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

Kana Kunihiro,^[a] Svetlana Heyte,^[b] Sébastien Paul,^[b] Thierry Roisnel,^[a] Jean-François Carpentier,^{*[a]} and Evgueni Kirillov^{*[a]}

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

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-diyl-bis(cyclohexylphosphine) (DCPF). A marked influence of water on the acrylate/propionate selectivity was noted. Turnover numbers [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, etc.) 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 CO_2 -incorporative reactions. Reductive carboxylation of unsaturated hydrocarbons with CO_2 and its direct insertion into C–H

[a]	K. Kunihiro, Dr. T. Roisnel, Prof. Dr. JF. Carpentier, Dr. E. Kirillov CNRS, Institut des Sciences Chimiques de Rennes (ISCR), UMR 6226
	Univ. Rennes 35042 Rennes Cedex (France) E-mail: jean-francois.carpentier@univ-rennes1.fr evqueni.kirillov@univ-rennes1.fr
[b]	Dr. S. Heyte, Prof. Dr. S. Paul CNRS, Centrale Lille, Univ. Artois, UMR 8181—UCCS—Unité de Catalyse et Chimie du Solide Univ. Lille F-59000 Lille (France)
D	Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.202005083.

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 and Ping 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 1,8-diazabicyclo[5.4.0]undec-7-ene (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 turnover number (TON) of 10 was disclosed by Limbach and co-workers with a Ni(COD)₂/diphosphine (COD: 1,5cyclooctadiene) system and NaOtBu as base.^[24] Upon utilizing less nucleophilic sodium phenoxides and Zn-dust as reductant,



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

Chem. Eur. J. 2021, 27, 3997 - 4003

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the same group achieved TON up to 107 (Scheme 1).^[25] Following a similar strategy, Vogt and co-workers developed a process with a Ni-DCPP (1,3-bis(dicyclohexylphosphino)propane) catalyst relying on β -H elimination induced by a strong Lewis acid;^[26] in the presence of (over)-stoichiometric amounts of Lil, 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 co-workers employed a similar approach by using a phenoxide base $(3-FC_6H_4ONa)$ 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 co-workers 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-gasshift reaction in the presence of H₂ or alcohols. Very recently, Iwasawa and co-workers reported the synthesis of acrylate alkali metal salts with Ru-based catalysts (Scheme 1);^[36] TON up to 15 was achieved using 1000 equiv. of Cs₂CO₃ as base in DMA (dimethylacetamide) 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 highthroughput 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 [bond dissociation energy (BDE) = 460 kJ mol⁻¹]^[38] and the relatively 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



Scheme 2. Possible products of the coupling reaction of CO_2 with C_2H_4 in the presence of Et₂SiH.

(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 carboxy-lation 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(sil-yl ester) copolymers, of interest as fouling-resistant coatings and self-polishing materials.^[40,41]

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)(PPh₃)₃, [Ru(p-cymene)Cl₂]₂, [Rh(noctanoate),2], Wilkinson's catalyst and a set of diphosphine ligands with variable stereo-electronic features (Scheme 3). A monohydrosilane, HSiEt₃, 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 ($P_{total} = 20$ bar); Et₃SiH (0.86 mmol); $[precursor]_0 = [ligand]_0 = 0.5 mol \% vs. hydrosilane;$ reaction temperature = 100 °C; reaction time = 16 h. Crude reactions mixtures were analyzed automatically by GC-FID (FID: flame ionization detector) and GC-MS.



 $\mbox{Scheme 3.}\xspace$ Main \mbox{Ru}^{II} and $\mbox{Rh}(I,II)$ precursors and diphosphine ligands used in this study.

Chem. Eur. J. 2021, 27, 3997 – 4003

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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 CO₂ 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 ethyland hydrosilane, that is hydrosilylation ene and dehydrogenative coupling, yielding the corresponding tetraethylsilane (TES) and triethylvinylsilane (TEVS).^[43] The analytical techniques developed in this study (see the Supporting Information 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 Supporting Information).

