Journal of Organometallic Chemistry 749 (2014) 379–386

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Low valent palladium benzoquinone complexes bearing different spectator ligands. The versatile coordinative capability of benzoquinone

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ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form
10 October 2013
Accepted 11 October 2013

Keywords:
Palladium olefin complexes
Benzoquinone hapticity
Olefins exchange equilibria

ABSTRACT

The synthesis of some benzoquinone palladium complexes bearing different spectator ligands was carried out and the hapticity of the coordinated olefin was inferred from the features of their ^1H and ^{13}C NMR spectra. It was shown that benzoquinone coordinates either η^2 and η^4 and that its coordinative choice is not easily predictable, although the η^2 coordination seems to be predominant in the presence of rigid ancillary ligands. The coordinative capability of benzoquinone was tested by means of thermodynamic and kinetic reference reactions and its slightly enhanced inertness with respect to the isofunctional naphthoquinone was assessed. Finally, the re-crystallization by slow diffusion at low temperature of diethylether in a dichloromethane solution of the complex $[Pd(\eta^2\text{-bq})(TTbQ\text{-}Me)]$ (bq = benzoquinone, TTbQMe = 8-*t*-Butylsulfanyl-2-methyl-quinoline) allows the separation of the dimer $[Pd_2(\eta^2\text{-bq})(TTbQ\text{-}Me)_2]$ whose solid state structure was resolved.

1. Introduction

The Pd(0) olefin derivatives are of paramount importance among all the palladium catalysts since they represent or are often identified as the active catalytic species in a variety of cross-coupling reactions [1]. On the basis of the original work of Dewar and Chatt and Duncanson [2] the palladium(0)–olefin bond was extensively studied from theoretical, structural [3], and synthetic points of view [4]. In particular, our group have in some cases measured the degree of stability imparted to the palladium(0) complexes by different olefins. The evaluation of the stability was based on the equilibrium constant of the direct exchange between olefins according to the following reaction [5a,b]:

$$\left[Pd\left(\eta^2-ol_1\right)(L-L')\right] + ol_2 \rightleftharpoons \left[Pd\left(\eta^2-ol_2\right)(L-L')\right] + ol_1 \qquad (1)$$

A summary of the general results suggesting a comprehensive order of coordinative properties of the most used electron-poor olefins based on the complex $[Pd(\eta^2\text{-nq})(Neocup)]$ (nq = naphthoquinone; Neocup = neocuproine) together with an indication of the dependence of such an order on the nature of the ancillary ligands, was recently reported [6]. Finally a general overview on the features of the Pd(0) olefin derivatives bearing labile or hemilabile spectator ligands was reviewed [7]. However, among the number of studied complexes the benzoquinone derivatives are not very abundant [8] and no quantitative data on its coordinative capability can be found in the literature. This fact probably depends on the nature of benzoquinone whose hapticity might be either η^2 or η^4 and consequently, formation of dimeric [8c] or oligomeric species via the unengaged olefinic vinylic bond cannot be excluded *a priori* [8e]. Moreover a further complication can arise from the fact that benzoquinone and its isofunctional naphthoquinone can give dimeric oxygen bridged species [8d]. We therefore decided to prepare some palladium(0) complexes with benzoquinone with the aim of setting its coordinative capability in the rank of the olefin stability order so far assessed [6] and understanding the structural features of the synthesized derivatives. The benzo- and naphthoquinone palladium complexes we have prepared are reported in the following Scheme 1.

2. Results and discussion

2.1. General considerations

The palladium(0) olefin complexes were obtained according to protocol (a) of Ref. [7] by the concomitant addition of the appropriate alkene (ol) and ligand (L–L′) to Pd_2DBA_3 [9] in anhydrous

