

# Lightly fluororous $[\text{Pd}(\text{OAc})_2\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})_3\}_2]$ in the methoxycarbonylation of styrene: Formation, performance and stability of the catalyst system

Jeroen J.M. de Pater<sup>a,b</sup>, Berth-Jan Deelman<sup>a,c,\*</sup>, Cornelis J. Elsevier<sup>b,1</sup>, Gerard van Koten<sup>a</sup>

<sup>a</sup> *Organic Chemistry and Catalysis, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands*

<sup>b</sup> *Van't Hoff Institute for Molecular Sciences, Molecular Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands*

<sup>c</sup> *ARKEMA Vlissingen B.V., P.O. Box 70, NL-4380 AB Vlissingen, The Netherlands*

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## Abstract

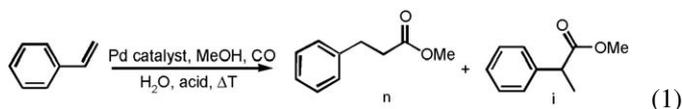
The fluororous palladium(II) complex,  $[\text{Pd}(\text{OAc})_2\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})_3\}_2]$ , has been prepared and characterized. Its application in the catalytic methoxycarbonylation of styrene in an MeOH/CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub> mixture (1/1 v/v) has been explored and its activity was compared to that of  $[\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2]$ . The fluororous complex showed a lower activity but a significantly higher selectivity towards the *branched* product. Investigation of both the conversion-versus-time and *i:n* ratio-versus-time profiles showed an unusual behaviour in the case of the fluororous complex, which has been ascribed to the formation of a dinuclear species for the fluororous complex.

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**Keywords:** Fluororous; FBS; Triarylphosphine; Palladium; Methoxycarbonylation; Styrene; Catalyst recycling

## 1. Introduction

The methoxycarbonylation of vinyl-arenes is an interesting topic for academic research and has been performed industrially [1–5]. In this process, a transition metal species catalyzes the formation of methyl esters from alkenes, CO and MeOH (Eq. (1)):



The most active catalysts for this reaction are based on palladium(II) and phosphine ligands. Both monodentate [1–4] and bidentate phosphine ligands [5] can be used, while addition of strong acids like *p*-toluenesulfonic acid or triflic acid is needed to boost activity. An important issue is the selectivity towards either

the linear (*n*) or branched (*i*) product. The branched esters are of interest to the pharmaceutical industry because they are precursors for an important class of non-steroidal, anti-inflammatory drugs like naproxen [6] and ibuprofen [7]. In order to comply with legislation, these compounds should be obtained in pure form and be devoid of even traces of catalyst remaining in the product. Furthermore a high selectivity towards the branched product is desirable.

A number of catalysts have been used for this reaction, some of which give a high selectivity towards the desired branched product. Generally these reactions suffer from low reaction rates, because of the low temperatures required to obtain good selectivities. Raising the reaction temperature leads to higher rates indeed, but also to a complete loss or even a reversal in selectivity providing more of the *linear* product. A further aspect that has been addressed in several studies during recent years is catalyst recycling. This research is mainly stimulated to deal with the high palladium loadings (0.1–5 mol%) that are needed to get high conversions in reasonable reaction times. In most cases catalyst recycling was attempted by performing the reaction in an aqueous biphasic solvent system, in which the catalyst was preferentially dissolved in the aqueous phase whereas the sub-

\* Corresponding author. Tel.: +31 113 617000; fax: +31 113 612984.

E-mail addresses: [berth-jan.deelman@arkemagroup.com](mailto:berth-jan.deelman@arkemagroup.com) (B.-J. Deelman), [else@science.uva.nl](mailto:else@science.uva.nl) (C.J. Elsevier).

<sup>1</sup> Fax: +31 20 5256456.

strates and products are present in the second, mostly organic phase. Consequently, alkoxy-carbonylations under biphasic conditions are limited to those substrates that have a relatively good solubility in the aqueous phase [8,9].