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 [DCPB: 1,4bis(dicyclohexylphosphino)butane], Ru(H)(Cl)(CO)(PPh₃)₃/PP₃, Ru(H)(Cl)(CO)(PPh₃)₃/DPPF (1,1'-ferrocenediyl-bis(diphenylphosphine)), [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, CO_2 , 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 1,1'-ferrocene-diylbis(cyclohexylphosphine) (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(dicylohexylphosphine) ligand on the catalytic performance was undertaken under the above-defined reaction conditions. When using DCPM (bis(dicyclohexyl)phosphino methane) 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 (1,2-bis(dicyclohexylphosphino)entrylene-bridged DCPP (1,3-bis(dicyclohexylphosphino)propane)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 PR_2 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,

Table 1. Catalytic results from batch experiments. ^[a]										
Entry	Precursor/ligand (1:1, 0.5 mol%)/additive [mol%] (vs. HSiEt ₃)	Conv. HSiEt ₃ ^[b] [mol %]	TON ^[c] [mol(product)mol(Ru) ⁻¹]							
			Route A	Route A products Route B and C produc				lucts		
			A1	P1	F1	TES	TEVS	E		
1	[Ru(p-cymene)Cl ₂] ₂ /DCPB	>98	0	0	0	180	traces	traces		
2	$Ru(H)(CI)(CO)(PPh_3)_3/PP_3$	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(p-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 /DCPP	81	traces	traces	1.0	8	66	26		
10 ^[d]	$Ru(H)(CI)(CO)(PPh_3)_3/DC^pPB^{[d]}$	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), $[Si-H]_0 = 0.43 \text{ mol } L^{-1}$, $[Ru]_0 = [ligand]_0 = 0.002 \text{ mol } L^{-1}$, CO_2/C_2H_4 1:1 mol mol⁻¹, $P(CO_2) + P(C_2H_4) = 20$ 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] TON as determined by GC-FID using *n*-dodecane as internal standard. [d] $DC^PPB = 1,4$ -bis(dicyclopentylphosphino)butane. [e] 4 h.

although A1 and P1 were still formed in small amounts, a significant difference in selectivity was observed as compared to DCPB (see Supporting Information, 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 vs. 10).

Evaluation of the temperature was conducted on the most efficient catalytic system in order to further optimize conversion and selectivity (see Table S4, Supporting Information, 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 Martin 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)(CI)(DCPB)(PPh₃), which is an obvious anticipated product from the combination of Ru(H)(CO)(CI)(PPh₃)₃ and DCPB. Following the procedure of Jia and co-workers,^[53] the precursor Ru(H)(CO)(CI)(PPh₃)₃ was refluxed in the presence of the ligand DCPB (1:1 mol ratio) in toluene under argon. Upon work-up (see Supporting Information) and subsequent recrystallization of the crude product, single-crystals of the expected Ru(H)(CO)(CI)(PPh₃)(DCPB) were recovered; its identity was established unambiguously by multinuclear NMR spectroscopy, MS (see Supporting Information), and an X-ray diffraction study (see Figure 1).

However, the NMR spectra of the crude reaction mixture revealed that $Ru(H)(CO)(CI)(PPh_3)(DCPB)$ is not necessarily the



Figure 1. Molecular structure of $Ru(H)(CO)(CI)(PPh_3)(DCPB)$ with thermal ellipsoids set at 50% probability.

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)(CI)(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 approximately 77% of the total hydrides.^[54] On the other hand, in the presence of water [40 equiv. vs. $Ru(H)(CO)(CI)(PPh_3)_3$ and DCPB], the NMR spectra evidenced a more selective formation of Ru(H)(-CO)(CI)(PPh₃)(DCPB) (\approx 80% of the total; Figures 2 c,d).^[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)(CI)(PPh₃)(DCPB) or its ferrocenyl analogue Ru(H)(-CO)(CI)(PPh₃)(DCPF) (see Supporting Information 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 CO_2 with C_2H_4 , 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

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Communication doi.org/10.1002/chem.202005083



Figure 2. a) ¹H NMR and b) ¹H{³¹P} NMR spectra of the hydride region (400 MHz, [D₈]toluene, 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, [D₈]toluene, 25 °C) of the crude product obtained from the reaction of Ru(H)(CO)(Cl)(PPh₃)₃, DCPB and H₂O (1:1:40).

and dihydrido ruthenium precursors/DCPB combinations allow to reach encouraging TON toward silylesters. A slight difference in selectivity is anyhow observed between the two systems: the use of $Ru(H)_2(CO)(PPh_3)$ minimizes route C product formation.

