Catalysis

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Cooperative Ligand Effects in Phase-Switching Homogeneous Catalysts**

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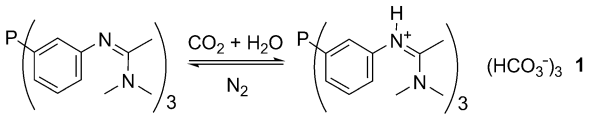
Homogeneous catalysis is usually carried out by using a metal complex that contains ligands that solubilize the complex and control the selectivity of the reaction. Apart from simple ligands, such as carbon monoxide or halides, these complexes usually contain only one other type of ligand. Noyori-type hydrogenation catalysts often contain diamines and (di)phosphine ligands and both are required to obtain the desired reactivity and selectivity.[1] Less usual are systems which give one product when one ligand is used, but the outcome is altered by adding a second ligand, which gives cooperative effects. We have recently reported two such cooperative effects. Xantphos is a bidentate phosphine ligand which has a wide bite angle and hence a high selectivity for the linear product in the hydroformylation of alkenes.[2] The products of these reactions are invariably aldehydes. When PEt_3 is used as the supporting ligand for alkene hydroformylation in alcoholic solvents, alcohols rather than aldehydes are the products, but the linear selectivity is poor.[3] By using a mixture of PEt_3 and xantphos, it is possible to obtain high selectivity towards the linear alcohol products.[4] We have demonstrated that only xantphos, which controls the regioselectivity, is coordinated to the metal atom during the early part of the reaction, but PEt_3 coordinates later in the cycle and directs the formation of alcohol products. In a second example, a xantphos ligand that is tagged with an imidazolium group (xantphos′) together with a sulfonated triphenylphosphine (PPh_3') were used for hydroformylation of alkenes in supercritical fluid/ionic liquid flow systems.[5] The metal/PPh_3' complex alone gives a high rate of reaction with poor linear selectivity, whereas the xantphos ligand alone gives a high linear selectivity at a lower rate of reaction. By using the two together we obtained intermediate linear selectivity at a similar rate of reaction to the experiments that were performed with xantphos alone. These results suggest that both PPh_3' and xantphos′ are coordinated to the metal atom in the resting state of the catalyst. Herein, we report a third example in which two ligands that are tagged with amidate groups, trisSwitchPhos **1**[6] and an amidated xantphos ligand **2**, give a high selectivity and allow the catalyst to be efficiently switched from the organic phase into the aqueous phase by bubbling CO_2 through the reaction mixture.



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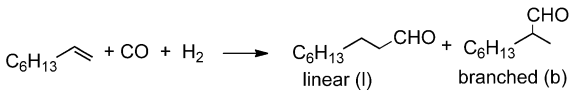
Scheme 1. Reversible switching of **1** into and out of the aqueous phase by bubbling CO_2 and N_2, respectively, through the reaction mixture.

We recently reported[6] that **1** is soluble in toluene and, in the presence of [Rh(acac)(CO)$_2$] (acac = 2,4-pentanedione), catalyzes the fast hydroformylation of 1-octene (Scheme 2). The catalyst can then be switched into the aqueous phase by



Scheme 2. Hydroformylation of 1-octene and the linear (desired) and branched products.

bubbling CO_2 through the reaction mixture. After phase separation and the addition of fresh toluene, the catalyst can be switched back into the organic phase by bubbling N_2 through the mixture at 60 °C (Scheme 1). The only problem with this system was that the linear selectivity was low (linear/branched (l/b) ca. 2.8:1, Table 1, entries 1–3) even when 50-fold excess of the phosphine relative to rhodium was used. To develop a switchable system that also gives a high linear selectivity, we synthesized xantphos ligands that are tagged with the same dimethylacetamidate groups as **1**.

Ligand **2** was synthesized by the route shown in Scheme 3, which is similar to that used to synthesize **1.** **2** was then combined with [Rh(acac)(CO)$_2$] for the hydroformylation of 1-octene in toluene. As expected, the rate of the hydroformylation reaction (Table 1, entries 4 and 5, see also Figure S1 in the Supporting Information) was lower than in the reaction catalyzed by **1** (Table 1, entries 1 and 2), but the linear selectivity was excellent (l/b = 19.5). As is common in reactions with xantphos ligands, significant amounts of isomerized alkene were obtained.

