Palladium-catalyzed carbonylative synthesis of carboxylic acid anhydrides from Alkenes

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Palladium-Catalyzed Synthesis of Symmetric Carboxylic Acid Anhydrides from Alkenes with *in situ* Generated Carboxylic Acids

*Carboxylic acid anhydrides are well known for their non-corrosive and mild acylating nature, and readily react with nucleophiles – alcohols, amines and thiols. We recently reported a carbonylative synthesis of acid anhydrides from alkenes with carboxylic acids as nucleophiles (Chapter 2). However, its synthesis of symmetric anhydrides requires the corresponding C_{n+1} carboxylic acid, which is not readily available in most of the cases. To overcome this challenge, we herein describe a strategy to synthesize symmetric acid anhydrides via in situ generated carboxylic acids from the alkene itself. It is known that the use of cheap and inexpensive formic acid (FA) reacts with alkene and CO to form carboxylic acids. Application of our catalytic conditions and modulating the alkene:formic acid ratio to at least 2:1 resulted in the formation of symmetric acid anhydride up to 70%, which was increased to 88% on varying the ratio to 3:1 - as represented in the case of the model substrate, styrene (**1**). Further studies showed minimal influence of different phosphine ligands on the regioselectivity of the acid anhydrides formed (approximately 60% linear-linear (**3nn**), 35% linear-branched (**3bn**) and 5% branched-branched (**3bb**)) resulting in an overall ~80% linearity. The catalytic process was applied to various alkenes, simple and with functional groups, to produce moderate to excellent yields as observed by their NMR yield or the corresponding amide produced on derivatization. A one-pot derivatization of the reaction mixtures provided access to various acyl molecules including phenolic esters, primary amides, thioesters and ketones, which otherwise require special conditions or are difficult to obtain via carbonylation chemistry.*

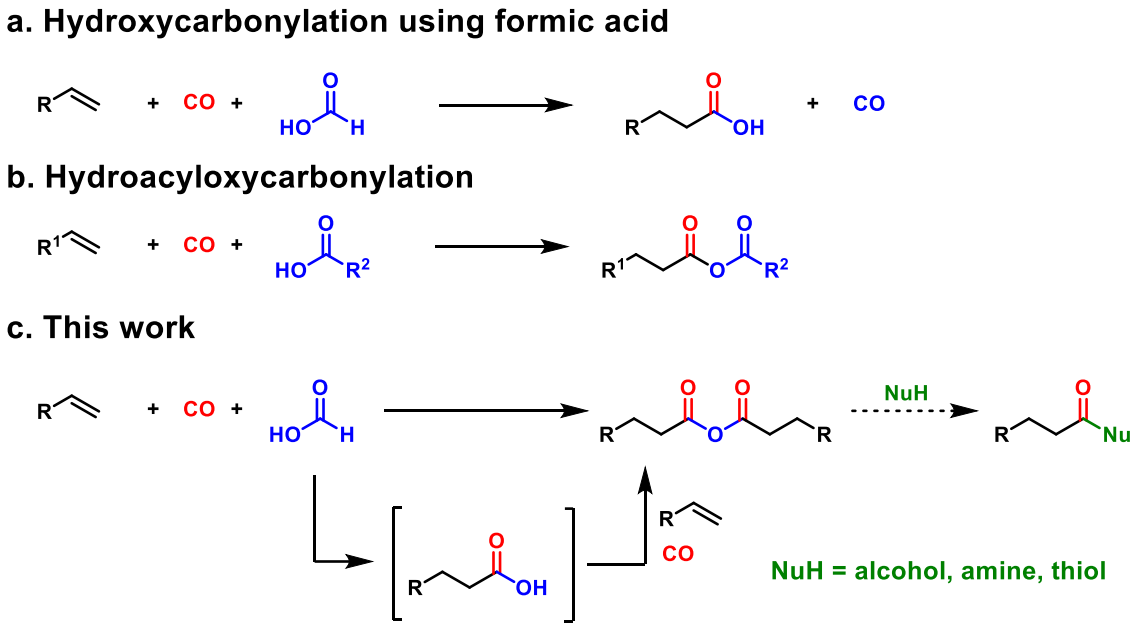
This chapter will be submitted for publication.

3.1. Introduction

Symmetric carboxylic acid anhydrides are vital electrophilic acylating reagents used in chemical synthesis of various fine chemicals, pharmaceuticals and polymers. The mild nature and effective chemical reactivity of anhydrides have established them as widely favored acylating agents in organic synthesis. As a result, they are employed, for example, as reagents in peptide chemistry to facilitate N-acylation processes.[1] It is important to use symmetric acid anhydrides in acylation processes, as it avoids the generation of by-products resulting from an attack on the undesired acyl group in mixed anhydrides.[2]

The conventional synthesis of symmetric anhydrides involves the activation of carboxylic acids by reagents such as thionyl chloride,[3,4] carbodiimides,[5] and triphosgene;[6] the use of these reagents generates by-products, and thus reduce the atom efficiency of the reaction. The development of metal-catalyzed carbonylation of alkenes with carbon monoxide as a cheap and abundant C1 feedstock has emerged as a sustainable and highly atom-economical synthesis for acyl-bearing molecules. Applying this concept, we established a facile palladium-catalyzed carbonylative synthesis of carboxylic acid anhydrides from alkenes with carboxylic acid as co-substrates (hydroacyloxycarbonylation) as described in Chapter 2.[7]

