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Hydroformylation of olefins and reductive carbonylation of aryl halides with syngas formed *ex situ* from dehydrogenative decarbonylation of hexane-1,6-diol†

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A variety of primary alcohols have been investigated as convenient substrates for the *ex situ* delivery of carbon monoxide and molecular hydrogen in a two-chamber reactor. The gaseous mixture is liberated in one chamber by an iridium-catalysed dehydrogenative decarbonylation of the alcohol and then consumed in the other chamber in either a rhodium-catalysed hydroformylation of olefins or a palladium-catalysed reductive carbonylation of aryl halides. Hexane-1,6-diol was found to be the optimum alcohol for both reactions where moderate to excellent yields were obtained of the product aldehydes. A relatively low pressure of 1.5–2.4 bar was measured in the closed system during the two transformations.

Introduction

The mixture of carbon monoxide and molecular hydrogen (*i.e.* syngas) is a very useful feedstock in chemistry and can be applied in a number of transformations such as the Fischer–Tropsch process,[1] the hydroformylation of alkenes[2] and the reductive carbonylation (formylation) of aryl halides.[3] However, for applications in organic chemistry the high toxicity of carbon monoxide constitutes a severe problem especially because a high pressure of syngas is often required. As a result, there has been a significant interest in finding alternative ways to generate and deliver syngas to a reaction mixture. This has led to the development of several syngas surrogates which are molecules that release syngas *in situ*.[4] These surrogates include formaldehyde, carbon dioxide and derivatives of formic acid where the last two also require a reducing agent.[4,5] However, the challenge is to combine the syngas-releasing reaction with the syngas-consuming reaction in the same pot. An alternative strategy is to separate the two transformations into two reaction vessels which are connected by a tube allowing syngas to flow from one vessel to another. This two-chamber setup for *ex situ* generation of carbon monoxide has been especially developed by the Skrydstrup group and applied in a number of carbonylation reactions[6] including the reductive carbonylation of aryl halides where 9-methylfluorene-9-carbonyl chloride served as the carbon monoxide source and potassium formate as the hydride source.[7] However, it would be desirable to have a cheaper and more easily available syngas surrogate for use in this system.

We have recently combined the dehydrogenation of a primary alcohol and the decarbonylation of the resulting aldehyde into one transformation where carbon monoxide and molecular hydrogen are produced in a 1 : 1 ratio together with the one-carbon shorter alkane.[8] This dehydrogenative decarbonylation is catalysed by 2.5% of $[Ir(coe)_2Cl]_2$, 5% of *rac*-BINAP and 10% of LiCl in mesitylene saturated with water at reflux (164 °C). The transformation has been applied to a variety of primary alcohols and functional groups such as ethers, esters, imides and aryl halides are stable under the reaction conditions while olefins are partially saturated.[8] The mechanism is believed to involve two separate catalytic cycles with the same iridium(I)-BINAP species where the first removes molecular hydrogen from the primary alcohol and the second cleaves carbon monoxide from the resulting aldehyde.

We envisioned that the dehydrogenative decarbonylation from an alcohol could serve as the syngas-releasing reaction in one chamber with a hydroformylation or a reductive carbonylation as the syngas-consuming reaction in the other chamber. Very recently, the same setup was used for generating syngas at 210 °C from polyols in the hydroformylation of styrene, but the transformation was often accompanied by significant reduction to ethylbenzene as a side reaction.[9] Accordingly, we here describe our development of commercially available alcohols as precursors for carbon monoxide and molecular hydro-

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gen in the synthesis of aldehydes from alkenes and aryl halides.

Results and discussion

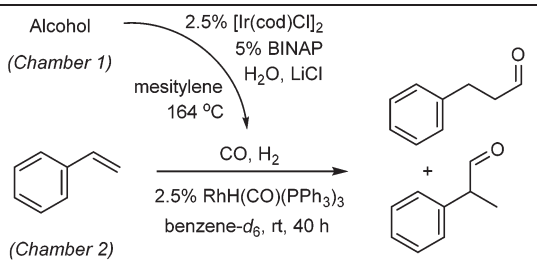
The iridium-catalysed dehydrogenative decarbonylation of a primary alcohol requires a temperature of at least 150 °C in order to produce syngas at a reasonable rate.[8] However, the hydroformylation of olefins and the reductive carbonylation of aryl halides are usually performed at significantly lower temperatures. As a result, the two chambers in the reactor will have to operate at different temperatures and the original design from the Skrydstrup group was therefore slightly modified. A longer connecting tube was employed between the two chambers and a coldfinger was installed in the syngas-releasing chamber to allow for the higher temperature and to prevent mesitylene from diffusing into the syngas-consuming chamber (see ESI†). In this way, the iridium-catalysed dehydrogenative decarbonylation could be studied under the optimised conditions with a variety of alcohols in the first chamber. In the second chamber the hydroformylation of styrene was selected for the first experiments and the complex $RhH(CO)(PPh_3)_3$ was chosen as the catalyst since it has shown high activity at both low temperature and pressure.[10] During the optimisation the hydroformylation was carried out in benzene-d_6 which allowed for quick determination of the yields by ^{1}H NMR spectroscopy.

