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Synthesis of novel olefin complexes of palladium(0) bearing monodentate NHC, phosphine and isocyanide spectator ligands

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ABSTRACT

We have synthesized and characterized seventeen new bis-NHC, mixed NHC–phosphines or NHC–isocyanides Pd(0) olefin complexes that can potentially act as catalysts. The complexes were characterized by standard spectroscopic methods and elemental analysis and in two cases by SC-XRD technique. We have analyzed with particular care the thermodynamic and kinetic conditions governing the one-pot synthesis of the mixed complexes. In this respect we tried to validate our results by a dedicated computational study on the mutual distribution of the isomers that could be potentially formed. However, the computational result is not clear-cut owing to the not significant value of the calculated ΔG_0. Finally, in one case we have measured the rate of the exchange reaction between not particularly encumbered olefins.

1. Introduction

Owing to their stability toward heat, moisture and air and their low toxicity [1], NHC ligands have been quite recently recognized as the real alternative to phosphines in the preparation of stable palladium catalysts [2]. Since the discovery [3] and the synthesis of the first stable NHC derivatives [4] the easy tune-up of the steric hindrance of the substituents at the imidazolic nitrogen [5] has allowed their detailed synthetic planning.

In addition, owing to the easy shift between the two reasonably stable oxidation states Pd(0) and Pd(II) [6], the use of palladium derivatives as homogeneous catalysts particularly in the field of the homo- and hetero-cross coupling is widespread [7]. Obviously, the performance of the catalyst can be improved by a wise structural planning which should induce a remarkable reactivity and an adequate stability throughout the turnover processes. A possible solution overcoming these conflicting features might be the synthesis of a Pd(0) pro-catalyst characterized by an easily displaceable olefin and stabilized by strong ligands. In such a way the labile olefin should promote the oxidative addition of organic halides, thereby triggering the overall catalytic process.

The characteristics of the palladium–olefin bond is clearly crucial since it represents a balance between the thermodynamic stability of the catalyst and its reactivity which is often kinetically controlled. [8].

In this respect, we have prepared and fully characterized a number of palladium(0) olefin bis-NHC, mixed NHC-phosphines or NHC-isocyanides derivatives to be tested as catalysts in future investigations. Notably, the one-pot synthesis of complexes bearing two different spectator ligands represents a remarkable and not trivial synthetic challenge, beside allowing the fine tuning of the electronic and steric features of the derivatives which are very important in planning catalysts [9]. We already came across a similar problem in the case of Pd(II) [10] and therefore we decide to extend our investigation to Pd(0) derivatives. In the following Scheme 1 we report the olefins and the starting thiopyridine palladium and silver carbene complexes described in the present paper.

2. Results and discussion

2.1. General remarks

The complexes **1a-d** [11], **1e**, **5a** [12], **3** and **4** [13] were synthesized according to published procedures. The preparation of the imidaziolium salt 1,3-bis(4-methylbenzyl)-2,3-dihydro-1*H*-imidazole bromide and its derivative **2** will be described in Section 4.

2.2. Bis-carbene complexes

In a previous paper [14] we have reported the synthesis and characterization of some palladium (0) bis-carbene complexes stabilized by maleic anhydride. It was apparent that the steric request of the carbene ligands and the nature of the starting palladium

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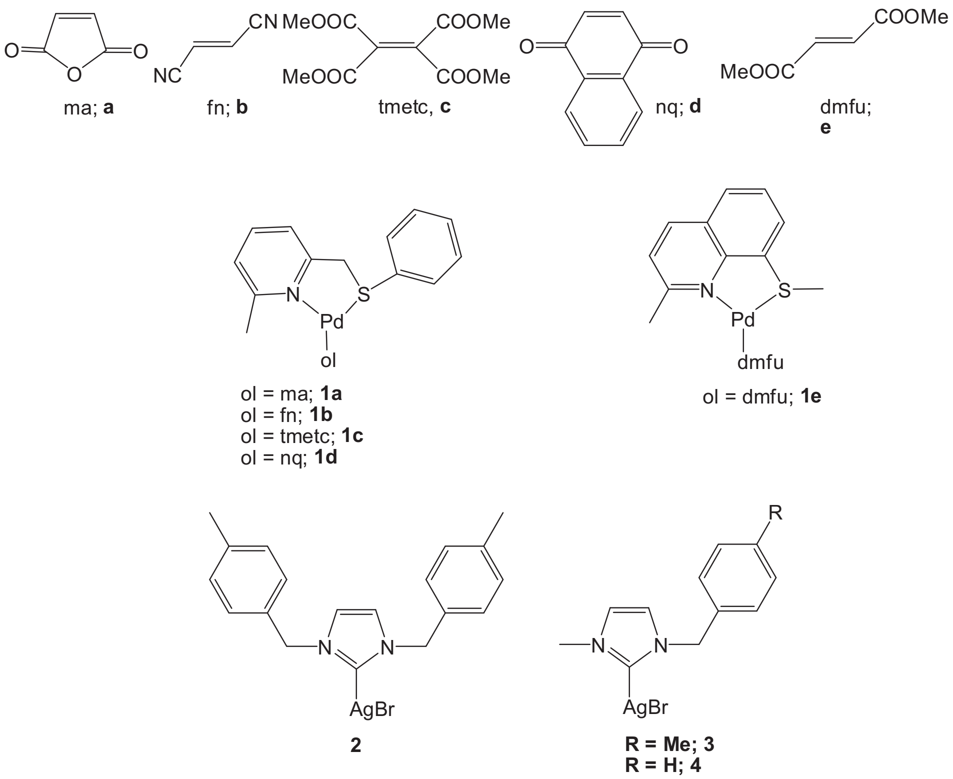

