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Reppe-Carbonylation of Alkenes with Carboxylic Acids: A Catalytic and Mechanistic Study

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In this work, a green-catalytic procedure is used to demonstrate the synthesis of long-chain anhydrides. This is accomplished by the carbonylation of alkenes with carboxylic acids. Anhydrides are important intermediates, finding specific applications as acetylation agents. The process is catalyzed by a Pd phosphine catalyst system in the presence of an acid promotor. Through optimization experiments, the importance of the phosphine ligand and acid promotor is demonstrated, without which the catalyst shows no activity. Although the yield was limited because of catalyst deactivation (42%), to the best of our knowledge, the synthesis of long-chain anhydrides through this route have not been reported previously. It therefore represents a significant result. Isolation of the anhydrides were also successfully demonstrated, however, as a result of the sensitivity of the anhydrides to water, the isolated yields were much lower than the HPLC yield. Furthermore, a mechanistic study by means of HP-NMR (High Pressure Nuclear Magnetic Resonance) spectroscopy provided significant insights into the mechanism of the reaction.

Introduction

Anhydrides are important organic intermediates both in research and in industry.[1] They are widely been used as acetylation agents for the synthesis of esters[2–6] and amides[4–6] as well as dehydrating agents.[1] A further application of anhydrides is in the synthesis of epoxy resins, which are widely been used as insulating materials.[7] Recently, Seidensticker and co-workers reported on the carbonylative telomerization of 1,3-butadiene with carboxylic acids. This produced mixed 3,8-nonadienoic anhydrides which were directly used as acetylation agents for the synthesis of amides.[8]

Acetic anhydride can be produced via the ketene process,[1] oxidation of acetaldehyde[1] or via the carbonylation of methyl acetate.[1,9] The ketene process can also be used for the synthesis of long chain anhydrides.[10] Furthermore, long chain anhydrides can be prepared via the reaction of acetic anhydride with higher carboxylic acids under heating.[11] Moreover, the reaction of acyl chlorides with higher carboxylic acids under basic conditions also produces long chain anhydrides.[12–14]

A further approach towards the synthesis of long chain anhydrides, which is scarcely reported, is by the Reppe-carbonylation of alkenes with carboxylic acids (Figure 1).[15–17]

The Reppe-carbonylation is a well-established approach for the synthesis of various carbonyl containing compounds.[18] It involves the carbonylation of alkenes (or alkynes) in the presence of a nucleophile. Various nucleophiles can be used, ranging from water, alcohols, amines, thiols and acids, allowing for the synthesis of carboxylic acids, esters, amides, thioesters and anhydrides respectively.[19–22,15–17] The Reppe-carbonylation is a more attractive approach towards the synthesis of anhydrides, in comparison to the approaches alluded to earlier (ketene process and the reaction of acetic anhydrides and acyl chlorides with higher carboxylic acids). This is attributed to the fact that it is based on catalysis and therefore circumvent the use of stoichiometric reagents such as basses and salts. Furthermore, the Reppe-carbonylation is 100% atom efficient and therefore do not generate stoichiometric amounts of waste. In addition to these, the substrates which are used can be obtained from renewable sources. It therefore conforms to the principles of green chemistry.

Previously, Pd-based catalysts have been used for the intermolecular Reppe-carbonylation of 3-butenoic acid for the production of methylsuccinic anhydride and glutaric anhydride while Mo-based catalysts have been used for the synthesis of propionic anhydride from ethylene and propionic acid (Figure 1).[15–17] Drawing inspiration from this, we focused on expanding this by using long chain alkenes and long chain carboxylic acids. By doing this, it can provide a synthesis route towards long chain anhydrides.

