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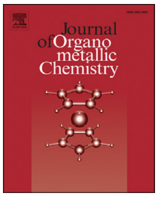

Addition of halogens and interhalogens on palladacyclopentadienyl complexes stabilized by pyridyl–thioether N–S spectator ligands

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ABSTRACT

We have studied from the experimental and theoretical point of view the oxidative addition of halogens (I_2 and Br_2) and interhalogens (ICl and IBr) on palladiumcyclopentadienyl complexes bearing heteroditopic pyridyl–thioether spectator ligands.

Addition of I_2 or of a stoichiometric amount of Br_2 to a $CDCl_3$ solution of the starting palladacyclopentadienyl complexes yields the expected palladium–σ–butadienyl derivatives. The bromide derivative in the presence of a further excess of Br_2 gives the wanted dibromo–(E, E)–σ–butadienyl and the pyridylthioether palladium(II) dibromide species. The rates of these reactions have been determined.

When the interhalogens are used as oxidizing agents the thermodynamically hampered species is formed at first. Only in the case of the reaction of IBr is the formation of the energetically hampered derivative followed by partial isomerization to the most stable complex. The rate of isomerization and the related equilibrium constant between isomers have been measured. On the basis of the experimental evidence and the computational approach we have proposed a plausible energetic path yielding the first formed unexpected species.

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

1. Introduction

The ease and versatility characterizing the Pd(0)/Pd(II) catalyzed cross coupling reactions have promoted in the past decade a number of studies, as witnessed by the available vast literature [1]. Conversely, the redox reactions involving the Pd(II)–Pd(IV)–Pd(II) conversions have been less investigated and are usually limited to the addition of halogens or organic halides in catalytic [2] or stoichiometric [3] processes often yielding conjugated dienes as their final products.

The conjugated dienes are important compounds contained in many natural and bioactive products. In this respect, some synthetic approaches based on catalytic protocols involving palladium complexes have been developed [4]. We are deeply interested in the mechanistic features of reactions involving Pd(IV) intermediates which in our opinion still represent a promising field worth of detailed investigations [3d-e]. As a matter of fact, a thorough knowledge on the nature of the cited elusive intermediates can give a marked impulse to the design of new Pd(II)/Pd(IV) catalytic cycles [2c], although from the original articles of Canty [5] new advances in the isolation of stable Pd(IV) species were achieved [2c and Refs. therein].

Palladacyclopentadienyl derivatives bearing different spectator ligands have been often studied owing to their potential capability to give σ–butadienyl derivatives and thence conjugated dienes [2–3,6]. In particular, our group has recently focused its interest on the oxidative attack of di–halogens on palladacyclopentadienyl complexes with monodentate isocyanides [3d] and phosphoquinoline [3e] as ancillary ligands. In the latter case, the peculiarity of the reaction course resulting in an unexpected widening of the coordinative ring drove us to extend our investigation to the oxidative reactions of halogens and inter-halogens on palladacyclopentadienyl derivatives bearing pyridylthioethers as spectator ligands. Moreover, for the sake of completeness, we have investigated the displacement of the halide-substituted conjugated dienes by exhaustive oxidative elimination of the starting complexes with

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bromine in excess. We have therefore tried to determine how the structure of the well known pyridylthioether ancillary ligands could affect the reaction rate since it was often shown that the overall reactivity of the pyridylthioether derivatives is strongly influenced by the electronic and steric properties imparted by the substituents to the ancillary ligands themselves [6g,7]. The ligands, the complexes and the reactions described in the present paper are reported in the following Scheme 1.