After adding water (Figure 1 a i) and then bubbling CO_2 through the mixture, some of the catalyst transferred into the aqueous phase. However, even after prolonged exposure to

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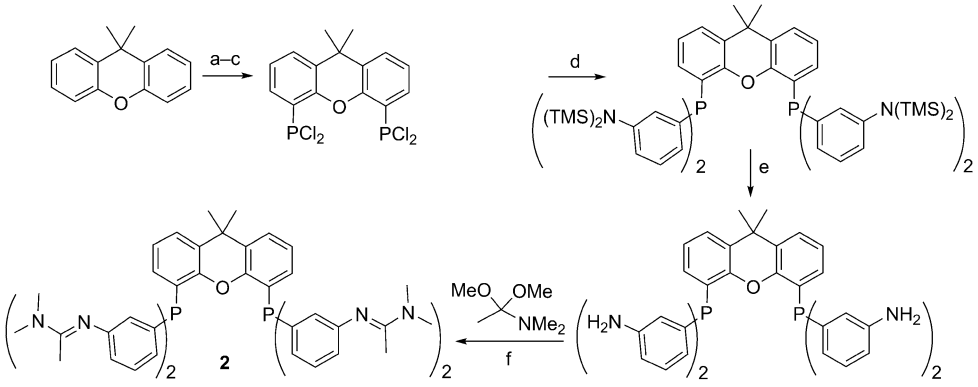
Table 1: Results from the hydroformylation of 1-octene catalyzed by rhodium complexes that contain ligands (L) **1**[6] or **2** alone or **1** and **2** together.[a]

Entry	L	Cycle	Aldehydes [%]	Octene Isomers [%]	l/b	$k/10^{-4}$ s^{-1}	$[Rh]_{org}$ [ppm][d]	$[Rh]_{aq}$ [ppm][e]
1	**1**[b]	1a	92.8	3.2	2.9	34	1.9	0.4
2	**1**[b]	1b				26		
3	**1**[b]	2	94.4	1.2	2.8	22	0.7	0.3
4	**2**	1a	84.1	12.2	19.5	5.0	[c]	
5	**2**	1b				4.5		
6	**2**	2	57.4	13.5	16.1	1.3		
7	**1/2**	1a	80.6	11.5	16.4	1.9	5.0	0.3
8	**1/2**	1b				2.3		
9	**1/2**	2	68.5	10.7	16.0	1.5	8.2	1.6

[a] Reaction conditions: 100 °C, 20 bar, $CO/H_2 = 1:1$, stirring rate = 1000 rpm, $[Rh] = 10^{-3}$ mol dm^{-3}, $[\mathbf{1}] = [\mathbf{2}] = 2.2 \times 10^{-3}$ mol dm^{-3}, toluene (8 mL), 1-octene (2 mL), the product solutions from cycles 1a and 1b, which are repeats of one another in each case; were combined for analysis and switching; [b] $[\mathbf{1}] = 5 \times 10^{-2}$ mol dm^{-3}; [c] Visually very high, not measured. [d] Conc of rhodium remaining in the organic phase after phase switching. [e] Conc of rhodium remaining in the aqueous phase after phase switching.



Scheme 3. Synthesis of **2**: a) THF, BuLi, −78 °C to RT, 24 h; b) $(NEt_2)_2PCl$, −78 °C to RT, 24 h; c) $HCl_{(g)}$, 0 °C, 15 min; d) 3-[bis(trimethylsilyl)amino]phenylmagnesium chloride, −78 °C to RT 12 h, 55 °C, 12 h; e) MeOH, reflux, overnight; f) Microwave, 160 °C, 1 h. TMS = trimethylsilyl.

bubbling CO_2, the organic phase remained quite orange (Figure 1a ii). After phase separation, the addition of fresh toluene to the water layer, and bubbling N_2 through the mixture, the aqueous phase decolorized as the catalyst transferred back into the toluene phase (Figure 1a iii). This new organic phase promoted the hydroformylation reaction at a much lower rate of reaction than in the first runs as a result of the lower catalyst concentration, but the l/b ratio remained high (16.1, Table 1, entries 4 and 5 versus entry 6, see also Figure S1 in the Supporting Information). It is clear from the poor phase switching that the number of amidine groups in the catalyst (four for $[RhH(CO)_2(\mathbf{2})]$) is too small to confer sufficient solubility on the protonated form in water. This is in line with previous results for catalysts that contain ligands similar to **1**, in which at least six amidine groups are required for efficient phase switching.[6,7]