The alkenes and the alkynes which are used in the Reppe-carbonylation is widely and easily available. Therefore, given the potential advantages associated with this approach in comparison to the approaches listed previously (ketene process and the reaction of acetic anhydrides and acyl chlorides with

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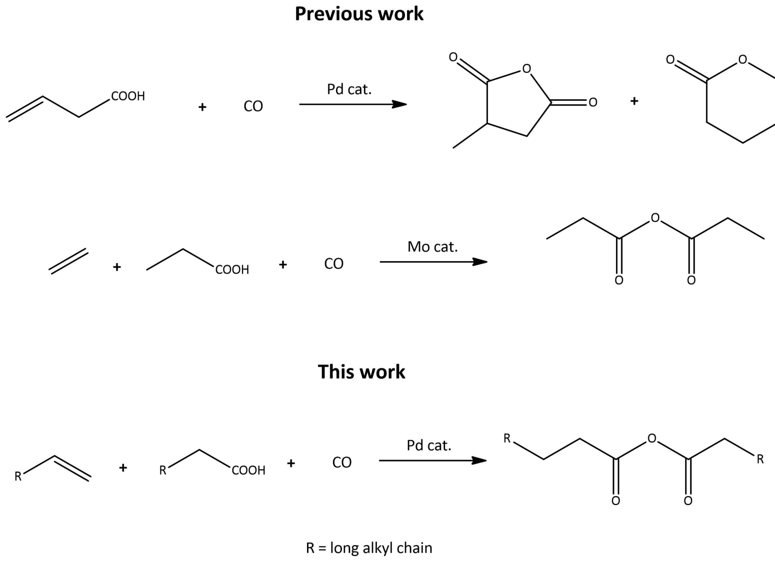
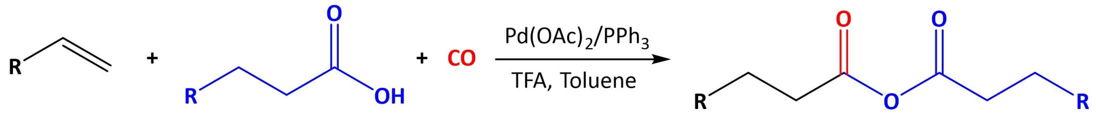


Figure 1. Synthesis of anhydrides via the Reppe-carbonylation of olefins in the presence of carboxylic acids.[15–17]

Table 1. Optimization of the loading of Pd, PPh_3 and TFA.[a]

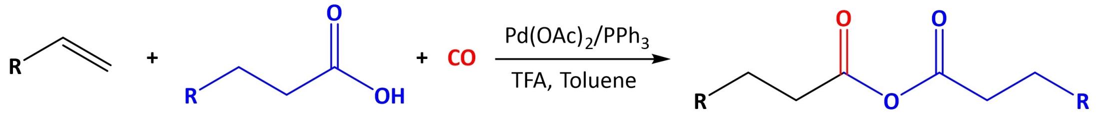


R = C_6H_{13}

Entry	Pd [mol %]	Pd : PPh_3	Pd : TFA	Yield [%]	TON[b]
1	1	1 : 20	1 : 40	37	37
2	0.5	1 : 20	1 : 40	23	46
3	0.2	1 : 20	1 : 40	17	88
4	0.2	–	1 : 40	0	0
5	0.2	1 : 5	1 : 40	16	79
6	0.2	1 : 10	1 : 40	16	83
7	0.2	1 : 20	–	0	0
8	0.2	1 : 20	1 : 20	6	30

[a] Conditions: $V_{total} = 2$ mL, $c_{1\text{-octene}} = 0.8$ mol/L, $c_{\text{nonanoic acid}} = 0.88$ mol/L, 700 rpm, T = 100 °C, t = 16 h, $p_{CO} = 50$ bar. [b] TON = ((mole of product)/(mole of Pd))

Table 2. Effect of temperature, pressure and reaction time on the yield of nonanoic anhydride.[a]



R = C_6H_{13}

Entry	Temperature [°C]	Pressure [bar]	Time [h]	Yield [%]	TON[b]
9	100	50	16	17	88
10	125	50	16	28	140
11	150	50	16	42	211
12	150	30	16	23	114
13	150	40	16	38	192
14	150	50	4	27	137
15	150	50	8	39	195

[a] Conditions: $V_{total} = 2$ mL, $c_{1\text{-octene}} = 0.8$ mol/L, $c_{\text{nonanoic acid}} = 0.88$ mol/L, 700 rpm, Pd : 1-octene (1 : 500, 0.2 mol %), Pd : PPh_3 (1 : 20), Pd : TFA (1 : 40). [b] TON = ((mole of product)/(mole of Pd)).

