# **ORGANOMETALLICS**

# Water-Soluble-Phosphines-Assisted Cobalt Separation in Cobalt-Catalyzed Hydroformylation

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**ABSTRACT:** The hydroformylation of octene-1 and the removal of  $Co_2(CO)_8$  and  $HCo(CO)_4$  from the reaction products including commercial C9 OXO-product were studied under biphasic conditions using an aqueous solution of different electron-donating sulfonated phosphine  $R_nP(C_6H_4$ -*m*-SO<sub>3</sub>Na)\_2 (n = 0, 1, 2; R = Me, Bu, Cp) ligands. Depending on the electronic and steric properties of the phosphines, 6–70 ppm residual cobalt concentrations could be achieved in the organic phase under 10 bar of  $CO/H_2$  (1:1) at 75 °C. The formation of several water-soluble-phosphine-substituted cobalt carbonyl species including  $Co_2(CO)_6(TPPTS)_2$ ,  $HCo(CO)_3(TPPTS)$ ,  $HCo(CO)_2(TPPTS)_2$ , and  $[Co(CO)_3(TPPTS)_2]^+[Co(CO)_4]^-$  were identified and monitored by *in situ* IR and NMR spectroscopy.

# ■ INTRODUCTION

The hydroformylation of olefins to aldehydes (oxo-aldehydes) has become one of the most important industrial homogeneous catalytic processes (Scheme 1).<sup>1</sup> Although different transition



metals can be used as catalysts,<sup>2</sup> cobalt and rhodium have been the preferred commercial catalysts in the absence or the presence of phosphine ligands.<sup>3</sup> The unmodified cobalt catalyst was discovered by Otto Roelen 75 years ago and has been used for the hydroformylation of olefin mixtures successfully to produce oxo-aldehydes by Esso (now ExxonMobil) for decades. The alkyl-phosphine-modified cobalt catalyst process was developed by Shell, which resulted in the *in situ* hydrogenation of the oxo-aldehydes to oxo-alcohols.<sup>4a</sup> In the case of rhodiumbased systems, the unmodified rhodium catalyst was used commercially by ICI for decades.<sup>3</sup> The triphenylphosphinemodified rhodium catalyst was commercialized by Union-Carbide (now Dow Chemical) and has become the most frequently used technology for the selective hydroformylation of  $\alpha$ -olefins to linear oxo-aldehydes.<sup>5</sup>

The efficient separation of the homogeneous oxo catalysts has been a formidable challenge for all commercial systems; a significant part of the research work has been directed toward the development of novel catalytic systems with facile catalyst recycling through molecular level control. Biphasic systems based on water,<sup>6</sup> fluorous<sup>7</sup> and ionic liquids,<sup>8</sup> and supercritical carbon dioxide<sup>9</sup> have been tested successfully as reaction media to facilitate catalyst recycling.<sup>10</sup>

Tertiary phosphines  $(PR_3)$  are the most important and widely used ligands to modify the properties of transition metal catalysts. The physical and chemical properties including the solubilities of phosphine ligands can be fine-tuned by controlling the structure of their substituents.<sup>11</sup> The first industrial aqueous biphasic system using the trisulfonatedtriphenylphosphine (TPPTS)-modified rhodium catalyst, the

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heart of the Rurhchemie/Rhône-Poulenc process (Scheme 2), was developed by Kuntz<sup>12</sup> and commercialized by Cornils.<sup>13</sup>



A typical plant produces more than  $6 \times 10^5$  tons of butanal annually, and depending on the propene quality, a conversion of 99% with an n/i ratio of approximately 95:5 of the crude butanal can be maintained. The process successfully utilizes the high and low solubility of propene or normal- and iso-butanals in water, respectively. The catalyst leaching has been kept at a very low level because of the easy and efficient aqueous/organic phase separation.<sup>13</sup>