Scheme 1. Starting ligands and silver carbene complexes.

complexes did represent the critical point in the planning of the synthesis [10]. For such a reason, in order to carry out the transmetalation process, we have chosen derivative **2** (^{1}H and ^{13}C{^{1}H} NMR spectrum in Fig. S1, Supplementary Material) and the complexes **1a–d** as the palladium reactive species. As a matter of fact, on the basis of our experience, [14] the encumbered complex **2** could still react with derivatives **1a–d** characterized by the lability of the 2-methyl-6-(phenylthiomethyl)pyridine ligand to give the bis carbene species **5a–d** [15]. The process yielding the derivatives **5b–d** is fast (10 min in the case of the most hindered **5c**) and the precipitation of AgBr indicates an almost immediate reaction. The ^{1}H NMR spectra of the complexes clearly point to the coordination of the olefin whose protons resonate as a singlet thanks to the equivalence of the ancillary ligands and at higher field than those of the uncoordinated alkenes. Such a feature is also confirmed by the ^{13}C {^{1}H} NMR spectra of the complexes displaying a marked upfield singlet ($\Delta\delta = 70 \div 100$ ppm) ascribable to the coordinated olefinic carbons. As for the carbene, the AB system related to the $C\underline{H}_2N$ and the signals of the coordinated carbon at about 190 ppm are clearly observable. The consistent elemental analysis and the IR spectra complete the characterization of such species (see Section 4 and Fig. S2 in Supplementary Material).

2.3. Mixed complexes, general considerations

The direct synthesis of square planar complexes bearing two different monodentate spectator ligands is not always obvious. In order to obtain pure mixed species not contaminated by derivatives bearing the same two ancillary ligands it is necessary to meet a specific energetic condition. In particular the ΔG° of formation of the heteroleptic species must be reasonably lower than the ΔG° of formation of both the two species bearing the same ligands and therefore the thermodynamics of formation of the heteroleptic complex is crucial. In this respect it was suggested that such a condition can be obtained by the use of strong ligands possibly exerting an extra-stabilizing push and pull effect [9]. However, as was suggested in the case of palladium(II) derivatives, the kinetic aspect of the problem is not always negligible as can be deduced from the reactions describing the whole process [10a] summarized in Scheme 2:

As a matter of fact, under favorable thermodynamic condition we can have different results as a function of different combinations of the rates of the reaction reported in Scheme 2.

In this respect, it is worth noting that the processes involving the complex AgBrNHC are strongly conditioned by the complex nature of the transmetalation reaction [16] and therefore reaction 1, which does not concern the transmetalation process but rather the exchange between ligands, is very probably the fastest one [10a,11a] (see Scheme 3).

Under this hypothesis we can envisage four different possibilities:

(i) Reaction 3 is faster than reaction 2. In this case we will observe the formation of the mixed complex only.
(ii) Reaction 2 is faster than reaction 3 and reaction 4 does not occur. In this case we will obtain the two bis-substituted species [$L_2Pd(\eta^2$-ol)] and [$(NHC)_2Pd(\eta^2$-ol)].
(iii) The rate of reaction 3 is comparable with that of reaction 2 and reaction 4 does not occur. We will obtain all the species, *i.e.* two bis-substituted and one heteroleptic species in variable concentrations.
(iv) *Reaction 4* occurs, the final species obtained will be again the mixed complex only independently of the rate of the reaction.

In order to verify whether the behavior observed in the case of Pd(II) complexes is generally valid, we tried to synthesize by direct