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Ruthenium-Catalyzed Coupling Reactions of CO₂ with C₂H₄ and Hydrosilanes towards Silyl Esters

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Dedicated to Prof. Pierre H. Dixneuf for his outstanding contribution to organometallic chemistry and catalysis.

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Abstract: A series of in situ-prepared catalytic systems incorporating Ru(II) precursors and bidentate phosphine ligands has been probed in the reductive carboxylation of ethylene in the presence of triethylsilane as reductant. The catalytic production of propionate and acrylate silyl esters was evidenced by high-throughput screening (HTS) and implemented in batch reactor techniques. The most promising catalyst systems identified were made of Ru(H)(Cl)(CO)(PPh₃)₃ and 1,4-bis(dicyclohexylphosphino)butane (DCPB) or 1,1'-ferrocene-diylbis(cyclohexylphosphine) (DCPF). A marked influence of water on the acrylate/propionate selectivity was noted. Turnover numbers (TON, mol.mol(Ru)⁻¹) up to 16 for acrylate and up to 68 for propionate were reached under relatively mild conditions (20 bar, 100 °C, 0.5 mol% Ru, 40 mol% H₂O vs. HSiEt₃). Possible mechanisms are discussed.

The use of cheap and non-toxic carbon dioxide for C–C coupling with unsaturated substrates (alkenes, alkynes, epoxides...) constitutes a valuable synthetic route toward carboxylic acids and carbonates, which are commodities and highly versatile starting materials toward fine chemicals.^[1–3] Unfortunately, due to the inherent stability of CO₂, highly reactive and difficult to handle organometallic co-reagents are often needed.^[4] To circumvent these waste-producing synthetic routes, tremendous efforts have been paid over the last 40 years, eventually leading to efficient achievements in transition-metal catalyzed CO₂-incorporative reactions. Reductive carboxylation of unsaturated hydrocarbons with CO₂ and its direct insertion into C–H bond to give carboxylic moieties have become powerful alternatives to usual methodologies.^[5–7] Moreover, synthesizing carboxylic derivatives from inexpensive starting materials such as ethylene is an attractive and cost-efficient transformation.^[8] Pioneering studies reported by Lapidus *et al.* in 1978 proved the feasibility of transforming C₂H₄ and CO₂ into propionic acid using Rh and Pd catalysts in the presence of HBr under very harsh conditions (Scheme 1).^[9] This discovery revolutionized and encouraged new developments in this area. The synthesis of acrylic acid, a very important base chemical used in the preparation of a variety of (co)polymers, was subsequently described in the 1980s.^[10–23] When mixing ethylene and CO₂ in presence of DBU and Ni complexes, Hoberg *et al.* reported the first isolation of a stable nickelalactone intermediate,^[18] yet, the reaction was not catalytic. The first catalytic synthesis of sodium acrylate with a

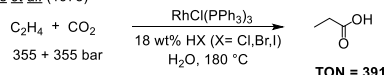
TON of 10 was disclosed by Limbach and coworkers with a Ni(COD)₂/diphosphine system and NaOtBu as base.^[24] Upon utilizing less nucleophilic sodium phenoxides and Zn-dust as reductant, the same group achieved TON up to 107 (Scheme 1).^[25] Following a similar strategy, Vogt and coworkers developed a process with a Ni-DCPP catalyst relying on β-H elimination induced by a strong Lewis acid,^[26] in the presence of (over)-stoichiometric amounts of LiI, NEt₃ and Zn-dust, regeneration of the active Ni-DCPP catalyst species was achieved, affording acrylate metal salts with TON up to 21. Very recently, Bernskoetter and coworkers employed a similar approach by using a phenoxide base (3-FC₆H₄ONa) with TON up to 82.^[27] Carboxylation reactions of alkenes using other metal-based catalysts such as Mn, W, Fe and Rh, have also been studied and supported by theoretical studies, bringing insights to the reaction mechanisms.^[28–34] For example, Leitner and coworkers reported a catalyst system involving [RhCl(CO)₂]₂ coupled with CH₃I as promoter and H₂ as reductant for the “hydrocarboxylation” of alkenes (Scheme 1).^[35] Actually, this route is based on a carbonylation reaction in which the active C1 synthon (CO) is released *via* a reverse water-gas-shift reaction in the presence of H₂ or alcohols. Very recently, Iwasawa's group reported the synthesis of acrylate alkali metal salts with Ru-based catalysts (Scheme 1);^[36] TON up to 15 were achieved using 1000 equiv of Cs₂CO₃ as base in DMA under 3 bar C₂H₄/CO₂. Hence, although promising activities and selectivities were achieved, most of the above protocols are plagued by the use of stoichiometric amounts of metal co-reagents.