The use of aqueous systems is limited by the solubility of the olefins in water, which depends on the structure of the olefins.14 The replacement of the water-soluble ligands of HRh(CO)(TPPTS)<sub>3</sub> with a fluorous phosphine P- $[CH_2CH_2(CF_2)_5CF_3]_3$  led to the development of the first fluorous biphasic hydroformylation system.<sup>15</sup> The HRh(CO)- $(P[CH_2CH_2(CF_2)_5CF_3]_3)_3$  was successfully tested in the continuous hydroformlyation of decene-1 using the toluene/  $C_6F_{11}CF_3$  system as the reaction media. The normal/iso ratio of 8:1 was achieved, and the fluorous system efficiently moderated the rhodium loss at the 1 ppm rhodium per mole of aldehyde level. The rhodium leaching was further reduced by the application of the  $P[p-C_6H_4-(CH_2)_8(C_6F_{13})]_3$  ligand.<sup>16</sup> The use of fluorous-phosphine-modified Rh catalysts for the hydroformylation of octene-1 in supercritical carbon dioxide has resulted in a homogeneous environment, in which many low- or medium-polarity olefins and catalysts can be dissolved (Scheme 3).<sup>9b</sup> Although the supercritical fluid can readily be removed at lower pressures, it does not overcome the original catalyst/product separation problem.

Due to the very low vapor pressure of ionic liquids, they have been used as alternative solvents.<sup>17</sup> The first hydroformylation reaction in molten salts using a Pt-based catalyst was reported by Parshall in 1972.<sup>18</sup> Both the Rh(CO)<sub>2</sub>(acac)/PPh<sub>3</sub> system and the rhodium complex of the sodium salt of the sulfonatedphenylphosphines were found to be active hydroformylation catalysts applying ionic liquids as solvents as well;<sup>19,20</sup> however the conversions were very low. The immobilization of the solution of rhodium catalysts in an ionic liquid–organic biphasic environment was reported by Mehnert.<sup>21</sup>

The unmodified cobalt-based catalyst has been used for the hydroformylation of olefins to oxo-aldehydes with a typical normal/iso (or n/i) ratio of 2. The three main cobalt species of the organic phase of any unmodified cobalt-based process are  $HCo(CO)_{4}$ ,  $Co_2(CO)_{8}$ , and the acyl- $Co(CO)_4$  species, which could be formed by the reaction of HCo(CO)<sub>4</sub> and  $\alpha$ -olefins.<sup>22</sup> Since the  $\alpha$ -olefins react faster than the internal olefins,  $HCo(CO)_4$  and  $Co_2(CO)_8$  are the only observable species at high conversion level in a typical reaction mixture. While the volatile  $HCo(CO)_4$  can be removed at lower pressures, the separation of  $Co_2(CO)_8$  from the reaction mixture is difficult. Two processes have been developed for the removal of cobalt at the industrial scale. The first involves the decobalting of the crude oxo mixture after depressurization by the addition of oxygen and organic acid (HCOOH or AcOH).<sup>23</sup> The second method starts with the treatment of the crude reaction mixture with a diluted aqueous solution of NaHCO<sub>3</sub> to convert  $HCo(CO)_4$  to  $Na[Co(CO)_4]$ , which can be then protonated by the controlled addition of diluted sulfuric acid.<sup>2</sup>

The tributyl-phosphine-modified cobalt catalyst system was developed in the late 1950s,<sup>4</sup> which forms an active and stable catalyst even at lower syngas pressures (20-100 bar) and produces alcohols rather than aldehydes.<sup>25,26</sup> The concentration of branched alcohols and aldehydes can be decreased by increasing the concentration of PBu<sub>3</sub>.<sup>27</sup> Because of the higher thermal stability of the tributyl-phosphine-modified cobalt catalyst, the hydroformylation can be performed at higher temperatures, which assists the formation of alcohols with similar selectivity. Although, the higher syngas pressure should favor the aldehyde formation, this influence could be compensated by applying higher hydrogen partial pressure.<sup>28</sup> Water has been shown to have dramatic effects on the tributylphosphine-modified cobalt catalyst including a higher rate of alcohol formation and a water-dependent alcohol/aldehyde ratio. It was shown that the maximum alcohol concentration can be achieved at 14 v/v % of water.  $^{29}$ 