First, simple primary alcohols were included as syngas sources in the first chamber (Table 1). Pentan-1-ol, heptan-1-ol, dodecan-1-ol and 2-phenylethanol all gave full conversion of styrene and resulted in ≥97% yield of the two aldehyde products (entries 1–4). Benzyl alcohol, on the other hand, gave a slightly lower yield of 92% since the reaction was accompanied by 8% reduction to ethylbenzene (entry 5). This can be explained by the higher stability and slower decarbonylation of benzaldehyde as compared to aliphatic aldehydes.[8,11] The result is a higher initial H_2 : CO ratio with benzyl alcohol than with aliphatic alcohols and thus more reduction to ethylbenzene is observed. Several α,ω-diols were also included in the alcohol screening where hexane-1,6-diol and dodecane-1,12-diol both gave ≥97% yield (entries 6 and 7). The branched alcohol 2-methylpropane-1,3-diol reacted slowly and only gave 55% conversion of styrene (entry 8).

Besides simple alcohols, carbohydrates would also be a very attractive syngas source since they can potentially undergo complete degradation into carbon monoxide and molecular hydrogen. Unfortunately, D-sorbitol and glycerol afforded very little of the desired aldehydes and the reactions were accompanied by significant reduction to ethylbenzene (entries 9 and 10). The gas development from the dehydrogenative decarbonylation of D-sorbitol and glycerol was measured in a separate flask and only about one equivalent was liberated. The poor conversion could be due to the limited solubility of D-sorbitol and glycerol in mesitylene at 164 °C. Attempts were made to improve the solubility by adding phenylboronic acid or dibutyltin oxide as hydroxyl complexing agents, but these experiments did not lead to additional syngas formation.

Therefore, hexane-1,6-diol was selected as the syngas source for general use since it gives complete conversion in the hydroformylation and is easy to handle as a solid. It is a very cheap substrate which is produced commercially by hydrogenation of adipic acid. The only byproduct from the dehydrogenative decarbonylation is butane which evaporates after unsealing the two-chamber reactor. The butane formation was confirmed by ^{1}H NMR of the hydroformylation reaction immediately after

Table 1 Alcohols as syngas source for the hydroformylation reaction



Entry	Alcohol	Equiv. of alcohol	Aldehyde yield[a] (%)	Linear : branched[a]	Ethylbenzene yield[a] (%)
1	Pentan-1-ol	2	98	5 : 3	2
2	Heptan-1-ol	2	100	5 : 4	0
3	Dodecan-1-ol	2	97	5 : 4	3
4	2-Phenylethanol	2	100	1 : 1	0
5	Benzyl alcohol	2	92	5 : 4	8
6	Hexane-1,6-diol	1	100	5 : 4	0
7	Dodecane-1,12-diol	1	97	5 : 4	3
8	2-Methylpropane-1,3-diol	1	55	2 : 1	0
9	D-Sorbitol	0.3	4	7 : 3	13
10	Glycerol	0.5	24	7 : 3	6

[a] Determined by ^{1}H NMR.

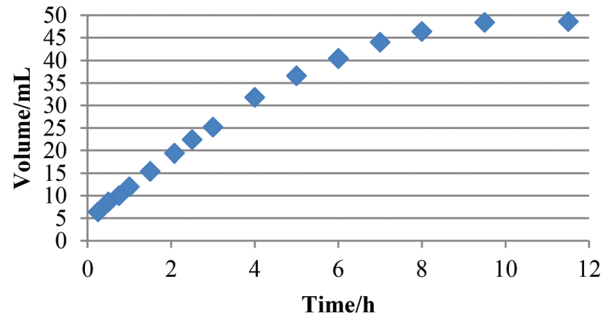


Fig. 1 Gas formation as a function of time.

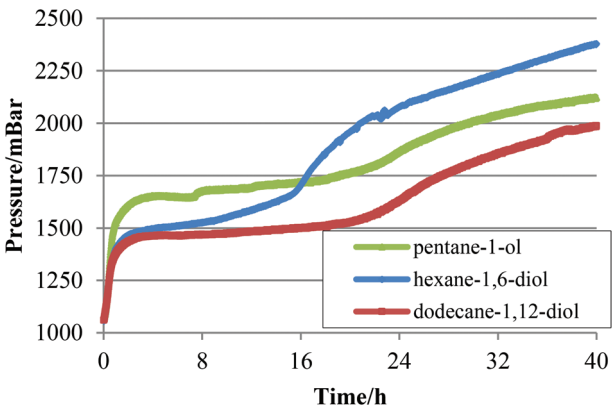


Fig. 2 Pressure in two-chamber reactor during the hydroformylation of styrene.

opening the system. The gas development during the dehydrogenative decarbonylation was measured by reacting 0.5 mmol of hexane-1,6-diol in a Schlenk tube connected to a burette filled with water. A total gas volume of 48.6 mL was collected which corresponds to approximately 2.0 mmol (Fig. 1).

