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Note

Kinetic investigation of a PC(sp^3)P pincer palladium (II) complex in the Heck reaction

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Abstract

An investigation of the kinetics of the Heck reaction between 4-iodoanisole and styrene catalysed by {*cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]-cyclohexane} palladium (II) iodide (**1**) has been performed in DMF-d_7 solution. Based on mercury poisoning experiments a heterogeneous palladium catalyst formed from the $PC_{sp^3}P$ Pd(II) pre-catalyst is proposed. Saturation behaviour with respect to the olefin concentration suggests a mechanism consisting of a pre-equilibrium association of the olefin followed by a rate determining reaction with aryl halide. The equilibrium constant for the olefin association, K_1, and the rate constant for the subsequent oxidative addition step, k_2, were determined to $(5.7 \pm 2.5) \times 10^{-3}$ and $18.4 \pm 2.7\ M^{-1}\ s^{-1}$, respectively.

Keywords: Palladium; Pincer complexes; Heck reaction; Kinetics; Heterogeneous catalysis

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1. Introduction

Carbon–carbon bond coupling reactions have become one of the most important tools in organic synthesis [1]. Among these the palladium-catalysed vinylation of aryl halides, the so-called Heck-reaction, occupies a prominent position since it involves functionalisation of a C–H bond [2].

Since the early work by Moulton and Shaw [3], cyclometallated phosphine-based pincer ligands have developed into powerful and important ligands for organometallic catalysts in C–C bond forming reactions [4–7]. In 1997, Milstein and co-workers [8] found that PCP pincer complexes could be applied as catalysts in the Heck reaction under aerobic conditions without degradation of the catalyst. This observation has inspired many others since pincer-based metal complexes seem to strike a unique balance of stability *vs.* reactivity. Thus, they have been applied in a large number of interesting reactions such as dehydrogenation [9], Karasch addition [10,11], ketone reduction [12], asymmetric aldol [13,14] and Heck reaction [8,15–18]. Recently, we also reported on the application of PCP pincer complexes in the Stille cross-coupling reaction [19].

In the large majority of cases the PCP backbone consists of an aromatic ring and only a few complexes with an aliphatic backbone, i.e., $PC_{sp^3}P$ pincer complexes, have been reported. The catalytic activity of such $PC_{sp^3}P$ pincer complexes has been investigated by Milstein and co-workers [8] and in our laboratory [18]. The general conclusion has been that an increased electron density on the metal centre, caused by coordination of an sp^3 carbon instead of an sp^2 carbon, increases the catalytic activity [8,18,20].

The mechanism of operation and the nature of the ECE complexes in catalysis is the subject of some debate [21]. Beside the classical Pd(0)/Pd(II) cycle [4,22–26] several authors have reported the involvement of a Pd(II)/Pd(IV) cycle [8,27,28]. Recently a study of a

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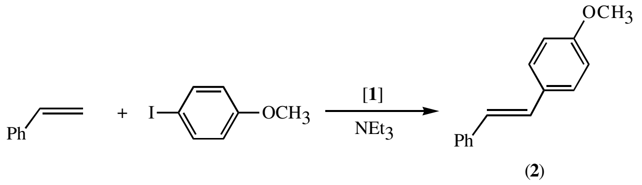

Scheme 1.

ditopic double pincer palladacycle with SCS pincer coordination was reported [29] and it was concluded that the reaction most probably is homogeneous. On the other hand, in our work on the Stille reaction [19], we concluded that the reaction is heterogeneous and that the PCP complexes only act as a source for catalytically active metallic palladium species. Eberhard reached the same conclusion in his work on the Heck reaction catalyzed by a series of PCP complexes with phosphite functionalities [30].

Thus, there seems to be no unanimous picture of the mechanistic role of pincer complexes in these reactions, and we decided to investigate this feature, using the $PC_{sp^3}P$ pincer complexes with their reported higher activity and thermal robustness. Here, we report a kinetic and mechanistic investigation of the catalytic reaction between styrene and 4-iodoanisole in DMF-d_7 solution using the $PC_{sp^3}P$ complex {*cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexane}–palladium (II) iodide (**1**) as catalyst in the Heck reaction, cf. Scheme 1.

