

A water-soluble diphosphine ligand with a large ‘natural’ bite angle for two-phase hydroformylation of alkenes

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Abstract

The concept of a large ‘natural’ bite angle in chelating diphosphines has been extended to two-phase alkene hydroformylation by the use of a water-soluble diphosphine based on a xanthene-type backbone. The recently developed diphosphine Xantphos was modified with water-soluble groups by controlled sulfonation in fuming sulfuric acid to form 2,7-bis(SO₃Na)-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (2,7-bis(SO₃Na)-Xantphos) exclusively. The application of this ligand in the two-phase rhodium-catalyzed hydroformylation of alkenes led to the selective formation of linear aldehydes. Some data are reported on the hydroformylation of propene, hex-1-ene and 4-styrenesulfonate. Recycling experiments showed the catalyst to be active up to five cycles. For comparison, the two-phase catalytic results are also given with TPPTS as the ligand. Furthermore, the coordination behaviour of the in situ formed catalytic species HRh(2,7-bis(SO₃Na)-Xantphos)(CO)₂ was studied by high-pressure NMR spectroscopy which indeed showed the desired bis-equatorial coordination of the ligand to the rhodium center. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Homogeneous catalysis has many characteristics that are favorable for commercial application. However, homogeneous catalysts are usually sensitive to air and moisture, this as well as the difficulty in separating the catalyst system from organic products, complicates the application of homogeneous catalysis in the chemical industry.

It is now well-known that separation and recycling of homogeneous catalysts is readily

achieved by applying two-phase catalysis. This methodology first achieved commercial success in the Shell higher olefin process [1]. In the ethylene oligomerization step, the nickel catalyst is dissolved in butanediol and the oligomeric alk-1-enes separate as an immiscible phase which is easily removed from the catalyst. More recently the Ruhrchemie–Rhône Poulenc Process based on rhodium–TPPTS (TPPTS = trisodium salt triphenylphosphine trisulfonate) catalysts for the hydroformylation of propene in water demonstrated the value of water as a solvent in a major homogeneously catalyzed reaction [2]. The success of the latter process

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stems from the extraordinary water solubility imparted to the catalyst by TPPTS. The potential for further application of two-phase catalysis has stimulated the development of many new hydrophilic phosphines [3,4]. Chelating diphosphines often show a higher selectivity and even a higher activity in the hydroformylation of alkenes. For example, BISBI and Xantphos both yield catalysts of high selectivity compared to triphenyl phosphines. Water-soluble versions of BISBI, namely BISBIS [5] and an analogous BISBI type phosphine with pendant groups $-p\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_3\text{-C}_6\text{H}_5$ (**I**) [6] as well as water-soluble BINAP type phosphines such as a BINAP analogue (**II**) of **I** [6] and BINAS-Na [7] also show improved selectivity and activity compared to TPPTS [8] in the two-phase hydroformylation of propene (see Fig. 1).

We recently developed [9] diphosphines based on xanthene-type backbones such as Xantphos (**1**, Fig. 2) showing an enhanced selectivity for

linear aldehydes, which was ascribed to the large ‘natural’ bite angle. In order to combine high selectivity and easy separation, we have chosen to modify Xantphos with water-soluble groups. We show here that Xantphos is selectively disulfonated to yield **2** and that water-soluble rhodium catalysts of **2** retain the exceptional selectivity toward linear aldehydes observed with **1** in nonaqueous solvents.

2. Results and discussion

2.1. Synthesis of 2,7-bis(SO_3Na)-Xantphos (**2**), high-pressure NMR spectroscopy on $\text{HRh}(\mathbf{2})(\text{CO})_2$ (**3**) and the synthesis of $\text{HRh}(\mathbf{2})\text{CO}(\text{PPh}_3)$ (**4**)

A widely used method to obtain water-soluble phosphines is the controlled sulfonation in fuming sulfuric acid [10,11]. However, this