In the present study, we aimed at identifying – using High-Throughput Screening (HTS) techniques – effective catalytic systems for the carboxylation of ethylene in the presence of alternative, readily available co-reagents, namely hydrosilanes (Scheme 2).^[37] The favored formation of the Si–O bond (BDE = 460 kJ.mol⁻¹)^[38] and the relative facile activation of the Si–H bond (BDE = 314 kJ.mol⁻¹) make hydrosilanes (such as Et₃SiH)^[38] good reductants under relatively mild conditions. We thus envisioned that such reactants may enable release of the free acrylate product from a putative metallalactone intermediate, formed by the activation of CO₂ via oxidative cyclization with ethylene.^[39] Moreover, the highly tunable reactivity of hydrosilanes and the ease of handling (stable liquids) make them interesting competitive reducing agents as compared to metals and organometallic hydrides and alkyls. Thus, the above

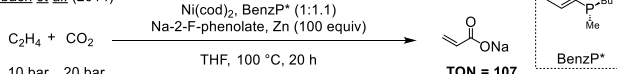
process involving hydrosilanes as reductants can constitute a reliable model for related carboxylation processes operating with H_2 and intermediated by metal-hydrido complexes. Also, silyl acrylate esters issued from this process are valuable precursors in the synthesis of poly(silyl ester) copolymers, of interest as fouling-resistant coatings and self-polishing materials.^[40,41]

Previous works

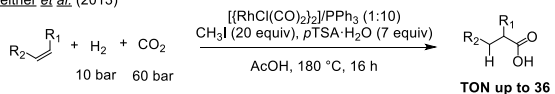
Lapidus *et al.* (1978)



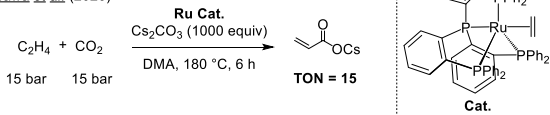
Limbach *et al.* (2014)



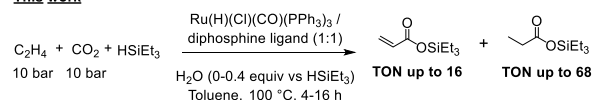
Leitner *et al.* (2013)



Iwasawa *et al.* (2020)



This work

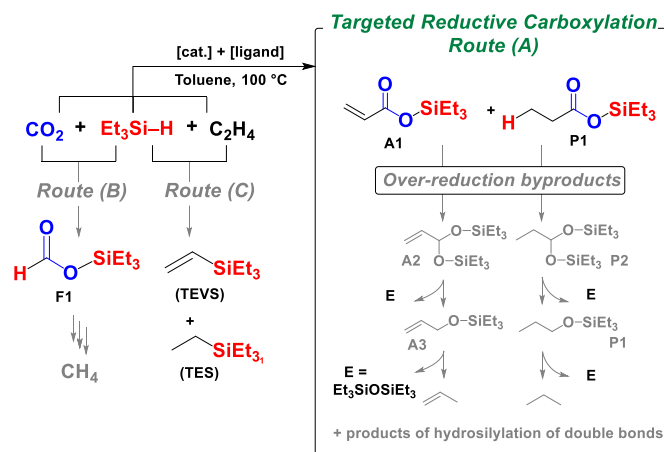


Scheme 1. Previous reports of metal-mediated carboxylation of olefins and present work