As it is possible that at least some of the resting state of the catalyst might contain both **1** and **2**, especially during phase switching when CO is absent, $[RhH(CO)(\mathbf{1})(\mathbf{2})]$[5] would contain seven amidine groups. Therefore, we attempted the hydroformylation reaction and phase switching in the presence of both ligands ($Rh:\mathbf{2}:\mathbf{1} = 1:2.2:2.2$). The hydroformylation of 1-octene occurred at a rate that was slightly lower than with **2** alone, but the linear selectivity was high at 16.4 (Table 1, entries 7 and 8, see also Figure S2 in the Supporting Information). On adding water and bubbling CO_2 through the reaction mixture, the organic phase completely decolorized (Figure 1b ii), which indicated that the catalyst transferred into the aqueous phase to a much higher extent than in the absence of **1**. Analysis of the product-containing organic phase by inductively coupled plasma mass spectrometry (ICPMS) showed that only 5 ppm of rhodium was present. This is higher than in the experiments with **1** alone, but much lower than with **2** alone. The phases were separated and the aqueous phase that contained the catalyst was treated with more toluene. Bubbling N_2 through the mixture at 60 °C caused the yellow color to be transferred from the water into the toluene (Figure 1b iii), which left only 0.3 ppm of rhodium in the aqueous phase. The toluene phase was then used for the hydroformylation of 1-octene and gave a very similar rate of reaction and linear selectivity to that obtained in the first runs (Table 1, entries 7 and 8 versus entry 9, see also Figure S1 in the Supporting Information). The catalyst could be reextracted, again with low levels of rhodium left in the phases from which the catalyst was switched (Figure 1c, Table 1, entry 9).

To investigate which ligands are coordinated to rhodium during the catalytic cycle and phase switching when **1** and **2** are used together, a series of NMR experiments were performed with PPh_3 and xantphos. The unsubstituted ligands were used to avoid problems with precipitation or phase transfer on bubbling CO_2 through the solution, or possible exchange with hydride species in D_2O. We believe this is an appropriate model, as we have shown that the properties of phosphines that are substituted with *meta*-amidine groups are similar to those of the unsubstituted phosphine.

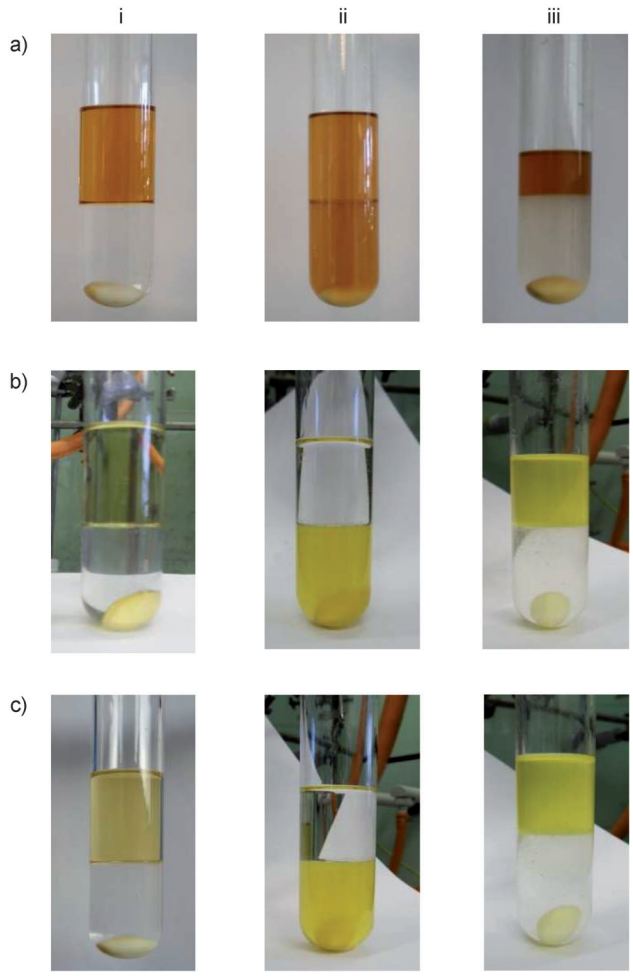


Figure 1. Phase switching after the hydroformylation of 1-octene catalyzed by rhodium complexes of a) **2**; b) **2** and **1** combined, cycles 1a and 1b; c) **2** and **1** combined, cycle 2. i) Reaction solution with water added. ii) After bubbling CO_2 through the mixture for 1.5 h. iii) After phase separation, addition of fresh toluene, and bubbling N_2 through the mixture at 60 °C for 1.5 h. The top (organic) phase from b iii) was used for the hydroformylation of 1-octene to give the product phase shown in c i).