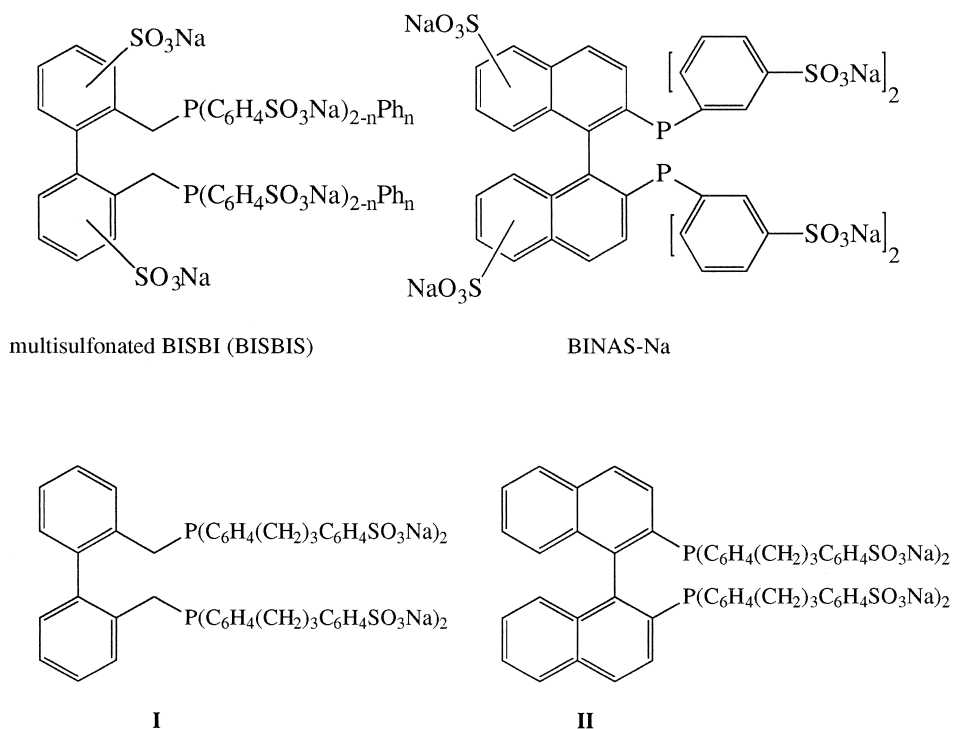


Fig. 1. Water-soluble diphosphine ligands inducing high selectivity in the rhodium catalyzed hydroformylation of alkenes.

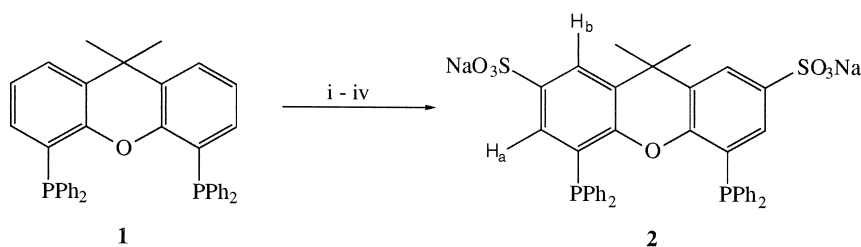


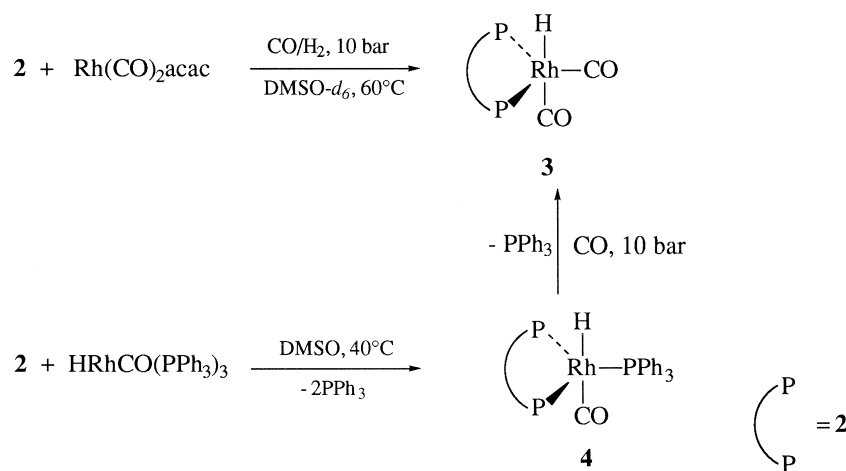
Fig. 2. Synthesis of sulfonated Xantphos (**2**). Reagents and conditions: (i) 25% $\text{SO}_3/\text{H}_2\text{SO}_4$, 5°C to RT; (ii) triisooctylamine, toluene; (iii) NaOH; (iv) neutralization, MeOH-extraction, EtOH.

