

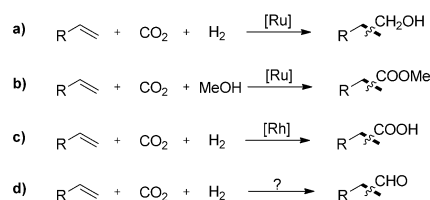


Rhodium-Complex-Catalyzed Hydroformylation of Olefins with CO₂ and Hydrosilane

Xinyi Ren, Zhiyao Zheng, Lei Zhang, Zheng Wang, Chungu Xia,* and Kuiling Ding*

Abstract: A rhodium-catalyzed one-pot hydroformylation of olefins with CO₂, hydrosilane, and H₂ has been developed that affords the aldehydes in good chemoselectivities at low catalyst loading. Mechanistic studies indicate that the transformation is likely to proceed through a tandem sequence of poly(methylhydrosiloxane) (PMHS) mediated CO₂ reduction to CO and a conventional rhodium-catalyzed hydroformylation with CO/H₂. The hydrosilyl-mediated reduction of CO₂ in preference to aldehydes was found to be crucial for the selective formation of aldehydes under the reaction conditions.

Over the past decades, the catalytic reduction of CO₂ has been extensively explored to generate energy-rich small molecules such as formic acid, carbon monoxide, methanol, and methane.^[1,2] Several innovative methods for reductive transformations of CO₂ have also recently emerged, which combine CO₂ reduction with C–C, C–N, or C–O bond formation and significantly broaden the range of chemicals accessible from CO₂.^[3] Of particular interest in this vein is the use of CO₂ as a surrogate for highly toxic and flammable CO, which is currently produced from fossil fuels and used in a myriad of industrial carbonylation processes.^[4] The efficient reduction of CO₂ to CO and the subsequent valorization of the CO thus obtained would be of great value in sustainable chemistry but the deoxygenative cleavage of the O=CO bond is difficult owing to its high bond strength (532 kJ mol⁻¹).^[5] Several catalytic transformations involving the use of CO₂ for carbonylative alkene functionalization have emerged recently, providing elegant approaches to useful chemicals such as carboxylic acids,^[6] esters,^[7] and alcohols^[8] (Scheme 1a–c). It is noteworthy that aldehydes, despite their fundamental importance in chemical industry and organic synthesis, represent a missing link and have not been obtained



Scheme 1. Transition-metal-catalyzed carbonylation of olefins with CO₂.

by reductive transformation of olefins in the presence of CO₂ (Scheme 1d). Presumably, the hydrogenation propensity of ruthenium catalysts or the high temperatures used in the rhodium-catalyzed reverse water gas shift (RWGS) process^[9] in these studies have precluded the isolation of these valuable aldehydes.

As part of our ongoing studies on CO₂ transformations,^[10] we sought to develop a catalytic alkene hydroformylation^[11] with CO₂ as the CO surrogate. As hydrosilanes have been used as viable reductants for CO₂ transformations,^[12] we began the study with 1-hexene (**1a**) as the substrate and poly(methylhydrosiloxane) (PMHS, *M_w* = 1900) as the reductant under 25 bar of H₂/CO₂ (4:1). A quick survey of reaction conditions indicated that Lewis basic *N*-methylpyrrolidone (NMP) was the optimal solvent for the reaction whereas only the isomerization/hydrogenation products were observed for the reactions in toluene and THF (see the Supporting Information). Gratifyingly, at 100 °C with KF as the additive and Rh(acac)(CO)₂/PPh₃ as the catalyst, **1a** was fully converted within 12 h to afford the aldehydes **2a** and **2a'** in 54% yield with a 78:22 linear to branched ratio (*l/b*), along with significant amounts of isomerized alkenes (**Iso**, 24%) and the hydrogenation product (**H**, 3%; Table 1, entry 1). In contrast, the reaction was very sluggish in the absence of any phosphine ligands (entry 2), indicating a critical ligand acceleration effect. Whereas diphosphine **L2** and BINOL-derived bis(phosphoramidite) **L3** only led to modest yields of the desired aldehydes (entries 3 and 4), the reactions with bis(phosphoramidite)s **L4** and **L5**, which bear a fused spirobisindane backbone, gave aldehydes **2a/2a'** in good yields and high regioselectivity for the linear product (entries 5 and 6). **L5** turned out to be optimal in terms of both catalytic activity and chemo/regioselectivity, and was thus used in our further studies. The use of other hydrosilanes, for example, PhSiH₃, Ph₂SiH₂, or PhMe₂SiH, afforded less satisfactory results (entries 7–9). No aldehyde was observed in the absence of PMHS (entry 10), indicating that the hydrosilane is essential for the transformation. Interestingly, the reaction also proceeded in the absence of H₂, albeit in a largely

