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Preliminary communication

THE PREPARATION OF *trans*-[CHLORO{1,4-BIS(*p*-METHOXYPHENYL)-1,4-DIAZA-1,3-BUTADIENE-2-YL}BIS (TRIPHENYLPHOSPHINE)-PALLADIUM(II)]

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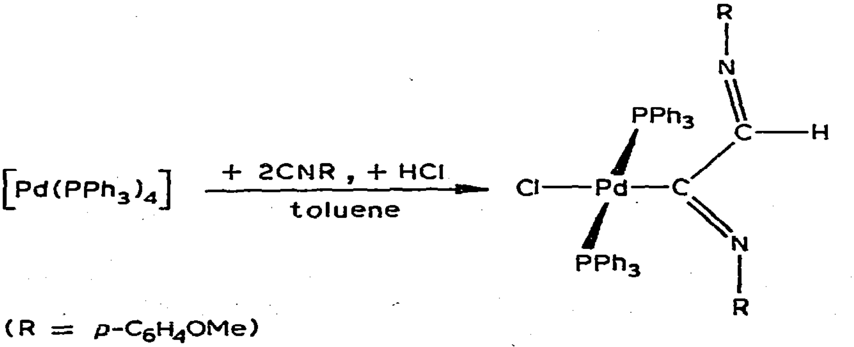
Summary

The title compound was prepared by reaction of [$Pd(PPh_3)_4$] with two equivalents of CN-*p*-C_6H_4OMe in toluene and successive addition of ethanolic HCl (molar ratio Pd/HCl 1/1) at −70°C. Some typical reactions of the 1,4-diaza-1,3-butadiene-2-yl group are reported.

In the course of our study on the coordination properties of organometallic 1,4-diazabutadienes, we have previously described the preparation of a variety of palladium(II) complexes containing a σ-bonded 1,4-diaza-3-methylbutadiene-2-yl group either with different ancillary ligands at the Pd center or with different substituents at the imino nitrogen atoms [1—4]. We now report (eq. 1) the preparation of a related palladium(II) compound in which the 3-methyl group on the 1,4-diazabutadiene-2-yl moiety is replaced by a hydrogen atom.



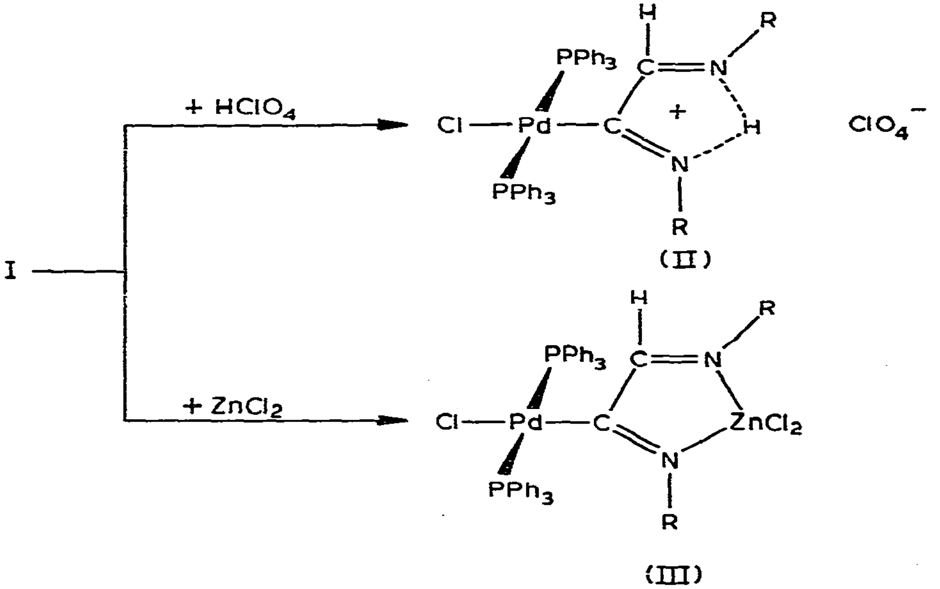
(1)

(I)

The reaction is carried out in two steps under dinitrogen. The isocyanide ligand is first added to a stirred suspension of [Pd(PPh$_3$)$_4$] (molar ratio Pd/CNR 1/2) to give a red-brown solution containing palladium(0) isocyanide species (probably [Pd(CNR)(PPh$_3$)$_3$] and [Pd(CNR)$_2$(PPh$_3$)$_2$], $\nu(\mathrm{C{\equiv}N})$ 2065(sh), 2050vs, 2020(sh) cm^{-1}) and a small amount of free isocyanide ($\nu(\mathrm{C{\equiv}N})$ 2124 cm^{-1}). In the second step, ethanolic HCl is added dropwise at −70°C (Pd/HCl 1/1). The mixture is then allowed to warm slowly (ca. 2 h) to room temperature, to give the final product I in 50—55% yield (based on the amount of starting complex [Pd(PPh$_3$)$_4$]). The formation of I may be formally explained by a "double" insertion of the isocyanide into a Pd—H bond generated in situ through oxidative addition of HCl to palladium(0). The hydrido complex [PdHCl(PPh$_3$)$_2$] has in fact been obtained by addition of HCl to [Pd(CO)(PPh$_3$)$_3$] [5], and the single insertion of isocyanide into a Pt—H bond has already been reported [6].

The formulation of I is based on elemental analysis, molecular weight, IR and ^{1}H NMR spectra and on some typical reactions of the 1,4-diaza-1,3-butadiene-2-yl group. The IR spectrum shows two C=N stretching vibrations at 1613 and 1539 cm^{-1} respectively, and a ν(Pd—Cl) band at rather low frequency (274 cm^{-1}), due to the high *trans*-influence of the σ-bonded diazabutadienyl moiety [1].

Complex I can be easily monoprotonated by HClO$_4$ and gives a 1/1 adduct with ZnCl$_2$ (eq. 2).



(2)

In the ^{1}H NMR spectra (CDCl$_3$) of I and II the signal δ (N=C—H) is masked by the strong resonances of PPh$_3$, but it can be observed as a singlet at 7.59 ppm in the spectrum of the binuclear complex III.

Further work is in progress in order to investigate the nature of the intermediates involved in reaction 1 and the coordination abilities of the 1,4-diazabutadiene-2-yl group.

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