An alternative biphasic separation technique based on fluorous biphasic systems (FBS) and fluorous catalysts [10–13] has not yet been explored for metal-catalyzed alkoxy-carbonylation reaction. It is obvious that the dissolution of polar transition metal catalysts in the fluorous phase requires their functionalization with perfluoroalkyl groups, which will increase the fluorophilicity of the precursor complexes. In this paper we present our attempts to use the FBS technique for the methoxy-carbonylation of styrene.

To study the effect of perfluoroalkyl tail-functionalization on the catalytic performance and stability of Pd-based alkoxy-carbonylation reactions, a lightly fluorous palladium complex  $[\text{Pd}(\text{OAc})_2\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-R}_{\text{F}6})_3\}_2]$  ( $\text{R}_{\text{F}6} = \text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ ) (**2**) was prepared and its performance in the methoxy-carbonylation of styrene was compared with the well-studied non-fluorous analogue  $[\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2]$  (**1**). A related fluorous Pd(0) complex,  $[\text{Pd}(0)(\text{P}\{\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}_3)_2(\text{MA})]$  (MA: maleic anhydride), was found to be too unstable in the methoxy-carbonylation of styrene [28]. The successful application of lightly fluorous P, N ligands in the Pd-catalyzed methoxy-carbonylation of phenylacetylene, in regular solvents as well as supercritical  $\text{CO}_2$ , was recently published [29].

## 2. Experimental

### 2.1. General remarks

All reactions were performed using standard Schlenk techniques under dinitrogen atmosphere. Diethyl ether, *n*-hexane and *n*-pentane were distilled from Na/benzophenone prior to use.  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{CaH}_2$ . MeOH was distilled from  $\text{Mg}(\text{OMe})_2$ .  $\text{CF}_3\text{C}_6\text{H}_5$  was distilled from  $\text{P}_2\text{O}_5$  and stored on molsieves under a dinitrogen atmosphere.  $\text{CDCl}_3$  (Cambridge Isotopes Laboratories, CIL) was degassed and stored under a dinitrogen atmosphere on molsieves. Deuterated methanol (CIL) was distilled from  $\text{NaOCD}_3$  and stored on molsieves under a dinitrogen atmosphere.  $[\text{Pd}(\text{OAc})_2]$  (Degussa),  $\text{PPh}_3$ , *p*-toluene sulfonic acid monohydrate and *n*-decane (Acros) were used as received. Styrene was passed over a short column of neutral alumina (Merck) immediately prior to use. CO (Hoekloos, Praxair, >99.9% purity) was used as received. Standard  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Varian Unity-INOVA 300 MHz, a Varian Mercury 200 MHz or a Varian Mercury-VxWorks 300 MHz spectrometer.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the fluorous complex were recorded on a Varian Unity-INOVA 500 MHz spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the residual solvent peak,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra externally to  $\text{H}_3\text{PO}_4$  (85%) and  $^{19}\text{F}$  NMR spectra externally to  $\text{CFCl}_3$ . Quantitative GC analysis were performed on a Varian 3300 Gas Chromatograph, equipped with J&W Scientific Inc. DB-5 column (30 m, 0.320 mm internal diameter) and a FID-detector (280 °C), using  $\text{N}_2$  as the carrier gas and attached to a Varian 4400 integrator. Elemental analyses were carried out

by H. Kolbe Mikroanalytisch Laboratorium, Mülheim an der Ruhr.  $\text{P}\{\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}_3$  was synthesized as reported [14].

*Note.* Little is known yet about the toxicology of fluorous phosphines and their metal complexes. It is therefore recommended that proper personal protection measures are taken as a precaution when working with these kinds of compounds. Because of their amphiphilic nature, especially contact with the skin should be avoided.