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Table 1: Hydroformylation of 1-hexene with CO₂, silane, and H₂.^[a]

$$n\text{C}_4\text{H}_9\text{CH=CH}_2 + \text{H}_2 + \text{CO}_2 \xrightarrow[\text{100}^\circ\text{C, 12 h}]{\text{Rh(acac)(CO)}_2, \text{Rh/L} = 1:3, \text{PMHS, KF, NMP}} n\text{C}_4\text{H}_9\text{CH}_2\text{CH}_2\text{CHO} + n\text{C}_4\text{H}_9\text{C(CH}_3\text{)CHO}$$

Entry	Si-H	L	Conv. [%] ^[b]	2a + 2a' [%] ^[b]	l/b ^[b]	Iso ^[b] [%]	H ^[b] [%]
1	PMHS	L1	100	54	78:22	24	3
2	PMHS	–	42	5	84:16	4	0
3	PMHS	L2	100	38	86:14	18	16
4	PMHS	L3	100	25	96:4	13	36
5	PMHS	L4	100	52	87:13	15	7
6	PMHS	L5	100	60	89:11	13	8
7	PhSiH ₃	L5	96	53	88:12	17	3
8	Ph ₂ SiH ₂	L5	100	54	90:10	18	16
9	PhMe ₂ SiH	L5	53	0	–	18	6
10	–	L5	87	0	–	53	11
11 ^[c]	PMHS	L5	91	32	91:9	38	0
12 ^[d]	PMHS	L5	100	52	91:9	24	9
13 ^[c-d]	PMHS	L5	98	19	88:12	35	0

[a] Reaction conditions: 1-hexene (10 mmol), S/C = 10000 (wherein S/C is the molar ratio of substrate to Rh), Rh(acac)(CO)₂ (0.001 mmol), ligand (0.003 mmol), Si-H (20 mmol), KF (1.0 mmol), H₂/CO₂ = 20/5 bar, 100 °C, 12 h, NMP (10 mL). [b] Determined by GC analysis with decane (0.5 mmol) as the internal standard. Iso = isomerized alkenes, H = hexane. Control experiments suggested that approximately 10 mol% of the starting alkene were lost as partially alkylated polysiloxane by hydrosilylation with PMHS (see the Supporting Information). [c] The reaction was conducted in the absence of H₂. [d] Without KF.

reduced aldehyde yield (entries 11 vs. 6). In the absence of KF, 2a/2a' were obtained in slightly lower yield (52%, entry 12). The yield declined drastically to 19% when both KF and H₂ were omitted from the reaction (entry 13).

A range of unfunctionalized alkenes were then subjected to the optimized reaction conditions (Table 2). Terminal olefins with an aliphatic substituent demonstrated similar reactivity profiles irrespective of the length of the carbon chain, affording the corresponding aldehydes in moderate to good yields (51–70%) and good linear regioselectivities (l/b = 81:19–90:10), accompanied by minor amounts of the isomerized (Iso) and hydrogenated (H) products (entries 1–8). Poor reactivity was observed for 2-octene, an internal olefin, for which the reaction gave the isomeric nonanals in modest yield (entry 9). Better results were attained in the reaction of cyclopentene, wherein the aldehyde was obtained in 29% yield (entry 10). Finally, the hydroformylation of styrene furnished the corresponding aldehydes in moderate yield (47%) favoring the branched isomer, along with a substantial amount of the hydrogenation product (41%, entry 11).