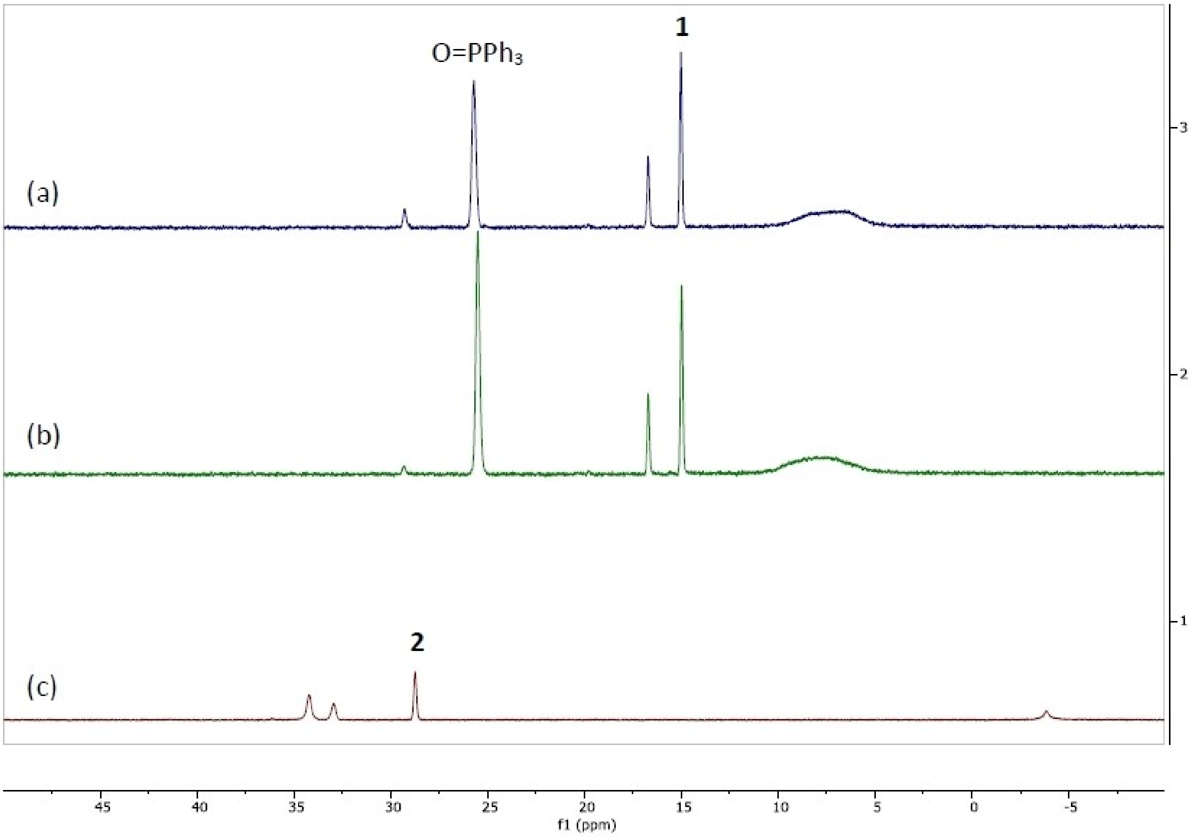


Figure 2. Monitoring the reaction via $^{31}P\{^1H\}$ Spectroscopy at room temperature. (a) $Pd(OAc)_2 + PPh_3$ (5 eq) in Tol-d8, (b) $Pd(OAc)_2 + PPh_3$ (5 eq) + CO (5 bar) in Tol-d8, (c) $Pd(OAc)_2 + PPh_3$ (5 eq) + CO (5 bar) + TFA (10 eq) in Tol-d8.

higher carboxylic acids), as well as the fact that it is rarely reported in literature, this paper deals with the synthesis of long-chain anhydrides using alkenes raging from C_6–C_{10} with nonanoic acid.