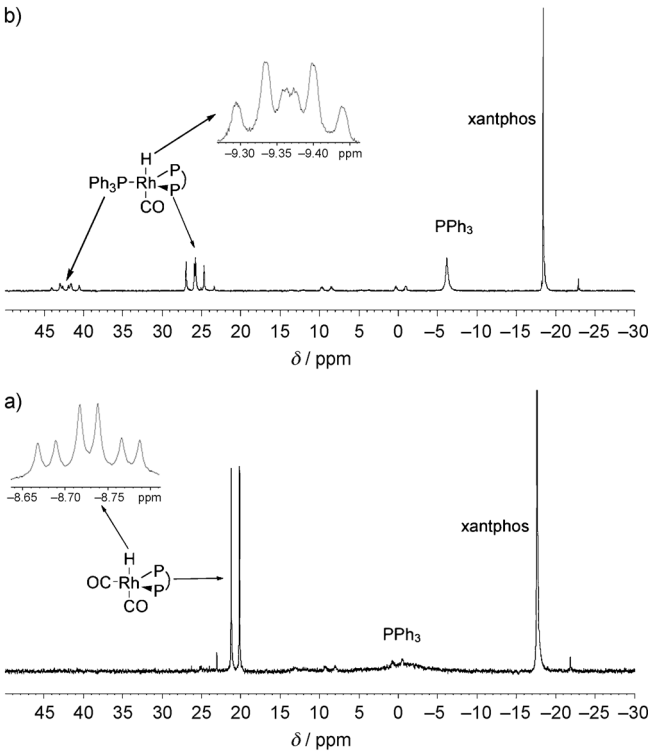


Figure 2. $^{31}P\{^1H\}$ NMR and the hydride region of the ^1H NMR spectra (inset) that were measured at room temperature for a mixture of $[Rh(acac)(CO)_2]$, PPh_3, and xantphos (1:2:2) a) Under CO/H_2 (1:1, 15 bar) and b) The solution from a) after bubbling CO_2 through the solution for 15 min.

For example, the ν_{CO} absorptions for *trans*-$[RhCl(CO)(\mathbf{1})_2]$ and for *trans*-$[RhCl(CO)(PPh_3)_2]$ are 1970 cm^{-1} and 1964 cm^{-1}, respectively, which suggests that there is slightly less electron density on the rhodium atom in the complex with **1** than there is on the rhodium atom in the complex with PPh_3. Consistent with this, the phosphorus atom in **1** resonates at a slightly higher frequency in the ^{31}P NMR spectrum ($\delta = -3.8$ ppm)[6] than the phosphorus atom in PPh_3 ($\delta = -5.9$ ppm), but the phosphorus atom in the protonated form of **1** resonates at a slightly lower field ($\delta = -6.6$ ppm)[6] than the phosphorous atom in PPh_3. Similarly, **2** gives a ^{31}P NMR resonance at $\delta = -16.5$ ppm, compared with the reported shift for xantphos of −17.5 ppm.[2] We do not anticipate that the *meta*-substituted amidate groups will change the steric properties of the ligands significantly.

The $^{31}P\{^1H\}$ NMR and ^1H NMR spectra (Figure 2a) of a solution that contains $[Rh(acac)(CO)_2]$, PPh_3, and xantphos (1:2:2) under CO/H_2 (1:1, 15 bar) has resonances that are identical to those reported for a solution of $[RhH(CO)_2$-(xantphos)][2] together with free xantphos and free PPh_3. The signal that is generated by PPh_3 is very broad, but sharpens on cooling or heating (Figure S2 in the Supporting Information), whereas the other resonances remain sharp throughout. The only other significant resonances are two weak, broad doublets centered at $\delta = 8.6$ ppm ($^1J_{P,Rh} = 150$ Hz) and 0.1 ppm ($^1J_{P,Rh} = 155$ Hz).