In summary, we have investigated the metal-catalyzed synthesis of esters from C_2H_4 , CO_2 , 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 ruthenalactone^[36] from C_2H_4 and CO_2 by oxidative addition is proposed as a key step in cycle P1. The P-Ru-P bite



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

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 ruthenalactone 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 $\beta\text{-hydride}$ elimination to give TEVS along with a hydrido-ruthenium intermediate. Both ruthenium species may be involved in the carboxylation processes, for example, through capture of CO₂ by the silyl-ruthenium. Such hypothetic 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.

Acknowledgements

This research project was supported by the ANR-17-CE06-0006-01 "CO22CHEM". The authors are indebted to Dr. Elsa Caytan from Rennes 1 University (UMS SCANMAT, Rennes, France) for NMR analyses, to Dr. Stephan Behrens from Leibniz Institute for Catalysis (Rostock, Germany) for his experimental contribution and to Prof. Franck Dumeignil (Univ. Lille) for stimulating discussions and sharing expertise. The REALCAT platform is benefiting from a state subsidy administrated by the French National Research Agency (ANR) within the frame of the 'Future Investments' program (PIA), with the contractual reference 'ANR-11-EQPX-0037'. The European Union, through the

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ERDF funding administered by the Hauts-de-France Region, has co-financed the platform. Centrale Lille, the CNRS, and Lille University as well as the Centrale Initiatives Foundation, are thanked for their financial contributions to the acquisition and implementation of the equipment of the REALCAT platform.

Conflict of interest

The authors declare no conflict of interest.

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

- S. Patai, *The Chemistry of Acid Derivatives*, Wiley, Chichester, New York, 1979.
- [2] L. J. Gooßen, N. Rodríguez, K. Gooßen, Angew. Chem. Int. Ed. 2008, 47, 3100–3120; Angew. Chem. 2008, 120, 3144–3164.
- [3] H. Maag, Prodrugs Chall. Rewards Part 1, Eds.: V. J. Stella, R. T. Borchardt, M. J. Hageman, R. Oliyai, H. Maag, J. W. Tilley, Springer New York, New York, NY, 2007, pp. 703–729.
- [4] Y. Zhang, S. N. Riduan, Angew. Chem. Int. Ed. 2011, 50, 6210–6212; Angew. Chem. 2011, 123, 6334–6336.
- [5] M. Börjesson, T. Moragas, D. Gallego, R. Martin, ACS Catal. 2016, 6, 6739-6749.
- [6] Y. Tsuji, T. Fujihara, Chem. Commun. 2012, 48, 9956-9964.
- [7] A. Pinaka, G. C. Vougioukalakis, Coord. Chem. Rev. 2015, 288, 69-97.
- [8] E. Kirillov, J.-F. Carpentier, E. Bunel, Dalton Trans. 2015, 44, 16212– 16223.
- [9] A. L. Lapidus, Y. Y. Ping, Russ. Chem. Rev. 1981, 50, 63.
- [10] H. Hoberg, D. Schaefer, J. Organomet. Chem. 1982, 236, C28-C30.
- [11] H. Hoberg, D. Schaefer, B. W. Oster, J. Organomet. Chem. 1984, 266, 313–320.
- [12] H. Hoberg, D. Schaefer, J. Organomet. Chem. 1983, 251, c51-c53.
- [13] R. Alvarez, E. Carmona, D. J. Cole-Hamilton, A. Galindo, E. Gutierrez-Puebla, A. Monge, M. L. Poveda, C. Ruiz, J. Am. Chem. Soc. 1985, 107, 5529–5531.
- [14] H. Hoberg, K. Jenni, C. Krüger, E. Raabe, Angew. Chem. Int. Ed. Engl. 1986, 25, 810–811; Angew. Chem. 1986, 98, 819–820.
- [15] H. Hoberg, Y. Peres, A. Milchereit, J. Organomet. Chem. 1986, 307, C38– C40.
- [16] H. Hoberg, K. Jenni, J. Organomet. Chem. 1987, 322, 193-201.
- [17] H. Hoberg, S. Gross, A. Milchereit, Angew. Chem. Int. Ed. Engl. 1987, 26, 571–572; Angew. Chem. 1987, 99, 567–569.
- [18] H. Hoberg, Y. Peres, C. Krüger, Y.-H. Tsay, Angew. Chem. Int. Ed. Engl. 1987, 26, 771–773; Angew. Chem. 1987, 99, 799–800.
- [19] H. Hoberg, Y. Peres, A. Milchereit, S. Gross, J. Organomet. Chem. 1988, 345, C17-C19.
- [20] H. Hoberg, D. Bärhausen, J. Organomet. Chem. 1989, 379, C7-C11.
- [21] H. Hoberg, A. Ballesteros, A. Sigan, J. Organomet. Chem. 1991, 403, C19-C22.
- [22] H. Hoberg, A. Ballesteros, A. Sigan, C. Jegat, A. Milchereit, Synthesis 1991, 1991, 395–398.
- [23] H. Hoberg, A. Ballesteros, A. Sigan, C. Jégat, D. Bärhausen, A. Milchereit, J. Organomet. Chem. 1991, 407, C23-C29.
- [24] M. L. Lejkowski, R. Lindner, T. Kageyama, G. É. Bódizs, P. N. Plessow, I. B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk, M. Limbach, *Chem. Eur. J.* 2012, *18*, 14017–14025.
- [25] N. Huguet, I. Jevtovikj, A. Gordillo, M. L. Lejkowski, R. Lindner, M. Bru, A. Y. Khalimon, F. Rominger, S. A. Schunk, P. Hofmann, M. Limbach, *Chem. Eur. J.* 2014, 20, 16858–16862.
- [26] C. Hendriksen, E. A. Pidko, G. Yang, B. Schäffner, D. Vogt, *Chem. Eur. J.* 2014, 20, 12037–12040.
- [27] K. B. Uttley, K. Shimmei, W. H. Bernskoetter, Organometallics 2020, 39, 1573-1579.

