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Preliminary communication

CARBENE—PALLADIUM(II) COMPLEX INTERMEDIATE IN THE HETEROCYCLE SYNTHESES; PALLADIUM(II)-CATALYZED REACTION OF AMINOALCOHOL WITH ISONITRILE

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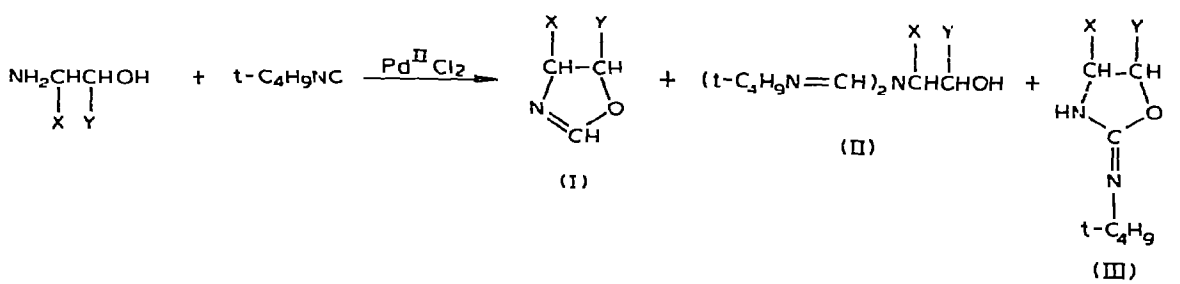
Summary

Carbene coordinated palladium(II) complexes were prepared by the reaction of 1 mole of $Pd^{II}Cl_2$, 2 moles of t-butyl isocyanide and 1 mole of β-aminoalcohol such as β-aminobutanol, methyl *L*-threonate and *o*-aminophenol. Pyrolysis at 200° gave the corresponding 2-oxazolines in high yields; treatment with various ligands was also examined.

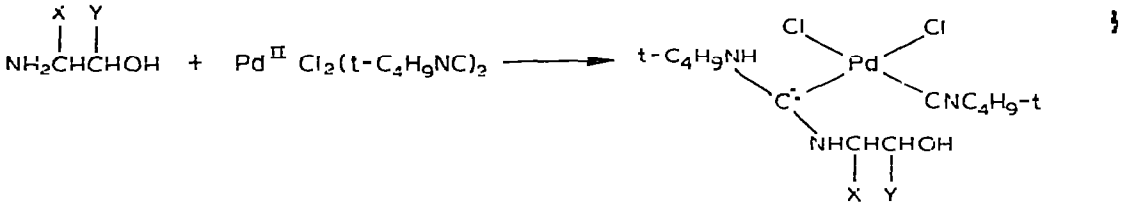
It has been previously reported [1] that the reactions of various β-aminoalcohols such as β-aminobutanol, methyl *L*-threonate and *o*-aminophenol with t-butyl isocyanide are catalyzed by $Pd^{II}Cl_2$ to produce 2-oxazolines (I) in high yields along with diamidide (II), and III as minor by-products (< 5 %).

We have found that carbene-coordinated palladium(II) complexes (IV) are intermediates in the oxazoline synthesis.



Carbene-coordinated palladium(II) complex (IV) was prepared by the reaction of a mixture of t-butyl isocyanide and $Pd^{II}Cl_2$ or $Pd^{II}Cl_2(t\text{-}C_4H_9NC)_2$ with β-aminoalcohol at room temperature. For instance, a mixture of 10 mmol of t-butyl isocyanide and 5 mmol of $Pd^{II}Cl_2$ in 4 ml of THF was treated with 5 mmol of methyl *L*-threonate ($[\alpha]_D^{13}$ +3.4°) in 4 ml of THF at room temperature.

The reaction mixture, after being treated with Norit, was concentrated and triturated with ether to precipitate carbene palladium(II) complex IVa. Complex IVa was reprecipitated from chloroform solution with ether (Yield 88 %; $[\alpha]_D^{25}$ −29°).