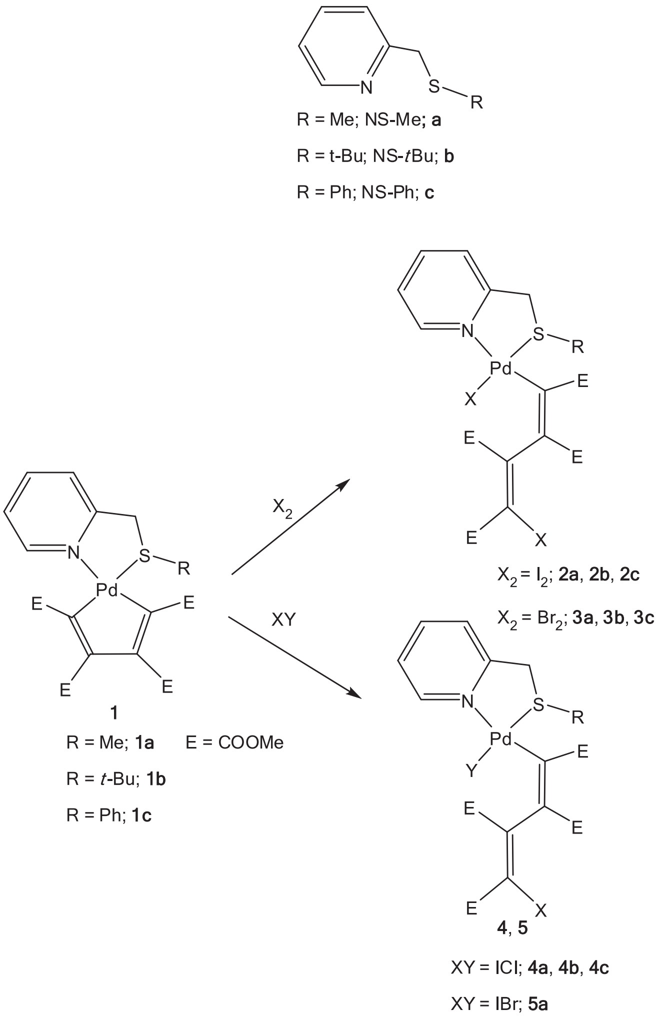
2. Results and discussion

2.1. General considerations

The ligands NS-R (R = Me, *t*-Bu, Ph) [7] and the complexes **1a**–**c** [8], were obtained according to published protocols by adding the appropriate ligand to the polymer $[PdC_4(COOMe)_4]_n$ [9]. The complexes **2a**–**c**, **3a**–**c**, **4a**–**c** and **5a** are newly synthesized compounds.

2.2. Reactions of complexes **1a**–**c** with I_2

Addition under inert atmosphere (Ar) of a slight excess of I_2 to a solution of complexes **1a**–**c** in anhydrous CH_2Cl_2 yields the (E, E)–σ–butadienyl derivatives **2a**–**c**. The reactions are fast and complete and proceed through two steps consisting in the formation of the Pd(IV) intermediate bearing two apical iodides followed by reductive elimination with the consequent opening of the cyclopentadienyl ring and formation of the σ–butadienyl derivatives [3b]. All the σ–butadienyl complexes are stable and isolable, although in the presence of excess iodine ($[$**2a**–**c**$]/[I_2] = 1/10$) a further and very slow reaction yielding the free 1,4–diiodobuta–1,3–diene (DIBD) and the $[Pd(NS\text{-}R)I_2]$ complexes occurs ($t_{1/2} \approx 4$ months).



Scheme 1. Ligands, starting complexes, halogens, interhalogens and reaction products.

The structure of complexes **2a**–**c** can be deduced on the basis of their ^1H and ^{13}C NMR spectra and from analogy with the spectra of similar σ-butadienyl derivatives [3e,7c]. In particular, the σ–coordinated butadienyl fragment is identified by the presence of four signals ascribable to $COOC\underline{H}_3$ protons resonating at different frequencies of the same groups of the original palladacyclopentadienyl species (Fig. 1SI in Supplementary). Moreover, the iodide coordinated to palladium induces a remarkable down-field shift of the *ortho* proton of the pyridine ring of the pyridylthioether ligands which resonates at ca. 9.6 ppm.

The structure of complexes **2a**–**c** was also identified by the ^{13}C NMR spectra recorded at RT since the four different carbons of the $-O\underline{C}H_3$, $\underline{C}O$ and $\underline{C}=\underline{C}$ groups resonate at very different frequencies from those of the cyclopalladate derivative precursors. Moreover, the terminal butadienyl carbon bound to iodide is particularly diagnostic owing to its low field resonance (ca. 100 ppm) (See Experimental and Fig. 2 SM in Supplementary material).

The resonance of the *ortho* pyridine proton (9.6 ppm) represents a marker identifying the structure of only one of the two possible geometric isomers. It is worth noting that a similar chemical shift was always detected in all the palladium complexes bearing a halide *cis* to the pyridine nitrogen of the ancillary ligands [6g,7a]. The formation of the uniquely observable isomer is strictly correlated to the sulfur *trans*–influence which is higher than that of nitrogen. The sulfur *trans*–influence determines the position of the cyclopentadienyl ring opening and consequently the formation of only the derivatives **2a**–**c** (see Scheme 1). The displacement of the carbon *trans* to sulfur by iodide is also responsible for the observed diastereotopicity at RT of the $C\underline{H}_2-S$ protons of the complexes **2a** and **2b**. The reduced *trans*–influence of iodide with respect to carbon renders the Pd–S bond of complexes **2a** and **2b** stronger than that of complexes **1a**–**c**. Consequently the rate of inversion of the sulfur absolute configuration [10] slows down [7c] (Fig. 1 SM in Supplementary material). An exception is represented by the $C\underline{H}_2S$ protons of the complex **2c**. This complex, bearing an electron-withdrawing phenyl group coordinated to sulfur, does not display similar behavior owing to the reduced strength of the Pd–S bond. Therefore complex **2c** behaves as complexes **1a**–**c** and its $C\underline{H}_2S$ protons resonate as a singlet at RT.

The low temperature NMR spectra of complexes **2** deserve a further comment. Owing to the perpendicular position of the σ–butadienyl fragment and that of the sulfur substituents which can be on the same or opposite side with respect to the main coordination plane [7c], the presence in solution of the *endo* and *exo* isomers can be detected from the splitting of the several signals at low temperature (Fig. 1).

The isomeric distribution of complex **2b** is strongly unbalanced (15/1), the *exo* being the less hindered and therefore the most probable isomer, owing to the steric interference exerted by the bulky *t*–Bu group.

2.3. Reactions of complexes **1a**–**c** with Br_2

Addition of a stoichiometric amount of bromine to complexes **1a**–**c** yields derivatives **3a**–**c**. In this case, however, the concentration of bromine is crucial since an excess causes a further reaction of the complexes **3a**–**c** (see later).

The ^1H and ^{13}C NMR spectra of the complexes **3a**–**c** are easily