method poses severe problems with respect to the precise control of the position and number of sulfonate substituents and therefore a mixture of sulfonated products is often obtained. Another problem is the formation of phosphine oxides which are difficult to separate from the products [12]. The sulfonation of **1**, however, gives a high yield of 2,7-bis(SO_3Na)-Xantphos (**2**) when the reaction conditions are carefully controlled. Specifically the addition of **1** to an oleum solution (25% SO_3 in H_2SO_4) must be done slowly and the temperature maintained at 5°C . The reaction was monitored by $^{31}\text{P}\{\text{H}\}$ NMR which indicated that during sulfonation the monosulfonated product is formed. Pure product is obtained by a work-up procedure similar to that described by Herrmann et al. [13] (Fig. 2). EtOH was used to remove small traces of the corresponding phosphine oxide.

The ^1H NMR spectrum of **2** in D_2O consists of two singlet signals in the aromatic region for H_a and H_b (7.98 and 6.95 ppm, respectively) which clearly indicates that the sulfonate groups are positioned *meta* to the phosphorus atoms and *para* to the oxygen atom.

High-pressure NMR experiments establish that the compound $\text{HRh}(\text{2})(\text{CO})_2$ (**3**) is prepared in situ when a 1:1 mixture of $\text{Rh}(\text{CO})_2(\text{AcAc})$ and **2** in $\text{DMSO}-d_6$ is pressurized to 10 bar with CO/H_2 (1:1). When the solution is heated overnight at 600°C , **3** is obtained exclusively as indicated by NMR spectroscopy (see Section 4). The $^{31}\text{P}\{\text{H}\}$ spectrum at room temperature consists of a sharp doublet at 22.18 ppm (J_{RhP}

= 121.1 Hz) for the bidentate phosphine ligand. The ^1H spectrum shows a double triplet in the hydride region (-9.27 ppm, $J_{\text{RhH}} = 7.3$ Hz, $J_{\text{PH}} = 13.1$ Hz). The small J_{PH} coupling constant indicates that the ligand is coordinated to rhodium predominantly in the desired bis-equatorial fashion. All of these data are in agreement with those expected for **3** and are very similar to those found for $\text{HRh}(\text{1})(\text{CO})_2$ [9]. Remarkably, when the sample is stored under an argon atmosphere (1 bar) overnight, the hydride species can still be detected by ^1H and ^{31}P NMR spectroscopy (about 20%). A similar experiment was performed in D_2O , however, according to the ^1H and ^{31}P NMR spectra, **3** was only partially formed after 16 h at 60°C . We suggest that the AcAc anion dissociates to a greater extent in DMSO. Since the hydroformylation reactions were performed in water, the catalyst was incubated overnight at 120°C to facilitate formation of **3** (see Section 4). A more stable hydride species is prepared from the reaction of **2** with $\text{HRhCO}(\text{PPh}_3)_3$ to yield $\text{HRh}(\text{2})\text{CO}(\text{PPh}_3)_3$ (**4**) as a yellow powder (Fig. 3). The $^{31}\text{P}\{\text{H}\}$ spectrum in CD_3OD of **4** consists of a double doublet at 29.77 ppm ($J_{\text{RhP}} = 148.2$ Hz, $J_{\text{PP}} = 126.7$ Hz, $J_{\text{PH}} = 13.0$ Hz) for the bidentate phosphine ligand and a double triplet at 47.05 ppm for PPh_3 ($J_{\text{RhP}} = 149.2$ Hz, $J_{\text{PP}} = 126.4$ Hz, $J_{\text{PH}} = 18.1$ Hz). The small J_{PH} and the coupling constants between the diphosphine-P and the PPh_3 show that the ligands coordinate in the equatorial plane. When **4** is treated with CO pressure (10 bar) in D_2O , the

Fig. 3. Synthesis of **3** and **4**.

biscarbonyl complex **3** forms exclusively, which shows that **4** is a useful precursor to the catalytically active rhodium complex of **2**.