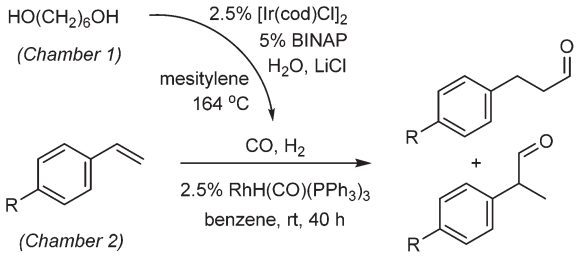
The pressure during the hydroformylation of styrene was measured continuously by attaching a manometer to the second chamber. The initial pressure with hexane-1,6-diol was about 1.5 bar which slowly rose to 2.4 bar during the reaction (Fig. 2). Similar values were measured with pentan-1-ol and dodecane-1,12-diol and in all cases a sudden increase in pressure was observed after 15–25 h. This probably illustrates the time at which the hydroformylation has gone to completion.

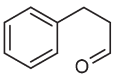
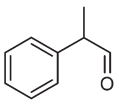
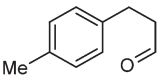
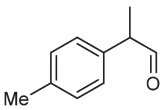
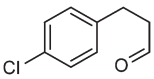
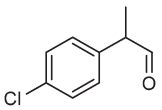
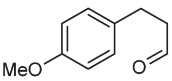
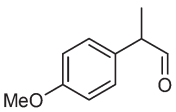
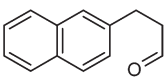
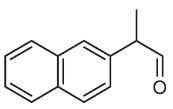
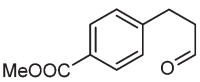
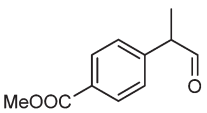
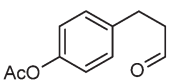
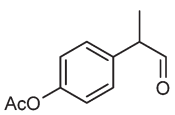
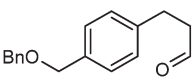
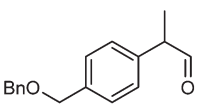
The two aldehydes from the hydroformylation of styrene were separated and isolated in a combined yield of 83% (Table 2, entry 1). The optimised conditions were also applied to a number of other alkenes to give aldehyde yields between 85 and 96% (entries 2–8). The ratio between the linear and the branched aldehyde is in line with the previous experiments with $RhH(CO)(PPh_3)_3$ at low temperature and pressure.[10] These results clearly illustrate that hexane-1,6-diol can be used as a syngas source in the hydroformylation reaction.

We then switched to the reductive carbonylation reaction to investigate whether a similar cheap alcohol could be employed for syngas delivery in this transformation. It has previously been shown that the reductive carbonylation of aryl halides can be performed at moderate pressure and temperature with $Pd(OAc)_2$ and cataCXium A (di-1-adamantyl-*n*-butylphosphine).[12] These conditions were therefore selected for chamber two where *p*-bromoanisole (**1**) was chosen as the substrate for the exploratory experiments. The reaction was performed in toluene where the conversion of **1** as well as the yield of *p*-anisaldehyde (**2**) and anisole (**3**) were determined by GC. In chamber one a number of different alcohols were subjected to the dehydrogenative decarbonylation (Table 3). Only high-boiling alcohols were investigated since an experiment with ethanol gave small amounts of ethyl *p*-anisate due to alcohol diffusion into the second chamber. The simple alcohols pentan-1-ol, heptan-1-ol and dodecan-1-ol gave decent yields of the desired aldehyde, but it was not possible to achieve full conversion of *p*-bromoanisole (entries 1–3). Complete consumption was obtained with 2-(2-naphthyl)ethanol and benzyl alcohol which both gave good yields of *p*-anisaldehyde (entries 4 and 5). Benzyl alcohol resulted in a larger amount of anisole than 2-(2-naphthyl)ethanol which is presumably due to the increased stability of benzaldehyde resulting in a higher initial $H_2:CO$ ratio. Several diols were also investigated where poor results were obtained with 2-methyl- and 2,2-dimethylpropane-1,3-diol (entries 6 and 7). The same was observed with butane-1,4-diol and pentane-1,5-diol where a low selectivity between **2** and **3** was also attained (entries 8 and 9). The latter is most likely caused by cyclisation of the diols into five- and six-membered hemiacetals after the dehydrogenation which makes the decarbonylation more demanding.[13] Hexane-1,6-diol and dodecane-1,12-diol both gave complete conversion and high yields of *p*-anisaldehyde (entries 10–13). No improvement was observed by increasing or decreasing the amount of hexane-1,6-diol. As a result, hexane-1,6-diol was again selected for general use and the scope of the transformation investigated on a variety of aryl halides.

