

The addition of halogens and interhalogens on palladacyclopentadienyl complexes bearing quinolyl-thioether as spectator ligands. A kinetic and computational study



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ARTICLE INFO

Article history:

Received 17 February 2016

Accepted 6 April 2016

Available online 13 April 2016

Keywords:

Thioquinoline-palladiumcyclopentadienyl complexes

Kinetic study

Halogens

Interhalogens

Dienes extrusion

ABSTRACT

We have studied the oxidative addition of halogens (I_2 and Br_2) and interhalogens (ICl and IBr) on complexes of the type $[Pd(\text{thioquinoline})C_4(\text{COOMe})_4]$, (thioquinoline = 8-(methylthio)quinoline, 8-(*t*-butylthio)quinoline, 2-methyl-8-(methylthio)quinoline, 2-methyl-8-(*t*-butylthio)quinoline).

The expected palladium(thioquinoline)- σ -butadienyl derivatives have been obtained by the stoichiometric addition of I_2 and Br_2 to a solution of the starting palladacyclopentadienyl complexes. The bromine in excess induces the extrusion of the di-bromo-(*E*, *E*)- σ -butadiene and the formation of the thioquinoline palladium(II) di-bromide species. The kinetics and mechanism of these reactions have been determined.

Except for one case which was analyzed in detail by a computational study, the oxidative addition of the interhalogens ICl and IBr yields the species that is less predictable from the thermodynamic point of view. In general the computational approach justifies the reaction progress and allows an interpretative clue suggesting a kinetically governed path to the reaction products.

Finally, the solid state structures of two reaction products were resolved and reported.

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1. Introduction

Owing to their potential ability to give σ -butadienyl derivatives as the products of the oxidative addition of organic halides or halogens, palladacyclopentadienyl complexes have often been studied from the catalytic [1] and stoichiometric [2] point of view. The reaction entails the Pd(II)–Pd(IV)–Pd(II) conversion which was by far less studied than that involving the Pd(0)–Pd(II) process [3]. For such a reason we think that any attempts at shedding light on the still debated Pd(IV) intermediate should be of remarkable interest. Moreover, the possibility to obtain dienes with a *Z*–*Z* configuration by further addition of organic halides or halogens to the σ -butadienyl complexes extends the range of synthetic available methodologies based on acetylene coupling [4]. In this respect we have recently published three studies of the reactivity of some palladacyclopentadienyl complexes bearing isocyanides, phosphoquinolines and pyridylthioethers as ancillary ligands with halogens and interhalogens. In any case we have obtained interesting results. In the first study we have measured the rates of

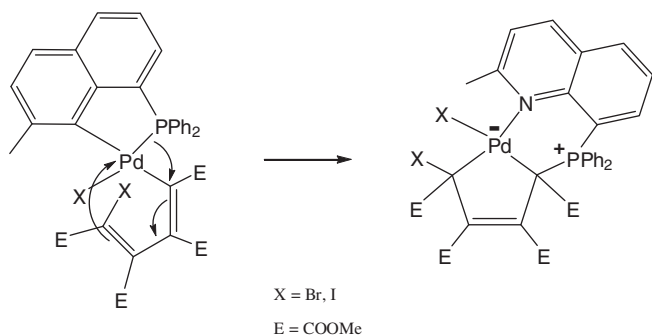
intramolecular conversion of the intermediate *trans*-diiodo palladium(IV) into the *cis*-diisocyanide-tetramethyl pallada-1-iodobuta-1,3-diene-1,2,3,4-tetracarboxylate and its subsequent isomerisation to the *trans*-isomer [2d]. The second investigation was characterized by the peculiar evolution of the initially formed σ -butadienyl complex, consisting in an intermolecular attack of the phosphorus originally coordinated to the metal on the sp^2 carbon of the σ -butadienyl fragment with the consequent widening of the phosphoquinoline coordinating ring and the unexpected final formation of a zwitterionic species (Scheme 1) [2e].

Finally, we have studied the palladacyclopentadienyl complexes bearing pyridylthioethers as spectator ligands reacting with halogens and interhalogens to give the σ -butadienyl derivatives as final products. However, in the case of interhalogens the final product was not the predictable one but rather the less thermodynamically stable species [2h].

The intriguing aspects of these studies prompted us to undertake a further investigation on palladacyclopentadienyl complexes bearing thio-quinoline based spectator ligands reacting with halogens and interhalogens. In the present study, we tried to establish how the combination between the structure of the ancillary ligand

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Scheme 1. Intermolecular attack of the phosphorus on the sp^2 carbon of the σ -butadienyl fragment and final formation of a zwitterionic species [2e].

and the sulfur atom might influence the overall reactivity of the complexes themselves and investigate whether the formation of the less stable σ -butadienyl and/or zwitterionic species can be considered a general trend. Furthermore, we have studied the kinetics in detail and surmised a plausible mechanism for the reaction between the σ -butadienyl complexes and Br_2 in excess leading to the extrusion of 1,4-dibromobuta-1,3-diene.

The ligands, the investigated complexes, the halogens, the interhalogens and the products of the oxidative addition are reported in Scheme 2.

