

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 $\{cis\text{-}1,3\text{-bis}[(di\text{-}tert\text{-}butyl\text{-}phosphino)methyl]\text{-cyclohexane}\}$ palladium (II) iodide (**1**) has been performed in $DMF\text{-}d_7$ 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.

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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].

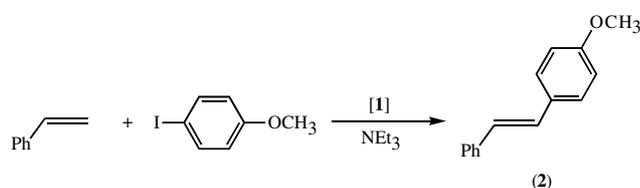
Since the early work by Moulton and Shaw [3], cyclometallated phosphine-based pincer ligands have developed into powerful and important ligands for organometallic catalysts in C–C bond forming reactions [4–7]. In 1997, Milstein and co-workers [8] found that PCP pincer complexes could be applied as catalysts 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}³P 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}³P 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 CaH₂ 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, ¹³C and ³¹P 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-, ¹³C NMR) or H₃PO₄ 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 Na₂CO₃ 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 ³¹P 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 precipitate. 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, CH₃), 7.00 (d, ³J_{H-H} = 8.5 Hz, 2H, *m*-H, Ph-OMe), 7.17 (d, ³J_{H-H} = 16.5 Hz, 1H, CH), 7.25 (t, ³J_{H-H} = 8.0 Hz, 1H, *p*-H, Ph), 7.27 (d, ³J_{H-H} = 16.5 Hz, 1H, CH), 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, Et₃N, 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) × 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) × 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 Et₃N, 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

integrated generating kinetic traces, which were fitted to single exponentials using the KaleidaGraph software.

3. Results and discussion

3.1. General observations

The β -substituted styrene **2** was isolated in 83% yield in the coupling reaction between 4-bromoanisole and styrene using **1** as catalyst. The only product observed was the E-isomer, and there was no indication of any other regio- or stereo isomer. We have earlier reported that the coupling between PhI and styrene catalysed by **1** (as the trifluoroacetate complex) has a regioselectivity of approximately 90% in favour of the E-isomer. The NMR data of **2** reported in the literature are rather brief and in agreement with our findings [31]. We were able to assign all peaks in the ^1H NMR spectrum and the trans configuration is most clearly seen in the large olefinic coupling constant (16.5 Hz), vide supra.

The fate of complex **1** in the reaction above was followed by ^{31}P NMR spectroscopy. Thus, the single peak (δ 76.8) from **1** was totally converted to a new single peak at higher field (δ 75.0) within 3 h. No further change was observed when the reaction was complete, and we interpret this as an iodo for bromo substitution at the metal centre. As expected, no such change of the ^{31}P NMR peak was seen in the kinetic investigation, where an aryl iodide was employed.

In order to find proper reaction conditions for the kinetic measurements different substrates and bases were considered. A qualitative investigation of the reaction conditions clearly shows that 4-iodoanisole is a more reactive substrate than 4-bromoanisole, which is in line with earlier results [35]. The influence from the use of different bases is also noteworthy, but the results were somewhat unexpected in view of what has been reported [18,36,37]. In general, the literature results point to inor-

ganic bases as superior, but for the present reaction in DMF, we found that triethylamine was the base of choice, due to the higher reactivity observed and the advantage of having a homogeneous reaction mixture in the kinetic investigations.

In no case was any reaction observed when **1** and either of the substrates were mixed separately, i.e., both substrates are required to activate the catalytic process. Finally it was noted that these reactions require an inert atmosphere; under ambient conditions the catalytic activity disappeared, most probably because of decomposition of the catalyst.

3.2. Kinetics and mechanism

All kinetic experiments were performed with 4-iodoanisole and styrene in large excess compared to the palladium precursor at 160 °C, cf. Scheme 1. The choice of substrate enables the monitoring of the reaction by means of ^1H NMR spectroscopy. Thus, the intensity of the strong singlet at δ 3.79, belonging to the methoxy group of 4-iodoanisole, decreased as a new downfield (δ 3.84) peak grew in with the formation of the reaction product **2**. Styrene was always used in at least ten-fold excess over aryl halide and under these conditions the reaction is finished within 15 h. The concentration of both styrene and complex **1** was varied and the kinetic traces were fitted to single exponentials, cf. Fig. 1, showing that the reaction is first order in aryl halide and giving observed rate constants as a function of styrene and palladium concentrations, cf. Figs. 2 and 3. All observed pseudo first-order rate constants are given in Tables 1 and 2. Using the aryl halide in excess over styrene gave very low conversion and as seen from Fig. 1(a) conversion is far from 100% at lower styrene concentrations.