2. Experimental

2.1. General procedures and materials

All experiments were carried out using standard high-vacuum line or Schlenk techniques or in a glove box under nitrogen. If nothing else is stated all commercially available reagents were used as received from Aldrich. Styrene was distilled from CaH_2 and stored in the glove box at −25 °C to prevent polymerisation. The complex {*cis*-1,3-bis[(di-*tert*-butylphosphino)methyl]cyclohexane} palladium (II) iodide (**1**) was prepared as described earlier [18]. All stock solutions were prepared and stored under nitrogen.

2.2. NMR measurements

The NMR spectroscopic measurements were performed in DMF-d_7 unless otherwise stated. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz (^1H). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^1H-, ^{13}C NMR) or H_3PO_4 as reference. J. Young NMR-tubes were purchased from J. Young (Scientific Glassware) Ltd.

2.3. Preparation of trans-(4-methoxyphenyl)-2-phenylethylene (2)

A J. Young NMR-tube was charged with 1.0 μL (8.0×10^{-6} mol) 4-bromoanisole and 1.0 μL (8.7×10^{-6} mol) styrene together with 1 mL DMF-d_7. Approximately one equivalent of complex **1** was dissolved in 0.500 mL DMF-d_7 and this solution was added to the NMR-tube. 9.7 mg (9.2×10^{-5} mol) of Na_2CO_3 was added and the reaction solution was heated to 160 °C. After 2 h an iodo for bromo substitution in complex **1** (to give the corresponding bromo-complex) was complete as indicated by ^{31}P NMR spectroscopy. After another 18 h at 160 °C a total consumption of the organic starting material was seen and 1 mL 20% HCl (aq) was added, leading to the formation of a white precipitatate. Extraction with diethylether and evaporation under reduced pressure gave an off-white crystalline product. The yield was 1.4 mg (6.6×10^{-6} mol, 83%) and the NMR signals were in accordance with the literature data for compound **2** [31]. ^1H NMR (DMF-d_7): δ 3.84 (s, 3H, C*H*3), 7.00 (d, $^3J_{H–H} = 8.5$ Hz, 2H, *m*-H, *Ph*–OMe), 7.17 (d,$^3J_{H–H} = 16.5$ Hz, 1H, C*H*), 7.25 (t,$^3J_{H–H} = 8.0$ Hz, 1H, *p*-H, *Ph*), 7.27 (d,$^3J_{H–H} = 16.5$ Hz, 1H, C*H*), 7.38 (t,$^3J_{H–H} = 8.0$ Hz, 2H, *m*-H, *Ph*–OMe), 7.60 (d,$^3J_{H–H} = 8.5$ Hz, 2H, *o*-H, *Ph*), 7.61 (d, $^3J_{H–H} = 8.0$ Hz, 2H, *o*-H, *Ph*).

2.4. Kinetic investigations

The kinetics of the catalytic reaction was studied using ^1H NMR spectroscopy. All equipment was rinsed with aqua regia prior to use. In a typical experiment, a J. Young NMR-tube was loaded with **1**, 4-iodoanisole, styrene, Et_3N, internal standard and solvent and placed in an oil bath at 160 °C. The reaction was monitored by ^1H NMR spectroscopy. The product was not separated and isolated, but characterized in situ. Ferrocene was used as internal standard, and all reactions were studied under pseudo-first-order conditions with an excess of the olefin (0.05–1.05 mol dm^{-3}) with respect to the aryl iodide ($(8.04–8.11) \times 10^{-3}$ mol dm^{-3}). To assure catalytic reaction conditions the concentration of the palladium (II) complex was at least one order of magnitude less ($(0.04–0.79) \times 10^{-3}$ mol dm^{-3}) than that of styrene and 4-iodoanisole. Stock solutions of all reagents in DMF-d_7 were used, except for the Et_3N, which was administered as received. Inhibition experiments were performed by adding approximately 0.1 g (5×10^{-4} mol) of elemental mercury to the reaction mixture [32,33]. In addition, experiments using cyclooctatetraene (COT) as catalyst inhibitor were also performed [34]. The amount of COT was approximately in 5-fold excess (0.35×10^{-3} mol dm^{-3}) relative to the amount of the catalyst (0.07×10^{-3} mol dm^{-3}), and was added at the start of the reaction. The ^1H NMR signals were