### 2.2. Synthesis of $[\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2]$ (**1**) [15]

In a typical experiment,  $[\text{Pd}(\text{OAc})_2]$  (0.24 g, 1.06 mmol) was dissolved in MeOH (20 mL). The  $[\text{Pd}(\text{OAc})_2]$  had dissolved in less than 30 s. Immediate addition of  $\text{PPh}_3$  (0.56 g, 2.12 mmol) to the orange solution resulted in the formation of a yellow suspension. After stirring for 5 min at room temperature all volatiles were evaporated *in vacuo*. The remaining orange-yellow solid was washed twice with  $\text{Et}_2\text{O}$  and dried, affording a yellow solid (0.73 g, 0.98 mmol, 92%). NMR-data ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) were in agreement with literature values [15].

### 2.3. Synthesis of $[\text{Pd}(\text{OAc})_2(\text{P}\{\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}_3)_2]$ (**2**)

In a typical experiment,  $\text{P}\{\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}_3$  (0.39 g, 0.26 mmol) was dissolved in a mixture of dichloromethane and methanol (1:2 v/v, 21 mL total volume). To this slightly turbid yellow solution was added  $[\text{Pd}(\text{OAc})_2]$  (0.029 g, 0.13 mmol). The solution immediately became orange and turbid. After 5 min, when the colour changed from orange to yellow, all solvents were removed *in vacuo*. The desired complex was isolated as a light-yellow solid (0.41 g, 0.12 mmol, 85%) after washing with *n*-pentane.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz):  $\delta$  0.29 (s, 36H,  $\text{Si}(\text{CH}_3)_2$ ), 0.74 (s, 6H,  $\text{H}_3\text{CCOO}^-$ ), 0.96 (m, 12H,  $\text{SiCH}_2$ ), 1.95 (m, 12H,  $\text{SiCH}_2\text{CH}_2$ ), 7.62 (m, 24H, aryl-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125.7 MHz):  $\delta$  -3.59 (s,  $\text{Si}(\text{CH}_3)_2$ ), 5.18 (s,  $\text{SiCH}_2\text{CH}_2$ ), 21.38 (s,  $\text{CH}_3\text{C}=\text{O}$ ), 25.98 (t,  $^2J_{\text{C-F}} = 25$  Hz,  $\text{SiCH}_2\text{CH}_2$ ), 114–121 (several m,  $\text{C}_6\text{F}_{13}$ -tail), 130.63 (t,  $J = 25$  Hz), 133.59 (m), 134.23 (m), 140.57 (s), 141.42 (s), 175.66 (s,  $\text{C}=\text{O}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.0 MHz):  $\delta$  15.6 (s, *trans*-complex); 17.3 (s, *cis*-complex). Elemental analyses: Calc. C: 37.83, H: 2.86, F: 46.68, P: 1.95, Pd: 3.35. Found C: 37.81, H: 2.94, F: 46.78, P: 1.93, Pd: 3.28.

### 2.4. Synthesis of $[\text{Pd}(\text{OAc})(\mu\text{-OAc})(\text{P}\{\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}_3)_2]$ (**3**)

A similar procedure as that for **2** was used, but now a palladium-to-phosphine ratio of 1:1 was used. Starting from  $\text{P}\{\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})\}_3$  (0.36 g, 0.25 mmol) and  $[\text{Pd}(\text{OAc})_2]$  (0.058 g, 0.25 mmol) the final product was obtained as a light-orange solid (0.25 g, 60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz):  $\delta$  0.29 (s, 36H,  $\text{Si}(\text{CH}_3)_2$ ), 0.70 (s, 12H,  $\text{H}_3\text{CCOO}^-$ ), 0.96 (m, 12H,  $\text{SiCH}_2$ ), 1.95 (m, 12H,  $\text{SiCH}_2\text{CH}_2$ ), 7.75 (m, 24H, aryl-H).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 81.0 MHz):  $\delta$  20.93. No suitable elemental analyses could be obtained.