The isolated yield from the conversion of *p*-bromoanisole was found to be 71% (Table 4, entry 1). A similar result was obtained with the corresponding iodide although the transformation required a longer reaction time (entry 2). The same reaction time was necessary for 4-bromoveratrole which afforded the aldehyde in 60% yield (entry 3). The reactions with 2-bromonaphthalene and 4-bromobiphenyl were uneventful and gave the aldehydes in 79 and 69% yield, respectively (entries 4 and 5). Substrates with electron-withdrawing substituents, however, reacted poorly due to competing dehalogenation (entries 6, 8 and 11). Some improvement could be achieved by lowering the temperature and increasing the reaction time (entries 7, 9 and 12). It has previously been observed that the chemoselectivity usually improves at a lower temperature.[12] An alternative strategy would be to increase the $CO:H_2$ ratio by including a hydrogen scavenger in chamber one. Norbornene, diphenylacetylene and benzophenone were investigated as scavengers in the reaction with *p*-bromochlorobenzene and the best result was obtained with 0.3 equivalent of diphenylacetylene as judged by GC. Under these modified

Table 2 Hydroformylation of olefins with hexane-1,6-diol as the syngas source



Entry	R	Linear product	Yield[a] (%)	Branched product	Yield[a] (%)
1	H		50		33
2	Me		52		41
3	Cl		53		35
4	MeO		44		49
5	—[b]		53		43
6	MeOOC		65		30
7	AcO		50		46
8	$BnOCH_2$		48		37

[a] Isolated yield. [b] 2-Vinylnaphthalene was used as the substrate.

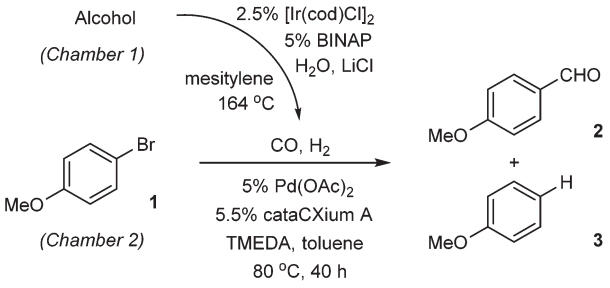
conditions a moderate yield was obtained with chloride and tosylate as the *para* substituent (entries 10 and 13). Similar results were attained with acetate, benzoate, silyloxy and benzyloxy in the *para* position (entries 14–17). These experiments again demonstrate that hexane-1,6-diol is a suitable source of syngas in a formylation reaction.

The pressure during the reductive carbonylation of 2-bromonaphthalene (with 0.3 equiv. of diphenylacetylene) was measured and found to be around 1.6 bar during the course of the reaction (Fig. 3). The slight decrease in pressure after about 8 h may indicate the time at which the active catalyst is formed and the reductive carbonylation commences. Mechanistic studies of the reaction have shown that palladium acetate is first converted into carbonyl and hydride complexes from which the catalytically active species is slowly released.[14]

Conclusions

In summary, we have presented a new application of the iridium-catalysed dehydrogenative decarbonylation of primary alcohols where the transformation serves as a syngas-releasing

Table 3 Alcohols as syngas source for the reductive carbonylation reaction



Entry	Alcohol	Equiv. of alcohol	Conversion of **1**[a] (%)	Yield of **2**[a] (%)	Yield of **3**[a] (%)
1	Pentan-1-ol	2	89	78	11
2	Heptan-1-ol	2	82	75	7
3	Dodecan-1-ol	2	85	77	8
4	2-(2-Naphthyl)ethanol	2	100	93	7
5	Benzyl alcohol	2	100	83	17
6	2-Methylpropane-1,3-diol	1	53	45	8
7	2,2-Dimethylpropane-1,3-diol	1	24	17	7
8	Butane-1,4-diol	1	42	25	17
9	Pentane-1,5-diol	1	34	17	17
10	Hexane-1,6-diol	1	100	92	8
11	Hexane-1,6-diol	0.75	25	16	9
12	Hexane-1,6-diol	1.5	100	85	15
13	Dodecane-1,12-diol	1	100	93	7

[a] Determined by GC.

reaction in a closed two-chamber setup. Hexane-1,6-diol was found to be a convenient syngas surrogate from which the gaseous mixture can be liberated continuously at low pressure. The transformation has been used for hydroformylation of olefins and reductive carbonylation of aryl halides to afford a variety of aldehydes in moderate to excellent yields.