Preliminary mechanistic studies were further performed on this catalytic system to gain insight

into the details of CO₂ hydrosilylation and alkene hydroformylation. Control experiments with CO₂ and PMHS in NMP at 100 °C for 12 h led to the in situ generation of CO, H₂, a minor amount of formic acid, and polymeric siloxanes, as determined by GC, ¹H and ¹³C NMR, and X-ray studies (see the Supporting Information for details). A plausible mechanistic manifold for the deoxygenative reduction of CO₂ with PMHS is shown in Scheme 2a. PMHS reduction of CO₂ is likely to proceed through initial formation of the silyl formate {HC(O)O-[Si]},^[13] which would readily decompose to the corresponding silanols {[Si]-OH} with simultaneous release of CO under prolonged heating.^[14] Alternatively, facile hydrolysis of the silyl formate affords formic acid,^[15] which may undergo decarbonylation to CO and water, decarboxylation to H₂ and CO₂, or a dehydrogenative coupling with PMHS to silyl formate and H₂. Irrespective of the exact nature of the CO₂ reduction, [RhCl(CO)(PPh₃)₂], a Rh complex bearing a CO ligand (Scheme 2b), was isolated from the reaction of CO₂ (1 atm) with RhCl(PPh₃)₃ in the presence of PMHS and KF in NMP at room temperature, and was structurally characterized by X-ray crystallography.^[16]

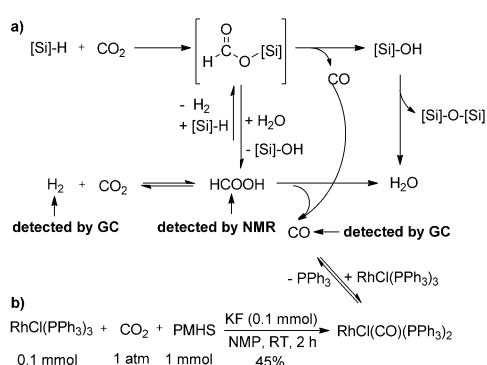
To confirm the source of the hydrogen in the aldehyde products, isotope-labeling experiments were performed by conducting the hydroformylation of 1h with D₂ instead of H₂ under the standard reaction conditions, and the deuterium incorporation in the aldehydes 2h and 2h' was determined by ¹H NMR analysis. As shown in Scheme 3a, the predominant formation of the CDO group (94%) for both the linear and branched aldehydes (2h and 2h') provides strong support for a conventional hydroformylation

Table 2: Substrate scope.^[a]

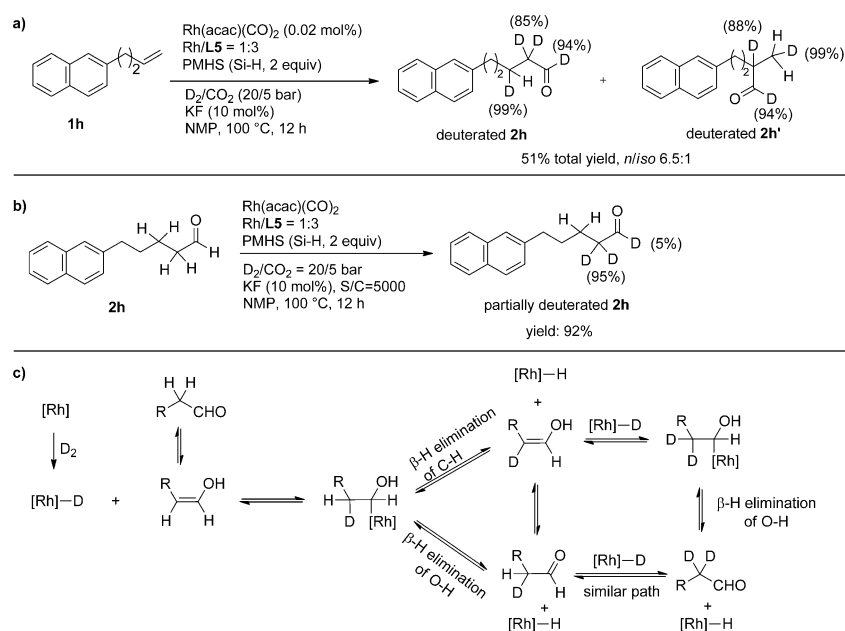
$$\text{R-CH=CH}_2 + \text{H}_2 + \text{CO}_2 \xrightarrow[\text{100}^\circ\text{C, 12 h}]{\text{Rh(acac)(CO)}_2, \text{Rh/L} = 1:3, \text{PMHS, KF, NMP}} \text{R-CH}_2\text{CH}_2\text{CHO}$$