## 2.5. Catalytic experiments

Standard catalytic runs were performed by using two autoclaves. One was a stainless steel autoclave with a total volume of 100 mL, equipped with a pressure gauge, a rupture disc assembly and a Swagelok™ connection towards the high pressure system. To prevent contamination of the solution with residues from the autoclave walls and bottom a glass insert was used in all reactions. The second autoclave was an in-house built stainless steel autoclave ( $V=50$  mL) [16], equipped with two borosilicate (Maxos 200) windows to allow visual inspection of the interior of the autoclave, a pressure transducer, temperature gauges inside the autoclave and the wall, a rupture disc assembly (set at 250 bar) and four heating elements in the wall for heating. In a typical experiment, a known amount of the appropriate catalyst precursor, 30 equiv. of *p*-toluenesulfonic acid monohydrate (*p*-TsOH), 600 equiv. of degassed water and 150 equiv. of styrene were mixed together in the appropriate solvent(s), giving a palladium concentration of  $\sim 2 \times 10^{-3}$  M. This solution was charged to the autoclave under nitrogen flow. After sealing the autoclave it was flushed three times with  $N_2$ , followed by three times flushing with CO. The autoclave was then heated to the desired temperature. The reaction was started by pressurizing the autoclave with 30 bar of CO. The content of the reactor was stirred using a magnetic stirring bar. When the reaction time had passed the autoclave was cooled with an icebath for 15 min. Subsequently, the pressure was carefully released during 10 min and the liquid phase was quantitatively analysed for reagents and products by GC using *n*-decane as an internal standard.

## 2.6. HP-NMR experiments

An in-house built 10 mm sapphire HP-NMR-tube [17,18], equipped with a titanium head which allows the introduction of gasses, was charged with 1.5 mL of a 1:1 solution of *d*4-methanol and  $CF_3C_6H_5$ , containing the catalyst precursor, styrene and the appropriate amounts of acid and  $H_2O$ . After sealing the tube and flushing with  $N_2$ , the tube was charged with CO (30 bar). The tube was transported to the NMR spectrometer, which was already warmed to 80 °C. After shimming  $^1H$  NMR spectra were recorded with 5 min intervals. After the desired reaction time the NMR-tube was ejected from the spectrometer and transported to a fumehood where the excess pressure was released.

*Note.* Since high pressures of CO are used, work should be conducted in a fumehood equipped with a CO detection system and sufficient ventilation capacity. Furthermore, laboratory personnel must never be directly exposed to the pressurized cell and sufficient personal protection must be ensured by employing proper safety shields.

## 3. Results

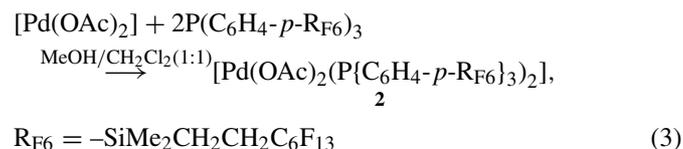
### 3.1. Synthesis of Pd-complexes

After the initial investigations by Drent and co-workers at Shell,  $[Pd(OAc)_2(PPh_3)_2]$  (**1**) has been successfully used by the group of Toniolo and co-workers as a catalyst precursor in the

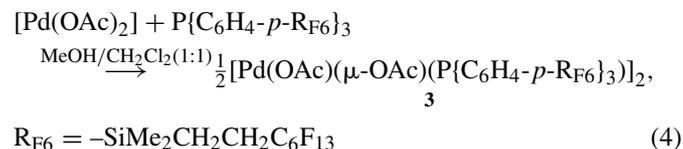
methoxycarbonylation of styrene [1]. We also used this approach successfully in the methoxycarbonylation of phenylacetylene by the related palladium acetate precursor  $[Pd(OAc)_2\{P(2-C_6H_5N)(C_6H_4-4-R_{F6})_2\}]$  [29].