Similarly to the biphasic rhodium recycling, several approaches based on biphasic catalysis have been reported for cobalt separation,<sup>30</sup> including aqueous<sup>31</sup> and fluorous systems.<sup>32</sup> Since TPPTS has been the most widely used watersoluble phosphine ligand, the synthesis of its cobalt complexes has been also reported including HCo(CO)<sub>3</sub>(TPPTS), HCo-(CO)<sub>2</sub>(TPPTS)<sub>2</sub>, [Co(CO)<sub>3</sub>(TPPTS)]<sup>-</sup>, and Co<sub>2</sub>(CO)<sub>6</sub>(TPPTS)<sub>2</sub>.<sup>33</sup> The reaction of Co<sub>2</sub>(CO)<sub>8</sub> with TPPTS results in the formation of [Co(CO)<sub>3</sub>(TPPTS)][Co-(CO)<sub>4</sub>]. The relatively stable Co<sub>2</sub>(CO)<sub>6</sub>(TPPTS)<sub>2</sub> undergoes base-induced disproportionation above pH = 10 to yield [Co(CO)<sub>3</sub>(TPPTS)]<sup>-</sup> as the only carbonyl-containing species. While the Co/TPPTS catalyst is less active than the Rh/TPPTS catalyst, it is superior for the hydroformylation of internal olefins under 20–105 bar of H<sub>2</sub>/CO (1:1) and at 130–





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190 °C. Aldehyde yields up to 75% could be realized with an n/ i ratio between 1 and 3. Depending on the reaction conditions, between 9 and 60 ppm of the total cobalt was found in the oxoproduct phase after catalyst separation. The biphasic hydroformylation of hexene-1 to heptanals using  $Co_2(CO)_6(TPPTS)_2$  resulted in 0.5–10% Co leaching; however, the application of glass as a catalyst support could reduce this value to 0.1%.<sup>31</sup> Although various types of sulfonated and carboxylated aryl phosphines have been tested for the hydroformylation of hexene-1,<sup>34</sup> the application of water-soluble-alkylphosphine-modified cobalt catalysts has not been studied yet.

#### RESULTS AND DISCUSSION

We report here the modification of the cobalt oxo process by the introduction of water-soluble phosphine ligands to assist the recycling of the cobalt catalyst and the *in situ* partial conversion of the aldehydes to the alcohols. The separation of the cobalt is based on the facile substitution of the carbonyl ligands of various cobalt carbonyls, mostly  $HCo(CO)_4$  and  $Co_2(CO)_8$ , by water-soluble phosphines, making all cobalt species preferentially water-soluble at lower syngas pressure (Scheme 4).





After the separation of the oxo product, the repressurization of the aqueous phase leads to the re-formation of the organicsoluble cobalt carbonyls and free water-soluble phosphines, which can be recycled to the oxo reactor (Figure 1). The presence of water and the water-soluble phosphine could provide additional benefits including better hot-spot control, *in situ* hydrogenation of the aldehydes to alcohols, and suppression of the side reactions involving the formation of water. The application of *in situ* spectroscopy could provide the molecular level information under reaction conditions in real time to structurally identify key intermediates of the catalytic cycle and develop the reaction network between substrates, catalyst precursor(s), intermediates, products, and side-products.<sup>35</sup> Although, several water-soluble-phosphines-modified cobalt carbonyl species have been prepared and characterized,<sup>33</sup> no *in situ* spectroscopic studies have been reported on their transformations yet.