Experimental section

General information

Gas chromatography was performed on a Shimadzu GCMS-QP2010S instrument fitted with an Equity 5, 30 m × 0.25 mm × 0.25 μm column. Flash column chromatography separations were performed on silica gel 60 (35–70 μm). NMR spectra were recorded on a Bruker Ascend 400 spectrometer. Chemical shifts were measured relative to the signals of residual $CHCl_3$ (δ_H 7.26 ppm) and $CDCl_3$ (δ_C 77.16 ppm). HRMS measurements were made using ESI with TOF detection.

General procedure for hydroformylation

To chamber 1 was added hexane-1,6-diol (118.2 mg, 1.0 mmol), $[Ir(cod)Cl]_2$ (16.8 mg, 0.025 mmol), *rac*-BINAP (31.1 mg, 0.050 mmol), LiCl (4.2 mg, 0.10 mmol) and 2.0 mL of mesitylene saturated with H_2O (150 ppm). To chamber 2 was added the olefin (1.0 mmol), $RhH(CO)(PPh_3)_3$[15] (23.0 mg, 0.025 mmol) and dry benzene (1.5 mL). The system was sealed with a coldfinger over chamber 1 and a screw cap over chamber 2. The two-chamber system was lowered into two separate oil baths, where the reaction in chamber 1 was stirred at 170 °C while the reaction in chamber 2 was stirred at rt. After 40 h the crude mixture in chamber 2 was purified directly by column chromatography (Et_2O–pentane) to isolate first the branched and then the linear aldehyde.

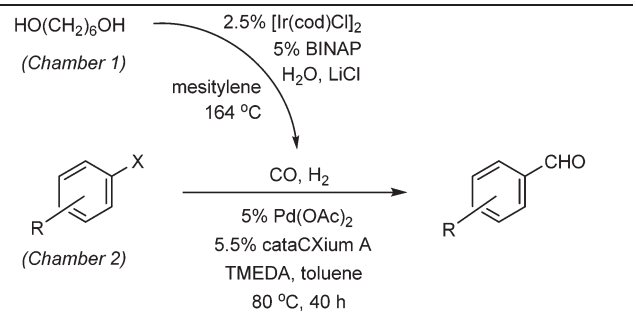
2-Phenylpropanal. R_f 0.50 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.69 (d, J = 1.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.31 (tt, J = 7.2, 1.2 Hz, 1H), 7.22 (dd, J = 7.2, 1.2 Hz, 2H), 3.64 (dq, J = 6.8, 1.2 Hz, 1H), 1.45 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 137.8, 129.2, 128.4, 127.6, 53.1, 14.7. MS m/z 134 $[M]^+$. NMR data are in accordance with literature values.[16]

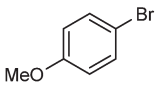
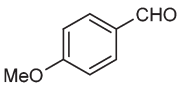
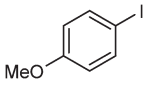
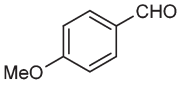
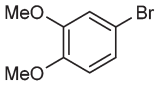
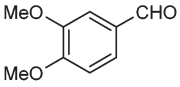
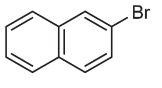
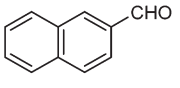
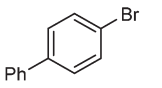
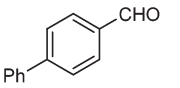
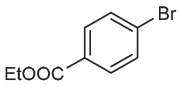
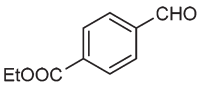
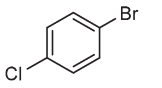
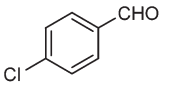
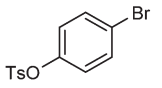
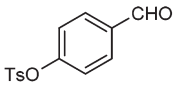
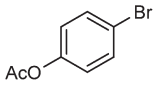
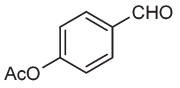
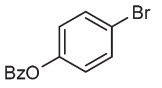
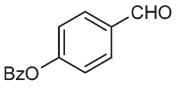
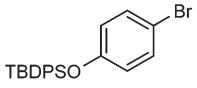
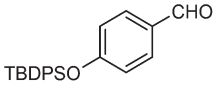
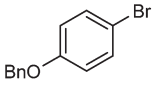
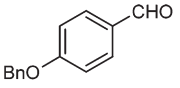
3-Phenylpropanal. R_f 0.37 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.83 (t, J = 1.2 Hz, 1H), 7.31 (tt, J = 6.8, 1.6 Hz, 2H), 7.25–7.18 (m, 3H), 2.97 (t, J = 7.6 Hz, 2H), 2.79 (dt, J = 7.6, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 140.4, 128.7, 128.4, 126.4, 45.4, 28.2. MS m/z 134 $[M]^+$. NMR data are in accordance with literature values.[17]

2-(4-Methylphenyl)propanal. R_f 0.48 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, J = 1.2 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.61 (dq, J = 7.2, 1.2 Hz, 1H), 2.37 (s, 3H), 1.44 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 137.1, 134.7, 129.9, 128.3, 52.7, 21.1, 14.7. MS m/z 148 $[M]^+$. NMR data are in accordance with literature values.[18]

3-(4-Methylphenyl)propanal. R_f 0.30 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.83 (t, J = 1.6 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 2.95 (t, J = 7.6 Hz, 2H), 2.77 (dt, J = 7.6, 1.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 137.3, 135.8, 129.3, 128.2, 45.4, 27.8, 21.0.