On depressurizing and passing CO_2 through the sample, the pale yellow solution became more orange, and the ^{31}P NMR spectra indicated the presence of $[RhH(CO)(PPh_3)$-(xantphos)][2] that has all of the phosphorous atoms in the equatorial plane of the trigonal bipyramid, together with a sharper signal for free PPh_3, and one for free xantphos. The small doublets that were detected when the solution was under CO/H_2 were still present. Bubbling CO_2 through the solution in the presence of water also gave $[RhH(CO)(PPh_3)$-(xantphos)] (Figure S4 in the Supporting Information). These experiments clearly show that xantphos is the only phosphine ligand in the coordination sphere of the metal atom under the high-pressure conditions of the catalytic reaction, but that both xantphos and PPh_3 are coordinated after bubbling CO_2 through the solution.

In conclusion, when ligands **1** and **2** are used for the rhodium-catalyzed hydroformylation of 1-octene, **2** controls the selectivity for the linear product, but **1** coordinates to rhodium in the resting state of the catalyst to allow successful phase switching into the aqueous phase through the formation

of the bicarbonate salt with CO_2. Thus, CO_2 has two roles: it affects the protonation of the amidine groups through the formation of carbonic acid by reaction with water, and it also removes CO from the system, which allows **1** to coordinate to the metal atom. When **1** and **2** are both present in the coordination sphere, there are seven amidines per rhodium atom, which is sufficient to allow efficient phase switching upon protonation of the amidines. The lower rate of hydroformylation of 1-octene when both ligands are present relative to when **2** is used alone, may arise because **1** can compete with the alkene for the vacant coordination site once CO is lost from [$RhH(CO)_2$(**2**)] to form the active species in the catalytic cycle. Some support for this suggestion comes from the broad PPh_3 resonance that was detected in the ^{31}P NMR spectrum under CO/H_2 (Figure 2a).

Experimental Section

All manipulations were carried out under dry N_2 by using standard Schlenk line and catheter tubing techniques.

4,5-Bis(dichlorophosphino-9,9-dimethylxanthene) was prepared by a literature procedure.[8]

4,5-Bis-(bis(3-aminophenyl)phosphino)-9,9-dimethylxanthene: 9,9-Dimethyl-4,5-bis-(dichlorophosphino)xanthene (2.00 g, 4.854 mmol, 1 equiv) was dissolved in THF (30 mL) and [bis(trimethylsilyl)amino]phenylmagnesium chloride (4.854 mL, 1M solution in THF) was slowly added at −40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h, then the reaction was stirred for an additional 12 h at 55 °C. The solvent was removed in vacuo to give a pale yellow oil. The crude product was dissolved in degassed methanol in a separate round-bottomed flask that was equipped with a reflux condenser. The mixture was heated at reflux for 18 h and the product was isolated by removing the solvent in vacuo. The crude product was recrystallized from methanol and dried in vacuo to give a fine white powder. Yield: 2.184 mmol, 45%.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$ (d, 2H, $J = 7.5$ Hz, Ar-H, xant), 7.01 (t, 2H, $J = 7.5$ Hz, Ar-H, xant), 6.93 (t, 4H, $J = 7.3$ Hz, Ar-H, Ph), 6.67 (d, 2H, $J = 7.0$ Hz, Ar-H, xant), 6.50–6.46 (m, 8H, Ar-H Ph), 6.28 (bt, 4H, Ar-H, Ph), 5.00 (s, 8H, NH_2), 1.57 ppm (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 152.4$ (d, $J = 9.6$ Hz, Ar-C), 148.7 (t, $J = 4.1$ Hz, Ar-C), 138.1 (t, $J = 6.0$ Hz, Ar-C), 132.6 (s, Ar-C), 130.0 (s, Ar-C), 129.1 (bs, Ar-C), 127.3 (s, Ar-C), 123.7 (s, Ar-C), 121.7 (t, $J = 10.0$ Hz, Ar-C), 119.5 (t, $J = 11.8$ Hz, Ar-C), 114.7 (s, Ar-C), 34.0 (s, 1C, $C(CH_3)_2$), 32.2 ppm (s, 2C, $C(CH_3)_2$); ^{31}P NMR(121 MHz, $CDCl_3$): $\delta = -19.18$ ppm (2P); MS (ESI): m/z: 661, 639 $[M+H]^+$; HRMS (ESI): m/z: calcd for $C_{39}H_{37}N_4OP_2$: 639.2446 $[M+H]^+$; found: 639.2457. Despite some contamination with solvents, this compound was used for the next step of the synthesis.