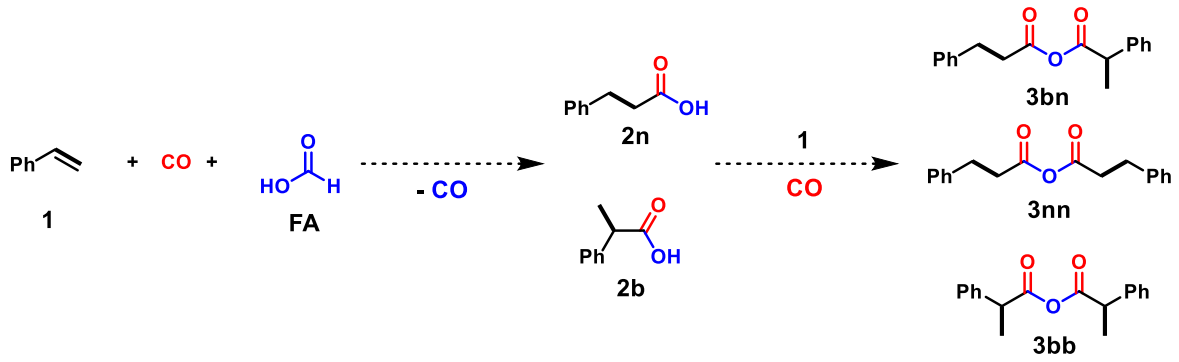
Carbonylative synthesis of carboxylic acids (hydrocarboxylation) is one of the prominent reactions in carbonylation chemistry.[8,9] Hydrocarboxylation of alkenes using formic acid (FA) in excess (at least 2.0 equivalents with respect to alkene) is one of the well-known synthetic strategies established and reported by several groups (Scheme 3.1.a).[10–15] The catalytic cycle involves formation of a mixed anhydride containing FA, which is known to be highly unstable and readily decomposes to release CO with formation of a carboxylic acid derived from the alkene. Taking this into account and based on the established catalytic conditions from our previous report on synthesis of acid anhydrides (Scheme 3.1.b), we envisaged a strategy to produce symmetric carboxylic acid anhydrides from alkenes without the need of an individually synthesized or isolated carboxylic acid co-substrate (Scheme 3.1.c). We herein present a palladium-catalyzed synthesis of symmetric carboxylic acid anhydrides from alkenes with *in situ* produced carboxylic acids.



Scheme 3.1. Proposed concept of carbonylative synthesis of symmetric acid anhydrides from alkenes without the need of corresponding carboxylic acid.

3.2. Results and Discussion

The reaction described in this chapter is a tandem reaction as shown in Scheme 3.2 using styrene (**1**) as a model substrate. In the first step, a carboxylic acid (phenylpropionic acid, **2n** or **2b**) is formed from a reaction of **1** with CO and FA. In the second step, the produced carboxylic acid will act as the nucleophile in the carbonylation of **1**, forming the carboxylic acid anhydride (phenylpropionic acid anhydride, **3nn**, **3bn** or **3bb**). To analyse the reactant and products in this reaction, we implemented NMR analysis to quantify **2** (**2n**, **2b**) and **3** (**3nn**, **3bn**, **3bb**), and GC analysis to quantify **1**. The yield% was calculated with respect to the limiting reagent (in most cases formic acid unless otherwise specified).



Scheme 3.2. Synthesis of anhydrides from styrene (**1**) and formic acid: intermediates and products.

Highly selective formation of linear acids or esters from alkenes can be achieved with a palladium-based catalytic system with the electron-rich and bulky ligand 1,2-bis(di-*tert*-butylphosphanylmethyl)benzene.[16] However, in our previous studies on carbonylative

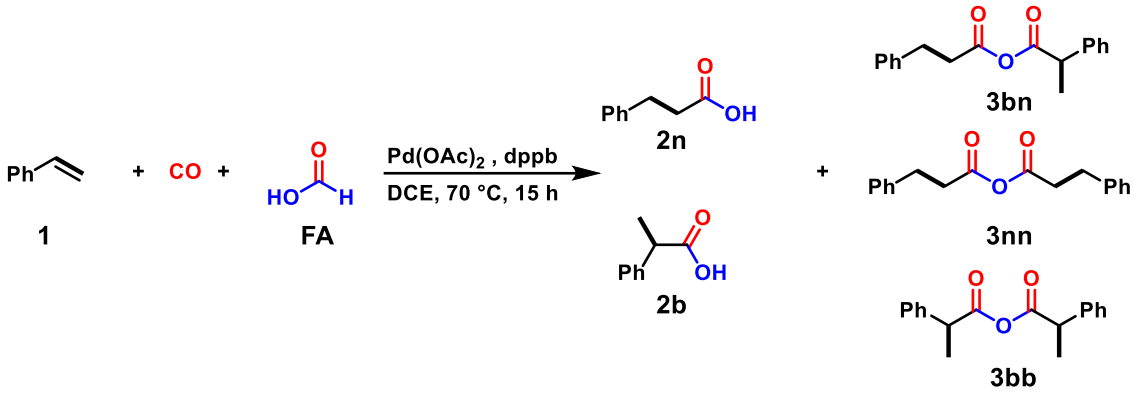
synthesis of imides and acid anhydrides, we found that use of electron-donating ligands in our catalytic system resulted in very slow catalysis and hence electron-withdrawing groups (such as phenyls) on phosphorus atoms was essential.[7,17] We also found that addition of strong acids was detrimental for catalysis; most likely it hampers formation of the carboxylate nucleophile. Based on this prior knowledge, for our initial trials in the current study we used the optimal conditions previously established for the carbonylation reaction of **1** with 3-phenylpropionic acid (**2n**): 1,4-bis(diphenylphosphanyl)butane (dppb) as the phosphine ligand, in combination with $Pd(OAc)_2$ as the pre-catalyst in 1,2-dichloroethane (DCE).

