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Preliminary communication

The mechanism of amination of η^3-allylpalladium complexes. An exploratory kinetic study

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Abstract

A kinetic study of the amination of chloro(η^3-methyl-2-butenyl)(triphenylphosphine)palladium (**1**) with dimethylamine shows that the rate is first order in complex **1** and second order in dimethylamine. At high amine concentrations this is also true for the amination of acetonitrile(η^3-3-methyl-2-butenyl)(triphenylphosphine)palladium tetrafluoroborate (**2b**) with benzylamine. These kinetic data, together with structural information from NMR during the reaction, suggest a common mechanism for the two reactions which involves rapid addition of the first equivalent of amine to the η^3-allyl system, followed by rate determining deprotonation of the intermediate.

Nucleophilic addition to η^3-allylpalladium complexes has been used extensively in organic synthesis [1]. One problem, which has only been partly solved, is control of regiochemistry [2]. The structure of the reactive intermediate is clearly important in this context. Trost and coworkers [3] and ourselves [4] have suggested that cationic complexes are formed as intermediates in the presence of strongly coordinating ligands such as phosphines, but in the reactions of η^3-allylpalladium chloride complexes this is not necessarily true [5]. Kinetic data should provide conclusive evidence on this point, but to our knowledge quantitative data are not available. We therefore decided to make an exploratory study of the kinetics of the amination of the mixed chloro-phosphine complex **1** with dimethylamine, a sufficiently slow reaction to be conveniently monitored by ^{1}H NMR spectroscopy at room temperature. For comparison, the amination of the cationic complex **2b** was also studied. Since the cationic complex is far more reactive ($> 10^2$) than the neutral complex **1**, benzylamine was used in the reactions with **2b**.

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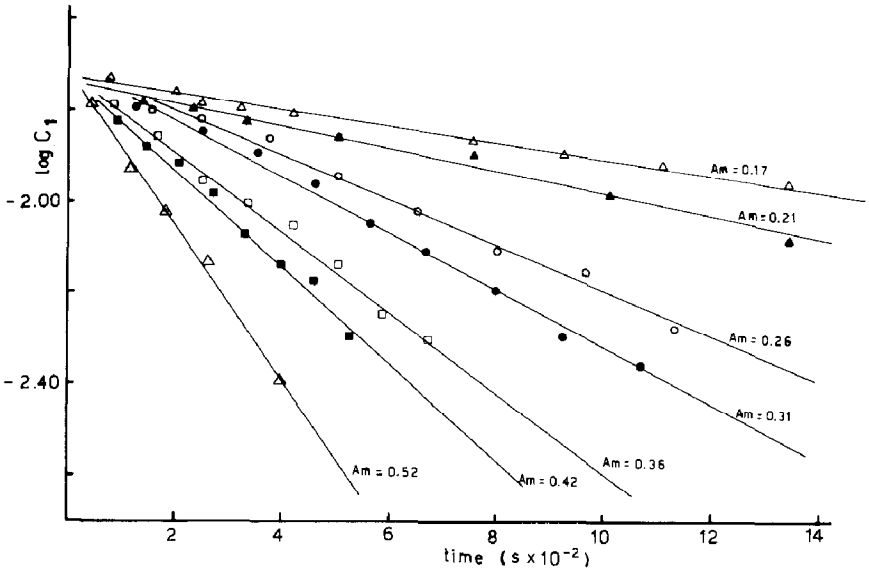


Fig. 1. Pseudo-first order plots for the reaction of **1** with dimethylamine. Am = C_{amine} (mol·l^{-1}).

The aminations were performed in an NMR tube at the probe temperature (25 °C) by adding a 8–25-fold excess of amine to an 0.020 *M* $CDCl_3$ solution of the complex. The relative concentrations of the product and substrate species were measured by integration of the methyl resonances of the allyl moieties, which are very well separated in the 200 MHz ^{1}H NMR spectrum of the reaction mixture. Fig. 1 and 2, show that the reaction is first order in the complex **1** and second order in amine.

Several mechanistic Schemes are compatible with this result. The most obvious is the formation of a cationic intermediate such as **2a** by displacement of chloride, followed by rapid addition of the second equivalent of amine to give **3**. To test this possibility, the influence of chloride ion (0.010–0.100 *M*, added as $Bu_4N^+Cl^-$) on the rate of amination was studied. Surprisingly, the addition of chloride was found to increase the reaction rate, strongly suggesting that a cationic intermediate is not involved [6*]. An alternative explanation is that a 5-coordinate species (**4**) is involved, but the NMR data clearly show that neither this complex nor the alternative 4-coordinate η^1-complex **5** is formed to appreciable extent (< 3% of the palladium species, cf. ref. 5a). Since there is no reason why these complexes would be vastly more reactive than the complex **1**, they seem unlikely as intermediates.

Final evidence against the reaction proceeding according to Scheme 1 is derived from the result of the amination of the cationic complex **2c**, which is rapidly and quantitatively formed in solution upon addition of 1 equivalent of benzylamine to the cationic complex **2b** (counter ion BF_4^-). At least at high amine concentrations ($\geq$ 0.4 *M*), the amination of **2c** is of first order in the complex and second order in amine [7*]. A reaction sequence that involves rapid and probably reversible addition of the first equivalent of amine to the η^3-allyl system followed by slow deprotonation of the intermediate **6** by the second equivalent, to give intermediate

* Reference number with asterisk indicates a note in the list of references.

