Tetrahedron Letters No. 43, pp 3733 - 3736, 1975. Pergamon Press. Printed in Great Britain.

AMINATION OF π-ALLYLPALLADIUM COMPOUNDS

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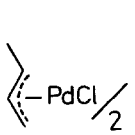
(Received in UK 25 July 1975; accepted for publication 15 September 1975)

The amination of 1,3-dienes (mostly in combination with the telomerisation of the dienes) is catalysed by complexes of nickel,[1,2,3] palladium[4] and rhodium.[5] These reactions have been postulated to proceed *via* π-allylmetal intermediates. The amination of a π-allylnickel complex was recently performed but the reaction was found to require more drastic conditions (2 h, 80°)[3] than those necessary for nickel-catalysed amination of butadiene (rapid at room temperature).[6]

In order to gain further insight into the mechanism of these aminations, a study of the reaction between π-allylpalladium complexes and amines was initiated. This seemed particularly interesting since a recent report on the synthesis of tris(triphenylphosphine)palladium(0) from the π-methallylpalladium chloride dimer and phosphine in the presence of benzylamine showed that *N*-methallylbenzylamine and *N,N*-dimethallylbenzylamine[7] were also formed during the reaction.



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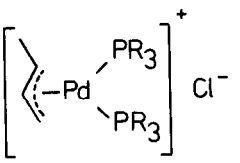

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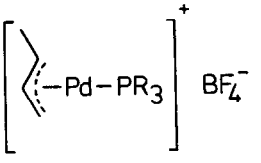

3

Using π-allylpalladium compounds (1) as the substrates, it was found that the amination with dimethylamine proceeded at a moderate rate at room temperature (Table I), but that the presence of strongly coordinating ligands like phosphines was required to ensure a high yield of amination product.

Variation of the phosphine-palladium ratio showed that the optimal ratio was 2:1. Under these conditions, the main palladium-containing species has been shown by conductivity measurements to be the ionic complex 2.[8,9] It thus appears that the formation of a positively charged complex is essential for the amination process to take place. This conclusion is further supported by the fact that the charged π-allylpalladium complex 3, obtained by the treatment of the complex 1 with silvertetrafluoroborate[10] in the presence of phosphine (optimal phosphine-palladium ratio 1:1), was very rapidly aminated by dimethylamine (Table II). Apparently then, π-allylpalladium complexes are sufficiently reactive to be likely intermediates in the amination of 1,3-dienes.

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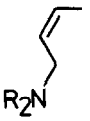

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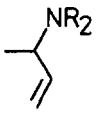
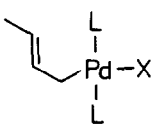


6

The products from the amination of the π-crotylpalladium species (2 and 3) were mainly the *trans*-amine 4 and small amounts of *cis*-amine 5 and a third isomer 6. It is not clear if this was due mainly to regioselectivity in the amination step or rapid isomerisation of the amine 6, as has been observed in the nickel-catalysed amination of butadiene.[2]

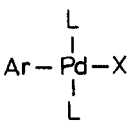
The actual mechanism for the amination of π-allylpalladium complexes is of interest, and several routes are possible for the reaction. The intermediacy of a π-allylamidopalladium complex or even the corresponding σ-allylpalladium complex 7a, which could undergo reductive elimination to give the amine, is attractive but seems unlikely since the arylpalladium complex 8 is stable in the presence of dimethylamine even at 170°. Under these conditions, the formation of the amido complex 8a appears likely. If reductive elimination to form carbon-nitrogen bonds were a favourable pathway for decomposition, the complex 8a would have yielded dimethylaminodiphenyl ether.

The contrast between the high reactivity of the π-allylpalladium complexes 2 and 3 and the stability of the arylpalladium complex 8 is, however, readily explained in terms of a mechanism involving nucleophilic substitution, which is generally slow with aromatic compounds. Although nucleophilic substitution at the sp^3-carbon of the σ-allyl complex 7 cannot be excluded,[11] direct nucleophilic attack on the π-allyl systems 2 and 3 appears more attractive, since this reaction is quite analogous to the reaction involving nucleophilic addition to complexed olefins.[12] In addition, an excess of phosphine, which could have been expected to increase the reaction rate of the σ-allylpalladium complex 7 by stabilizing the leaving group, palladium(0), actually strongly retards the amination. This effect is in complete accordance with a nucleophilic attack on the π-allyl systems of 2 and 3, since coordination with additional phosphine ligands would diminish the positive charge on these systems and thus their reactivity towards nucleophiles.



7 X=Cl

7a X=NR_2



8 X=Cl

8a X=NR_2

Ar = diphenylether

As an added point of interest, simple olefins are known to be readily convertible to π-allylmetal complexes.[13] Palladium-catalysed amination, in contrast to the use of a stochiometric quantity of palladium[12] has not yet been achieved despite much effort. A route *via* π-allyl complexes would perhaps make a truly catalytic process possible.

Table I. Yield of *trans*-crotyldimethylamine 4 after the addition of a ligand and *N,N*-dimethylamine to π-crotylpalladium chloride dimer in THF

Ligand (eqv./Pd)	Temperature	Yield (time) in %
-	20	22 (1 h)[a]
Bu_3P (1)	20	18 (21 h)
Bu_3P (2)	20	33 (45 min), 64 (85 min), 100 (12 h)
Bu_3P (4)	20	27 (19 min), 43 (24 h), 96 (1 week)
Biphos (1)	20	50 (17 min), 91 (2 h)
Ph_3P (2)	20	24 (1 h), 32 (7 h)[a]
Ph_3P (4)	20	38 (2 h)[a]
Ph_3P (1)	Reflux	69 (2 h)
Ph_3P (2)	Reflux	86 (2 h)

[a]No further increase at longer reaction times.

Table II. Yield of *trans*-crotyldimethylamine 4 after the addition of a ligand and *N,N*-dimethylamine to (π-crotyl)Pd^+ BF_4^- in 80 % aceton/water

Ligand (eqv./Pd)	Temperature	Yield (time) in %
-	20	33 (2 h)[a]
Ph_3P (1)	20	100 (10 min)
Ph_3P (2)	20	63 (9 min), 97 (1,5 h)

[a]No further increase at longer reaction times.

Acknowledgments

We thank The Swedish Board for Technical Development and KemaNord AB for financial support.

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