Acceleration of the Reductive Elimination Step in Pd-Catalysed Allylic Alkylation by Allylic Substrates

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Allylic electrophiles used in Pd-catalysed allylic alkylation greatly accelerate reductive elimination of η^3-allyl(organo)palladium(II) complexes, *via* a Pd$^{\mathrm{IV}}$ intermediate, to give the coupling products and η^3-allylpalladium(II) salts.

It has been suggested that Pd-catalysed allylic alkylation using 'non-stabilised' carbanions involves reductive elimination of either an η^3- or η^1-allyl intermediate [(**1**) or (**2**)], followed by oxidative addition of allylic substrates to Pd^0 species.[1] We present here evidence for the involvement of (**1**) in the C–C bond forming step which is *preceded* by the action of the allylic substrates.

The complexes (**1a**—**d**)† were synthesized from (**3**; R = H or Me, X = Cl) and R^2ZnCl in tetrahydrofuran (THF) at −78 to −50 °C. The phenyl and the dichlorophenyl analogues were stable at −50 and 0 °C, respectively, in solvents such as THF, CH_2Cl_2, and toluene. Above −20 or 15 °C, respectively, these analogues decomposed slowly to give rather low yields (*ca.* 30—50%) of (**4**) and R^2R^2, R^2H, hexa-1,5-diene, *etc.*

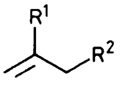
Addition of PPh_3 to a $CDCl_3$ solution of (**1a**—**d**) (P : Pd = 3 : 1) did not result in the formation of a new palladium species, even though the *syn–anti* proton exchange observed on the n.m.r. time scale[2] could be explained by the transient formation of (**2**) and its *trans* isomer.[3] Also, excess of PPh_3 did not accelerate the rate of formation of (**4**) significantly, although the product yields were improved to some extent. These results, together with the retarding effect of PPh_3 on the allylic substrate-induced reductive elimination, described below, suggest a very minor involvement (if at all) of the η^1-allylpalladium(II) species in the catalytic cycle when PPh_3 or weaker donors are used as ligands.

Of particular interest is that addition of (**5a**—**d**) to (**1a**) or (**1c**) induced rapid formation of (**4a**) or (**4c**) in very high yields (*ca.* 80—95%) even at −50 or 0 °C, respectively. The palladium complexes (**3**; R = H, X = Cl, Br, OAc, OPh) were formed at the same time. The initial rate of formation of (**4c**) obeyed second-order kinetics: first order with respect to (**1c**) and the allylic substrate.‡ The rate constant ($dm^3\,mol^{-1}\,h^{-1}$ in toluene at 0 °C) decreased in the order, 0.35 ± 0.04 (**5b**) > 0.22 ± 0.04 (**5d**) = 0.21 ± 0.03 (**5a**) > 0.045 ± 0.005 (**5c**).

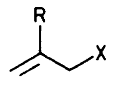
Significantly, it was found that the allylic substrate is incorporated in the coupling products. Thus, the reaction of (**1a**) or (**1c**) with (**5e**) in CH_2Cl_2 at −50 or 0 °C gave a higher amount of (**4b**) or (**4d**) than (**4a**) or (**4c**), respectively [(**4a**) : (**4b**) = (**4c**) : (**4d**) = *ca.* 1 : 2].§ On the other hand, the reaction of (**1b**) or (**1d**) with (**5a**) gave predominantly (**4a**) or (**4c**), respectively [(**4a**) : (**4b**) = *ca.* 3 : 1, (**4c**) : (**4d**) = *ca.* 5 : 1].§

These observations are consistent with a Pd$^{\mathrm{IV}}$ intermediate[4] formed by oxidative addition of the allylic substrates, with the allyl–methylallyl scrambling in this intermediate, if any, being slow under the conditions employed. An alternative path involving addition of PdR^2 to the C=C bond of the substrate followed by elimination of PdX[5] may be excluded, since the reaction of (**1c**) with $MeCH{=}CHCH_2Cl$ gave mainly $MeCH{=}CHCH_2C_6H_3Cl_2$-2,5 and (**4c**).