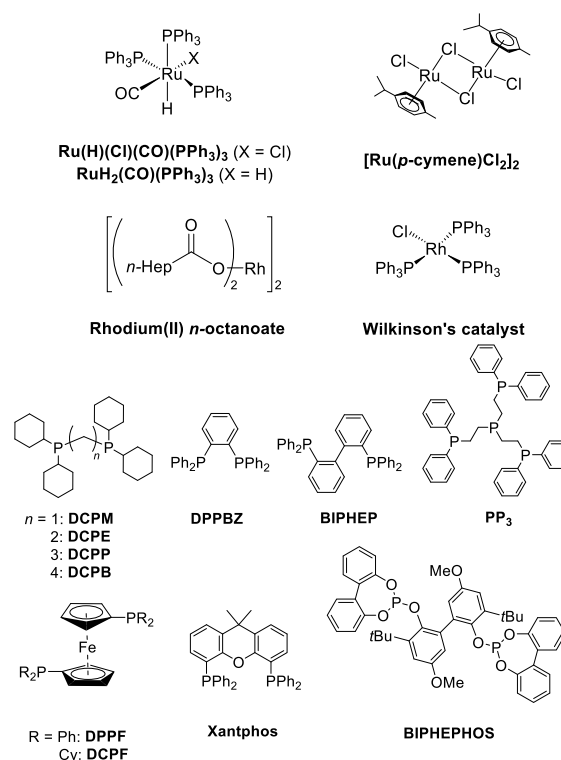
Our approach relied on the evaluation of combinations of various ligands, especially multidentate phosphines, with group 8 and 9 metal precursors, in the presence of different hydrosilanes. Using a combinatorial HTS facility, series of parallel 24 tests were performed, involving commercial metallic precursors such as $Ru(H)(Cl)(CO)(PPh_3)_3$, $[Ru(p\text{-cymene})Cl_2]_2$, $[Rh(n\text{-octanoate})_2]_2$, Wilkinson's catalyst and a set of diphosphine ligands with variable stereo-electronic features (Scheme 3). A monohydrosilane, $HSiEt_3$, was used for the screening. Based on the results of preliminary investigations, the following conditions were applied for the HTS experiments: solvent (toluene, 2 mL); equimolar C_2H_4 - CO_2 gas mixture ($P_{\text{total}} = 20$ bar); Et_3SiH (0.86 mmol); $[precursor]_0 = [ligand]_0 = 0.5$ mol% vs. hydrosilane; reaction temperature = $100^\circ C$; reaction time = 16 h. Crude reactions mixtures were analyzed automatically by GC-FID and GC-MS.

Scheme 2 summarizes the three possible different series of products that can form through the corresponding, competing reaction pathways, namely routes A, B and C. Thus, besides the reductive carboxylation reaction of ethylene (Route A) towards the targeted triethylsilyl propionate (**P1**) and acrylate (**A1**) products, subsequent over-reduction by-products can form, namely **P2**, **P3**, propane and **A2**, **A3**, propene, respectively, along with disiloxane **E**. Route B is the hydrosilylation reaction of CO_2 towards, first, triethylsilyl formate (**F1**) and, subsequently, the series of over-reduction products up to methane.^[42] However,

the main competitive pathway that we experienced comprises the two separate reactions between ethylene and hydrosilane, that is hydrosilylation and dehydrogenative coupling, yielding the corresponding tetraethylsilane (TES) and triethylvinylsilane (TEVS).^[43] The analytical techniques developed in this study (see SI for details) enabled unequivocal separation, authentication and quantification of most of the above possible products (except the gaseous ones); overall silane balance closures of 72-91% were obtained in most cases (see SI).



Scheme 2. Possible products of the coupling reaction of CO_2 with C_2H_4 in the presence of Et_3SiH .



Scheme 3. Main $Ru(II)$ and $Rh(I,II)$ precursors and diphosphine ligands used in this study.

During the first series of HTS tests, many combinations were found to enable high conversions (> 60%) of Et₃SiH. However, the targeted **P1** and **A1** products were not the major products obtained, as the Route C products (TES and TEVS) were detected in high yields. However, we were able to identify a few effective metal precursor/ligand combinations that produce quantifiable and, in some cases, remarkable amounts of the targeted **P1** and **A1**. In particular, the following Ru-based systems were pinpointed: Ru(H)(Cl)(CO)(PPh₃)₃/DCPB, Ru(H)(Cl)(CO)(PPh₃)₃/PP₃, Ru(H)(Cl)(CO)(PPh₃)₃/DPPF, [Ru(*p*-cymene)Cl₂]₂/DCPB and [Ru(*p*-cymene)Cl₂]₂/DPPF (Scheme 3). For the first time, these group 8 metal-based systems appeared to give a direct access to silyl esters from ethylene, CO₂ and hydrosilane, with moderate to high HSiEt₃ conversions.