- n, [28] I. Pápai, G. Schubert, I. Mayer, G. Besenyei, M. Aresta, Organometallics 2004, 23, 5252–5259.
 - [29] D. C. Graham, C. Mitchell, M. I. Bruce, G. F. Metha, J. H. Bowie, M. A. Buntine, Organometallics 2007, 26, 6784–6792.
 - [30] P. N. Plessow, A. Schäfer, M. Limbach, P. Hofmann, Organometallics 2014, 33, 3657 – 3668.
 - [31] W. Guo, C. Michel, R. Schwiedernoch, R. Wischert, X. Xu, P. Sautet, Organometallics 2014, 33, 6369–6380.
 - [32] G. Yang, B. Schäffner, M. Blug, E. J. M. Hensen, E. A. Pidko, *ChemCatChem* 2014, 6, 800–807.
 - [33] A. Julián, J. Guzmán, E. A. Jaseer, F. J. Fernández-Alvarez, R. Royo, V. Polo, P. García-Orduña, F. J. Lahoz, L. A. Oro, *Chem. Eur. J.* 2017, 23, 11898–11907.
 - [34] Y. Li, Z. Liu, J. Zhang, R. Cheng, B. Liu, *ChemCatChem* **2018**, *10*, 5669–5678.
 - [35] T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 2013, 52, 12119–12123; Angew. Chem. 2013, 125, 12341–12345.
 - [36] K. Takahashi, Y. Hirataka, T. Ito, N. Iwasawa, Organometallics 2020, 39, 1561–1572.
 - [37] To our knowledge, no examples have been reported so far dealing with the use of hydrosilanes as reductants in the reactions of ethylene and CO₂. On the other hand, some metal-catalyzed reactions of alkynes with CO₂ and HSiR₃ have been reported; see, for example: T. Fujihara, T. Xu, K. Semba, J. Terao, Y. Tsuji, *Angew. Chem. Int. Ed.* 2011, *50*, 523–527; *Angew. Chem.* 2011, *123*, 543–547.
 - [38] Hydrosilane Et₃SiH was selected as reductant because it features both high thermodynamic hydricity and kinetic nucleophilicity among other commercial analogues: a) M. Heiden, A. P. Lathem, *Organometallics* 2015, *34*, 1818–1827; b) M. Horn, L. H. Schappele, G. Lang-Wittkowski, H. Mayr, A. R. Ofial, *Chem. Eur. J.* 2013, *19*, 249–263; c) J. Xu, A. Krajewski, Y. Niu, Y. G. S. M. Kiruba, J. K. Lee, *Chem. Sci.* 2019, *10*, 8002–8008.
 - [39] A. Tortajada, F. Juliá-Hernández, M. Börjesson, T. Moragas, R. Martin, Angew. Chem. Int. Ed. 2018, 57, 15948–15982; Angew. Chem. 2018, 130, 16178–16214.
 - [40] J. A. Callow, M. E. Callow, Nat. Commun. 2011, 2, 244.
 - [41] X. Zhou, Q. Xie, C. Ma, Z. Chen, G. Zhang, Ind. Eng. Chem. Res. 2015, 54, 9559–9565.
 - [42] F. J. Fernández-Alvarez, L. A. Oro, ChemCatChem 2018, 10, 4783-4796.
 - [43] S. Lachaize, L. Vendier, S. Sabo-Etienne, Dalton Trans. 2010, 39, 8492– 8500.
 - [44] M.-N. Birkholz (née Gensow), Z. Freixa, P. W. N. M. van Leeuwen, Chem. Soc. Rev. 2009, 38, 1099–1118.
 - [45] C. Bruckmeier, M. W. Lehenmeier, R. Reichardt, S. Vagin, B. Rieger, Organometallics 2010, 29, 2199–2202.