*Varying **1**:FA ratio*. Ideally, the envisioned reaction should be carried out with an alkene to FA ratio of 2:1, as in the first step one equivalent of carboxylic acid **2** should be formed, which then acts as the nucleophile in the second step forming **3**. Thus, we started our investigations with a study to establish the optimal substrate to FA ratio, as we have shown in our previous work that the hydrocarbonylation of **1** with **2n** is an equilibrium reaction (with a calculated $\Delta G_{\text{gas-phase}}$ value close to zero) and benefits from the use of an excess of one of the substrates.

We began with testing our established catalytic conditions for anhydride synthesis from alkenes with FA in excess (Table 3.1, entry 1). As expected, this resulted in ~90% phenylpropionic acid (**2**, 82:18 **2n**:**2b**), which confirmed the instability of the produced formate anhydride. An equimolar ratio of **1**:FA resulted in the same yield of **2** with only a trace amount of **3nn** (Table 3.1, entry 2). As decomposition of the formate anhydride to **2** is accompanied by the formation of CO, overall the net reaction does not consume CO, as is nicely demonstrated by the absence of a CO pressure drop (Figure AII.1). The result of this reaction seems to indicate faster kinetics of the nucleophilic attack by FA than by carboxylic acid **2**, as hardly any anhydride is formed. However, it cannot be excluded that upon formation of **3** a subsequent disproportionation reaction with FA ultimately results in generation of more **2**.

Use of stoichiometric amounts (for the net desired reaction) of **1** and FA of 2:1 resulted in 70% yield of phenylpropionic anhydride (**3**) (Table 3.1, entry 3). This value is similar to the equilibrium yield reported in our previous work.[7] Increasing the molar ratio of **1**:FA to 3:1 led to formation of **3** with a yield of 86% (Table 3.1, entry 4; please note that this yield is calculated with respect to the limiting reagent FA, the yield based on **1** is 57%). With the same amount of catalyst, the reaction could be scaled to 30:10 mmol **1**:FA generating a yield of 88% (Table 3.1, entry 5). Overall, we observe that the linearity obtained in both steps of the reactions is 75 to 80%, as reflected in the approximate 4:1 ratio found for **2n**:**2b**, and **3nn**:**3bn**:**3bb** ratios approaching the statistically expected values of 64:32:4.

Table 3.1. Influence of relative substrate ratio on product formation.[a]