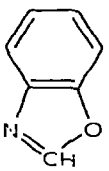
(IVa) X = CO_2CH_3 ; Y = CH_3
(IVb) X = C_2H_5 ; Y = H
(IVc) X,Y = o-aminophenol

Similarly, carbene complexes IVb and IVc were prepared by the reaction of a mixture of t-butyl isocyanide and $Pd^{II}Cl_2$ with β-aminobutanol and with *o*-aminophenol, respectively. The structures of IVa-IVc have been established by elemental analyses as well as IR and NMR spectra. (IVa: Anal. Found: C, 38.20; H, 6.53; Cl, 14.10; N, 8.89. $C_{15}H_{29}N_3O_3Cl_2Pd$ calcd.: C, 37.80; H, 6.13; Cl, 14.87; N, 8.81 %. IR (KBr): 3375, 3225, 3030, 2205, 1740, 1570 cm^{-1}. PMR ($CDCl_3$): δ 1.4 (d, 3H), 1.5 (m, 18H), 3.8 (s, 3H), 4.3 ~ 4.7 (m, 2H). ^{13}C NMR (CD_3OD with TMS): δ 21.0, 21.5 ($\underline{C}H_3CH$), 29.4, 31.8 (($\underline{C}H_3)_3C$), 53.0 ($O\underline{C}H_3$), 55.2, 55.9 (($CH_3)_3\underline{C}$), 67.9, 68.3 ($\underline{C}HNH$, $\underline{C}HOH$), 172.1, 172.7 ($\underline{C}OO$).) The IR spectra of IVa-IVc exhibited strong bands at 2205 cm^{-1}, due to the isonitrile ligand, and at 1545 ~ 1570 cm^{-1}, which is characteristic of a coordinating diaminocarbene ligand. This *cis*-configuration for complex IVa is indicated by the presence of two bands assigned to ν(Pd–Cl) at 287 and 321 cm^{-1}. During the course of our study, Boschi et al. [2] reported the preparation and characterization of carbene-palladium(II) complexes of this sort. Our spectral data of IVa-IVc are in agreement with those given by them. The 220 MHz PMR spectrum of IVa showed restricted rotation [3] about the C—N bonds of the carbene ligand; i.e., at least three singlet bands due to the t-butyl group of the carbene ligand were observed.

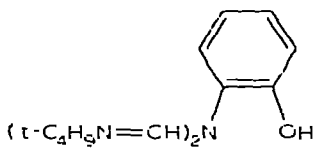
Pyrolysis of carbene—palladium(II) complexes (IV), which are stable at room temperature in air, gave the corresponding 2-oxazoline derivatives. For example, complex IVa in THF was heated in a sealed tube at 200° for 1 h, giving rise to 4-carbomethoxy-5-methyl-2-oxazoline (I: X = CO_2CH_3; Y = CH_3; $[\alpha]_D^{13}$ = +231°) in 77 % yield. Similarly, benzoxazole (V) was obtained in 75 % yield from the pyrolysis of IVc.

Next, treatment of the carbene—palladium(II) complex IVc with some ligands was examined from the mechanistic viewpoint of the production of 2-oxazoline. Complex IVc was stirred with 1 mole of t-butyl isocyanide in THF or with a mixture of 1 mole of t-butyl isocyanide and 1 mole of *o*-aminophenol in THF for 24 h at room temperature. The reaction mixture was extracted with ether to remove unchanged complex IVc. The IR and TLC analyses of the ether extract which was almost free from Pd-containing species (Pd contents is < 1 %

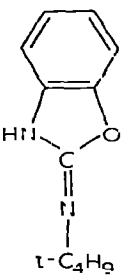
of used Pd^{II}) showed that benzoxazole (V) was not formed in the reaction. Then, the ether extract was subjected to GLC analysis (200°C), which, however, showed the formation of benzoxazole V (6%) with diamidide VI (69%) and VII (25%). (VI:PMR ($CDCl_3$ with TMS)δ1.35 (s, 9H), 1.47 (s, 9H), 6.5 (broad, 1H), 7.3 ~ 6.9 (m, 6H). VII:PMR ($CDCl_3$ with TMS): δ 1.46 (s, 9H), 7.4 ~ 6.9 (m, 4H).)



