

Preliminary communication

PALLADIUM(II)-PROMOTED 1,4-DIAMINATION OF 1,3-DIENES. STEREOCHEMISTRY OF AMINATION OF A π -ALLYLPALLADIUM COMPLEX

BJÖRN AKERMARK*, JAN-E. BÄCKVALL*, ANDERS LÖWENBORG and
 KRISTER ZETTERBERG

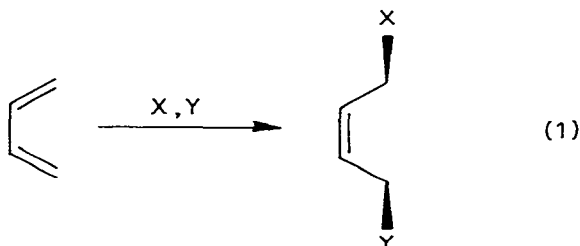
*Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm
 (Sweden)*

(Received November 13th, 1978)

Summary

Reaction of 1,3-dienes with bis(benzonitrile)palladium dichloride and dimethylamine gives 4-dimethylamino π -allylic palladium complexes, which on treatment with AgBF_4 or triphenylphosphine are attacked by excess dimethylamine on the face of the π -allyl group opposite to that occupied by palladium to give 1,4-diamines.

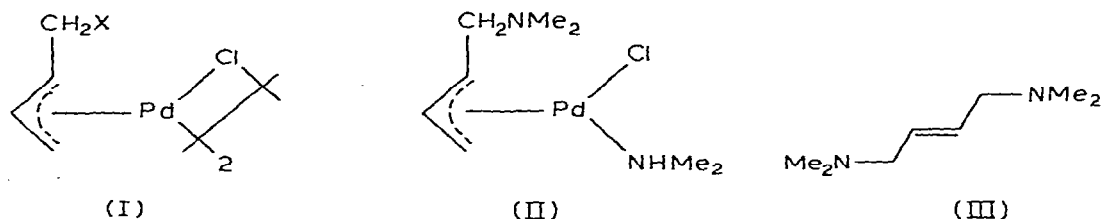
Methods for stereospecific vicinal *cis*-oxyamination and *cis*-diamination of alkenes have recently been developed by our group [1] and by Sharpless and his associates [2]. In view of the accessibility of 1,3-dienes* as substrates for organic reactions, similar 1,4-difunctionalizations of 1,3-dienes would have considerable synthetic potential (eq. 1).



We have previously studied the amination of both π -olefin [4,5] and π -allyl-palladium [6] complexes. It occurred to us that monoamination of butadiene might give an amino π -allylpalladium complex (I) [7] ($\text{X} = \text{NR}_2$), which should react with a second mole of amine to yield a diamine. Using 1,3-cyclohexadiene

*Recently several new interesting methods for the synthesis of 1,3-dienes have been developed; for example see: ref. 3.

as substrate it should even be possible to determine the overall steric course of the amination. This is of interest both for the synthetic applicability of the diamination reaction and for the determination of the mechanism of amination of π -allylpalladium systems. In this paper we show that 1,3-dienes can, indeed, be converted to 1,4-diamines (Table 1). An important aspect of the results is that the two amino groups are added in a *cis*-fashion to the diene system, indicating that palladium, in the intermediate π -allyl complex (e.g., II), is displaced by nucleophilic attack by external amine.



Amination of the monodentate π -complex* of butadiene in tetrahydrofuran (THF) at -40°C gave a pale yellow complex, which is tentatively assigned structure II. The π -allyl complex II was also obtained when I ($\text{X} = \text{Cl}$) was treated with dimethylamine at -40°C for 30 min. Attempts to bring II into reaction with excess amine were unsuccessful even at higher temperature. However, addition of triphenylphosphine and/or AgBF_4 at -40°C and heating the mixture under reflux for 30 min produced 1,4-bis(dimethylamino)but-2-ene (III) together with palladium(0). The use of tributylphosphine in place of triphenylphosphine gave lower yields. When butadiene was used in excess, 2,7-octadienylamine and octatriene were formed catalytically in side reactions (cf. ref. 9). The results from diamination of butadiene are given in Table 1. A similar dependence of phosphine and AgBF_4 was previously found [6] for the amination of π -crotylpalladium chloride. However, Table 1 reveals that addition of AgBF_4 seems to be more effective than addition of phosphine. In fact, the best result was obtained with two equivalents of AgBF_4 without added phosphine (entry 6). This is slightly different from the results of the previous study on π -crotylpalladium chloride, where at least one equivalent of phosphine was required for successful amination. Other dienes, for example 1,3-pentadiene (50%), isoprene (30%) and 1,3-cyclohexadiene (22%), were also shown to undergo the 1,4-diamination reaction with dimethylamine. However, 1,3-cyclooctadiene gave no diamination product under the conditions used.