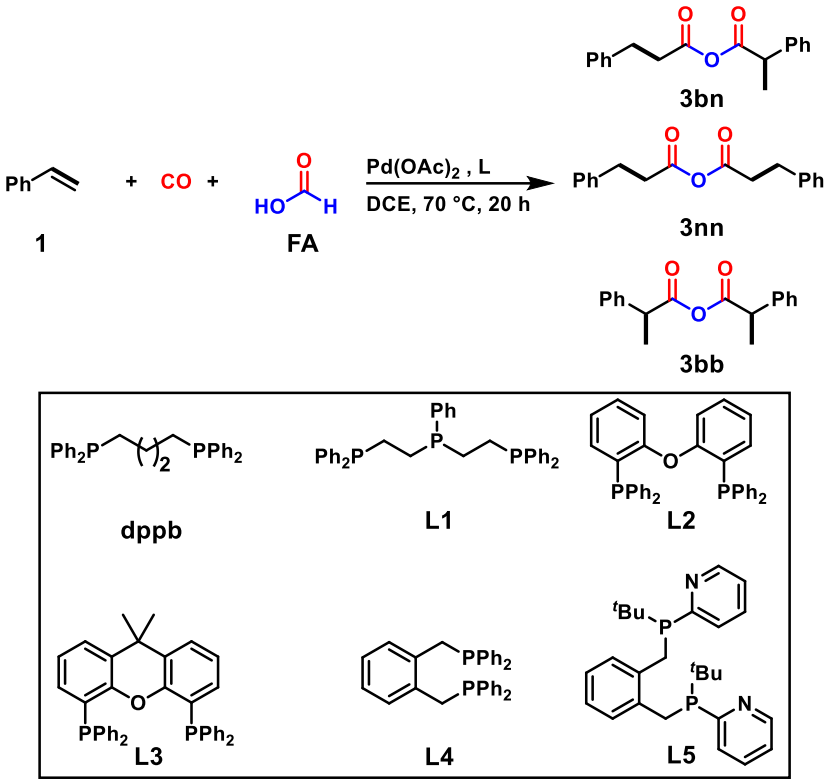


Entry	1:FA (mmol)	2 (mmol)	3 (mmol) (3nn:3bn:3bb)
1	5:10	4.5	0
2	5:5	4.6	Trace
3	10:5	1.3	3.5 (59:34:7)
4	15:5	1.0	4.3 (58:37:5)
5	30:10	1.5	8.8 (54:40:6)

[a] Reaction conditions: CO (50 bar), $Pd(OAc)_2$ (0.05 mmol), dppb (0.10 mmol), DCE (6 mL), 70 °C, 15 h. Amount of products and regioselectivity of **2** and **3** determined by quantitative NMR analysis with dibromomethane as internal standard (error ± 5%).

Influence on regioselectivity by ligands. We tested several phosphine ligands to study their influence on the reactivity and regioselectivity of the catalytic system (Table 3.2). A catalytic system comprising the tridentate ligand **L1** did not yield any product. Use of **L2** resulted in 82% yield of **3**, whereas use of **L3** resulted in a total anhydride yield of 72%, but at a reaction temperature of 85 °C. Rigid backbone, **L4** and **L5**, were tested for their activity. Interestingly, the xylene-based ligand **L4** resulted in 28% yield of **3** and 20% yield of **2** (also see Table AII.2, entry **L4**); apparently, the rigidity of the backbone significantly lowers the rate of the reaction. Similarly, the rate of the reaction comprising the catalytic system with **L5** is even lower, yielding only 16% of **3** and 60% of **2**, with a **2n**:**2b** ratio of 66:34 (also see Table AII.2, entry **L5**). In conclusion, the tested ligands mostly affect the rate of the reactions. Use of the more rigid **L4** or more electron-donating **L5** result in low yields of anhydride **3** and build-up of intermediate **2**. The linearity in products is approximately the same (75-80%) in all reactions with catalytic systems comprising phenyl-containing ligands, whereas use of **L5** leads to a lower linearity of about 65-70%.

Table 3.2. Influence of ligands on the yield and regioselectivity in the formation of anhydrides.



Entry	Ligand	Yield% of 3	3nn:3bn:3bb
1[a]	**dppb**	86	58:37:5
2	**L1**	0	-
3	**L2**	82	61:34:5
4[b]	**L3**	72	58:35:7
5[c]	**L4**	28	57:43:trace
6[c]	**L5**	16	47:53:trace

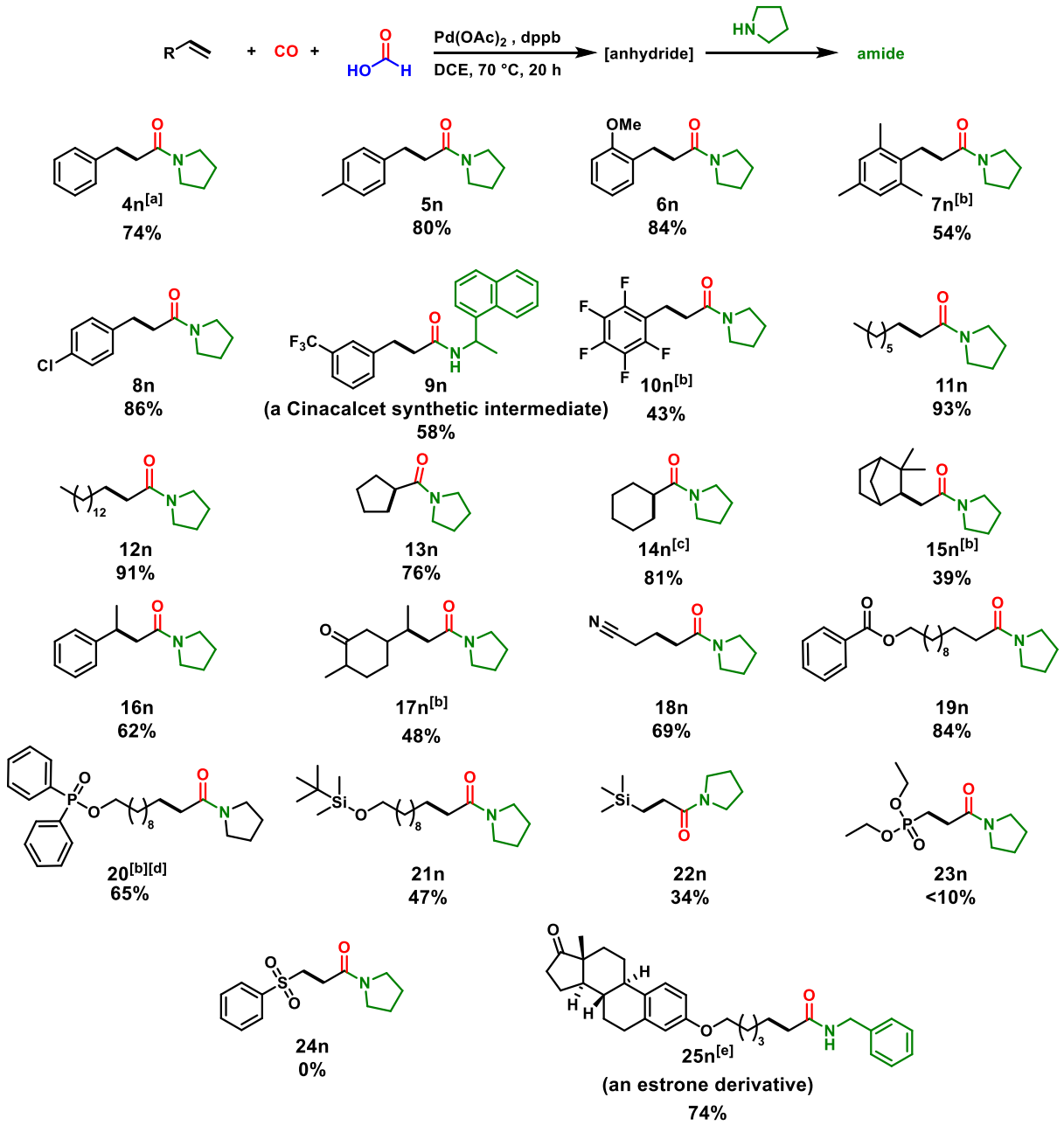
Reaction conditions: **1** (15.0 mmol), FA (5.0 mmol), CO (50 bar), $Pd(OAc)_2$ (0.05 mmol), ligand (0.10 mmol), DCE (6 mL), 70 °C, 20 h. Yield% (based on FA) and regioselectivity of **3** determined by NMR analysis with dibromomethane as internal standard. [a] 15 h instead of 20 h. [b] 85 °C instead of 70 °C. [c] **1** (7.5 mmol), FA (2.5 mmol), $Pd(OAc)_2$ (0.025 mmol), ligand (0.325 mmol).