For the synthesis of the fluoros pre-catalyst, we used the fluoros phosphine  $P(C_6H_4-p-R_{F6})_3$  that was already available from previous studies [14]. The common route for the synthesis of **1** involves the reaction of  $[Pd(OAc)_2]$  and  $PPh_3$  in boiling benzene for several hours [19]. When we initially employed this synthetic route we obtained **1** in 80–90% yield after precipitation and washing with *n*-hexane. This method, however, did not work for **2**. Instead, decomposition occurred and mixtures of compounds were obtained at these temperatures, presumably because of the low stability of compound **2** in boiling benzene [20]. Conducting the synthesis at lower temperatures was also not successful. In all cases mixtures of products were obtained, containing the desired product in minor amounts.

We therefore adopted the method published by Toniolo and co-workers in 1995, who prepared the complex  $[Pd(dppp)(OAc)_2]$  using MeOH as the solvent [15]. When applied to the synthesis of **1**, the desired complex could be obtained in a 92% yield (Eq. (2)). However, the fluoros ligand did not completely dissolve in MeOH. By changing the solvent to a 2:1 (v/v) mixture of MeOH and  $CH_2Cl_2$  (where  $CH_2Cl_2$  ensured that all of the fluoros phosphine had dissolved) and by applying short reaction times, the desired compound **2** was obtained in good yield (Eq. (3)) [22]:

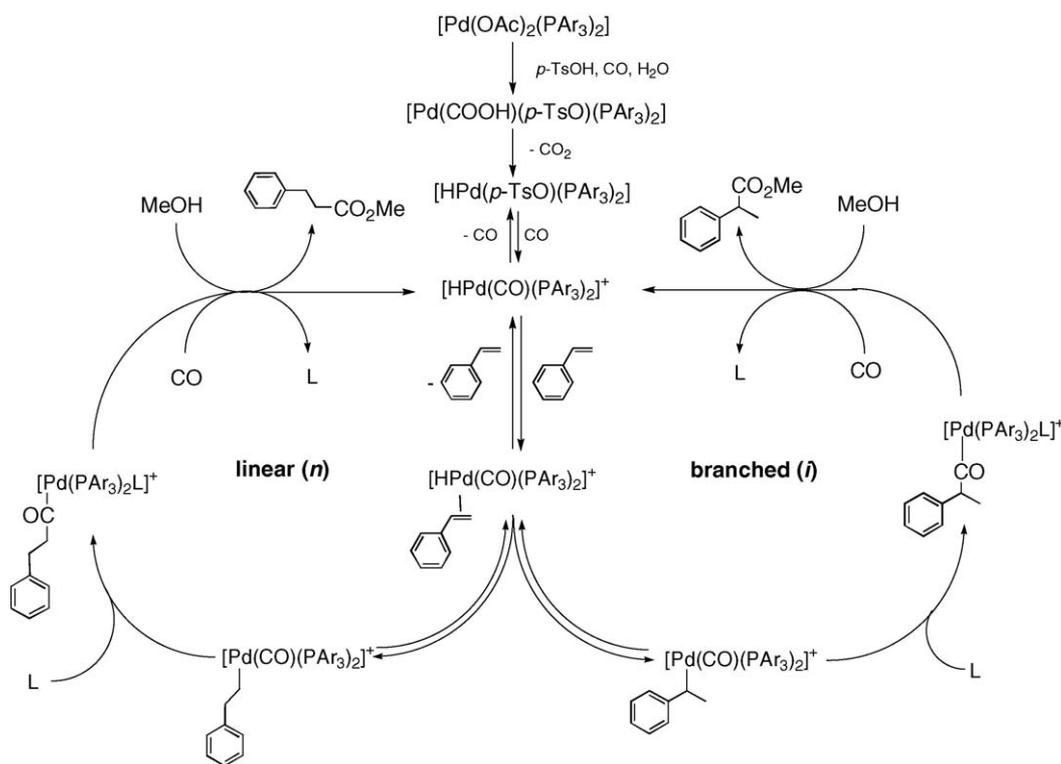


Complex **2** was characterized by  $^1H$ ,  $^{13}C\{^1H\}$  and  $^{31}P\{^1H\}$  NMR spectroscopy and by elemental analyses. In the NMR spectra some differences between **1** and **2** were apparent. Whereas for **1** only the *trans*-complex could be detected in its  $^{31}P\{^1H\}$  NMR spectrum at 25 °C (in  $CDCl_3$ ), the solution of **2** appeared to consist of a mixture of *trans*- and *cis*-isomers, the *trans*-isomer being the major species (90:10 *trans/cis*) [21]. The different propensity of **1** and **2** towards dimer formation is most interesting. Facile formation of dimeric  $[Pd(OAc)_2\{P(C_6H_4-p-R_{F6})_3\}]_2$  (**3**) already took place during the synthesis of **2**. Complex **3** was also synthesized independently (Eq. (4)) [23]:



Solubility studies involving **2** showed that this complex is soluble (more than 0.1 g/mL) in a variety of commonly used organic solvents (e.g., pentane, hexane, chloroform and dichloromethane). Furthermore, this compound is also soluble





Scheme 1. Catalytic cycle for methoxycarbonylation of styrene [1]. For all cationic palladium complexes the counteranion is  $p\text{-TsO}^-$ .  $L = \text{CO}$ ,  $\text{PAr}_3$  or  $\text{MeOH}$ .

selectivity of the reactions was found to be highly temperature dependent ( $i:n$  values of 1.86 (**1**) and 2.33 (**2**)), which is in line with previous observations for non-fluorous catalysts [25,26]. The fluorous complex **2** maintained a higher selectivity than non-fluorous **1** for the branched ester.

#### 4. Discussion

Several differences can be noted between non-fluorous complex **1** and fluorous complex **2**. Whereas **1** was observed as the *trans*-isomer only, **2** consisted of a mixture of *cis*- and *trans*-isomers. Furthermore **2** is less stable in solution than **1**, leading to formation of the dimeric complex **3** and free phosphine (Eq. (4)). For **1** the formation of the corresponding dimeric compound ( $[\text{Pd}(\text{OAc})_2(\text{PPh}_3)]_2$ ) was not observed. Although this was not further investigated, we think that the presence of the perfluoroalkyl groups is probably responsible for this behaviour. Formation of the dimeric compound in the case of **3** may lead to more favorable solvent–solute interactions.

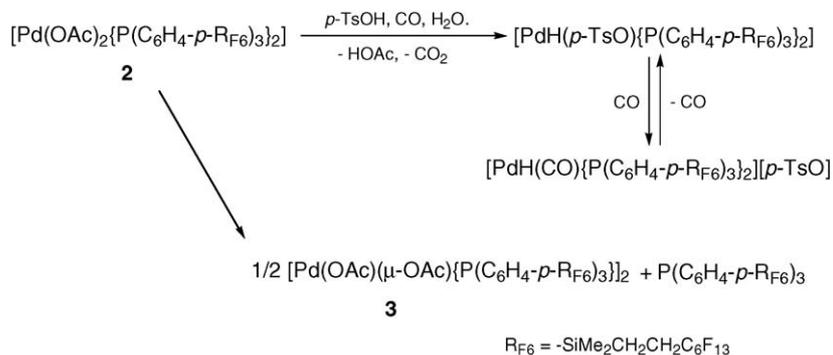
The use of the fluorous palladium complex **2** as a precursor in the methoxycarbonylation of styrene gave rise to a number of interesting phenomena. During the first 90 min of the process, a remarkable difference in reactivity between **1** and **2** was observed. Whereas for the former a high conversion (>95% after 90 min), and a constant  $i:n$  ratio are observed, **2** suffers from an induction period characterized by a lower conversion and a high but decreasing  $i:n$  ratio. After this initial phase the selectivity reaches a plateau at a level that is still higher than that of **1**. These results suggest that in the catalysis with **2** initially a species is

present which has a low activity, but a high selectivity towards the *i*-isomer. Gradually, during the first 90 min of the reaction a second species is formed, which has a higher activity but a lower selectivity towards the *i*-isomer.

To offer an explanation for this behaviour one has to consider the proposed catalytic cycle for the methoxycarbonylation of styrene as proposed in the literature in more detail (Scheme 1) [1].