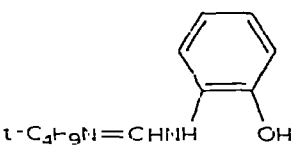
(V)



(VI)



(VII)



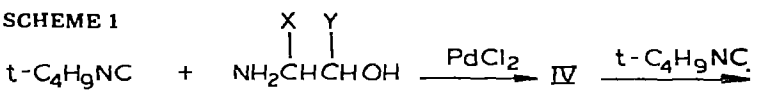
(VIII)

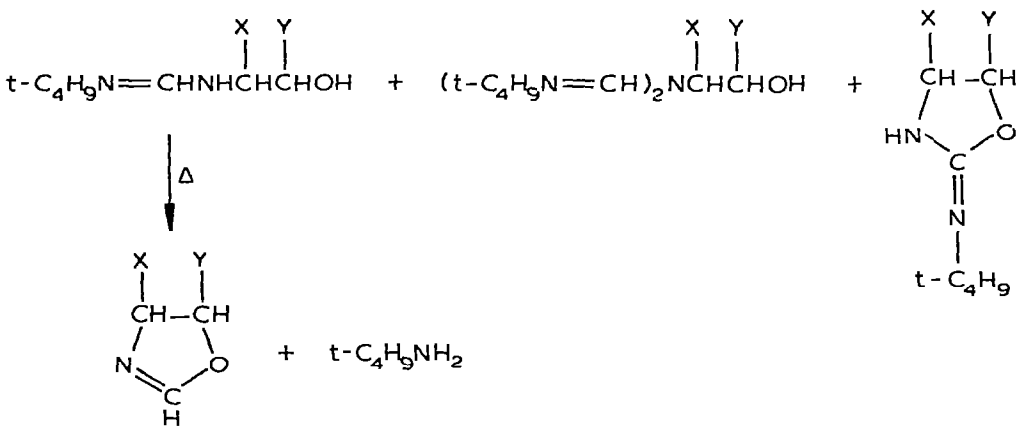
Similar results were obtained in the reactions of IVc with triphenylphosphine and with potassium cyanide. These observations may be taken to suggest that a species, which is thermally cyclized to give benzoxazole, is formed in the reaction of IVc with ligands at room temperature. We assume that the species is to be *N*-(*o*-hydroxy)phenyl-*N'*-t-butylformamidine (VIII), although it has not been isolated. In a separate experiment, VIII independently prepared, was thermally cyclized to produce benzoxazole (V) without any catalyst (VIII→V: 16% yield at 80°/4 h and quantitative yield at 200°/1 h). Thus, the above assumption was supported. (VIII: PMR (CD_3CN)δ 1.39 (s, 9H), 6.6 ~ 7.1 (m, 4H), 7.88 (s, 1H).)

Based upon the observations mentioned above, Scheme 1 can be presented as a possible reaction mechanism for the oxazoline syntheses.

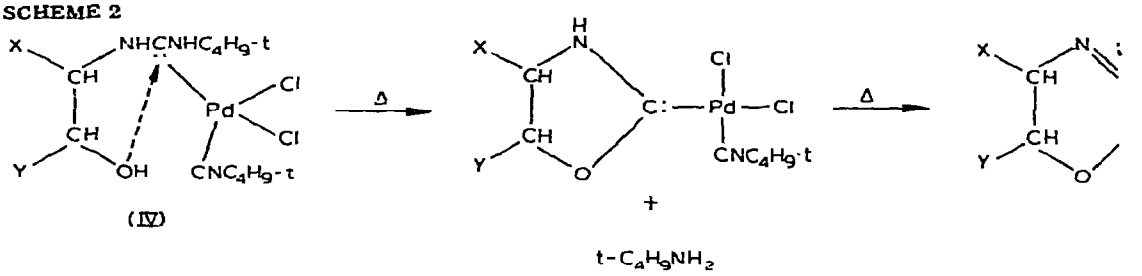
For the pyrolysis of the carbene complexes IV to produce oxazoline derivatives, however, an alternative mechanism may be operative (Scheme 2).

SCHEME 1





SCHEME 2



(IV)

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3 F. Bonati and G. Minghetti, J. Organometal. Chem., 59 (1973) 403.