These reactions using the “hit” catalyst combinations were next reproduced in batch experiments using 50 mL-autoclaves (entries 1–5, Table 1). The combination giving **A1** in higher amounts was Ru(H)(Cl)(CO)(PPh₃)₃/DCPB (entry 3, TON = 13). The related catalyst system based on the DCPF ligand – that has a more rigid ferrocenyl backbone but with a bite angle of 99 ° just slightly larger as compared to 94 ° for the butylene-bridged DCPB^[44] – returned quite similar results (Table 1, entries 3 vs. 6).

Evaluation of the influence of the alkylene chain length in the bidentate bis(dicyclohexylphosphine) ligand on the catalytic performance was undertaken under the above-defined reaction

conditions. When using DCPM instead of DCPB, high TON for the route C products were obtained, but **A1** and **P1** were not detected at all (entry 7). On the other hand, when using the homologous ethylene-bridged DCPE and propylene-bridged DCPD ligands, low amounts of the Route A products became detectable again (entries 8 and 9). These observations, highlighting a monotonous dependence of the TON for carboxylation products with the length of the alkylene backbone, suggest, not unexpectedly, that the P–Mt–P bite angle has a major influence on the activity and selectivity of the reaction.

Regarding the nature of the PR₂ moieties within the chelating fragment, a comparison between DPPF and DCPF shows that replacement of phenyl by cyclohexyl groups increases conversions from 16% to 49% as well as selectivities toward the Route A products (entries 5 vs. 6). In the case of DPPB ligand, although **A1** and **P1** were still formed in small amounts, a significant difference in selectivity was observed as compared to DCPB (see SI, Table S3). Whereas phenyl and cyclohexyl groups are rather similar in terms of steric bulkiness, PCy₂ moieties are much more basic than their PPh₂ counterparts, and this is known to dramatically affect both structural arrangement and reactivity of the [(P–P)Ru] fragment. Hence, in addition to the bite angle, basicity of the P residues is another key factor in this process. Replacing the cyclohexyl by cyclopentyl groups on the butylene-bridged chelating phosphine provided comparable results toward route A products (entries 3

Table 1. Catalytic results from batch experiments^[a]

Entry	Precursor / ligand (1:1, 0.5 mol%) / additive [mol%] (vs. HSiEt ₃)	Conv. HSiEt ₃ [mol%] ^[b]	TON (mol(product).mol(Ru) ⁻¹) ^[c]					
			Route A products		Route B and C products			
			A1	P1	F1	TES	TEVS	E
1	[Ru(<i>p</i> -cymene)Cl ₂] ₂ / DCPB	>98	0	0	0	180	traces	traces
2	Ru(H)(Cl)(CO)(PPh ₃) ₃ / PP ₃	29	0	0	0	traces	2	0
3	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPB	54	13	1.3	16	4	53	1.6
4	[Ru(<i>p</i> -cymene)Cl ₂] ₂ / DPPF	67	0	3	0	74	16	2
5	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DPPF	16	0.2	0.4	0	10	4	0.4
6	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPF	49	10	traces	0	3	26	3
7	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPM	>98	0	0	0	20	180	traces
8	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPE	55	traces	1.0	8.0	2.0	60	traces
9	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPD	81	traces	traces	1.0	8	66	26
10 ^[d]	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DC ^p PB ^[d]	44	12	2	9	4	48	traces
11	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPB / H ₂ O [10]	63	15	23	5	3	47	4
12	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPB / H ₂ O [20]	83	16	42	10	4	82	4
13	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPB / H ₂ O [40]	97	4	68	3	5	84	1
14	Ru(H)(Cl)(CO)(PPh ₃) ₃ / DCPB / H ₂ O [80]	89	0	48	14	6	108	traces
15	Ru(H) ₂ (CO)(PPh ₃) ₃ / DCPB	40	26	1	12	2	7	1
16 ^[e]	Ru(H) ₂ (CO)(PPh ₃) ₃ / DCPB / H ₂ O [20]	68	22	24	1	3	10	3

^[a] Reaction conditions: toluene (20 mL), [Si–H]₀ = 0.43 mol·L⁻¹, [Ru]₀ = [ligand]₀ = 0.002 mol·L⁻¹, CO₂/C₂H₄ 1:1 mol/mol, P(CO₂) + P(C₂H₄) = 20 bar; 16 h; results of at least duplicated experiments and averaged TON values. ^[b] Determined by integration of the ¹H NMR peaks vs. those of the standard ((Me₃Si)₄Si). ^[c] Turnover number as determined by GC-FID using *n*-dodecane as internal standard. ^[d] DC^pPB = 1,4-bis(dicyclopentylphosphino)butane. ^[e] 4h

vs. 10).