 - [46] S. Y. T. Lee, M. Cokoja, M. Drees, Y. Li, J. Mink, W. A. Herrmann, F. E. Kühn, ChemSusChem 2011, 4, 1275–1279.
 - [47] P. N. Plessow, L. Weigel, R. Lindner, A. Schäfer, F. Rominger, M. Limbach, P. Hofmann, Organometallics 2013, 32, 3327 – 3338.
 - [48] S. Y. T. Lee, A. A. Ghani, V. D'Elia, M. Cokoja, W. A. Herrmann, J.-M. Basset, F. E. Kühn, New J. Chem. 2013, 37, 3512–3517.
 - [49] D. Jin, P. G. Williard, N. Hazari, W. H. Bernskoetter, Chem. Eur. J. 2014, 20, 3205 – 3211.
 - [50] D. Jin, T. J. Schmeier, P. G. Williard, N. Hazari, W. H. Bernskoetter, Organometallics 2013, 32, 2152–2159.
 - [51] R. Fischer, J. Langer, A. Malassa, D. Walther, H. Görls, G. Vaughan, Chem. Commun. 2006, 2510-2512.
 - [52] M. Gaydou, T. Moragas, F. Juliá-Hernández, R. Martin, J. Am. Chem. Soc. 2017, 139, 12161–12164.
 - [53] S. H. Liu, S. T. Lo, T. B. Wen, I. D. Williams, Z. Y. Zhou, C. P. Lau, G. Jia, *Inorg. Chim. Acta* 2002, 334, 122–130.
 - [54] M. Meuresch, S. Westhues, W. Leitner, J. Klankermayer, Angew. Chem. Int. Ed. 2016, 55, 1392–1395; Angew. Chem. 2016, 128, 1414–1417.
 - [55] Based on the ³¹P NMR data (Figure S12), the addition of water to the crude reaction mixture containing Ru(H)(CO)(CI)(PPh₃)(DCPB)/PPh₃ results in the suppression of formation of the hydrido species at -8.00 ppm and favors higher proportion of Ru(H)(CO)(CI)(PPh₃)(DCPB).
 - [56] Putative [Ru(H)(OH)] species can be envisioned as well; see: a) M. J. Burn, M. G. Fickes, J. F. Hartwig, F. J. Hollander, R. G. Bergman, J. Am. Chem. Soc. 1993, 115, 5875–5876; b) Y. Arikawa, S. Nagae, J.-i. Morishita,

Chem. Eur. J. 2021, 27, 3997 – 4003

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K. Hiraki, M. Onishi, Angew. Chem. Int. Ed. 2005, 44, 5509–5513; Angew. Chem. 2005, 117, 5645–5649.

- [57] This has been particularly well evidenced in hydroformylation reactions, where the bite angle controls the axial/equatorial positioning of the different ligands in the coordination sphere of catalytic intermediates, and eventually affects interaction of the alkene with the metal center and subsequent steps, and hence activity and regioselectivity, see: P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, *Pure Appl. Chem.* **1999**, *71*, 1443–1452.
- [58] P. Dierkes, P. W. N. M. van Leeuwen, J. Chem. Soc. Dalton Trans. 1999, 1519–1530.

Manuscript received: November 24, 2020 Revised manuscript received: December 21, 2020 Accepted manuscript online: January 16, 2021 Version of record online: January 28, 2021