Table 4 Reductive carbonylation of aryl halides with hexane-1,6-diol as the syngas source



Entry	Substrate	Product	Yield[a] (%)
1			71
2[b]			73
3[b]			60
4			79
5			69
6 7[b,c]			20 35
8 9[b,c] 10[d,e]			27 56 47
11 12[c,f] 13[d,e]			33 56 62
14[d,e]			49
15[d,e]			54
16[d,e]			44
17[d,e]			65

[a] Isolated yield. [b] Reaction time 90 h. [c] Temperature 60 °C in chamber 2. [d] 0.3 Equiv. of diphenylacetylene added to chamber 1. [e] Reaction time 64 h. [f] Reaction time 114 h.

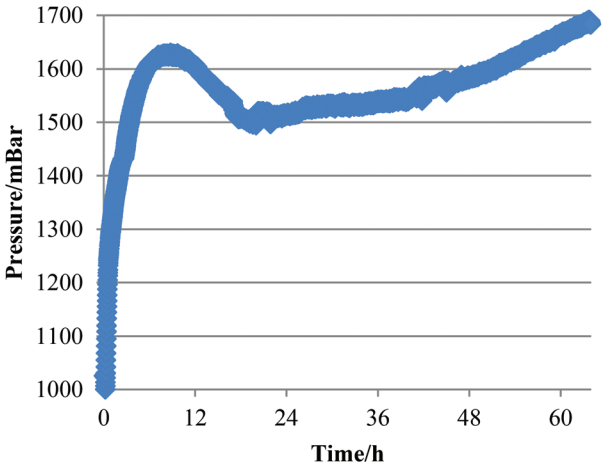


Fig. 3 Pressure in two-chamber reactor during reductive carbonylation of 2-bromonaphthalene.

MS *m*/*z* 148 $[M]^+$. NMR data are in accordance with literature values.[18]

2-(4-Chlorophenyl)propanal. R_f 0.45 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, J = 1.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.62 (dq, J = 7.2, 1.2 Hz, 1H), 1.43 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 136.3, 133.6, 129.7, 129.3, 52.4, 14.7. MS *m*/*z* 168 $[M]^+$. NMR data are in accordance with literature values.[16]

3-(4-Chlorophenyl)propanal. R_f 0.24 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.78 (t, J = 1.6 Hz, 1H), 7.24 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 2.75 (dt, J = 7.2, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 138.9, 132.0, 129.7, 128.7, 45.1, 27.4. MS *m*/*z* 168 $[M]^+$. NMR data are in accordance with literature values.[19]

2-(4-Methoxyphenyl)propanal. R_f 0.49 (Et_2O–pentane 1 : 10). ^1H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, J = 1.6 Hz, 1H), 7.13 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.58 (dq, J = 7.2, 1.2 Hz, 1H), 1.41 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 159.1, 129.7, 129.5, 114.6, 55.4, 52.2, 14.8. MS *m*/*z* 164 $[M]^+$. NMR data are in accordance with literature values.[16]

3-(4-Methoxyphenyl)propanal. R_f 0.35 (Et_2O–pentane 1 : 10). ^1H NMR (400 MHz, $CDCl_3$): δ 9.81 (t, J = 1.6 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.91 (t, J = 7.6 Hz, 2H), 2.74 (dt, J = 7.6, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 158.2, 132.4, 129.3, 114.1, 55.3, 45.6, 27.4. MS *m*/*z* 164 $[M]^+$. NMR data are in accordance with literature values.[20]

2-(2-Naphthyl)propanal. R_f 0.46 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.78 (d, J = 1.2 Hz, 1H), 7.90–7.82 (m, 3H), 7.70 (s, 1H), 7.56–7.49 (m, 2H), 7.34 (dd, J = 8.4, 1.6 Hz, 1H) 3.81 (dq, J = 6.8, 1.2 Hz, 1H), 1.57 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 135.2, 133.7, 132.7, 128.9, 127.8, 127.2, 126.5, 126.3, 126.2, 53.1, 14.7. MS *m*/*z* 184 $[M]^+$. NMR data are in accordance with literature values.[16]