Results and Discussion

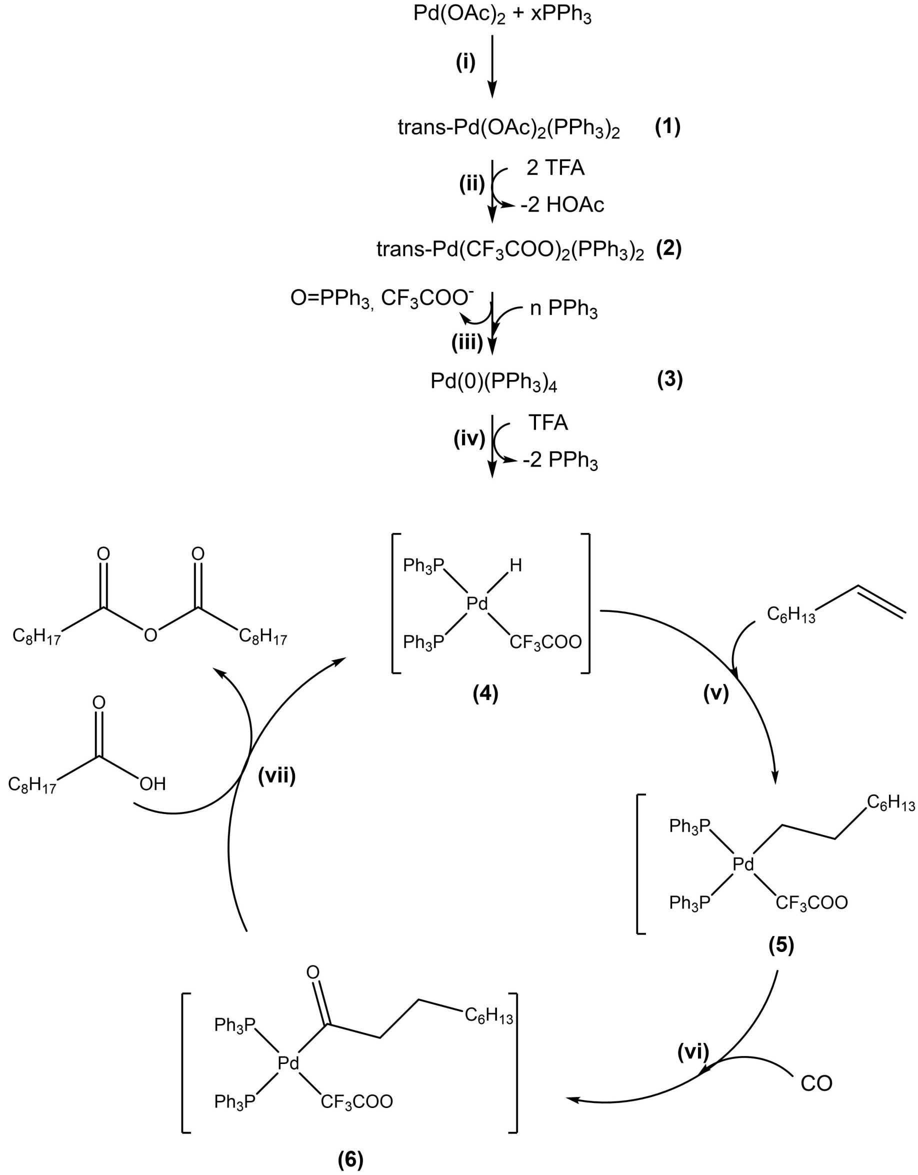
Catalyst development and optimization

As a model reaction, we studied the carbonylation of 1-octene in the presence of nonanoic acid, in order to produce the symmetric anhydride, nonanoic anhydride (Table 1). 1-Octene is widely been used in carbonylation reactions, including hydroformylation.[23–28]