2.2. 2,7-bis(SO₃Na)-Xantphos in the Rh-catalyzed hydroformylation

The results from the catalytic hydroformylation of propene, hex-1-ene and 4-styrene sulfonate with the new rhodium-**2** complex are presented in Table 1. Recycling experiments were also done and these results are given in Table 2. Both for hex-1-ene and propene high selectivities for the formation of linear aldehydes are observed ($l/b = 32.5$). For hex-1-ene

no isomerization is observed. In all cases relatively low activities are found. This observation is attributed to mass transfer limitation of the substrates and in the case of propene also to the low pressure which was used. The activity and selectivity of the reaction was found to be independent of the ligand to rhodium ratio in similar systems (when $L/\text{Rh} > 2$) [9]. Higher activities, however, are observed when the water-soluble 4-styrene sulfonate is used as the substrate. Linear and branched aldehydes ($l/b = 0.67$; 20%) and the hydrates (10%) are formed in addition to poly(4-styrenesulfonate) (70%) [14]. The conversion is quantitative within 3 h, which indicates that the rhodium catalyst system is

Table 1

Rhodium-catalyzed hydroformylation of propene, 1-hexene and *p*-(SO₃Na)-styrene using water-soluble diphosphine ligand **2**

Ligand	Substrate	Conversion (%)	Selectivity to aldehydes (%)	l/b	TOF ^a
2 ^b	propene	67	100	30.2	310
TPPTS ^b	propene	51	100	16.0	500
2 ^c	1-hexene	13	100	34.7	24
2 ^d	<i>p</i> -(SO ₃ Na)-styrene	100	19.8	0.67	670

^aTOF: (mol aldehydes)/(mol Rh · h); determined at 30% conversion (1-hexene at 10% conversion); the selectivity towards the formation of aldehydes was 100% in the case of propene and hex-1-ene and 20% for 4-styrenesulfonate.

^bReaction conditions: $T = 120^\circ\text{C}$, $p = 9$ bar propene and 10 bar $\text{CO}/\text{H}_2 = 1/1$, $[\text{Rh}] = 0.2$ mM, $L/\text{Rh} = 5/1$, $\text{Sub}/\text{Rh} = 9500/1$.

^cReaction conditions: $T = 120^\circ\text{C}$, $p = 19$ bar $\text{CO}/\text{H}_2 = 1/1$, $[\text{Rh}] = 0.13$ mM, $L/\text{Rh} = 5/1$, $\text{Sub}/\text{Rh} = 3000/1$, decane was used as internal standard.

^dReaction conditions: $T = 120^\circ\text{C}$, $p = 19$ bar, $\text{CO}/\text{H}_2 = 1/1$, $[\text{Rh}] = 0.2$ mM, $L/\text{Rh} = 5/1$, $\text{Sub}/\text{Rh} = 9500/1$.

Table 2
Recycling of the catalyst **3** with propene as the substrate^a

Cycle	Conversion (%)	Linear aldehyde (%)	<i>l/b</i>	TOF ^b
1	76	96.8	30.2	170
2	73	97.2	34.7	280
3	81	97.3	36.0	310
4	79	97.5	39.0	420
5	100	97.4	34.8	440

^aReaction conditions: $T = 120^{\circ}\text{C}$, $p = 9$ bar propene and 10 bar $\text{CO}/\text{H}_2 = 1/1$, $[\text{Rh}] = 0.2$ mM, $L/\text{Rh} = 5/1$, $\text{Sub}/\text{Rh} = 9500/1$.

^bTOF: (mol aldehydes)/(mol Rh · h); determined at 30% conversion.

highly active in one-phase hydroformylation. From the recycling experiment it is clear that the formation of the catalyst system in water is slow which is in accordance with the observation that after each cycle activity is increased. Furthermore, the catalyst system is remarkably stable. After each cycle (80% conversion), the autoclave was depressurized and the contents was transferred to a Schlenk flask under argon. The organic layer was separated and the water phase was reinjected in the flushed autoclave which was then pressurized with propene (9 bar) and CO/H_2 to 19 bar, and heated to 120°C . The fifth cycle was run to 100% conversion. In the next cycle no activity for the catalyst was observed, which indicates that in the absence of substrate the catalyst decomposes.

3. Conclusion

The results reported here show that the new water-soluble diphosphine **2** is easily obtained without formation of phosphine oxides and its structure is unambiguously established by NMR spectroscopy. The new rhodium catalyst system **3**, derived from **2** and $\text{Rh}(\text{CO})_2(\text{AcAc})$, is catalytically active and highly regioselective in hydroformylation reactions of alkenes. Recycling experiments show **3** to be stable under hydroformylation conditions. Furthermore, the higher regioselectivity to the linear aldehyde, which is

ascribed to the favorable size of the bite angle in the unsulfonated analog **1**, is retained in water.