Entry	Alkene	Conv. [%] ^[b]	Aldehydes ^[b] [%]	l/b ^[b]	Iso [%] ^[b]	H [%] ^[b]
1	1-hexene (1a)	100	60	89:11	13	8
2 ^[c]	propene (1b)	–	59	81:19	–	–
3 ^[c]	1-butene (1c)	–	57	84:16	–	–
4	1-pentene (1d)	99	58	89:11	16	8
5	1-heptene (1e)	99	70	90:10	12	8
6	1-octene (1f)	80	59	86:14	7	10
7	1-decene (1g)	99	52	85:15	5	20
8 ^[d]	2-(but-3-en-1-yl)naphthalene (1h)	99	51	85:15	17	22
9	2-octene (1i)	82	11	22:78 ^[e]	60	0
10	cyclopentene (1j)	60	29	–	–	–
11	styrene (1k)	98	47	36:64	2	41

[a] Alkene (10 mmol), Rh(acac)(CO)₂ (0.001 mmol), L5 (0.003 mmol), PMHS (Si-H, 20 mmol), KF (1.0 mmol), H₂/CO₂ = 20/5 bar, 100 °C, 12 h, NMP (10 mL). [b] Determined by GC analysis with decane as the internal standard. [c] Alkene (20 mmol), PMHS (Si-H, 40 mmol), S/C = 10000, 24 h. [d] S/C = 5000, total yield of the isolated aldehydes. [e] 1-/2-/3-CHO = 22:58:20.



Scheme 2. a) Proposed mechanism for the hydrosilylation of CO_2 to CO , H_2 , HCOOH , and siloxanes. b) Formation of the rhodium carbonyl complex $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ from the reaction of $\text{RhCl}(\text{PPh}_3)_3$ with CO_2 and PMHS.



Scheme 3. Deuterium-labeling experiments with D_2 under the standard reaction conditions. a) $\text{Rh}^1/\text{L5}$ catalyzed hydroformylation of **1h**. b) $\text{Rh}^1/\text{L5}$ catalyzed H/D exchange of **2h**. c) Proposed mechanism for the H/D exchange at the α -position of the aldehyde.

pathway, wherein the D atom in the CDO moiety necessarily originates from D_2 . The incorporation of a single D atom at the β -carbon atoms of the aldehydes with a similar deuteration ratio (99%) is also consistent with this mechanism.^[17] These results imply that CO , generated in situ by CO_2 reduction with PMHS, was effectively utilized in combination with H_2 for the hydroformylation. Hence, the possibility of PMHS-derived silyl formate acting as a formyl transfer agent can be virtually ruled out for the present reaction system. Further isotope-labeling experiments on the H/D exchange of 5-(naphthalen-2-yl)pentanal (**2h**), performed under the standard conditions with D_2 , revealed that little H/D exchange (5%) occurred on the CHO moiety of the aldehyde (Scheme 3b). The negligible H/D exchange in the present case indicates that the aldehyde is virtually resistant to retro-

hydroformylation,^[18] which is further corroborated by the fact that no deuterium was incorporated in the β -positions of deuterated **2h**. The high percentage of deuterium incorporation at the α -carbon atoms of the product aldehydes in Scheme 3a and b illustrates the high reactivity of the α -hydrogen atoms, which readily undergo a sequence of Rh-mediated β -H elimination and reinsertion equilibria to finally deliver the α -deuterated aldehydes (Scheme 3c).^[19]

On the other hand, the excellent yield (92%) of isolated α -dideuterated 5-(naphthalen-2-yl)pentanal (**2h**) shown in Scheme 3b is also consistent with the generally good yields of the aldehydes shown in Table 2. Indeed, under the standard reaction conditions, 1-octanal (**2e**) was found to be almost inert to hydrosilylation, and remained largely intact (97% by GC analysis) after 12 h under these conditions. In contrast, **2e** was fully consumed in the absence of CO_2 under otherwise identical reaction conditions (see the Supporting Information). These results suggest that the aldehyde, once generated by hydroformylation, is not reduced further to the alcohol as the excess of CO_2 present in the reaction system reacts in preference to the aldehyde with the residual PMHS reagent.