Evaluation of the temperature was conducted on the most efficient catalytic system in order to further optimize conversion and selectivity (see Table S2, SI, for details). Below 80 °C, route C products were mostly formed. At 120 °C and above, the selectivity for Route A products decreased to the benefit of Route B and C products; hence, the reaction was better conducted at 100 °C.

In the literature, co-reagents such as bases,^[24] methylating reagents,^[45–48] Lewis acids^[49,50] or phosphine ligands^[51] are often added to promote cleavage of metallalactones and release of the free acrylate products. Hence, to identify conditions for a more selective production of the desired carboxylation products, we investigated the influence of several additives such as Al(OTf)₃, KPF₆, CsF, KF. Yet, no significant variations were observed in the presence of such additives. On the other hand, addition of water much affected triethylsilane conversion and selectivities towards Route A products (entries 11–14). With only 0.1 equiv (vs. HSiEt₃) of H₂O, a slightly higher conversion of HSiEt₃ and a dramatic increase in the formation of **P1** were observed (compare entries 11 and 3). With more water (0.2 and 0.4 equiv), the formation of propionate was favored over acrylate with higher corresponding TONs of 42 and 68 (entries 12 and 13, respectively). Yet, addition of 0.8 equivalent did not seem to be beneficial to the system, decreasing the overall TON to 48 (entry 14). It is still unclear how H₂O interferes (*vide infra*). Previous work by Ruben and co-workers explored the use of water in site-selective hydrocarboxylation of unsaturated hydrocarbons with CO₂: in the case of olefins, linear carboxylic acids are formed through hypothetical hydrometallation.^[52]

To get a better insight in the nature of the catalytically active species in our system, we targeted the synthesis of Ru(H)(CO)(Cl)(DCPB)(PPh₃), which is an obvious anticipated product from the combination of Ru(H)(CO)(Cl)(PPh₃)₃ and DCPB. Following the procedure of Jia and coworkers,^[53] the precursor Ru(H)(CO)(Cl)(PPh₃)₃ was refluxed in the presence of the ligand DCPB (1:1 mol ratio) in toluene under argon. Upon work-up (see SI) and subsequent recrystallization of the crude product, single-crystals of the expected Ru(H)(CO)(Cl)(PPh₃)(DCPB) were recovered; its identity was established unambiguously by multinuclear NMR, MS (see SI) and an X-ray diffraction study (see Figure 1).

However, the NMR spectra of the crude reaction mixture revealed that Ru(H)(CO)(Cl)(PPh₃)(DCPB) is not necessarily the major product arising from this combination. Depending on the reaction conditions, it is accompanied by the formation of several other hydrido species in variable amounts. In fact, the hydride region of the ¹H NMR spectrum featured, besides the doublet of triplets at –7.16 ppm from Ru(H)(CO)(Cl)(PPh₃)(DCPB), other sets of resonances at higher field (Figure 2a). This was even more obvious in the ¹H{³¹P} NMR spectrum (Figure 2b), that evidenced that those two, or possibly three, additional species account for ca. 77% of the total hydrides.^[54] On the other hand, in the presence of water (40 equiv vs Ru(H)(CO)(Cl)(PPh₃)₃ and DCPB), the NMR spectra evidenced a more selective formation of Ru(H)(CO)(Cl)(PPh₃)(DCPB) (ca. 80% of the total; Figures 2c and 2d).^[55] Although the exact nature of the additional species has not been identified yet,^[56] we assume that they account for,

at least to some extent, the different selectivities observed in the catalytic process. Surprisingly enough, preliminary catalytic experiments conducted with isolated batches of Ru(H)(CO)(Cl)(PPh₃)(DCPB) or its ferrocenyl analogue Ru(H)(CO)(Cl)(PPh₃)(DCPF) (see SI for synthesis and X-ray characterization) returned neither acrylate (**A1**) nor propionate (**P1**) silyl esters, but the other side products. This may suggest that the other hydride species are the actual active ones in the coupling of CO₂ with C₂H₄, although we refrain at this stage to overspeculate.