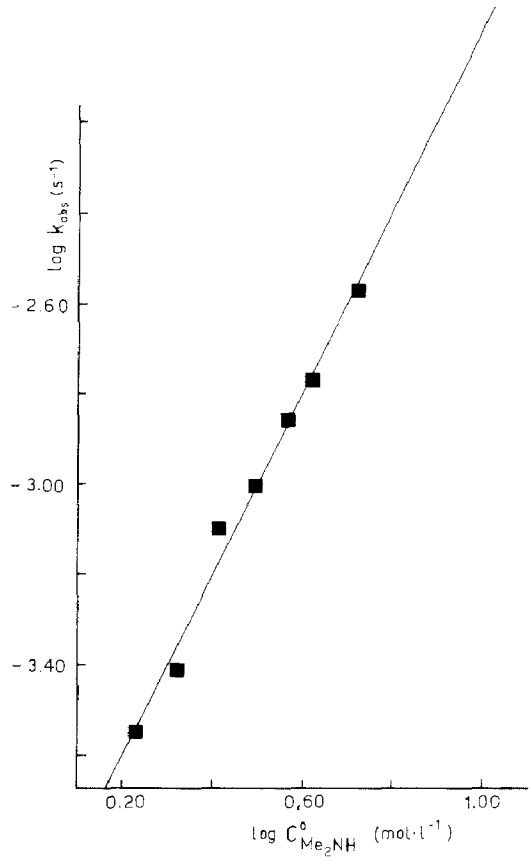
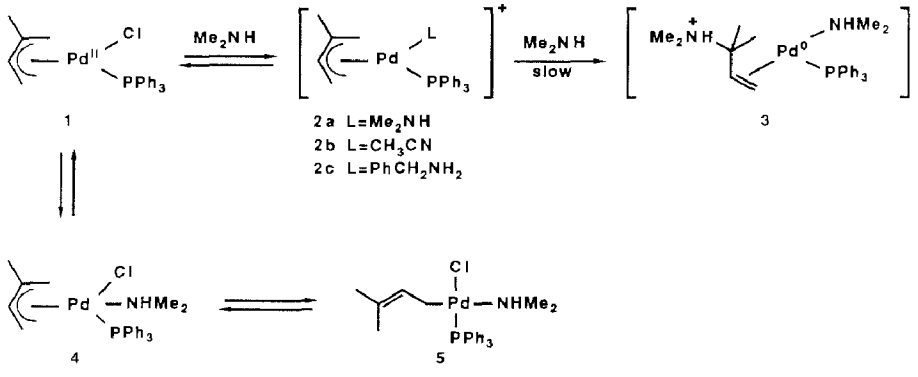
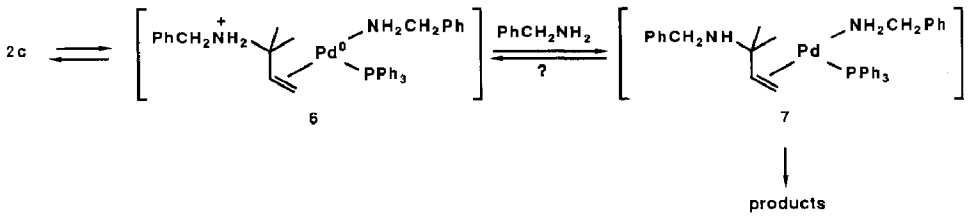


Fig. 2. Plot of log k_{obs} versus log C°_{amine} for the reaction of **1** with dimethylamine. The slope of the straight line is 2.0.



Scheme 1

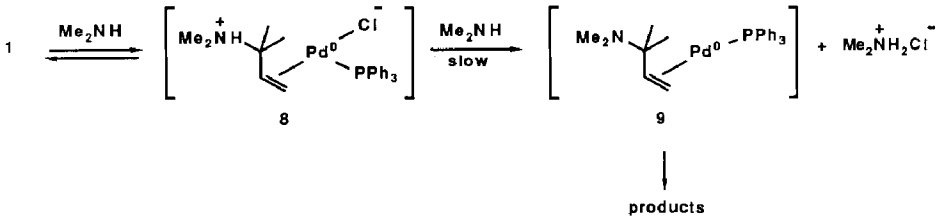
7, is compatible with the kinetic result (Scheme 2). It is noteworthy that the



Scheme 2

palladium-promoted amination of simple olefins, as well as of 1,5-dienes, appears to proceed by a similar reaction path [8,9].

A similar sequence appears very probable also for the amination of neutral η^3-allyl complexes. This is illustrated in Scheme 3 for the complex **1**. In the first



Scheme 3

step, which is fast and probably reversible, the first equivalent of amine is added to the η^3-allyl system to generate a zwitterionic complex **8**. This is deprotonated by a second equivalent in the slow step to give the neutral intermediate **9** which then decomposes to the amine product and palladium metal. Scheme 3 is compatible with all available experimental facts. It is clearly unlikely that cationic species are intermediates in amination of chloride complexes such as **1**. The reversibility indicated in the reaction of the cationic complex **2b** suggests that thermodynamic control of the regiochemistry may be important, in addition to charge control, and further studies are necessary to establish the relative importance of these two factors.

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References and notes

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6 The role of the added chloride is not clear at this point. Tentative explanations include chloride-promoted deprotonation of species such as **8** and displacement of the coordinated olefin from intermediates such as **9** by chloride.
7 At amine concentrations lower than 0.4 *M*, the reactions seem to reach an equilibrium. The reason for this is not clear.
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