The addition of Hg(I) to the reaction mixture resulted in almost total loss of catalytic activity. Hence, less than 20% of the 4-iodoanisole was converted to (4-methoxyphenyl)-2-phenylethylene after 8 h. Mercury is known to

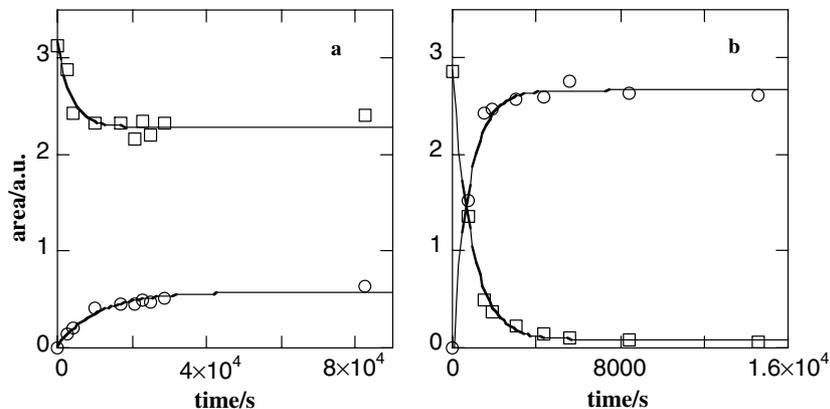


Fig. 1. Observed intensities of 4-iodoanisole (\square) and **2** (\circ) as a function of time at 160 °C when: (a) $[\text{styrene}] = 0.05 \text{ mol dm}^{-3}$; (b) $[\text{styrene}] = 1.05 \text{ mol dm}^{-3}$. General reaction conditions were: $[\text{Pd}] = 0.07 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{4-iodoanisole}] = 8.04 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{ferrocene}] = 2.76 \times 10^{-3} \text{ mol dm}^{-3}$. Solid lines denote the best fit to a single exponential using KaleidaGraph.

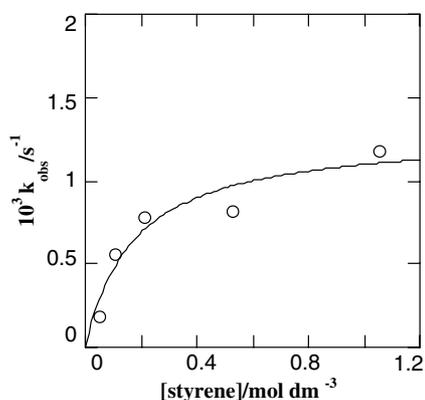


Fig. 2. Observed pseudo-first-order rate constants for the reaction in Scheme 1 as a function of [styrene] in DMF- d_7 solution at 160 °C. The values are reported as means of the reactant decay and the product formation. Complete data and further reaction conditions are reported Table 1. The solid line denotes the best fit to Eq. (1), where $K_1 = (5.7 \pm 2.5) \times 10^{-3} \text{ M}^{-1}$, and $k_2 = 18.4 \pm 2.7 \text{ M}^{-1} \text{ s}^{-1}$.

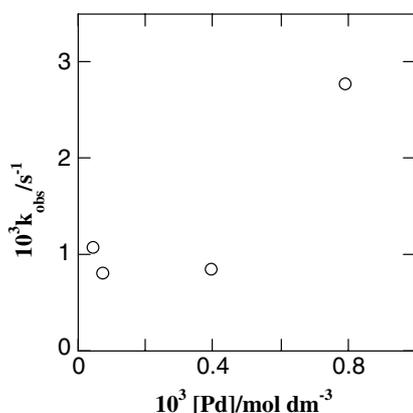


Fig. 3. Observed pseudo-first-order rate constants for the reaction in Scheme 1 as a function of [Pd] in DMF- d_7 solution at 160 °C. The values are reported as means of the reactant decay and the product formation. Complete data and further reaction conditions are reported in Table 2.