We found that an initial catalyst system consisting of $Pd(OAc)_2$, PPh_3 and trifluoroacetic acid is capable of catalyzing the Reppe-carbonylation of 1-octene with nonanoic acid in the presence of 50 bar CO (Entry 1). In order to optimize the catalyst concentration, the effect of the Pd loading (0.2–1 mol%) on the yield of the nonanoic anhydride was investigated (Entries 1–3), while keeping the ratio of Pd:PPh_3 (1:20) and Pd:TFA (1:40) constant. With a decrease in the concentration of the catalyst, the yield of the nonanoic anhydride decreased since less catalyst are available to catalyze the reaction. However, decreasing the catalyst loading from 0.5 mol% (Entry 2) to 0.2 mol% (entry 3) only led to a 6% decrease in the yield, while as expected, a much higher TON is obtained when using 0.2 mol%.

Next, the effect of PPh_3 on the yield of nonanoic anhydride was investigated (Entries 3–6), using a 0.2 mol% catalyst loading and a Pd:TFA ratio of 1:40. Similar yields of the nonanoic anhydride was obtained when 5–20 equivalents of PPh_3 was used (Entries 3, 5–6), however, in the absence of PPh_3 (Entry 4), the catalyst is completely inactive. This is attributed to catalyst deactivation, since the reaction solution turned black with the formation of a black residue.[29] The PPh_3 is therefore necessary to stabilize the active catalyst.

Next, different equivalents of TFA was used (0, 20 and 40 equivalents, Entries 3, 7–8), with a catalyst loading of 0.2 mol% and a Pd:PPh_3 ratio of 1:20. As expected, in the absence of TFA, no catalytic activity was obtained (Entry 7), since the TFA is necessary in the activation of the catalyst, responsible for the formation of a Pd–H species.[30] Using 20 eq of TFA (Entry 8) produces lower yield of the nonanoic anhydride. This is attributed to the lower concentration of TFA in solution, which leads to a slower activation of the catalyst and therefore a subsequent lower activity.



Scheme 1. Possible mechanism for the Reppe-carbonylation of 1-octene with nonanoic acid.[41]

After establishing the optimum amount of $Pd(OAc)_2$, PPh_3 and TFA, the effect of temperature, pressure and reaction time were evaluated (Table 2).

With an increase in the temperature from 100 to 150 °C, the yield increases from 17% to 42% at 150 °C, with a TON of 211. Lower yield of the nonanoic anhydride was obtained at lower pressures (Entries 11–13). At lower pressures, the concentration of CO in solution is most likely lower.[31] Therefore, the carbonylation step in the catalytic cycle is slower which leads to a slower reaction and hence a lower yield of the anhydride. The yield of nonanoic anhydride is 27% after 4 h and 39% after 8 h (Entry 14 and 15). However, from 8–16 h, the yield only increased by ~3% (Entry 11 and Entry 15). The catalytic activity is therefore quite high in the initial stages of the reaction but slows down over time. This is indicative of catalyst deactivation.[32] As a result of catalyst deactivation, subsequent experiments were evaluated for 8 h reaction time.

Different Pd precursors were evaluated in the carbonylation of 1-octene with nonanoic acid (Table S2). However, all the Pd(II) precursors produced similar yield of nonanoic anhydride, except for $PdCl_2$. The lower activity of $PdCl_2$ is attributed to its lower solubility in toluene, which therefore leads to a lower concentration of Pd in solution. In the case of the other Pd precursors, the similar activities possibly indicate that the active species is the same for all the Pd precursors. The trifluoroacetate anion can replace the different anions while it can further operate as a weakly coordinating anion, stabilizing the active species.[33–34] A lower yield of the nonanoic anhydride was also obtained using a Pd(0) precursor ($Pd_2(dba)_3$).