First, a single-phase cobalt-catalyzed hydroformylation of octene-1 was performed for comparison. A solution of 25 mL of octene-1 in 30 mL of *n*-hexane was placed in a 250 mL highpressure reactor, equipped with a high-pressure SiComp IR probe attached to a ReactIR 1000 in situ reaction analysis instrument. The reaction mixture was pressurized with CO/H<sub>2</sub> (1:1) to reach 100 bar at 100 °C. The presence of a band of 1octene at 1656 cm<sup>-1</sup> was observed (Figure 2a). After the addition of a solution of 0.982 g (2.87 mmol) of  $Co_2(CO)_8$  in 10 mL of *n*-hexane under 102 bar of  $CO/H_2$  (1:1), the bands at 2070 and 2030  $\text{cm}^{-1}$  appeared due to  $\text{Co}_2(\text{CO})_8$  and  $HCo(CO)_4$  After a few minutes new peaks appeared at 2005 and 2103 cm<sup>-1</sup>, indicating the formation of the acyl-cobalt species. The band at 1733 cm<sup>-1</sup> showed the formation of the nonanals (Figure 2a). The n/i ratio was 2.1 at 95% olefin conversion after 1.5 h.

We also investigated the possible effect of changing the order of the addition of octene-1 and  $Co_2(CO)_8$ . A solution of 1.04 g (3.04 mmol) of  $Co_2(CO)_8$  in 55 mL of *n*-hexane was placed in a 250 mL high-pressure reactor, equipped with a high-pressure SiComp IR probe attached to a ReactIR 1000 instrument. The reaction mixture was pressurized with  $CO/H_2$  (1:1) to reach 100 bar at 100 °C. The formation of  $HCo(CO)_4$  could be observed by the appearance of the bands at 2030, 2053, and 2117 cm<sup>-1</sup>. After reaching the equilibrium between  $Co_2(CO)_8$ and HCo(CO)<sub>4</sub>, 25 mL (160 mmol) of octene-1 was added, resulting in the transient formation of the acyl-cobalt species  $(2005 \text{ and } 2103 \text{ cm}^{-1})$  and the formation of nonanals (1733)cm<sup>-1</sup>) with the same conversion and selectivity (Figure 2b) as observed in the previous experiment. Thus, we have confirmed that the order of the addition of the olefin and the catalyst has no effect on product formation, as expected.

Next, we studied the biphasic hydroformylation of octene-1 (64 mmol) with TPPTS-modified cobalt catalyst using  $Co_2(CO)_8$  (2.9 mmol) in 45 mL of *n*-hexane and TPPTS (5.8 mmol) in 10 mL of water under 100 bar CO/H<sub>2</sub> (1:1) at 100 °C (TPPTS/Co = 1). While the *in situ* IR studies have



Figure 1. Proposed process for water-soluble-phosphine-assisted cobalt recycling.



Figure 2. One-phase hydroformylation reactions of octene-1.

shown the full conversion of octene-1 to nonanals, GC-MS measurements confirmed the formation of normal- and isononanals (n/i = 3.2). Only trace amounts of nonanols and nonanoic acids could be detected. After the phase separation of the reaction mixture, the aqueous phase was reused as the catalyst phase under the same conditions, which resulted in similar product composition with full conversion of octene-1. Although *in situ* IR did not show the presence of  $HCo(CO)_4$  in the organic phase, the octene-1 could be converted to nonanals in the presence of the Co/TPPTS catalyst system operating at 100 bar of CO/H<sub>2</sub> (1:1) and 100 °C. <sup>31</sup>P NMR of the aqueous phase revealed the presence of several TPPTS-containing cobalt species including Co<sub>2</sub>(CO)<sub>6</sub>(TPPTS)<sub>2</sub> at 70.0 ppm,  $[Co(CO)_3(TPPTS)_2]^+[Co(CO)_4]^-$  at 57.5 ppm, HCo-(CO)<sub>3</sub>(TPPTS) at 58.4 ppm, HCo(CO)<sub>2</sub>(TPPTS)<sub>2</sub> at 56.6 ppm, HCo(CO)(TPPTS)<sub>3</sub> at 55.6 ppm, TPPTS-oxide at 35.6 ppm, and TPPTS at -4.2 ppm.<sup>33</sup> It should be noted that the substitution of  $HCo(CO)_4$  with TPPTS was performed in THF containing 5-10% H<sub>2</sub>O as solvent, and no biphasic system was reported.3