Table 1
Reaction conditions and rate constants at 160 °C in DMF- d_7 solvent^a

$10^3/\text{M}$	$10^4 k_1/\text{s}^{-1}$			$10^4 k_2/\text{s}^{-1}$		
	[Pd]	[Ar-X] ^b	[Olefin] ^c	[Base] ^d	Reactant ^b	Product ^e
0.07	8.04	50.0	144		2.75 ± 0.83	0.90 ± 0.18
0.07	8.04	105	144		9.27 ± 3.26	1.89 ± 0.28
0.07	8.04	210	144		4.66 ± 0.51	6.37 ± 0.65
0.07	8.04	524	144		8.58 ± 0.49	7.83 ± 1.66
0.07	8.04	1050	144		11.1 ± 0.6	12.5 ± 1.1

Both constants for the reactant decay and the product formation are displayed.

^a [Ferrocene] = 2.76 mM in all measurements.

^b Ar-X = reactant = 4-iodoanisole.

^c Olefin = styrene.

^d Base = NEt₃.

^e Product = *trans*-(4-methoxyphenyl)-2-phenylethylene.

Table 2
Reaction conditions and rate constants at 160 °C in DMF- d_7 solvent^a

$10^3/\text{M}$	$10^4 k_1/\text{s}^{-1}$			$10^4 k_2/\text{s}^{-1}$		
	[Pd]	[Ar-X] ^b	[Olefin] ^c	[Base] ^d	Reactant ^b	Product ^e
0.04	8.04	524	144		10.4 ± 1.2	11.1 ± 2.6
0.07	8.04	524	144		8.58 ± 0.49	7.83 ± 1.66
0.39	8.04	524	144		9.84 ± 0.31	7.55 ± 1.35
0.79	8.04	524	144		31 ± 3	25 ± 10

Both constants for the reactant decay and the product formation are displayed.

^a [Ferrocene] = 2.32 mM in all measurements.

^b Ar-X = reactant = 4-iodoanisole.

^c Olefin = styrene.

^d Base = NEt₃.

^e Product = *trans*-(4-methoxyphenyl)-2-phenylethylene.

amalgamate Pd colloid [33] and to verify the Hg(I) poisoning experiments, also cross-experiments with addition of cyclooctatetraene (COT) were performed. Agreement between the two tests provides a good indication that the results are valid [34]. Even though we see a substantial inhibition with COT (cf. Fig. 4) we interpret our results in favour of a heterogeneous rather than a homogenous catalytic process. It is known that COT can inhibit also heterogeneous catalysts (in this case presumably by competing with styrene for active sites) but any homogeneous palladium(0) compounds are expected to react with COT and become completely inactive [32]. Complete inhibition by 2 equiv. of a 1,4 diene has been reported for an aromatic PCP-complex in the Heck reaction, but in that case no cross-experiment with mercury was performed [38]. Recently, we reported a mechanistic investigation on the Stille cross-coupling that pointed strongly to a heterogeneous system where the palladium particles were formed from an aromatic PCP-Pd(II) pre-catalyst [19]. The observations on the current Heck system speak in favour of a

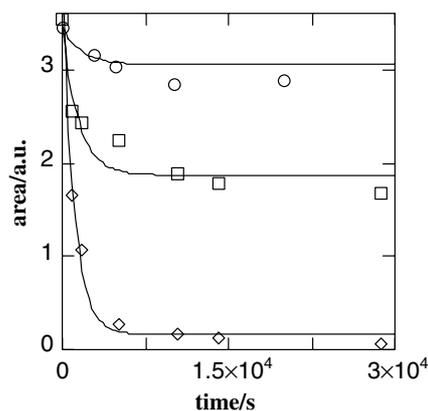


Fig. 4. Observed intensities of 4-iodoanisole as a function of time at 160 °C in DMF- d_7 with addition of Hg(I) (○), with addition of COT (□) and without any additive (◇). Reaction conditions: [Pd] = $0.07 \times 10^{-3} \text{ mol dm}^{-3}$; [styrene] = $0.524 \text{ mol dm}^{-3}$; [4-iodoanisole] = $8.04 \times 10^{-3} \text{ mol dm}^{-3}$; [ferrocene] = $2.76 \times 10^{-3} \text{ mol dm}^{-3}$.