4. Experimental

4.1. General

All synthetic operations and catalyst preparations were carried out under an argon atmosphere by using standard Schlenk techniques. The organic solvents were carefully dried and freshly distilled prior to use. Methanol was distilled from CaH_2 and distilled deionized water was degassed by five cycles of vacuum boiling and readmission of argon. Hex-1-ene was purchased from Aldrich and poured through a neutral alumina column prior to use. Propene was purchased from Indugas Praxair (purity 2.5) and was used as received. 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos) [9] and $(\text{PPh})_3\text{Rh}(\text{H})(\text{CO})$ [15] were prepared according to literature procedures.

^1H NMR (300 MHz), ^{13}C NMR (75.5 MHz) and ^{31}P NMR spectra (121.5 MHz, referenced to external 85% H_3PO_4) were recorded on a Bruker AMX-300 spectrometer. High-pressure NMR spectra, ^1H NMR (300.1 MHz) and ^{31}P NMR spectra (121.5 MHz, referenced to external 85% H_3PO_4) were recorded on a Bruker DRX-300 spectrometer. Mass spectrometry was measured on a JEOL JMS-Sx/SX102A. Melting points were measured on a Gallenkamp MFB-595 melting apparatus. Gas chromatography was performed on a Carlo Erba GC 6000 Vega series or an Interscience Mega 2 series apparatus (split/splitless injector, J&W, DB1 30 m column, film thickness 3.0 mm, carrier gas 70 kPa of He, FID detector).

The hydroformylations were carried out in a 170 ml RVS autoclave, equipped with a substrate inlet vessel, a liquid sample valve, baffles and a mechanical stirrer (Medimex). The temperature was controlled by an electronic heating mantle. Samples were removed via the liquid

sample valve and analyzed by temperature-controlled gas chromatography or ^1H NMR spectroscopy.

4.2. Synthesis of 2,7-bis(SO_3Na)-Xantphos (**2**)

In a typical experiment, Xantphos (1 g, 1.73 mmol) was added slowly to oleum (2.9 ml, 25% SO_3) in 4 h at 5°C . After the addition was complete, the resulting brownish solution was warmed to RT. After 16 h, 15 ml degassed ice water was added slowly to the solution which resulted in a white suspension. Another 20 ml of water was added and the resulting yellowish solution was poured into a vigorously stirred solution of triisooctylamine (54 mmol, 2.3 ml) in 10 ml of toluene. The toluene layer was washed twice with water and a solution of NaOH (6.25 M) was slowly added until pH 12 was reached. The water layer was decanted and neutralized with a 3 M H_2SO_4 solution. Evaporation gave a white solid which was poured into refluxing MeOH. After 30 min the white suspension was carefully filtrated and the resulting clear solution was evaporated to dryness resulting in a pale yellow solid. Further purification was accomplished by refluxing the solid in EtOH which after decantation and evaporation gave a white solid. Yield: 1.03 g (1.31 mmol; 76%). ^1H NMR (CD_3OD ; ppm): δ 8.00 (s, 2H, ArH), 7.28–7.18 (m, 22H, ArH), 1.69 (s, 6H, $\text{C}(\text{CH}_3)_2$). $^{13}\text{C}\{\text{H}\}$ NMR (CD_3OD ; ppm): δ 154.6 (t, $J = 9.3$ Hz), 142.1, 138.0 (t, $J = 6.0$ Hz), 135.2 (t, $J = 10.1$ Hz), 131.1, 129.9, 129.6, 128.3, 128.0, 126.0, 36.2 ($\text{C}(\text{CH}_3)_3$), 32.1 (CH_3). $^{31}\text{P}\{\text{H}\}$ NMR (CD_3OD ; ppm): δ -14.7. (Found: C, 57.8; H, 4.2; S, 8.2. Calc. for $\text{C}_{39}\text{H}_{30}\text{Na}_2\text{O}_7\text{P}_2\text{S}_2$: C, 58.3; H, 4.0; S, 8.2%). Exact mass (FAB): m/z 783.7165 [$\text{M} + \text{H}$] (Calc. for $\text{C}_{39}\text{H}_{31}\text{Na}_2\text{O}_7\text{P}_2\text{S}_2$: 783.7168). M.p. $> 300^\circ\text{C}$ (decomposition).