In order to observe the formation of these cobalt species, we have monitored the reaction of  $HCo(CO)_4$ , the precursor of the catalytically active unsaturated cobalt carbonyl {HCo- $(CO)_3$ , with TPPTS by *in situ* IR under carbon monoxide at room temperature. A solution of 1.54 mmol of  $HCo(CO)_4$  in 5 mL of *n*-hexane was prepared by the reaction of  $NaCo(CO)_4$ and gaseous HCl at -78 °C under nitrogen. After the removal of NaCl by filtration and warming the solution to room temperature, the solution was first treated with less than one equivalent (1 mmol) of TPPTS dissolved in 5 mL of water. While the color of the aqueous phase changed from colorless to light orange and then to dark brown, the rapid decrease of the amount of  $HCo(CO)_4$  in the organic phase could be observed. All  $HCo(CO)_4$  could be removed from the solution by the addition of 1 mL of an aqueous solution of 0.875 mmol of TPPTS, resulting in a P/Co ratio of 1.21 (Figure 3 and Figure 4).

The <sup>31</sup>P NMR measurement of the aqueous phase indicated the formation of  $Co_2(CO)_6(TPPTS)_2$  (69.6 ppm), HCo- $(CO)_3(TPPTS)$  (61.0 ppm),  $[Co(CO)_3(TPPTS)_2]^+[Co <math>(CO)_4]^-$  (58.3 ppm), and HCo $(CO)_2(TPPTS)_2$  (57.2 ppm). Free TPPTS could not be observed, as expected. The addition of 0.875 mmol of TPPTS resulted in the formation of  $Co_2(CO)_6(TPPTS)_2$  (69.7 ppm), HCo $(CO)_2(TPPTS)_2$  (57.2 ppm), and  $[Co(CO)_3(TPPTS)_2]^+[Co(CO)_4]^-$  (58.3 ppm). The excess of TPPTS at -4.8 ppm and the presence of TPPTS oxide at 35.4 ppm could also be detected. Thus, HCo $(CO)_4$ 





**Figure 3.** Removal of 1.54 mmol of  $HCo(CO)_4$  in 5 mL of *n*-hexane by the addition of an aqueous solution of TPPTS (1 mmol and then 0.875 mmol) under 1 bar of CO at room temperature.

can be removed from the organic phase by using an aqueous solution of more than one equivalent of TPPTS under biphasic conditions.

Although the formation of  $Co_2(CO)_2$  was not observed in the organic phase, the possibility of its removal by TPPTS was also confirmed by the addition of 5 mL of an aqueous solution of 0.4 mmol of TPPTS to 0.2 mmol of  $Co_2(CO)_8$  in 5 mL of *n*octane under 1 bar of CO/H<sub>2</sub> (1:1) at 50 °C (Figure 5). The <sup>31</sup>P NMR of the aqueous phase indicated that the main cobalt species were  $Co_2(CO)_6(TPPTS)_2$  (69.6 ppm) and [Co-(CO)<sub>3</sub>(TPPTS)<sub>2</sub>]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> (58.3 ppm).

Thus, we have demonstrated that both  $HCo(CO)_4$  and  $Co_2(CO)_8$  can be removed from the organic phase with an aqueous solution containing at least one equivalent of TPPTS with respect to cobalt under biphasic conditions. On the basis of our in situ IR results and the relevant reported reactions of cobalt carbonyls with tertiary phosphines,  $\hat{}^{33,36}$  the proposed reactions of the aqueous cobalt recycling can be summarized as depicted in Scheme 5. In the absence of  $\alpha$ -olefins, the two main cobalt species are  $HCo(CO)_4$  and  $Co_2(CO)_8$  under oxo conditions, both of which can be converted to water-soluble TPPTS-containing cobalt species by substitution reactions at lower syngas pressures and transfer of the cobalt from the product organic phase to the aqueous phase. Since these substitution reactions are reversible, both  $HCo(CO)_4$  and  $Co_2(CO)_8$  can be regenerated at higher syngas pressures, resulting in the transfer of the cobalt from the aqueous phase to the organic phase.