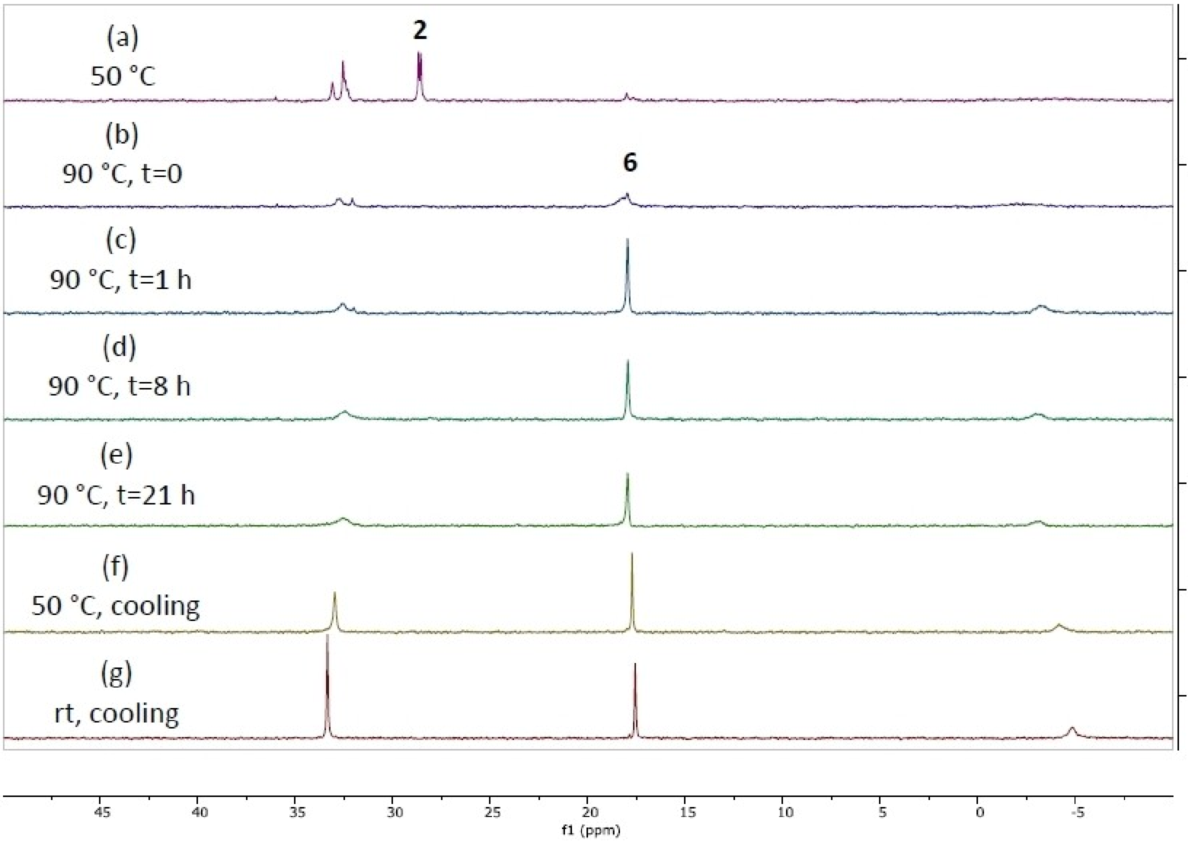


Figure 3. Monitoring the reaction via $^{31}P\{^1H\}$ NMR spectroscopy at elevated pressure and temperature. $Pd(OAc)_2$, PPh_3 (5 eq), CO (30 bar), TFA (10 eq), 1-octene (10 eq) and nonanoic acid (10 eq).

Using PTSA (*p*-Toluenesulfonic acid) as acid additive had no significant effect on the yield of the nonanoic anhydride, in comparison to TFA.

