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Preliminary communication

Oligomerization of thiophene in the presence of $PdCl_4^{2-}$

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Abstract

In the presence of $PdCl_4^{2-}$ in alcohol/water (2/1) solution, thiophene oligomerized to form α,α-coupled bithiophene while 2,2′-bithiophene oligomerized to form α,α-coupled tetrathiophene as the major products. In the case of thiophene, two unstable intermediates were isolated and characterized by ^{1}H NMR as η^1,C-bonded and η^5,π-bonded thiophene-palladium(II) complexes. The mechanism of α,α-coupling of thiophene is thus proposed.

Non-substituted thiophene-metal complexes have been of substantial interest to chemists recently, particularly in attempts to study the mechanism of the hydrodesulfurization (HDS) process, which involves reactions via C–S bond activation, and of thiophene oligomerization, which involves reactions via C–H bond activation. A few examples of η^1,S-bonded [1] and η^5,π-bonded [2] complexes of thiophene have been identified or proposed. The η^5,π-bonded complexes appear to be generally more stable than the η^1,S-bonded complexes. η^2-Complexes [3] and η^4-complexes have also been proposed [2h,3,4]. Although η^1,C-bonded thiophene complexes of main group metals have long been known, only a few η^1,C-bonded complexes of transition metal have been reported. [5]

Recently we have studied the oligomerization of thiophene in the presence of $PdCl_4^{2-}$ and successfully isolated two intermediates. Because these two intermediates are fairly unstable, we were unable to obtain sufficient data to characterize them fully at the present time; however the ^{1}H NMR data and the results of metal content analysis give some important information.

Thiophene reacts over 24 h with $PdCl_4^{2-}$ in an alcohol/water (2/1) solution at room temperature to give primarily α,α-coupled terthiophene and bithiophene products (3 : 1 product ratio). In the course of product separation, two unstable species were isolated by TLC. The ^{1}H NMR spectrum of the first species shows three doublet–doublet sets with equal intensity. In the ^{1}H NMR spectrum, the first doublet–doublet set appears at δ 7.27 ppm with coupling constants J 1.5 Hz and 5.4 Hz. The second set appears at δ 7.07 ppm with coupling constants J 1.5 Hz and 3.9 Hz. The third doublet–doublet set appears at δ 6.89 ppm with coupling constants J 3.9 Hz and 5.4 Hz. From the chemical shift and coupling constant data,

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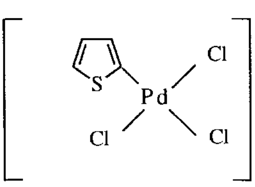
we can assign the double doublets to the thiophene protons on C-5, C-3, and C-4, respectively; a protonless substituent must be present on C-2. This species decompose gradually at room temperature even under nitrogen atmosphere to form 2,2′-bithiophene and palladium metal. Therefore, this species could be an intermediate, I or II, in bithiophene formation. However, an ICP-mass analysis of this species shows that it contains 18.38 ± 0.16% potassium and 25.15 ± 0.18% palladium. Therefore this species is the potassium salt of complex II.



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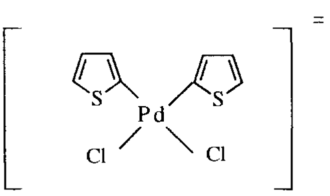
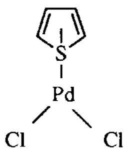


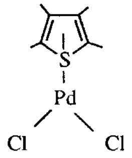
(I)

(II)

The ^{1}H NMR spectrum of the second unstable species shows two sets of multiplets with equal intensities at ~ 7.70 and 7.55 ppm. This species, containing 40.57 ± 0.32% palladium, decomposed gradually, only thiophene and palladium(II) chloride being recovered. Of several stable η^5,π-bonded thiophene complexes the NMR data were reported previously [2a,2b,2c,2e,2f,2g,2h]. It was found that thiophene complexes with a lower oxidation state metal center will cause the thiophene proton to shift up-field and those with a higher oxidation state metal center will cause the thiophene proton to shift down-field relative to uncoordinated thiophene, with proton resonances appearing at ~ 7.15 and 7.35 ppm. From the ^{1}H NMR chemical shift data and the decomposition products we conclude that the species could be an η^5-bonded thiophene-palladium complex (III). A similar complex (IV), which is stabilized by four methyl substituents on the thiophene, was prepared by Maithis in 1978 [2b].