Substrate Scope. Based on the commercial availability of the ligand dppb, and the fact that the different ligands result in more or less the same selectivity, a series of substrates were screened using the most active catalytic system dppb/$Pd(OAc)_2$ at an alkene:FA ratio of 3:1 and a catalyst loading of 1.0 mol% (Scheme 3.3). Since acid anhydrides are prone to degradation on isolation, the reaction mixtures were derivatized with pyrrolidine (unless specified otherwise) in basic conditions (see Section AII.5) to produce amides **4**; the amount of pure linear amide isolated by column chromatography is reported (provided yield% is related to FA as the limiting reagent, the numbers should be multiplied with 0.67 to obtain the yield% relative to alkene).

Linear amide **4n** was isolated in 74% yield from our benchmark reaction with **1**. The reaction can be applied to a large variety of styrene-based substrates, resulting in **5n**–**10n** in reasonable to high yields of 43-86%. In some of the reactions the NMR yield of the intermediate anhydride was significantly higher (Table AII.3), indicating that either the derivatization reaction or the isolation of the amide product is more difficult. The reaction with trimethylstyrene as the substrate appeared to be significantly slower, as observed from the CO pressure drop (still dropping after a reaction time of 36 h), leading to a yield of 54% **7n** on derivatization. The reaction with *m*-CF_3-styrene resulted in 68% of anhydride and was derivatized with another amine, (1R)-(+)-1-naphthylethylamine, providing **9n** in a yield of 58%. This compound **9n** is an intermediate in the synthesis of the Cinacalcet,[18,19] a drug used to treat hyperparathyroidism in patients on dialysis with chronic kidney disease.

Unactivated long-chain alkenes such as 1-octene and 1-pentadecene yielded 93% **11n** and 91% **12n**, respectively. Cyclic alkenes are also efficiently converted into their corresponding amides, yielding 76% **13n** and 81% **14n**. The sterically demanding substrate (±)camphene yielded 39% **15n** (2:1 endo:exo) after a reaction time of 36 h. The CO pressure drop indicated that the catalysis was slow. Geminal disubstituted alkenes, α-methylstyrene and dihydrocarvone, yielded 62% **16n** and 48% **17n** (after 36 h), respectively. The catalytic system was found to be tolerant to functional groups such as ether (**6n**), ketone (**17n**), nitrile (**18n**), ester (**19n**), phosphinate ester (**20**) and silyl-/silylether (**21n**, **22n**), and gave modest (34% **22n**) to excellent (84% **19n**) yields. However, vinyl-based substrates containing a sulfone or phosphate group at the vicinal position generated little (<10%) or no anhydride. Palladium black formation was observed in catalytic reactions with substrates containing silyl or silylether functional groups.