The mechanistic data obtained thus far seem to be largely consistent with a tandem process combining PMHS-mediated CO_2 hydrosilylation to CO and rhodium-catalyzed hydroformylation. However, further results on the hydroformylation of 1-hexene with CO as the sole carbonyl source suggest a somewhat more intricate scenario. Control experiments were conducted with 1-hexene under CO/H_2 (2/20 bar) in NMP at 100°C using $\text{Rh}(\text{acac})(\text{CO})_2/\text{L5}$ (**1a**/Rh = 5000, Rh/L5 = 1:3) as the catalyst to simulate the title reaction under the standard conditions. Surprisingly, only trace amounts of the aldehydes (< 3%) were detected by GC analysis after 12 h (see the Supporting Information). These intriguing results prompted us to further explore the role of formic acid in our

reaction. Notably, hydroformylation of 1-hexene with CO/H_2 (2/20 bar) in NMP in the presence of substoichiometric amounts of HCOOH or other Brønsted acids (methanesulfonic acid (MSA) or *para*-toluenesulfonic acid monohydrate (*p*-TsOH \cdot H_2O)) led to significantly improved yields (11–43%) of the aldehydes (see the Supporting Information). While we surmise that the acid might enhance the reaction by facilitating rhodium hydride formation,^[20] the exact role of the acid is, however, still unclear at the moment.

In conclusion, we have developed a highly efficient rhodium phosphoramidite catalyst system for the selective hydroformylation of olefins to aldehydes without formation of the corresponding alcohols. This system is based on the use of CO_2 and poly(methylhydrosiloxane), two nontoxic and inexpensive chemical waste products, as the carbonyl source

and hydrogen as a further reaction partner. To the best of our knowledge, this work represents the first method for the synthesis of aldehydes from alkenes and CO₂. Mechanistic studies revealed that the transformation is most likely to proceed through a one-pot tandem sequence of PMHS-mediated CO₂ reduction to CO followed by a conventional rhodium-catalyzed hydroformylation with CO/H₂. The reduction of CO₂ in preference to aldehydes with a hydrosilane was disclosed to be crucial for selective aldehyde formation. Further studies to understand the mechanistic details and extend this reaction to other types of ligands are underway in our laboratories.

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Keywords: aldehydes · carbon dioxide · hydroformylation · olefins · rhodium