The facile removal of cobalt from the products of industrial hydroformylation is indeed one of the key issues concerning



Figure 4. Removal of  $HCo(CO)_4$  (1.54 mmol) from *n*-hexane with an aqueous solution of TPPTS (5 mL) under 1 bar of CO at room temperature. Reaction profiles of the bands of  $HCo(CO)_4$ .



Figure 5. Removal of  $Co_2(CO)_8$  from *n*-octane with an aqueous solution of TPPTS.





product quality and process simplicity. We have investigated the removal of cobalt with water-soluble phosphines in commercial C9 OXO-product, which is a mixture of  $C_8$ -alkanes and branched olefins (10%),  $C_9$ -aldehydes,  $C_9$ -alcohols, and  $C_9$ -formate esters (53%),  $C_9$ -ethers (1%), ether alcohols (3%),  $C_9$ -acetals (31%), and other heavies (2%).<sup>37</sup> While the total cobalt

concentration is dictated by the required process performance, the total concentration of the water-soluble ligand can be adjusted to maximize the removal of the cobalt. We have therefore investigated the cobalt removal at two different concentrations of TPPTS while keeping the cobalt concentrations the same. Since the formation of phosphine-substituted cobalt carbonyls is strongly dependent on the concentration of carbon monoxide and the phosphine ligand, the cobalt concentration in the organic phase was also measured at a lower pressure of syngas and a higher concentration of TPPTS. Furthermore, our investigations were performed at 75 °C to enhance the formation of cobalt-phosphine species but operate at an easily and economically maintainable temperature by using industrial process water.

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The biphasic mixture of a solution of 1.62 mmol of  $Co_2(CO)_8$  in 55 mL of C9 OXO-product and an aqueous phase containing 4.6 mmol of TPPTS in 10 mL of water was heated under 100 bar of CO/H<sub>2</sub> (1:1) at 75 °C for 2 h. A sample taken from the organic phase showed 138 ppm cobalt (Table 1, entry 1). When the pressure was decreased from 100

Table 1. Cobalt Removal from the Organic Phase at 75 °C

entry	organic phase/mL	water (mL)	[Co] <sub>total</sub> (mol/L)	[Ligand] <sub>total</sub> (mol/L)	[Co] <sub>organic phase</sub> at 100 bar (ppm)	[Co] <sub>organic phase</sub> at 10 bar (ppm)
1	C9 OXO-product/55	10	0.05	TPPTS/0.07	138	70
2	C9 OXO-product/55	10	0.05	TPPTS/0.14	111	54
3	C9 OXO-product/45 + 10 mL <i>n</i> -hexane	10	0.025	TPPTS/0.07	37	19
4	C9 OXO-product/55	5	0.025	TPPTS/0.07	109	45
5	C9 OXO-product/55	5	0.025	CpDPPDS/0.07	107	43
6	C9 OXO-product/55	5	0.025	BuDPPDS/0.07	90	35
7	C9 OXO-product/55	5	0.025	Me <sub>2</sub> MPPMS/0.07	8	6

to 10 bar of CO/H $_2$  (1:1) at 75 °C, the cobalt concentration decreased in the organic phase to 70 ppm, as expected.