Oxidation (Br_2) of the generated complex II in the presence of dimethylamine also gave III in a reaction analogous to the recently reported [1b] formation of vicinal diamines from oxidation of β -aminoalkylpalladium complexes. However, yields of III were lower in these oxidation reactions, and several side-products were formed.

The stereochemistry of the overall reaction was studied with 1,3-cyclohexadiene as the substrate. 1,4-Diamination of 1,3-cyclohexadiene, starting from the π -complex IV* and using one equivalent each of triphenylphosphine and

* This complex, in which the diene is bound as a monodentate ligand, was prepared from the diene and $(\text{PhCN})_2\text{PdCl}_2$ at -40°C [8].

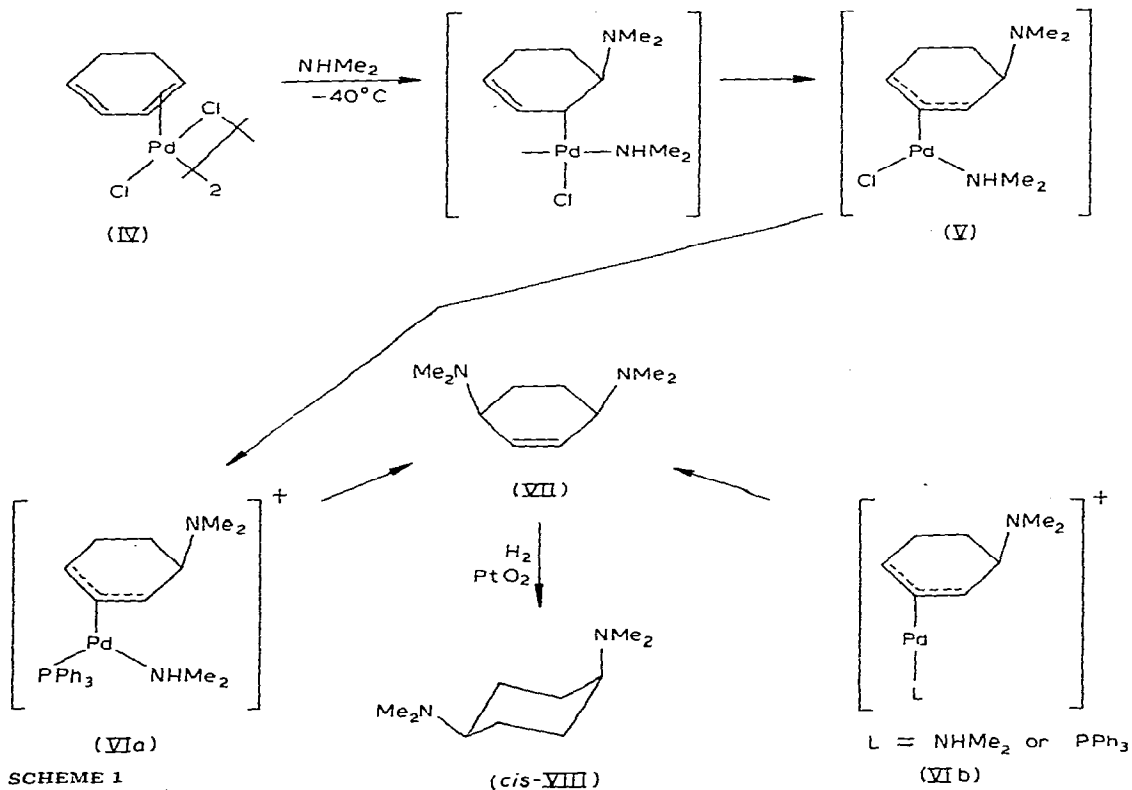
AgBF_4 , gave a sole product VII [22%, *m/e* 168 (M^+), NMR (CCl_4 , TMS) δ 1,6 (m, 4, CH_2CH_2), 2.22 (s, 12, two $\text{N}(\text{CH}_3)_2$), 2.8 (m, 2, two CH), 5.73 ppm (broad s, 2, $\text{CH}=\text{CH}$)], which on hydrogenation (PtO_2 , H_2) was transformed into *cis*-VIII. The saturated compound *cis*-VIII was identified by comparison with authentic samples of *cis*- and *trans*-VIII, prepared by Eschweiler-Clarke [10] alkylation of *cis*- and *trans*-1,4-diaminocyclohexane [11] respectively. GLC analysis showed that the product *cis*-VIII from 1,3-cyclohexadiene was >94% *cis*.