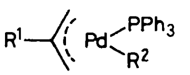
Under the conditions described above no reaction occurred between (**1c**) and benzyl chloride or methyl iodide which normally have reactivities toward nucleophiles comparable to or greater than (**5**). This result, together with the rather low



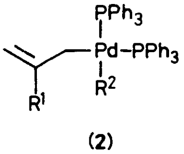
(**4**) **a**; $R^1 = H, R^2 = Ph$
b; $R^1 = Me, R^2 = Ph$
c; $R^1 = H, R^2 = C_6H_3Cl_2$-2,5
d; $R^1 = Me, R^2 = C_6H_3Cl_2$-2,5



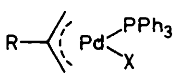
(**5**) **a**; R = H, X = Cl
b; R = H, X = Br
c; R = H, X = OAc
d; R = H, X = OPh
e; R = Me, X = Cl



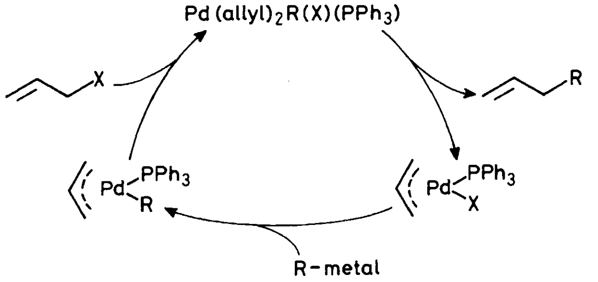
(**1**) **a**; $R^1 = H, R^2 = Ph$
b; $R^1 = Me, R^2 = Ph$
c; $R^1 = H, R^2 = C_6H_3Cl_2$-2,5
d; $R^1 = Me, R^2 = C_6H_3Cl_2$-2,5



(**2**)



(**3**)



Scheme 1. A specific structure for the Pd$^{\mathrm{IV}}$ intermediate is not intended.

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† Complexes (**1c**) and (**1d**) were fully characterised by elemental analyses and i.r. and ^1H n.m.r. spectroscopy, and (**1a**) and (**1b**) by comparison of their spectral data with those of (**1c**) and (**1d**).

‡ The rate was followed by monitoring the appearance of (**4c**) by g.l.c.; the initial concentration of (**1c**) was 0.02 mol dm^{-3} with a large excess of (**5**) (*ca.* 0.4—1.6 mol dm^{-3}). The kinetics showed a first-order dependence on [(**1c**)] up to *ca.* 2 half-lives. Second-order rate constants were obtained by plotting pseudo first-order rate constants [averages of 3 separate runs at a given concentration of (**5**)] against [(**5**)].

§ The approximate value at *ca.* 10—20% total conversion. The ratios at the earlier stages, though less accurate, showed similar product distribution patterns. As the reaction proceeded, the arylpalladium(II) species became a mixture of (**1a**)/(**1b**) or (**1c**)/(**1d**) with the relative amount of the starting complex decreasing, owing to facile exchange of R^2–Cl or allyl–methylallyl ligands between (**1**) and the reaction product (**3**; R = H or Me, X = Cl). This intermolecular ligand exchange was confirmed separately by ^1H n.m.r. spectroscopy.

sensitivity of the reaction rate to the leaving group, X of (**5**), indicates the importance of prior C=C bond co-ordination in the oxidative addition of (**5**).[6] Thus, the observation that the reductive elimination of (**1a**) and (**1c**) induced by (**5**) was retarded considerably by adding a very small amount of PPh_3 [P : (**5**) = 0.001 : 1] may be explained by the initial substitution of PPh_3 by (**5**) in (**1**). In any case, as for the formation of the allylpalladium(II) intermediate of type (**3**) from the allylic substrates in the catalytic cycle, a key step from a stereochemical point of view,[1,7] a new path not involving Pd^0 complexes must also be taken into account (Scheme 1).

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