4,5-Bis(-[3-(1-dimethylaminoethylideneamino) phenyl]phosphino}-9,9-dimethyl-9*H*-xanthene (**2**): 4,5-Bis-(bis(3-aminophenyl)-phosphino)-9,9-dimethylxanthene (0.5 g, 0.785 mmol, 1 equiv) was placed into a microwave reaction vessel that was equipped with a magnetic stirrer. The tube was sealed with a septum and purged with alternate vacuum and N_2 (three times). Dimethylacetamide dimethylacetal (2.14 g, 2.35 mL, 20 equiv) was added and the tube was heated at 160 °C for 1 h in a microwave oven (400 W at 2.45 GHz). The crude mixture was transferred to a Schlenk tube. The excess dimethylacetamide dimethylacetal and the methanol that was produced were removed in vacuo and the residue was redissolved in toluene. The toluene phase was washed with water (10 mL). After the water layer was removed, a further aliquot of water (15 mL) was added to the toluene phase and CO_2 was bubbled through the stirred, biphasic mixture for 1.5 h. The toluene phase was discharged and fresh toluene (15 mL) was added. N_2 was bubbled through the stirred, biphasic mixture for 1.5 h at 60 °C. The toluene was evaporated, then the waxy yellow solid was washed with hexane and dried in vacuo. The product was purified by column chromatography (9:1 CH_2Cl_2: MeOH, 2% v/v NEt_3) to give a yellow foam. Yield; 0.216 g, 30%.

$R_f = 0.64$ (9:1 CH_2Cl_2: MeOH, 2% v/v NEt_3); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.29$ (dd, 2H, $J = 7.9$, 1.3 Hz, Ar-H, xant), 7.09 (t, 4H, $J = 7.6$ Hz, Ar-H, Ph), 6.85 (t, 2H, $J = 7.6$ Hz, Ar-H, xant), 6.8 (m, 4H, Ar-H, Ph), 6.62 (d, 4H, $J = 8.1$ Hz, Ar-H, Ph), 6.57 (bdq, 2H, $J = 7.9$, 1.65 Hz, Ar-H, xant), 6.51 (bdq, 4H, J = 5.9,1.665 Hz, Ar-H, Ph), 2.91 (s, 24H, $NC(CH_3)N(CH_3)_2$), 1.66 (s, 12H, $NC(CH_3)N(CH_3)_2$), 1.58 ppm (s, 6H, $C(CH_3)_2$).^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 157.5 (s, 1C, $NC(CH_3)N(CH_3)_2$), 152.0 (t, $J = 9.3$ Hz, Ar-C), 151.8 (t, J = 3.3 Hz, Ar-C), 137.7 (dd, $J = 7.3$, 6.0 Hz, Ar-C), 132.2 (s, Ar-C), 129.0 (s, Ar-C), 128.3 (t, $J = 4.1$ Hz, Ar-C), 127.7 (dd, J = 11.5, 9.3 Hz, Ar-C), 126.7 (dd, $J = 12.6$ Hz, $J = 8.8$ Hz, Ar-C), 125.9 (s, Ar-C), 122.9 (s, Ar-C), 122.6 (s, Ar-C) 37.9 (s, 8C, $NC(CH_3)N(CH_3)_2$), 34.3 (s, 1C, $C(CH_3)_2$), 32.1 (s, 2C, $C(CH_3)_2$, 14.9 ppm (s, 4C, $NC(CH_3)N(CH_3)_2$). ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -16.5$ ppm (s, 2P). HRMS (ESI): m/z: calcd for $C_{55}H_{65}N_8OP_2$: 915.4712 $[M+H]^+$; found: 915.4714.