TABLE I

1,4-DIAMINATION OF BUTADIENE

Case	Ph_3P (equiv.) ^a	AgBF_4 (equiv.) ^a	Yield of III ^{b,c} (%)
1	1	0	15
2	2	0	20 (15 ^d)
3	0	1	40
4	1	1	48 (37 ^d , 45 ^e)
5	2	1	38
6	0	2	69 (84 ^e)
7	1	2	43 (29 ^d)
8	2	2	32 (27 ^d)

^a 1 equiv. = 1 mmol; the amount of palladium complex used was 1 mmol. ^b The yield of III using neither Ph_3P nor AgBF_4 was < 3%. ^c Yields were determined by GLC and are based on the amount of palladium used. Unless otherwise noted, 1/2 mmol (= 1 mmol Pd) of I (X = Cl) was suspended with a three-fold excess of butadiene at -40°C in THF (6 ml). Dimethylamine (7 mmol) in THF (3 ml) was added and after stirring at -40°C for 30 min Ph_3P and/or AgBF_4 was added. The reaction mixture was allowed to warm up and refluxed for 30 min. ^d $(\text{PhCN})_2\text{PdCl}_2$ was used. ^e After reaching room temperature the reaction mixture was allowed to stir at 20°C for 24 h.



A probable mechanism is shown in Scheme 1. Attack of amine on a double bond coordinated to palladium(II) has been shown [5] to take place from the side opposite to that of the metal. Thus attack of amine on the π -complex IV would produce the π -allyl complex V. The role of added phosphine or AgBF_4 appears to be to generate a positively charged complex VI. The π -allyl complex VI would be reactive enough to be attacked by amine on carbon (cf. ref. 6), and in this way give the unsaturated diamine VII. To account for the observed stereochemistry, attack of dimethylamine on VI must take place on the side remote from palladium. This is in contrast with suggestions [12] that nucleophiles such as alcohols or amines migrate from the metal to the coordinated allyl group, but consistent with our earlier suggestion [6,13] that amination of π -allylpalladium systems is a nucleophilic type of reaction, closely related to amination of π -olefin complexes [5]. The result is also consistent with the recent finding that some carbon nucleophiles, such as malonates, attack on the face of the π -allyl system opposite to that occupied by palladium [14].

We are currently investigating the generality of this type of reaction in which two substituents are introduced in the 1,4-positions of a diene system (eq. 1). Preliminary experiments show that 1-dimethylamino-4-methoxybut-2-ene is readily formed (49% isolated yield) from butadiene via complex I ($\text{X} = \text{OCH}_3$).

Acknowledgements

We thank the Swedish Natural Science Research Council and the Swedish Board for Technical Development for financial support.

References

- 1 (a) J.E. Bäckvall, *Tetrahedron Lett.*, (1975) 2225; (b) (1978) 163.
- 2 (a) K.B. Sharpless, D.W. Patrick, L.K. Truesdale and S.A. Biller, *J. Amer. Chem. Soc.*, 97 (1975) 2305; (b) K.B. Sharpless, A.O. Chong and K. Oshima, *J. Org. Chem.*, 41 (1976) 177; (c) A.O. Chong, K. Oshima and K.B. Sharpless, *J. Amer. Chem. Soc.*, 99 (1977) 3420.
- 3 R.C. Larock and B. Riefling, *J. Org. Chem.*, 43 (1978) 1468, and ref. therein.
- 4 B. Åkermark, J.E. Bäckvall, L.S. Hegedus, K. Zetterberg, K. Siirala-Hansén and K. Sjöberg, *J. Organometal. Chem.*, 72 (1974) 127.
- 5 B. Åkermark, J.E. Bäckvall, K. Siirala-Hansén, K. Sjöberg and K. Zetterberg, *Tetrahedron Lett.*, (1974) 1363.
- 6 B. Åkermark and K. Zetterberg, *Tetrahedron Lett.*, (1975) 3733.
- 7 For formation of complexes I where $\text{X} = \text{Cl}$, OMe or OAc , see: B.L. Shaw, *Chem. Ind. (London)*, (1962) 1190; S.D. Robinson and B.L. Shaw, *J. Chem. Soc.*, (1963) 4806; J.M. Rowe and D.A. White, *J. Chem. Soc. A*, (1967) 1451; K.A. Holder and P. Powell, *J. Organometal. Chem.*, 122 (1976) 275.
- 8 M. Donati and F. Conti, *Tetrahedron Lett.*, (1966) 1219.
- 9 J. Tsuji, *Accounts Chem. Res.*, 6 (1973) 8.
- 10 M.L. Moore, *Org. React.*, 5 (1949) 301.
- 11 A.T. Nielsen, *J. Org. Chem.*, 27 (1962) 1998.
- 12 (a) R. Baker, *Chem. Rev.*, 73 (1973) 487; (b) P.W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Academic Press, New York, Vol. II, 1975, p. 156-157.
- 13 B. Åkermark, M. Almemark, J. Almlöf, J.E. Bäckvall, B. Roos and A. Støgard, *J. Amer. Chem. Soc.*, 99 (1977) 4617.
- 14 (a) B.M. Trost and P.E. Strege, *J. Amer. Chem. Soc.*, 99 (1977) 1649; (b) B.M. Trost and L. Weber, *ibid.*, 97 (1975) 1611; (c) B.M. Trost, L. Weber, P.E. Strege, T.J. Fullerton and T.J. Dietsche, *ibid.*, 100 (1978) 3416.