Various monodentate phosphine ligands as well as the bidentate ligand, dppb (1,4-bis(diphenylphosphino)butane), were evaluated in the Reppe-carbonylation reaction. Similar yields were obtained using triphenylphosphine, tris(p-tolyl)phosphine and tricyclohexylphosphine. However, in the case of tris(pentafluorophenyl)phosphine and triphenylphosphite, the catalyst was completely inactive. Catalyst deactivation was observed in the case of tris(pentafluorophenyl)phosphine, evidenced by the formation of a black precipitate. Based on these results, we can conclude that it is the steric properties of these ligands which control the catalytic activity. There is therefore a sweet spot between ~140-170°, and outside these ranges, no activity is observed (triphenylphosphite = 128° and tris(pentafluorophenyl)phosphine = 184°).

In the case of the bidentate ligand, dppb, the catalytic activity is very reduced. This is most likely attributed to strong coordination of dppb to the Pd-centre and therefore inhibiting coordination of the substrates to the Pd-centre.

In addition to 1-octene, 1-hexene and 1-decene was also used as alkene substrates in the Reppe-carbonylation, in combination with nonanoic acid. The unsymmetrical anhydrides produced from 1-hexene and 1-decene undergoes disproportionation to symmetric anhydrides, as confirmed by GC-MS analysis(Figures S7–10, S12–15). These anhydrides were isolated via a basic extraction (extracting the acid with 1 M NaOH solution, anhydrides remain in organic phase), however, due to the sensitivity of the anhydrides to water, the isolated yields were very low (11–19%). This further limited the scope of the reaction.

Mechanistic Study

To gain an insight into the mechanism of the reaction, a ^{31}P NMR study was performed. This was done in the presence of $Pd(OAc)_2$, PPh_3 (5 eq), CO (5 bar), trifluoroacetic acid (TFA), 1-octene and nonanoic acid (10 eq each). The results is shown in Figure 2.

Upon mixing $Pd(OAc)_2$ with 5 equivalents of PPh_3, **1** (see Scheme 1) forms instantaneously, with a resonance at 15.02 ppm, as shown in (a). The formation of **1** from $Pd(OAc)_2$ and PPh_3 has been shown in the literature before.[35–38] However, under these conditions, rapid oxidation of PPh_3 to $O{=}PPh_3$ also occurs (resonance at 25.72 ppm). Lee and Lee has previously done an extensive study on the Pd-catalyzed oxidation of triphenyl phosphine to triphenyl phosphine oxide.[39] The resonance at 29.26 ppm is possibly a Pd complex containing triphenylphosphine oxide ($Pd(OAc)_2(OPPh_3)_2$).[39] The broad resonance at ~7 ppm is assigned to free PPh_3, which is possibly in equilibrium with coordinated PPh_3. PPh_3 normally produces a signal at −5.24 ppm (Figure S16). As a result of being in equilibrium with coordinated PPh_3, drifting of this signal is observed. No significant changes were observed upon introducing 5 bar of CO (b). In the presence of TFA, as shown in (c), $O{=}PPh_3$ is protonated and shifts to 34.25 ppm (Figure S21). A new resonance is observed at 28.75 ppm. This resonance is assigned to $Pd(CF_3COO)(PPh_3)_2$ (**2**), which forms as a result of the substitution of the acetate ligands of **1** with trifluoroacetate. The presence of **2** is further confirmed via ESI-MS analysis (Figure S25), while the substitution of acetate ligands with the acid has also been shown before.[33,40] Introducing 1-octene and nonanoic acid had no significant effect, with similar spectra observed as in the case of (c) (Figures S17-18).

Since no significant changes in the spectra were observed upon formation of **2**, subsequent studies were performed at elevated pressure (30 bar) and temperature (90 °C). The results of this study are shown in Figure 3.