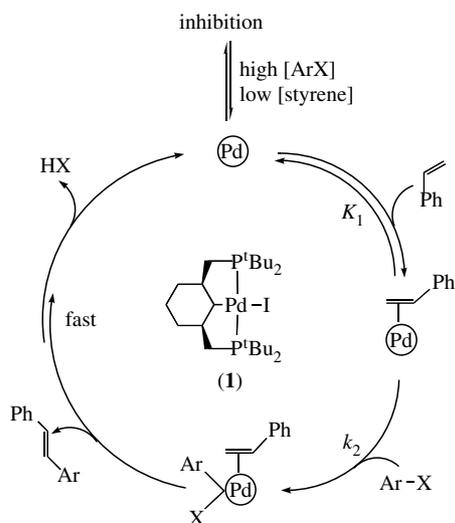
similar interpretation and a heterogeneous form of palladium as the active catalyst seems most reasonable.

From Fig. 3, we can see that although the errors are large the reaction rate is higher at high [Pd] indicating a dependence in palladium that is probably first order (vide infra). A heterogeneous catalytic cycle requires activation of the pre-catalyst and we know that this happens only to a small extent; almost all of the PCP complex is recovered after the reaction is over. Since the initiation mechanism is currently unknown it cannot be excluded that it is a varying degree of initiation from run to run that gives rise to the kind of results observed in Fig. 3. This deviation from linearity could then be taken as support for a heterogeneous catalysis. Fig. 2 displays smaller errors and there is a saturation behaviour with respect to styrene concentration. Assuming a heterogeneous catalytic system, a mechanism as shown in Scheme 2 can be proposed. A fast pre-equilibrium followed by an irreversible reaction with aryl halide will give the following rate law:

$$\text{rate} = k_{\text{obs}}[\text{ArX}]; \quad k_{\text{obs}} = \frac{K_1 k_2 [\text{pd}][\text{styrene}]}{1 + K_1 [\text{styrene}]} \quad (1)$$

In comparison to the classical Heck mechanism this means that we propose a reversed order of entry of the substrates, where the olefin is activated before the aryl halide [37]. If oxidative addition were to precede the olefin coordination this could not explain the observed saturation. Also, this is not a completely new notion and has been proposed by both Shaw and Jensen in the context of Pd(II)/Pd(IV) cycles [16,27].

The simple catalytic cycle cannot explain the inhibition (incomplete conversion) seen in runs where the styrene concentration was low. This inhibition might be explained by a competitive non-productive binding of aryl halide at higher aryl halide/styrene ratios.



Scheme 2.

Another possibility is that saturation of the active sites with olefin prevents the catalyst from aggregating and thus becoming inactive. It should be noted, though, that in no cases do we see any formation of palladium black.

It is clear that the kinetics (the aryl halide and olefin concentration dependencies) are completely compatible with a homogeneous catalytic cycle with initial reversible olefin activation, as proposed by Jensen. However, it fails to explain the inhibition experiments with mercury and the erratic dependence on palladium concentration. Also, contrary to our observation, in a homogeneous scheme it is expected that **1** would react with styrene in a stoichiometric reaction since we know from the kinetics that this equilibrium can be pushed to the right.

Eberhard has suggested that the decreased electronic density on the metal centre expected in phosphinite PCP complexes (compared to phosphines) will cause the complex to decompose more easily and therefore lead to a more active source of colloidal palladium [30]. In the current reaction system, the introduction of an aliphatic PCP ligand induces the opposite effect, i.e., the sp^3 carbon donates electrons more readily towards the metal centre as compared to the corresponding aromatic ones. Still, the results in [18] suggest that we get a more active catalyst compared to the aromatic phosphine system [8] (but less active than the phosphinites [16,30]). It is thus clear that we do not understand the initiation process of these complexes, but it seems that less robust compounds, such as **1** (which is more active under inert reaction conditions) or the phosphinite complexes, give more efficient catalytic process.

In conclusion we propose that **1** serves as a Pd(II) pre-catalyst forming small amounts of a catalytically active colloidal Pd species, although we have no direct evidence as to the nature of the active catalyst. The kinetics speak in favour of a heterogeneous mechanism consisting of a pre-equilibrium step involving association of the olefin followed by a rate determining oxidative addition step of the aryl halide.

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