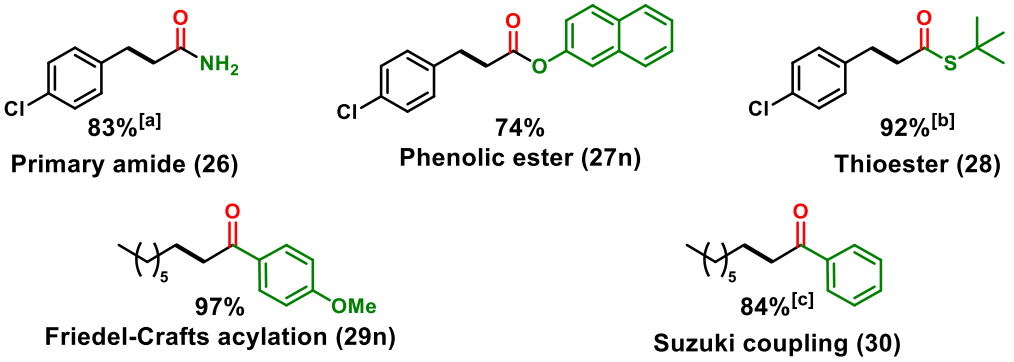
The reactions in this substrate scope were carried out using an excess of alkene (alkene:FA of 3:1), in order to drive the equilibrium to completion. However, whereas FA is readily available, very often the substrate alkenes are expensive or obtained after a multi-step synthetic route. The catalytic procedure was applied to an estrone derivative (scale: 2:1 mmol). For this reaction a catalyst loading of 2.5 mol% was used in order to obtain a reasonable rate for this dilute reaction, and 74% benzylamide **25n** was attained on derivatization with benzylamine.



Scheme 3.3. Synthesis of amides from alkenes and *in situ* generated carboxylic acid *via* carbonylation. Reaction conditions: alkene (3.0 equiv.; 15 or 7.5 mmol), FA (1.0 equiv.; 5 or 2.5 mmol), CO (50 bar), $Pd(OAc)_2$ (1.0 mol%), dppb (2.0 mol%), DCE (6.0 mL), 70 °C, 20 h. [a] 15 h instead of 20 h. [b] 36 h instead of 20 h. [c] alkene (3.0 equiv.; 30 mmol), FA (1.0 equiv.; 10 mmol), CO (50 bar), $Pd(OAc)_2$ (0.5 mol%), dppb (1.0 mol%), DCE (6.0 mL), 70 °C, 24 h. [d] presence of branched product, ratio of l:b 79:21. [e] alkene (2.0 mmol), FA (1.0 mmol), CO (50 bar), $Pd(OAc)_2$ (2.5 mol%), dppb (5.0 mol%), DCE (6.0 mL), 70 °C, 20 h. Yield% are based on FA.

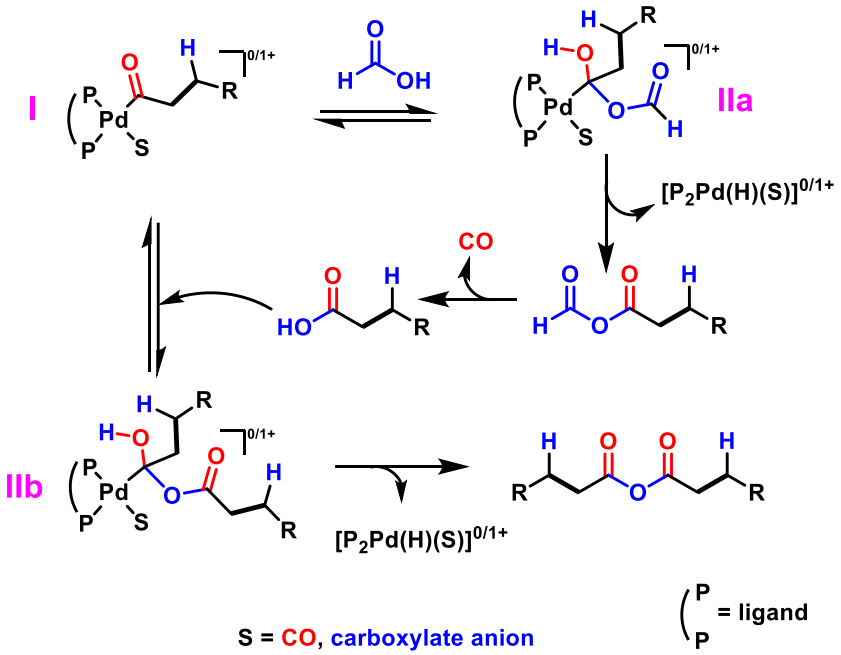
Applications. The reactivity of acid anhydrides allows access to molecules that may be otherwise difficult to obtain *via* classical hydrocarbonylation reactions, either due to low reactivity of the nucleophile or poisoning of the catalyst by the nucleophile. The synthesis of primary amides using ammonia as nucleophile in carbonylation reactions is challenging, owing to the basicity of ammonia hindering metal-hydride formation, and the deactivation of the metal catalyst by formation of unreactive ammine complexes.[20,21] With our catalytic procedure

generating intermediate anhydrides from alkenes and FA, a one-pot derivatization with ammonia resulted in 83% of the primary amide **26** in 79% linearity. Poorly nucleophilic alcohols such as β-naphthol reacted with our catalytic mixture to form ester **27n** in a yield of 74%. Thiols, which are often considered as poisons in palladium-mediated catalysis, can be used as nucleophiles to produce thioesters,[22] and indeed derivatization of a reaction mixture with *tert*-butylthiol resulted in 92% thioester **28** with 85% linear selectivity Finally, we were able to generate ketones in excellent yields *via* a Friedel-Crafts acylation with anisole (97%, **29n**), and a metal-catalyzed Suzuki coupling with phenylboronic acid (84%, **30**).