Upon heating the sample to 50 °C (spectrum a), a new resonance appeared at ~18 ppm. This resonance grew larger when the temperature was increased to 90 °C while this occurred at the expense of **2**, at ~28.6 ppm. Based on literature, this resonance belongs most likely to a Pd-acyl species, **6** (see Scheme 1), since it is known that the nucleophilic attack by the nucleophile (in this case the nonanoic acid), is the rate-determining step in the carbonylation of alkenes proceeding through the Pd–H mechanism.[40]

Based on these results, the following mechanism can be postulated (Scheme 1):

In the first step (**i**), the reaction of $Pd(OAc)_2$ with PPh_3 produces **1**. This is followed by the substitution of the acetate ligands by trifluoroacetate, in order to form **2**. It is known that PPh_3 is able to reduce Pd(II) to Pd(0).[36–39,42] In a report by Jutand and co-workers,[38] they demonstrated the formation of $Pd(0)(PPh_3)_n$ from $Pd(OAc)_2$ and PPh_3. It is therefore highly likely that this system also proceeds via a $Pd(0)(PPh_3)_n$ intermediate, since it is known that the Pd–H intermediate (**4**), is formed after the oxidative addition of the acid (TFA, trifluoroacetic acid) to the Pd(0) species.[43] **3** and **4** was not observed and most likely rapidly forms upon heating, since the only other intermediate detected is possibly the Pd-acyl species, **6**. Furthermore, no Pd–H intermediates were detected in ^1H NMR spectroscopy. Coordination of the alkene (**v**), followed by its insertion into the Pd–H bond produces the Pd-alkyl species, **5**. **6** is formed after the coordination and migration of CO (**vi**) into the Pd-alkyl bond. The catalytic cycle is complete after nucleophilic attack by the acid (**v**), producing the anhydride and regenerating **4**.

Additionally, the progress of the reaction was followed via ^1H NMR spectroscopy (Figure S26). Cosumption of 1-octene is quite rapid initially (0-1 h), however, it proceeded more steadily after this initial period. After ~20 h, the yield of nonanoic anhydride is around ~50%, while internal octenes are formed as a by-product as a result of the isomerization of 1-octene.

Conclusion

In this study, long-chain anhydrides were successfully synthesized through the carbonylation of alkenes with carboxylic acids. To the best of our knowledge, this is the first time that these anhydrides were synthesized via this approach. Moderate yields were obtained, owing possibly to catalyst deactivation. The carbonylation reaction works best with monodentate phosphine ligands, while bidentate ligands led to reduced yields. Upon performing the carbonylation reaction with 1-hexene and 1-decene, unsymmetrical anhydrides were obtained. However, these unsymmetrical anhydrides underwent dispropionation to the more stable symmetric anhydrides, as confirmed via GC-MS analysis. Furthermore, a mechanistic study was performed via HP NMR (High Pressure NMR). This allowed us to identify important reaction intermediates in the carbonylation reaction and as such, a possible mechanism was suggested.

Experimental Section

General experimental procedure

$Pd(OAc)_2$ (1.8 mg, 0.008 mmol) and PPh_3 (42 mg, 0.16 mmol) were weighed in air and transferred into a SCHLENK tube, where oxygen was removed by alternating application of vacuum and argon gas. The solids were dissolved in toluene (3,6 mL) and trifluoroacetic acid (TFA) (0.024 mL, 0.32 mmol) followed by 1-octene (0.63 mL, 4 mmol) and nonanoic acid (0.77 mL, 4.4 mmol) were added in an argon counterflow. 2 mL of this mixture were transferred to two 10 mL spectite autoclaves under SCHLENK conditions. Subsequently, the autoclaves were pressurized with 50 bar CO, placed into a preheated aluminium cone and stirred for 8 h at 700 rpm and 150 °C. After the reaction time, it was cooled down to room temperature and the pressure carefully released. The reaction mixture was transferred to a glass vial. 0.1 mL of this mixture was transferred to a GC vial, diluted with MeCN (0.9 mL) and analyzed via HPLC.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: Alkenes · Anhydrides · Carbonylation · Carboxylic acids · Palladium

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