- [1] a) M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, **2010**; b) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365; c) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510; *Angew. Chem.* **2011**, *123*, 8662; d) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709.
- [2] W. Wang, S. Wang, X. Ma, J. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703.
- [3] a) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933; b) A. Tlili, E. Blondiaux, X. Frogneux, T. Cantat, *Green Chem.* **2015**, *17*, 157; c) K. Thenert, K. Beydoun, J. Wiesenhal, W. Leitner, J. Klankermayer, *Angew. Chem. Int. Ed.* **2016**, *55*, 12266; *Angew. Chem.* **2016**, *128*, 12454.
- [4] a) *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Berlin, **2006**; b) *Modern carbonylation methods* (Ed.: L. Kollar), Wiley-VCH, Weinheim, **2008**.
- [5] *CRC Handbook of Chemistry and Physics*, 95th ed. (Ed.: W. M. Haynes), CRC, Boca Raton, FL, **2014–2015**.
- [6] T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2013**, *52*, 12119; *Angew. Chem.* **2013**, *125*, 12341.
- [7] L. Wu, Q. Liu, I. Fleischer, R. Jackstell, M. Beller, *Nat. Commun.* **2014**, *5*, 3091.
- [8] a) K.-I. Tominaga, Y. Sasaki, *Catal. Commun.* **2000**, *1*, 1; b) K.-I. Tominaga, Y. Sasaki, *J. Mol. Catal. A* **2004**, *220*, 159; c) Q. Liu, L. Wu, I. Fleischer, D. Selent, R. Franke, R. Jackstell, M. Beller, *Chem. Eur. J.* **2014**, *20*, 6888; d) M. Ali, A. Gual, G. Ebeling, J Dupont, *ChemCatChem* **2014**, *6*, 2224.
- [9] K. Tsuchiya, J. D. Huang, K. Tominaga, *ACS Catal.* **2013**, *3*, 2865, and references therein.
- [10] a) L. Zhang, Z. Han, X. Zhao, Z. Wang, K. Ding, *Angew. Chem. Int. Ed.* **2015**, *54*, 6186; *Angew. Chem.* **2015**, *127*, 6284; b) Z. Han, L. Rong, J. Wu, L. Zhang, Z. Wang, K. Ding, *Angew. Chem. Int. Ed.* **2012**, *51*, 13041; *Angew. Chem.* **2012**, *124*, 13218; c) Y. Xiao, Z. Wang, K. Ding, *Macromolecules* **2006**, *39*, 128; d) Y. Xiao, Z. Wang, K. Ding, *Chem. Eur. J.* **2005**, *11*, 3668.
- [11] a) *Rhodium Catalyzed Hydroformylation* (Eds.: P. W. N. M. van Leeuwen, C. Claver), Kluwer Academic Publishers, Dordrecht, **2000**; b) R. Franke, D. Selent, A. Boerner, *Chem. Rev.* **2012**, *112*, 5675.
- [12] F. J. Fernández-Alvarez, A. M. Aitani, L. A. Oro, *Catal. Sci. Technol.* **2014**, *4*, 611.
- [13] K. Motokura, M. Naijo, S. Yamaguchi, A. Miyaji, T. Baba, *Chem. Lett.* **2015**, *44*, 1217.
- [14] a) T. Morimoto, K. Kakiuchi, *Angew. Chem. Int. Ed.* **2004**, *43*, 5580; *Angew. Chem.* **2004**, *116*, 5698; b) L. P. Wu, Q. Liu, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 6310; *Angew. Chem.* **2014**, *126*, 6426.
- [15] K. Motokura, D. Kashiwame, A. Miyaji, T. Baba, *Org. Lett.* **2012**, *14*, 2642.
- [16] a) P. Svoboda, J. Hetflejš, *Collect. Czech. Chem. Commun.* **1975**, *40*, 1746; b) A. Ceriotti, G. Ciani, A. Sironi, *J. Organomet. Chem.* **1983**, *247*, 345.
- [17] It should be noted that even though H₂ has been detected by GC analysis in the reaction described above, it is statistically insignificant in comparison with the D₂ concentration in the system.
- [18] a) S. K. Murphy, J. W. Park, F. A. Cruz, V. M. Dong, *Science* **2015**, *347*, 56; b) S. Kusumoto, T. Tatsuki, K. Nozaki, *Angew. Chem. Int. Ed.* **2015**, *54*, 8458; *Angew. Chem.* **2015**, *127*, 8578.
- [19] M. Portnoy, D. Milstein, *Organometallics* **1994**, *13*, 600.
- [20] X. Fang, M. Zhang, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 4645; *Angew. Chem.* **2013**, *125*, 4743.

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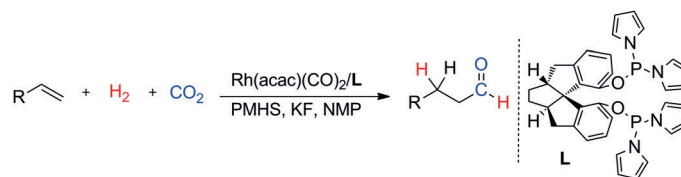
Communications



Hydroformylation

X. Ren, Z. Zheng, L. Zhang, Z. Wang,
C. Xia,* K. Ding* ———— ■■■■-■■■■

Rhodium-Complex-Catalyzed
Hydroformylation of Olefins with CO₂
and Hydrosilane



Hydroformylation with waste chemicals:
A rhodium phosphoramidite catalyst
enables the efficient hydroformylation of
olefins to aldehydes in the presence of
CO₂, hydrosilane, and H₂. This trans-

formation is likely to proceed through
poly(methylhydrosiloxane) (PMHS)
mediated CO₂ reduction to CO and
a conventional rhodium-catalyzed hydro-
formylation with CO/H₂.