Scheme 3. 4. One-pot derivatizations of catalytic reaction mixtures to synthesis amide, ester, thioester and ketones. [a] presence of branched product, l:b 79:21. [b] presence of branched product, l:b 85:15. [c] presence of branched product, l:b 92:8. Yield% is based on FA.

Mechanism. The carbonylation reaction with carboxylic acids as the nucleophiles most likely proceeds *via* the classical palladium-hydride[23,24] mechanism for the two cycles, first with FA as the nucleophile forming the formate anhydride that decomposes to a carboxylic acid, which then acts as the nucleophile in the second reaction (Scheme 3.5). Thus, in the first cycle acyl-palladium species **I** undergoes a nucleophilic attack by FA to form a formate-mixed anhydride *via* intermediate **IIa**. This formate acid anhydride is unstable at higher temperatures, decomposing to release CO and carboxylic acid. The CO released in this case compensates for the CO consumed and hence, we do not observe a drop in CO pressure when we use equimolar amounts of **1**:FA to form **2** (see Figure AII.1). The formed carboxylic acid may then act as a nucleophile reacting with **I** to form **IIb**, which yields the acid anhydride fully derived from two molecules of the alkene. Since the acid anhydride formed in the reaction may equilibrate with the regeneration of the reactants, an excess of the alkene may promote the reaction in the forward direction towards the desired product.



Scheme 3.5. Postulated mechanism of tandem hydroacyloxycarbonylation of alkenes to synthesize acid anhydrides.

3.3. Conclusion

In summary, a carbonylative synthesis is reported for the production of symmetric anhydrides from alkenes *via* tandem reaction using FA for *in situ* generation of a carboxylic acid. The catalytic procedure is applicable to a wide range of substrates and is tolerant to various functional groups to produce moderate to excellent yields of anhydrides that are derived from two molecules of the alkene substrate. Further, the anhydrides formed can be derivatized to amides, esters, thioesters and ketones by simple one-pot derivatization reactions. Moreover, a recent report on formation of two molecules of acyl derivative, instead of one, by electrophilic activation of symmetric acid anhydrides[25] further adds to the future scope for sustainability of this reaction.

3.4. References

(1) El-Faham, A.; Albericio, F. Peptide Coupling Reagents, More than a Letter Soup. *Chem. Rev.* **2011**, *111* (11), 6557–6602.
(2) Kim, J.; Jang, D. O. A Convenient Method for Synthesis of Symmetrical Acid Anhydrides from Carboxylic Acids with Trichloroacetonitrile and Triphenylphosphine. *Synth. Commun.* **2001**, *31* (3), 395–399.
(3) Adduci, J. M.; Ramirez, R. S. Anhydride Formation with Thionyl Chloride. *Organic Preparations and Procedures* **1970**, *2* (4), 321–325.
(4) Kazemi, F.; Kiasat, A. R. Dabco/SOCl 2 , Mild, and Convenient Reagent for the Preparation of Symmetrical Carboxylic Acid Anhydrides. *Phosphorus, Sulfur, and Silicon and the Related Elements* **2003**, *178* (10), 2287–2291.
(5) Selinger, Z.; Lapidot, Y. Synthesis of Fatty Acid Anhydrides by Reaction with Dicyclohexylcarbodiimide. *J. Lipid Res.* **1966**, *7* (1), 174–175.
(6) Kocz, R.; Roestamadji, J.; Mobashery, S. A Convenient Triphosgene-Mediated Synthesis of Symmetric Carboxylic Acid Anhydrides. *J. Org. Chem.* **1994**, *59* (10), 2913–2914.
(7) Ramakrishnan, A.; Romeijn, S. G.; Bouwman, E. Palladium-Catalyzed Synthesis of Carboxylic Acid Anhydrides from Alkenes. *J. Catal.* **2023**, *in press*, DOI: 10.1016/j.jcat.2023.115192.