By increasing the total TPPTS concentration in the reactor from 0.07 mol/L to 0.014 mol/L, the residual cobalt concentrations decreased to 111 and 54 ppm cobalt in the organic phase under 100 and 10 bar of  $CO/H_2$  (1:1) at 75 °C, respectively (Table 1, entry 2). When the polarity of the organic phase was decreased by the addition of *n*-hexane (10 mL) to the C9 OXO-product (45 mL), the residual cobalt concentrations decreased significantly to 37 and 19 ppm in the organic phase under 100 and 10 bar of  $CO/H_2$  (1:1) at 75 °C, respectively (Table 1, entry 3).

Next, we lowered the total cobalt concentration from 0.05 mol/L to 0.025 mol/L and decreased the volume of the aqueous phase from 10 mL to 5 mL. The residual cobalt concentrations were 109 and 45 ppm in the organic phase under 100 and 10 bar of  $CO/H_2$  (1:1) at 75 °C, respectively (Table 1, entry 4). This is similar to the results obtained in the presence 0.05 mol/L total cobalt concentration, indicating that the residual cobalt concentration in organic phase primarily depends on the Co/TPPTS ratio.

It should be emphasized that the removal of various cobalt species from the organic phase is the result of the substitution of their carbonyl ligands by water-soluble phosphines. The effectiveness of this step will depend on the basicity and the size of the phosphine.<sup>30</sup> The use of much more basic phosphines that have a small cone angle should result in even lower cobalt levels. The basicity of a phosphine with respect to TPPTS can be simply increased by the replacement of one or two of the *m*sulfonatophenyl groups with one or two alkyl substituents.<sup>38</sup> While the incorporation of appropriate alkyl substituent(s) can result in optimal basicity and steric property, the remaining msulfonatophenyl group can ensure good solubility in protic media.<sup>38</sup> Consequently, the sodium salts of cyclopentylbis(msulfonatophenyl)phosphine  $\{C_5H_9P(C_6H_4-m-SO_3Na)_2 \text{ or }$ CpDPPDS}, n-butylbis(m-sulfonatophenyl)phosphine {n-BuP- $(C_6H_4-m-SO_3Na)_2$  or BuDPPDS}, and dimethyl(m-m)sulfonatophenyl)phosphine  $\{(CH_3)_2P(C_6H_4-m-SO_3Na) \text{ or }$ Me<sub>2</sub>MPPMS} ligands were investigated for the removal of cobalt from C9 OXO-product. There was no significant difference between the final cobalt concentration levels by using the TPPTS (45 ppm)- and the CpDPPDS (43 ppm)modified catalyst system (Table 1, entries 4 and 5). Although there is a difference between their electronic parameters ( $\chi_{TPPTS}$ = 15.3 and  $\chi_{CpDPPDS}$  = 11.3), their steric properties are similar ( $\theta_{TPPTS}$  = 173° and  $\theta_{CpDPPDS}$  = 172°),<sup>38</sup> which could have influenced the equilibria between various cobalt carbonyl- and phosphine-substituted species. The electronic parameter of BuDPPDS ( $\chi_{BuDPPDS} = 12.5$ ) is similar to both TPPTS and CpDPPDS, but the cone angle is smaller ( $\theta_{BuDPPDS} = 153^{\circ}$ ), which resulted in better cobalt removal, indicating the beneficial

role of sterics in this reaction. Finally, by using the more electron-donating and less bulky Me<sub>2</sub>MPPMS ( $\chi = 10.8$ ,  $\theta_{Me2MPPMS} = 140^{\circ}$ ) the final cobalt concentration can be reduced to 6.0 ppm in the organic phase.