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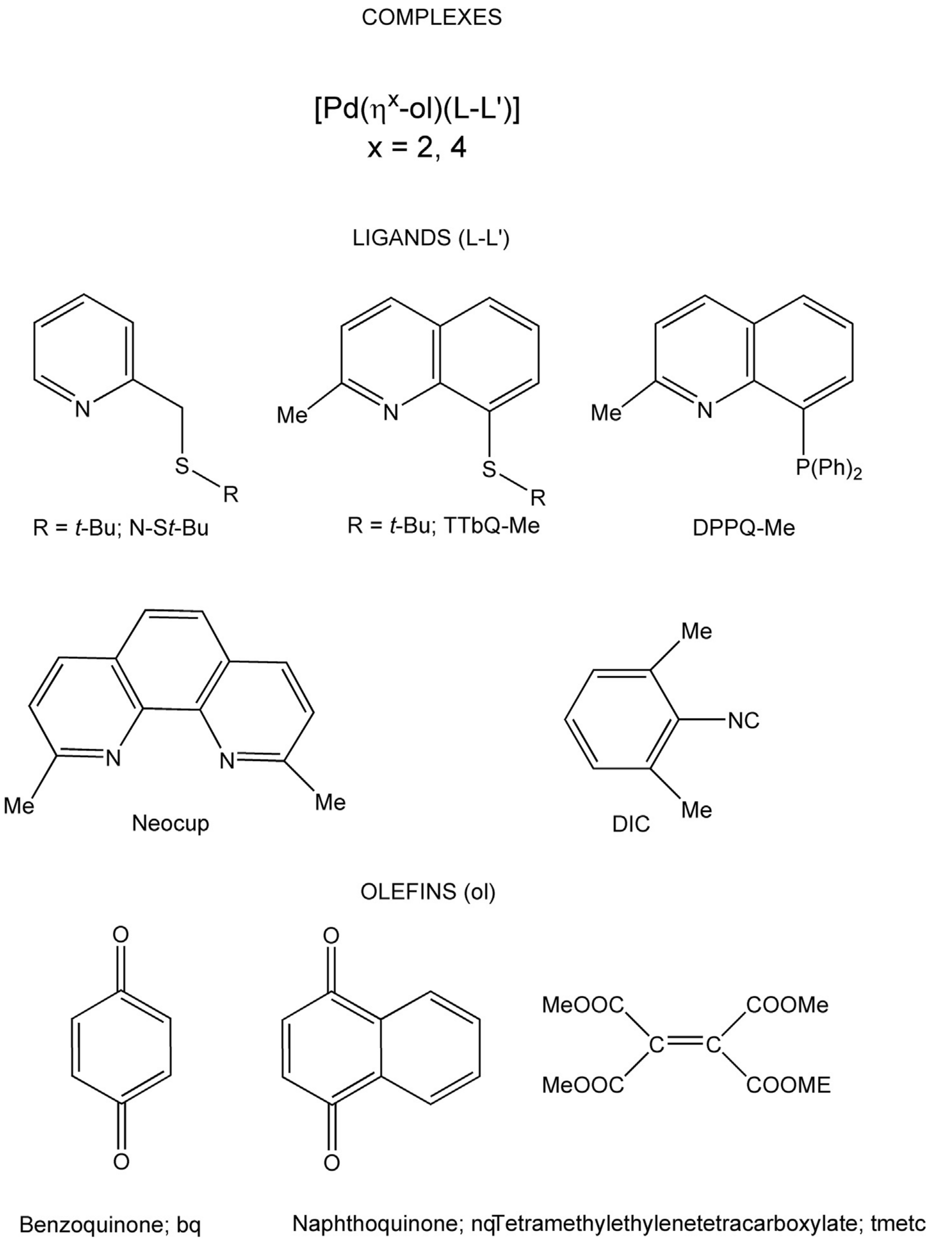
http://dx.doi.org/10.1016/j.jorganchem.2013.10.021



Scheme 1. Ligands and complexes synthesized and studied.

acetone under inert atmosphere (Ar), in the dark. The formation of the complexes was unequivocally apparent by comparison of their ^{1}H and ^{13}C NMR spectra with those of the free olefins and from their IR spectra. As a consequence of the marked metal–olefin back donation the chemical shifts of the protons and carbons of the coordinated olefins resonate at 1–2.5 and 40–80 ppm upfield with respect to the uncoordinated alkenes, respectively. Moreover, in the IR spectra of the Pd(0) derivatives the $\nu_{C=O}$ stretching are shifted at lower frequencies than those of the uncoordinated quinones ($\Delta\nu_{C=O} = 25 \div 30$ cm^{-1}).

2.2. *Complex [Pd(η^4-bq)(N–St-Bu)]*

We have firstly investigated the reaction between the flexible ligand N–St-Bu, the complex Pd_2DBA_3 and benzoquinone. The $CDCl_3$ ^{1}H NMR spectrum at 298 K of the isolated red compound indicated an equimolecular ratio between the N–St-Bu ligand and benzoquinone with the signal of the $C\underline{H}_2$-S system and of the four olefinic protons resonating as a singlet at 4.12 ppm and as an AB system centered at 5.63 ppm, respectively (Fig. 1a). Consistently, the olefinic carbons in the RT ^{13}C NMR spectrum resonate as a couple of signals at 100.0 and 103.8 ppm (Fig. 1b). Both NMR spectra can be explained by invoking the coordination of the olefin and the rapid inversion of the sulfur configuration of the pyridylthioether ligand. It is well known that the rapid inversion of the sulfur configuration can often be frozen [10] and therefore it might be possible to obtain some Supplementary information about the structure of the complexes by lowering the temperature. In Fig. 1c and d the low temperature (193 K) ^{1}H and ^{13}C NMR spectra of the complex are reported and in particular in Fig. 1c an AB system related to the diastereotopic $C\underline{H}_2$-S thioetheric protons can be detected at 4.12 ppm. This suggests that at 193 K the position of the