(8) Kalck, P.; Urrutigoïty, M.; Dechy-Cabaret, O. Hydroxy- and Alkoxycarbonylations of Alkenes and Alkynes. In *Catalytic Carbonylation Reactions*; Beller, M., Ed.; Topics in Organometallic Chemistry; Springer: Berlin, Heidelberg, 2006; pp 97–123.
(9) Brennführer, A.; Neumann, H.; Beller, M. Palladium-Catalyzed Carbonylation Reactions of Alkenes and Alkynes. *ChemCatChem* **2009**, *1* (1), 28–41.
(10) El Ali, B.; Alper, H. Formic Acid-Palladium Acetate - l,4-bis(diphenylphosphino)butane: An Effective Catalytic System for Regioselective Hydrocarboxylation of Simple and Functionalized Olefins. *J. Mol. Catal.* **1992**, *77*, 7-13.
(11) El Ali, B.; Alper, H. Palladium Acetate Catalyzed Synthesis of Cycloalkylacetic Acids by Regioselective Hydrocarboxylation of Methylenecycloalkanes with Formic Acid and l,4-bis(diphenylphosphino)butane . *J. Org. Chem.* **1993**, *58* (13), 3595–3596.
(12) Wang, Y.; Ren, W.; Shi, Y. An Atom-Economic Approach to Carboxylic Acids *via* Pd-Catalyzed Direct Addition of Formic Acid to Olefins with Acetic Anhydride as a Co-Catalyst. *Org. Biomol. Chem.* **2015**, *13* (31), 8416–8419.
(13) Okada, M.; Takeuchi, K.; Matsumoto, K.; Oku, T.; Choi, J.-C. Hydroxycarbonylation of Alkenes with Formic Acid Using a Rhodium Iodide Complex and Alkyl Ammonium Iodide. *Org. Biomol. Chem.* **2021**, *19* (40), 8727–8734.
(14) Okada, M.; Takeuchi, K.; Matsumoto, K.; Oku, T.; Yoshimura, T.; Hatanaka, M.; Choi, J.-C. Hydroxycarbonylation of Alkenes with Formic Acid Catalyzed by a Rhodium(III) Hydride Diiodide Complex Bearing a Bidentate Phosphine Ligand. *Organometallics* **2022**, *41* (13), 1640–1648.
(15) Ren, W.; Wang, M.; Guo, J.; Zhou, J.; Chu, J.; Shi, Y.; Shi, Y. Pd-Catalyzed Regioselective Branched Hydrocarboxylation of Terminal Olefins with Formic Acid. *Org. Lett.* **2022**, *24* (3), 886–891.
(16) Vondran, J.; Furst, M. R. L.; Eastham, G. R.; Seidensticker, T.; Cole-Hamilton, D. J. Magic of Alpha: The Chemistry of a Remarkable Bidentate Phosphine, 1,2-Bis(Di-Tert- Butylphosphinomethyl)Benzene. *Chem. Rev.* **2021**, *121* (11), 6610–6653.
(17) Limburg, B.; Gloaguen, Y.; de Bruijn, H. M.; Drent, E.; Bouwman, E. Palladium-Catalyzed Isomerization/(Cyclo)Carbonylation of Pentenamides: A Mechanistic Study of the Chemo- and Regioselectivity. *ChemCatChem* **2017**, *9* (15), 2961–2971.
(18) Bijukumar, G.; Maloyesh, B.; Bhaskar, B. S.; Rajendra, A. Efficient Synthesis of Cinacalcet Hydrochloride. *Synth. Commun.* **2008**, *38* (10), 1512–1517.
(19) Thiel, O. R.; Bernard, C.; Tormos, W.; Brewin, A.; Hirotani, S.; Murakami, K.; Saito, K.; Larsen, R. D.; Martinelli, M. J.; Reider, P. J. Practical Synthesis of the Calcimimetic Agent, Cinacalcet. *Tetrahedron Lett.* **2008**, *49* (1), 13–15.
(20) Roundhill, D. M. Transition Metal and Enzyme Catalyzed Reactions Involving Reactions with Ammonia and Amines. *Chem. Rev.* **1992**, *92* (1), 1–27.
(21) Zhao, J.; Goldman, A. S.; Hartwig, J. F. Oxidative Addition of Ammonia to Form a Stable Monomeric Amido Hydride Complex. *Science* **2005**, *307* (5712), 1080–1082.
(22) Gui, B.; Yee, K.-K.; Wong, Y.-L.; Yiu, S.-M.; Zeller, M.; Wang, C.; Xu, Z. Tackling Poison and Leach: Catalysis by Dangling Thiol–Palladium Functions within a Porous Metal–Organic Solid. *Chem. Commun.* **2015**, *51* (32), 6917–6920.
(23) Eastham, G. R.; Tooze, R. P.; Heaton, B. T.; Iggo, J. A.; Whyman, R.; Zacchini, S. Synthesis and Spectroscopic Characterisation of All the Intermediates in the Pd-Catalysed Methoxycarbonylation of Ethene. *Chem. Commun.* **2000**, *7*, 609–610.
(24) Clegg, W.; Eastham, G. R.; Elsegood, M. R. J.; Heaton, B. T.; Iggo, J. A.; Tooze, R. P.; Whyman, R.; Zacchini, S. Synthesis and Reactivity of Palladium Hydrido-Solvento Complexes, Including a Key Intermediate in the Catalytic Methoxycarbonylation of Ethene to Methyl Propanoate. *J. Chem. Soc., Dalton Trans.* **2002**, *17*, 3300–3308.
(25) Kumar, V.; Rana, A.; Lal Meena, C.; Sharma, N.; Kumar, Y.; Mahajan, D. Electrophilic Activation of Carboxylic Anhydrides for Nucleophilic Acylation Reactions. *Synthesis* **2018**, *50* (19), 3902–3910.