3-(2-Naphthyl)propanal. R_f 0.23 (Et_2O–pentane 1 : 20). ^1H NMR (400 MHz, $CDCl_3$): δ 9.83 (t, J = 1.2 Hz, 1H), 7.88–7.80

(m, 3H), 7.65 (s, 1H), 7.56–7.45 (m, 2H), 7.35 (dd, J = 8.4, 1.6 Hz, 1H), 3.12 (t, J = 7.6 Hz, 2H), 2.83 (dt, J = 7.6, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 137.9, 133.6, 132.1, 128.2, 127.6, 127.5, 126.9, 126.4, 126.1, 125.5, 45.1, 28.2. MS m/z 184 $[M]^+$. NMR data are in accordance with literature values.[21]

Methyl 4-(1-oxopropan-2-yl)benzoate. R_f 0.32 (Et_2O–pentane 1 : 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, J = 1.2 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 3.70 (dq, J = 7.2, 1.2 Hz, 1H), 1.46 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 166.8, 143.0, 130.4, 129.6, 128.5, 53.0, 52.3, 14.7. MS m/z 192 $[M]^+$. NMR data are in accordance with literature values.[16]

Methyl 4-(3-oxopropyl)benzoate. R_f 0.19 (Et_2O–pentane 1 : 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (t, J = 1.2 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 2.97 (t, J = 7.2 Hz, 2H), 2.78 (dt, J = 7.2, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 166.9, 145.9, 129.9, 128.4, 128.3, 52.1, 44.8, 28.0. MS m/z 192 $[M]^+$. NMR data are in accordance with literature values.[22]

4-(1-Oxopropan-2-yl)phenyl acetate. R_f 0.40 (Et_2O–pentane 1 : 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, J = 1.2 Hz, 1H), 7.21 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 3.63 (dq, J = 7.2, 1.2 Hz, 1H), 2.28 (s, 3H), 1.42 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 169.5, 150.1, 135.3, 129.4, 122.3, 52.4, 21.1, 14.7. MS m/z 192 $[M]^+$. ^{1}H NMR data are in accordance with literature values.[23]

4-(3-Oxopropyl)phenyl acetate. R_f 0.22 (Et_2O–pentane 1 : 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, J = 1.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.73 (dt, J = 7.6, 1.2 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 169.5, 149.0, 137.9, 129.2, 121.6, 45.1, 27.4, 21.0. MS m/z 192 $[M]^+$. NMR data for this compound are not known in the literature and HRMS data could not be obtained which is likely due to the instability of aliphatic aldehydes. Instead, the crude aldehyde mixture was reduced with $NaBH_4$ (20 mg, 0.53 mmol) in THF at 0 °C. The obtained alcohol had the following NMR data where the ^{1}H NMR values are in accordance with literature data.[24] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.68 (t, J = 6.4 Hz, 2H), 2.70, (t, J = 7.6 Hz, 2H), 2.29 (s, 3H), 1.92–1.82 (m, 2H), 1.37 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 148.9, 139.5, 129.5, 121.5, 62.3, 34.2, 31.5, 21.3.

2-(4-(Benzyloxymethyl)phenyl)propanal. R_f 0.41 (Et_2O–pentane 1 : 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, J = 1.6 Hz, 1H), 7.40–7.15 (m, 9H), 4.56 (s, 2H), 4.54 (s, 2H), 3.61 (dq, J = 7.2, 1.6 Hz, 1H), 1.42 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 138.2, 137.8, 137.1, 128.5, 128.5, 128.4, 127.8, 127.7, 72.3, 71.7, 52.8, 14.7. MS m/z 254 $[M]^+$. HRMS: m/z calcd for $C_{17}H_{18}O_2$ 277.1204 $[M + Na]^+$, found 277.1203.

3-(4-(Benzyloxymethyl)phenyl)propanal. R_f 0.22 (Et_2O–pentane 1 : 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, J = 1.2 Hz, 1H), 7.37–7.11 (m, 9H), 4.52 (s, 2H), 4.49 (s, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.71 (dt, J = 7.6, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 139.8, 138.3, 136.3, 128.4, 128.3, 128.1, 127.7, 127.6, 72.1, 71.8, 45.2, 27.8. MS m/z 254 $[M]^+$. HRMS: m/z calcd for $C_{17}H_{18}O_2$ 277.1204 $[M + Na]^+$, found 277.1204.