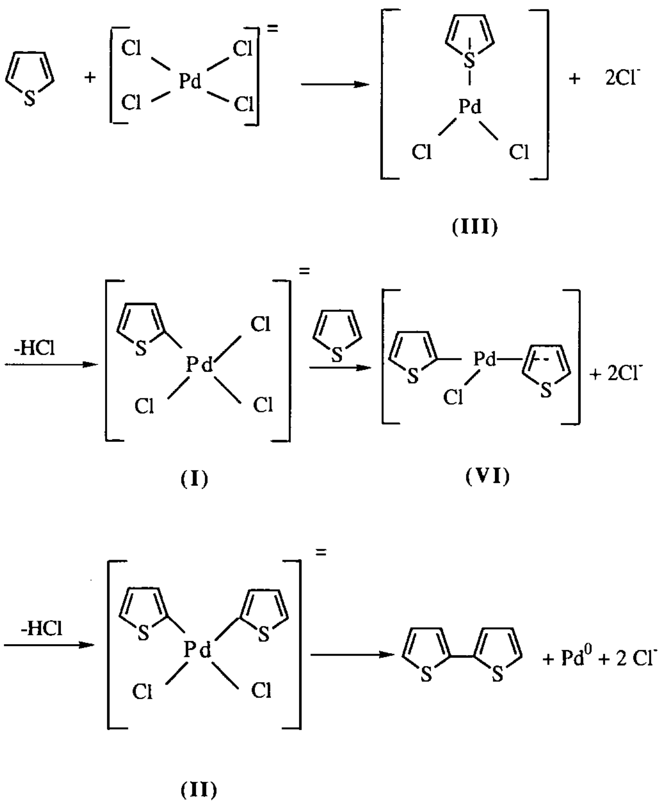


(III)



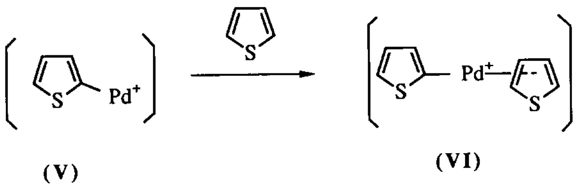
(IV)

In a typical reaction, 2.00 ml of thiophene (35.8 mmol) reacted with 0.5044 g (1.547 mmol) of K_2PdCl_4 in 50 ml of an ethanol/water (2/1) solution under nitrogen at room temperature for 24 hours. The reaction mixture was concentrated and extracted with chloroform. After the combined chloroform extract was concentrated, the reaction mixture was chromatographed with n-hexane on a 20 cm × 20 cm silica gel 60 plate (layer thickness 0.25 nm). 0.0540 g of 2,2′-bithiophene (0.325 mmol, 21.0% based on $PdCl_4^{2-}$) and 0.1324 g of α-coupled terthiophene (0.540 mmol, 69.9% based on $PdCl_4^{2-}$) were obtained as the two major products. Several minor products including trace amounts of α-coupled tetrathiophene (4.91 mg, 0.0263 mmol), palladium complex III (12.55 mg, 0.0298 mmol), and complex II (10.70 mg, 0.0312 mmol) were also isolated from the TLC plate.

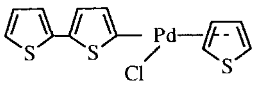


Scheme 1

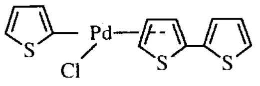
Rudakov and Ignatenko [6] have studied the coupling of thiophene in aqueous solution of palladium sulfate and palladium perchlorate and they suggested, from the kinetic isotope effects and the influence of acidity, that the coupling reaction should proceed through intermediates V and VI.



From these intermediates, we propose the mechanism for the coupling reaction of thiophene shown in Scheme 1. The 2,2′-bithiophene thus formed might react with $PdCl_4^{2-}$ further to form intermediate VII, or react with I to form another intermediate (VIII), which leads to terthiophene. In the thiophene coupling reaction, only trace amounts of α-tetrathiophene and the higher oligomers were found because an excess amount of thiophene was present and bithiophene is more bulky relative to thiophene. This steric effect is also found in the coupling reaction of 2,2′-bithiophene under the same conditions. The major product of this coupling reaction is α-tetrathiophene and the rate of coupling is slower than that in the thiophene case (50% yield based on $PdCl_4^{2-}$).



(VII)



(VIII)

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