4.3. In situ preparation of $\text{HRh}(\text{2})(\text{CO})_2$ (**3**); high-pressure NMR

$\text{Rh}(\text{CO})_2(\text{AcAc})$ (5 mg, 0.02 mmol) and **2** (15.2 mg, 0.02 mmol) were mixed in $\text{DMSO}-d_6$

(1.5 ml) which resulted in an orange solution. The solution was transferred into a 10 mm sapphire NMR tube equipped with a titanium head [16,17],^{1, 2} pressurized with CO/H_2 (10 bar) and heated to 60°C . A color change from orange to yellow was observed. The yield of **3** was quantitative as determined by ^1H NMR spectroscopy. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{DMSO}-d_6$; ppm): δ 22.2 (dd, $J_{\text{RhP}} = 121$ Hz). ^1H NMR ($\text{DMSO}-d_6$; ppm): δ 7.91 (s, 2H, ArH), 7.52–7.22 (m, 22H, ArH), 2.12 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), -9.27 (dt, 1H, $J_{\text{RhH}} = 7.3$ Hz, $J_{\text{PH}} = 13.1$ Hz, RhH).

4.4. Synthesis of $\text{HRh}(\text{2})\text{CO}(\text{PPh}_3)$ (**4**)

$\text{HRhCO}(\text{PPh}_3)_3$ (20 mg, 0.022 mmol) and **2** (17 mg, 0.022 mmol) were mixed in $\text{DMSO}-d_6$ (1 ml) at RT. The resulting yellow solution was stirred for an additional 3 h at 40°C after which the solvent was evaporated under high vacuum. The resulting yellow solid was twice washed with Et_2O and evaporated to dryness to give **4** as a yellow solid. Yield: 29.6 mg (94%, 0.02 mmol). $^{31}\text{P}\{\text{H}\}$ NMR ($\text{DMSO}-d_6$; ppm): δ 29.8 ($J_{\text{RhP}} = 148$ Hz, $J_{\text{PP}} = 127$ Hz), 47.1 ($J_{\text{RhP}} = 149$ Hz, $J_{\text{PP}} = 127$ Hz). ^1H NMR (CD_3OD ; ppm): δ 8.20 (s, 2H, ArH), 7.81–7.10 (m, 37H, ArH), 2.01 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), -9.77 (m, 1H, $J_{\text{RhH}} = 3.1$ Hz, $J_{\text{PH}} = 13.0$ Hz, $J_{\text{P'H}} = 18.1$ Hz, RhH).

4.5. Two-phase hydroformylation; recycling experiments

In the desired ratio, **2** and $\text{Rh}(\text{CO})_2(\text{AcAc})$ were mixed in 2 ml degassed water under argon. The resulting yellowish solution was transferred into the flushed (3 times) autoclave under argon, and 10 ml of degassed water was added.

¹ Note: Extreme caution should always be taken while working under high gas pressures, sufficient personal protection must be taken to prevent injuries during transport and handling of the high-pressure NMR tube.

² A 10 mm o.d. tube with 1 mm wall is employed. The Viton o-ring in the valve was replaced by Vespel.

The autoclave was pressurized to 12 bar with CO/H₂ and heated to 120°C overnight after which it was cooled to RT and depressurized. *Propene*: then the autoclave was pressurized with propene (9 bar) and with CO/H₂ to 19 bar. The autoclave was heated to 120°C and stirred for two days after which it was cooled to RT using an ice bath. The organic layer was separated and dissolved in C₆D₆ and analyzed by ¹H NMR spectroscopy. The conversion and TOFs were calculated from the pressure drop (see Table 1). Hex-1-ene and 4-styrene-sulfonate: then the desired amount of substrate and *n*-decane (internal standard) were placed in the substrate vessel and then pressed into the autoclave with 19 bar of CO/H₂. Samples were removed via the liquid sampling valve and analyzed by temperature-controlled gas chromatography and ¹H NMR spectroscopy. *Recycling experiment* (see Table 2): the experiment was performed similar to that described for propene. For each cycle after 80% conversion, the autoclave was depressurized and the contents was transferred to a Schlenk flask under argon. The organic layer was separated and the water phase was reinjected in the flushed autoclave which was then pressurized with propene (9 bar) and CO/H₂ to 19 bar, and heated to 120°C.

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