Hydroformylation reactions were carried out as described previously,[6] but by using [Rh(acac)$(CO)_3$] (1 mmol dm^{-3}) and **2** (2.2 mmol) with or without **1** (2.2 mmol) in toluene (8 mL). Once the catalytic system had equilibrated at 100 °C under CO/H_2 (1:1, 15 bar), 1-octene (2 mL) was injected by using a substrate injector and the pressure was adjusted to 20 bar. Gas was fed from a ballast vessel to maintain the pressure at 20 bar. The pressure in the ballast vessel was recorded electronically. After the reactions, the autoclave was cooled and depressurized. It was then opened and the contents were analyzed by GC-FID (HP-1 column, 30 m, I.D 0.25 mm, 0.25 μm thick film) that separated the compounds on the basis of boiling points. The recycling procedure was carried out as described previously.[6]

High-pressure ^1H NMR studies were carried out in a sapphire tube that was fitted with a dip-tube for bubbling gases into the reaction (Hydraulik und Industrie-Technic GmbH, Rostock). [Rh(acac)$(CO)_2$] (0.023 g, 0.089 mmol), PPh_3 (0.047 g, 0.18 mmol), and xantphos (0.18 mmol) were dissolved in [D_8]toluene (3 mL), which resulted in effervescence and an orange solution. The solution was heated to boiling and CO/H_2 (1:1) was bubbled through it for 2 min. This solution (2 mL) was transferred under CO/H_2 into the NMR tube, which was then pressurized with CO/H_2 (15 bar). $^{31}P\{^1H\}$ NMR and ^1H NMR spectra were recorded at room temperature, −70 °C, and 130 °C.

^1H NMR (400 MHz, [D_8]toluene, room temperature): $\delta =$ −8.8 ppm (dt, $J_{H,Rh} = 6.4$ Hz, $J_{H,P} = 14.8$ Hz [Rh*H*$(CO)_2$(xantphos)]), lit. $\delta = -8.5$ ppm (dt, $J_{H,Rh} = 6.4$ Hz, $J_{H,P} = 10$ Hz).[2] $^{31}P\{^1H\}$ NMR (121 MHz, [D_8]toluene, room temperature): $\delta = 20.7$ ppm (d, $J_{P,Rh} =$ 128 Hz, [RhH$(CO)_2$(xantphos)]), lit. $\delta = 21.1$ ppm (d, $J_{P,Rh} =$ 127 Hz),[2] −0.7 (br. s, PPh_3), −17.6 ppm (s, xantphos), lit. $\delta =$ −17.5 ppm.[2]

After cooling, the pressure was released and N_2 was bubbled through the solution to remove CO/H_2. CO_2 was then bubbled through the solution for 15 min before the NMR spectra were recorded again at room temperature, −80 °C, and 100 °C.

^1H NMR (400 MHz, [D_8]toluene, room temperature): $\delta =$ −9.4 ppm (ddt, $J_{H,Rh} = 1.0$ Hz, $J_{H,P(PPh_3)} = 20$ Hz, $J_{H,P(xantphos)} = 12$ Hz [Rh*H*$(CO)(PPh_3)$(xantphos)]), lit. $\delta = -9.1$ ppm (ddt, $J_{H,Rh} = 1.7$ Hz, $J_{H,P(PPh_3)} = 18$, $J_{H,P(xantphos)} = 12$ Hz).[2] $^{31}P\{^1H\}$ NMR (121 MHz, [D_8]toluene, room temperature): $\delta = 42.3$ ppm (ddd, $J_{P,Rh} = 167$ Hz, $J_{P,P} = 130$ Hz) [RhH$(CO)(PPh_3)$(xantphos)]), lit. $\delta = 42.7$ ppm (ddd, $J_{P,Rh} = 151$ Hz, $J_{P,P} = 119$ Hz, ddd as a result of second-order effects),[2] 25.2 ppm (dd, $J_{P,Rh} = 147$ Hz, $J_{P,P} = 130$ Hz)[2] [RhH$(CO)(PPh_3)$-(*xantphos*)]), lit. $\delta = 25.7$ ppm (dd, $J_{P,Rh} = 128$ Hz, $J_{P,P} = 119$ Hz),[2] −4.7 (br s, PPh_3), −17.6 ppm (s, xantphos).

Degassed water (1 mL) was added to the solution (1 mL) that remained once the NMR tube had been filled and CO_2 was bubbled through this mixture for 5 min. The orange organic phase was studied by ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopy. The NMR spectra of the

main species were identical to those that were obtained in the absence of water, except that the PPh_3 resonance was replaced by a broad signal between 0 and 20 ppm, two new signals, each a doublet of doublets, were detected between 12 and 20 ppm, and there was new weak doublet at 31.1 ppm ($J_{P,Rh} = 142$ Hz, see Figure S4 in the Supporting Information). Some ligand oxidation also occurred.

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