2. Results and discussion

2.1. General remarks

The ligands TMQ, TTBQ [5], TMQ-Me [6], TTBQ-Me [7], the polymer $[PdC_4(COOMe)_4]_n$ [8] and complex **1c** [6] were obtained according to published protocols. The complexes **1a**, **b**, **d** are newly synthesized species and were obtained by adding a small excess of the appropriate ligand to the polymer $[PdC_4(COOMe)_4]_n$ under inert atmosphere in anhydrous acetone. The formation of the complexes **1a–d** is deduced from their NMR spectra which display all the signals of the ligands and carboxymethyl groups at different frequencies than those of the uncoordinated ones. In particular, owing to the ditopicity of the spectator ligands, the COOMe groups resonate as four distinct signals within 3.5–4.0 ppm (see Section 4 and Fig. 1 SM in Supplementary Material).

2.2. Reactivity of complexes **1a–d** with I_2 and Br_2

Addition under inert atmosphere of a stoichiometric amount of I_2 or Br_2 to a solution of complexes **1a–c** in anhydrous CH_2Cl_2 yields the (*Z*, *Z*)- σ -butadienyl derivatives **2a–d** or **3a–d**, respectively. The reactions are fast and complete as can be seen from the immediate decolorization of the reaction mixture. A stoichiometric amount of halogens is crucial since an excess especially in the case of Br_2 , might induce a further reaction with the extrusion of the 1,4-dihalobuta-1,3-diene (see later). The σ -butadienyl complexes **2a–d** and **3a–d** are stable and isolable and their structure is inferred from the 1H and ^{13}C NMR spectra in which again, all the signals of the starting complexes **1a–d** are detected at shifted frequencies. Remarkably, the position of the pyridine proton H^2 in the case of complexes **2a–b** and **3a–b** (ligands TMQ and TTBQ) and that of the terminal butadienyl carbon coordinated to the halide in all the formed complexes is particularly diagnostic [6,9a]. Therefore, the structure of the complexes is immediately recognized since the low-field resonance of the terminal butadienyl carbon (~ 100 ppm, X = I; ~ 150 ppm, X = Br), of the quinolinic H^2 (10.15–10.25 ppm, X = I; 9.85–9.96 ppm, X = Br) and to

a lesser extent of the pyridine methyl substituent (complexes **2c–d**, **3c–d**), indicate the exclusive formation the isomer bearing the halide *trans* to the pyridine nitrogen (see Scheme 2, Section 4 and Fig. 2 SM in Supplementary Material). Owing to the position of the σ -butadienyl fragment and the substituent at sulfur which can occupy the same or opposite side of the main plane of the complexes two rotamers (*exo* and *endo*) are possible. The existence of the rotamers in different concentration due to the different stability can be revealed by low temperature NMR, as can be seen in the spectrum of complex **2a** recorded at 223 K (see Fig. 3 SM in Supplementary Material). The isomeric choice (halide *cis* to pyridine nitrogen) and the existence of rotamers was confirmed by the resolved solid state structure of the *exo* rotamer of complex **3a** reported in Fig. 1 (the solid state structure will be discussed later).

In summary, the thioquinoline palladacyclopentadienyl complexes behave very similarly to the analogous pyridylthioether derivatives when reacting with halogens. In the Supplementary Material (Fig. 4 SM) we report the results of a computational study related to the energy involved in the above described reactions which parallels and confirms the results we and other authors have obtained in previously published articles [2b,2h]. In particular it is noteworthy that:

- (i) The σ -butadienyl derivatives are more stable than the starting reagents (Fig. 4a, b SM, [2b,2h]).
- (ii) The reactions of the palladacyclopentadienyl complexes with Br_2 are thermodynamically favored with respect to those with I_2 (Fig. 4a, b SM, [2b,2h]).
- (iii) Owing to the energy difference between the two possible isomers, the opening of the pentadienyl ring only occurs *trans* to the thioquinoline sulfur with the consequent formation of only one regioisomer (Fig. 4c, d SM, [2h]).

2.3. Reactivity of complexes **1a–d** with ICl and IBr

The thioquinoline derivatives react with the interhalogens ICl and IBr to give selectively the isomers bearing Cl and Br, respectively coordinated to palladium, whereas I is in any case obviously bound to the terminal dienyl carbon. Remarkably, the displacement of pentadienyl ring again takes place *trans* to the thioquinoline sulfur (see Scheme 2). Therefore, only one of the four possible isomers is obtained in any case considered and these findings confirm the previously observed results obtained with the pyridylthioether derivatives [2h].

The 1H NMR spectra of the complexes **4** and **5** confirms the nature of the isomers since the resonance of the quinolyl H^2 in the interval 9.64–9.74 and 9.85–9.96 ppm is typical of a complex bearing a chloride or bromide *cis* to quinoline ring, respectively. [[2h] and Refs. therein] (see also Section 4 and Fig. 6 SM in Supplementary Material section). Moreover the ^{13}C low-field resonance of the terminal butadienyl carbon at ca. 100 ppm ($=C-I$) is a further indication that the complexes with the bromide or chloride coordinated to palladium are formed.

In the case of complex **4a** we were able to obtain crystals suitable for a diffractometric determination of its solid state structure which is reported in Fig. 2. Again, the structure will be discussed further on.

The regioisomers **4a–d** are stable and isolable and a slow isomerization process is detectable only after different but in any case significant time intervals.

As for the derivatives obtained by adding IBr to **1a–d** complexes, only the species **5a**, **b**, **d** can be separated pure from the reaction mixture. However the latter display an enhanced tendency to isomerise to the most stable isomer (*i.e.* with I

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