, *i.e.* π-electron withdrawing ability of the auxiliary ligand is also operative in determining the ease of Eq. 1. Presumably, the fact that **1e** is more reactive than **1a**, which in turn is more reactive than **1f**, is ascribed to the decreasing order of the π-acidic nature of the ligand,[9)] $P(OPh)_3 > PPh_3 > AsPh_3$. Such lowering of the barrier to the C-C coupling by the more π-acidic ligand becomes especially prominent in the olefin-promoted reductive elimination of **1**.[5a,10)]

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6) All kinetic runs in this work were carried out under nitrogen by observing the appearance of the coupling products by GLC, with the initial concentrations of the complexes being in the range, 0.01 - 0.04 M.

7) The arsine complex **1f** was prepared in a manner similar to that for **1a** and **2**,[5b)] and fully characterized similarly. The other complexes were formed in solutions by adding the appropriate L to **1f** ([L]/[**1f**] ≥ 6) whereby complete ligand exchange was unambiguously confirmed by ^{1}H NMR spectra.

8) Less satisfactory stoichiometry and kinetic behaviors were observed in the reaction in the presence of only small amounts of L. This may have been caused by Pd-black which precipitated as the reaction proceeded. With sufficient amounts of L added the reaction mixture remained completely homogeneous.

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10) Preliminary kinetic studies of this reaction suggest that an intermediate of the type, $Pd(\eta^3-C_3H_5)(olefin)(C_6H_3Cl_2-2,5)$ plays a key role in accomplishing the C-C coupling where olefins may be strongly π-acidic ones such as maleic anhydride or acrylonitrile; H. Kurosawa and M. Emoto, unpublished results.

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