Additional *in situ* catalytic experiments were conducted using the dihydro Ru(H)₂(CO)(PPh₃) precatalyst. Indeed, in presence of Et₃SiH, the mono-hydride Ru(H)(CO)(Cl)(PPh₃)₃ precursor is reduced to the dihydrido one and is therefore present within the reaction medium. Consequently, its evaluation in catalysis was undertaken. In combination with DCPB ligand (entry 15), a better selectivity was obtained toward route A product in comparison to the mono-hydride/DCPB catalytic combination (entries 3 vs 15). When adding 0.2 equivalent of water to the system, an increase of the overall route A TONs was observed (27 to 46, entries 15 vs 16). In brief, both mono and dihydrido ruthenium precursors/DCPB combinations allow to reach encouraging TON toward silylesters. A slight difference in selectivity is anyhow

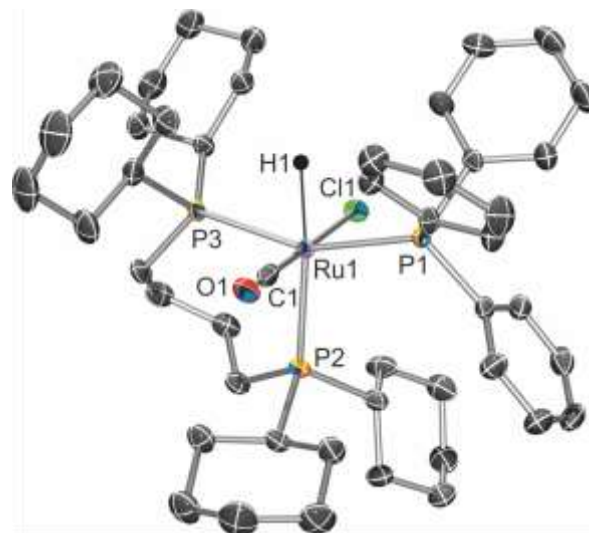


Figure 1. Molecular structure of Ru(H)(CO)(Cl)(PPh₃)(DCPB) with thermal ellipsoids set at 50% probability.

observed between the two systems: the use of Ru(H)₂(CO)(PPh₃) minimizes route C product formation.

In summary, we have investigated the metal-catalyzed synthesis of esters from C₂H₄, CO₂ and HSiEt₃. Using HTS, we have identified that the Ru(H)(Cl)(CO)(PPh₃)₃/DCPB combination enables to achieve moderate conversion and selectivity toward triethylsilyl propionate and acrylate. In agreement with the formation of the targeted silylester products (route A), a combination of two ruthenium catalytic cycles is tentatively proposed in Scheme 4, as a working hypothesis (among others). Formation of the ruthenialactone^[36] from C₂H₄ and CO₂ by oxidative addition is proposed as a key step in cycle P1. The P–Ru–P bite angle of ligand can have a major influence on the feasibility of this step, stability of the metallacycle and thus, on the overall activity and selectivity of the reaction.^[24]

Such influence has been well established in many other catalytic processes.^[57,58] Subsequent ruthenolactone cleavage by hydrosilane shall result in the formation of the mixed hydrido/alkyl intermediate. The latter may undergo a reductive elimination to give **P1** or afford **A1** via β -H elimination step within the second cycle A1. At this point, addition of water can affect the selectivity of the process by stabilizing the intermediate leading to the formation of **P1** via reductive elimination step. Also, formation of TEVS suggests that silyl-ruthenium is one of the active species in the overall process; such species may undergo ethylene insertion and β -hydride elimination to give TEVS along with a hydrido-ruthenium intermediate. Both ruthenium species may be involved in the carboxylation processes, e.g. through capture of CO₂ by the silyl-ruthenium. Such hypothetical scenarios are currently explored by DFT computations; the results will be discussed in a forthcoming paper.

Current efforts are directed at challenging such mechanistic scenarios through DFT computations as well as at identifying the different Ru species generated from the combination in the absence or presence of water, preparing and isolating them, and assessing their intrinsic reactivities.