General procedure for reductive carbonylation

In a two-chamber system, hexane-1,6-diol (118 mg, 1.00 mmol), $[Ir(cod)Cl]_2$ (16.8 mg, 0.025 mmol), *rac*-BINAP (31.0 mg, 0.050 mmol), LiCl (4.2 mg, 0.10 mmol) and mesitylene (2.0 mL, saturated with H_2O) were added to chamber 1. To chamber 2 were added the aryl halide (1.00 mmol), Pd $(OAc)_2$ (11.2 mg, 0.050 mmol), cataCXium A (19.7 mg, 0.055 mmol), TMEDA (0.30 mL, 2.00 mmol) and dry toluene (2.0 mL). The two-chamber system was flushed with argon. The system was sealed with a coldfinger over chamber 1 and a screw cap over chamber 2. Chamber 1 was heated to 170 °C while chamber 2 was heated to 80 °C. After 40 h, the system was allowed to reach rt and the pressure was released upon opening of the system. The suspension in chamber 2 was filtered through a silica plug and the filter cake was rinsed with EtOAc. The filtrate was concentrated and purified by column chromatography (Et_2O–pentane) to afford the aldehyde product.

4-Anisaldehyde (2). R_f 0.25 (Et_2O–pentane 1 : 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 164.7, 132.1, 130.1, 114.4, 55.7. MS m/z 136 $[M]^+$. NMR data are in accordance with literature values.[5a]

3,4-Dimethoxybenzaldehyde. R_f 0.28 (Et_2O–pentane 1 : 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.41 (dd, J = 8.2, 1.8 Hz, 1H), 7.36 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 154.5, 149.6, 130.1, 126.9, 110.4, 108.9, 56.2, 56.0. MS m/z 166 $[M]^+$. NMR data are in accordance with literature values.[5a]

Naphthalene-2-carbaldehyde. R_f 0.28 (Et_2O–pentane 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 1H), 8.35 (s, 1H), 8.07–7.86 (m, 4H), 7.68–7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 136.6, 134.7, 134.3, 132.8, 129.68, 129.27, 129.3, 128.2, 127.2, 122.9. MS m/z 156 $[M]^+$. NMR data are in accordance with literature values.[5a]

Biphenyl-4-carbaldehyde. R_f 0.30 (Et_2O–pentane 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.67–7.62 (m, 2H), 7.52–7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5. MS m/z 182 $[M]^+$. NMR data are in accordance with literature values.[5a]

Ethyl 4-formylbenzoate. R_f 0.20 (Et_2O–pentane 1 : 15). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.19 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 165.7, 139.2, 135.6, 130.3, 129.6, 61.7, 14.4. MS m/z 178 $[M]^+$. NMR data are in accordance with literature values.[5d]

4-Chlorobenzaldehyde. R_f 0.26 (Et_2O–pentane 1 : 30). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.88–7.73 (m, 2H), 7.57–7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 141.1, 134.9, 131.1, 129.6. MS m/z 140 $[M]^+$. NMR data are in accordance with literature values.[5a]

4-(4-Methylbenzenesulfonyloxy)benzaldehyde. R_f 0.29 (Et_2O–pentane 1 : 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.86–7.80 (m, 2H), 7.77–7.68 (m, 2H), 7.33 (dd, J = 8.6, 0.6 Hz,

2H), 7.20–7.13 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 154.0, 146.0, 135.0, 132.2, 131.4, 130.1, 128.6, 123.2, 21.9. MS *m*/*z* 276 $[M]^+$. R_f 0.29 (Et_2O–pentane 1 : 3). NMR data are in accordance with literature values.[7]

4-Formylphenyl acetate. R_f 0.25 (Et_2O–pentane 1 : 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.86–7.82 (m, 2H), 7.23–7.18 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 168.8, 155.4, 134.1, 131.3, 122.5, 21.2. MS *m*/*z* 164 $[M]^+$. NMR data are in accordance with literature values.[25]

4-Formylphenyl benzoate. R_f 0.30 (Et_2O–pentane 1 : 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.13–8.06 (m, 2H), 7.89–7.81 (m, 2H), 7.59–7.51 (m, 1H), 7.46–7.38 (m, 2H), 7.34–7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 164.5, 155.7, 134.10, 134.07, 131.3, 130.3, 128.9, 128.8, 122.6. MS *m*/*z* 226 $[M]^+$. NMR data are in accordance with literature values.[26]

4-((*tert*-Butyldiphenylsilyl)oxy)benzaldehyde. R_f 0.28 (Et_2O–pentane 1 : 20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.77–7.60 (m, 6H), 7.52–7.33 (m, 6H), 6.93–6.81 (m, 2H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 161.3, 135.5, 132.1, 131.8, 130.39, 130.36, 128.1, 120.4, 26.5, 19.6. MS *m*/*z* 360 $[M]^+$. NMR data are in accordance with literature values.[27]

4-(Benzyloxy)benzaldehyde. R_f 0.22 (Et_2O–pentane 1 : 10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.88–7.80 (m, 2H), 7.49–7.33 (m, 5H), 7.12–7.04 (m, 2H), 5.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.7, 136.0, 132.0, 130.1, 128.8, 128.4, 127.5, 115.2, 70.3. MS *m*/*z* 212 $[M]^+$. NMR data are in accordance with literature values.[28]

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