Before the catalysis starts, a cationic palladium hydride complex has to be formed, which takes several steps, all involving mononuclear Pd species. Since we observed during the synthesis of **2** that this compound easily forms the dimeric complex  $[\text{Pd}(\text{OAc})(\mu\text{-OAc})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{R}_{\text{F}_6})_3\}]_2$  (**3**), such a process may also compete with palladium hydride formation during catalysis (Scheme 2). Compound **3** is likely to be converted further to analogous tosylate complexes under the action of the excess of  $p\text{-TsOH}$ .

When tested independently, pre-catalyst **3** gave a low conversion but a high  $i:n$  ratio. The observed rate and  $i:n$  profiles for **2** in the first 90 min can be explained when the formation of compound **3** as a competing catalyst precursor is taken into account. We see, however, that after these 90 min, activity increases and the  $i:n$  ratio remains constant when **2** is used as the precursor complex. We can qualitatively account for this by assuming a situation where mononuclear diphosphine species derived from **2** and monophosphine complexes derived from dinuclear **3** are competing catalysts. The reaction profile for **2** reflects the different stability of these species and is possibly further complicated by residual activity of decomposition products. When the reac-

Scheme 2. Possible reactions during formation of the active species from **2**, leading to formation of **3**.

tion is performed with pure **3** as the precursor, this is not possible and we see only the poor activity but good selectivity of the species derived from **3**.

Another interesting feature of the use of fluororous complex **2** compared to **1** is that, even after the initial induction period, it gave a higher selectivity for the branched product. This is rather surprising, since one would expect that introduction of the fluororous phosphines in the active species would lead to increased steric bulk around palladium, which would favor the linear ester (Scheme 1). However, we saw earlier that complex **2** in solution consists of a mixture of *cis*- and *trans*-isomers, whereas **1** appears as a solution of purely the *trans*-isomer. This tendency of the fluororous complexes to form the *cis*-isomer could very well play a role during catalysis as well. Although both pathways in Scheme 1 involve *cis*-bis(phosphine)palladium intermediates in which the acetate anions are replaced, the tendency of the fluororous catalyst precursor **2** to form more of the *cis*-coordinated complex, despite opposing steric considerations, may be indicative of less steric crowding induced by the fluororous ligand and could be the origin of the higher *i:n* ratio obtained with the catalyst system derived from **2**. Although only speculative at this point, the minimization of the number of solvent–solute interactions and consequently an optimization of energetically more stabilizing solvent–solvent interactions that result from pairing-up of the fluortails in a *cis*-coordination mode, may play a role here [27].

Although there are significant differences between fluororous **2** and conventional precursor **1**, these do not rule out catalyst recycling by the FBS techniques. However, thermal instability and Pd black formation is a major obstacle for recycling of an active catalyst system. Hence, Pd systems that are more resistant to Pd(0) formation are clearly desirable.

## 5. Conclusions

We have synthesized the fluororous complex  $[\text{Pd}(\text{OAc})_2\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})_3\}_2]$  (**2**) in good yield and purity. In solution this complex is less stable than its non-fluororous analogue  $[\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2]$  (**1**), leading to the formation of  $[\text{Pd}(\text{OAc})(\mu\text{-OAc})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})_3\}_2]$  (**3**). The mononuclear complex **2** was employed as a catalyst precursor in the methoxycarbonylation of styrene where it gave rise to a lower activity, but a higher selectivity towards the

branched product when compared with non-fluororous **1**. The observed conversion-versus-time and *i:n* ratio-versus-time profiles showed a remarkably different behaviour between the fluororous and non-fluororous complex, especially in the early stages of the reaction. The differences can be explained in terms of competing species derived from **2** and **3** in case of the fluororous complex **2**. The present results demonstrate that fluororous Pd-complexes that are active in the methoxycarbonylation of styrene can be prepared. However, as initial experiments under fluororous biphasic conditions failed due to Pd black formation, catalyst stability and recycling need further investigation.

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