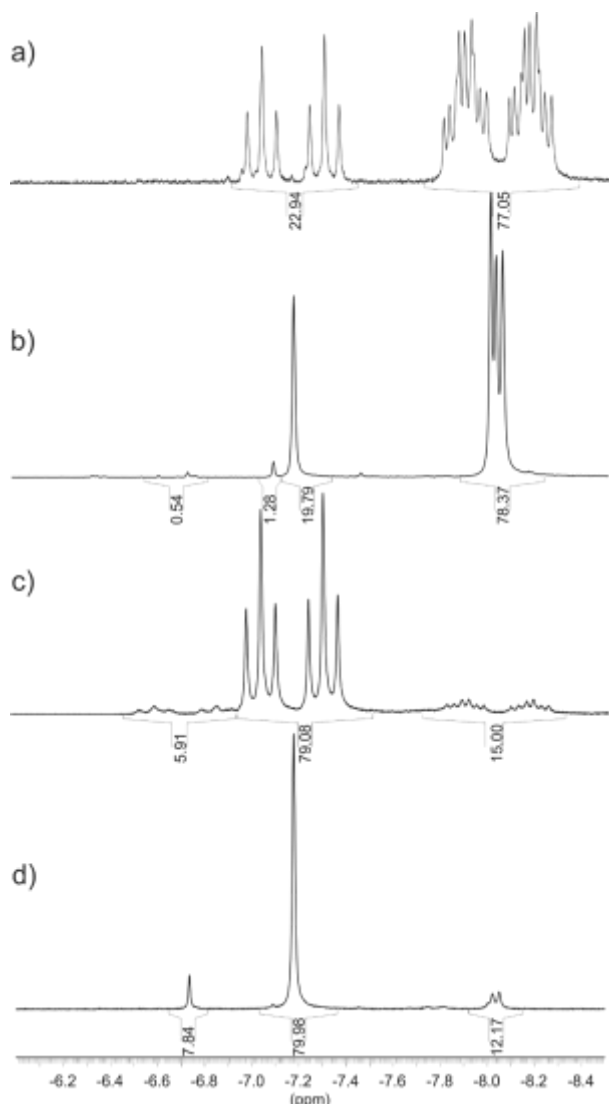
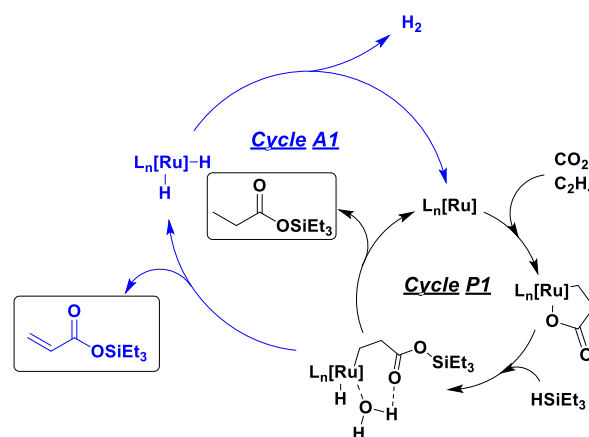


Figure 2. a) ¹H NMR and b) ¹H(³¹P) NMR spectra of the hydride region (400 MHz, toluene-*d*₆, 25 °C) of the crude product obtained from the reaction of

Ru(H)(CO)(Cl)(PPh₃)₃ and DCPB (1:1); c) ¹H NMR and d) ¹H(³¹P) NMR spectra of the hydride region (400 MHz, toluene-*d*₆, 25 °C) of the crude product obtained from the reaction of Ru(H)(CO)(Cl)(PPh₃)₃, DCPB and H₂O (1:1:40).



Scheme 4. Possible mechanisms for triethylsilyl acrylate (**A1**) and propionate (**P1**) formation.

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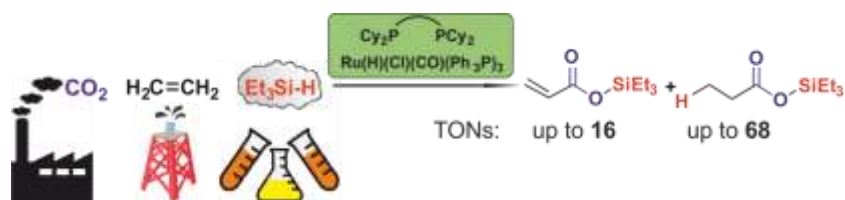
Keywords: carbon dioxide fixation • ethylene • reductive carboxylation • hydrosilylation • high throughput screening

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Reductive carboxylation of ethylene in the presence of triethylsilane as reductant was achieved upon using in situ-prepared catalytic systems incorporating Ru(II) precursors and bidentate phosphine ligands.