# CONCLUSIONS

It was demonstrated that  $Co_2(CO)_8$  and  $HCo(CO)_4$  can be removed from the hydroformylation product phase including the commercial C9 OXO-product by using a sulfonated watersoluble tertiary phosphine ligand under biphasic conditions. The efficiency of the separation is strongly affected by the electronic and steric properties of the phosphine ligands, the Co/phosphine ratio, the polarity of the organic phase, and the total syngas pressure. Depending on the nature of the phosphines, 6-70 ppm cobalt concentrations could be achieved in the organic phase under 10 bar of  $CO:H_2$  (1:1) at 75 °C. It was confirmed that the order of the addition of cobalt and olefin has no effect on the product formation in cobaltcatalyzed hydroformylation. The formation of several cobalt carbonyls including  $Co_2(CO)_6(TPPTS)_2$ , HCo- $(CO)_3(TPPTS)$ ,  $HCo(CO)_2(TPPTS)_2$ , and [Co- $(CO)_3(TPPTS)_2]^+[Co(CO)_4]^-$  was observed by investigating the reaction of  $Co_2(CO)_8$  and  $HCo(CO)_4$  with TPPTS using in situ IR and NMR spectroscopy.

#### EXPERIMENTAL SECTION

Hexane, methanol, and hydrochloric acid were obtained from Molar Chemicals Ltd., Budapest, Hungary. The octane and octene-1 were purchased from Aldrich Chemical and used as received without further purification.  $Co_2(CO)_8$  was obtained from Strem Chemical Co. and purified by recrystallization from deoxygenated *n*-hexane under carbon monoxide atmosphere. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker-Avance 250 MHz NMR instrument using H<sub>3</sub>PO<sub>4</sub> as reference. GC measurements were performed on an HP-5890 GC with an HP-5 capillary column equipped with an FID detector using cyclohexane as internal standard. GC-MS was performed on an HP-6890 instrument equipped with 5973 MSD. *In situ* IR measurements were performed by using a ReactIR 1000 infrared instrument equipped with a SiComp probe head (ASI, a Mettler Toledo Company). The AAS measurements were performed on a Perkin-Elmer 310 atomic absorption spectrometer at an atomization temperature of 2500 °C and at a detection wavelength of 240.7 nm.

detection wavelength of 240.7 nm. TPPTS<sup>39</sup> and HCo(CO)<sub>4</sub><sup>35a</sup> were prepared by published methods. The disodium salt of butylbis(*m*-sulfonatophenyl)phosphine (Bu-DPPDS), the sodium salt of dimethyl(*m*-sulfonatophenyl)phosphine (Me<sub>2</sub>MPPMS), and the disodium salt of cyclopentylbis(*m*sulfonatophenyl)phosphine (Cp-DPPDS) were prepared according to our previous work<sup>11</sup> (detailed experimental procedure and characterization of the disodium salt of cyclopentylbis(*m*sulfonatophenyl)phosphine in ref 38). All manipulations were performed by using standard Schlenk techniques.

Hydroformylation of Octene-1 in Organic/Aqueous Biphasic Conditions with in Situ IR Measurement. The two-phase

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hydroformylation reaction consisting of 1.04 g (2.9 mmol) of  $Co_2(CO)_8$  in 45 mL of *n*-hexane and 3.3 g (5.8 mmol) of TPPTS in 10 mL of water was placed in a 250 mL high-pressure reactor, equipped with a high-pressure IR probe attached to a ReactIR 1000 infrared instrument. The reaction mixture was pressurized with CO/ $H_2$  (1:1) to reach 100 bar at 100 °C. After 2 h 10 mL of 1-octene was added to the reaction mixture. The reaction mixture was cooled to room temperature after 3 h. The two phases were separated and analyzed by GC and NMR. The aqueous phase was used as catalyst phase without any further modification in the next investigation of hydroformylation of 20 mL (128 mmol) of 1-octene in 30 mL of *n*-hexane (100 bar of CO/H<sub>2</sub>).

General Procedure for Cobalt Removal from C9 OXO-Product under Biphasic Conditions. In a typical experiment 1.6 mmol of Co<sub>2</sub>(CO)<sub>8</sub> was dissolved in 55 mL of C9 OXO-product under nitrogen at room temperature. The solution was combined with 5 mL of an aqueous solution of 4.9 mmol of TPPTS followed by transfer with vacuum into the 100 mL stainless steel reactor equipped with a Parr 4870 temperature controller. The water was treated and has been stored under nitrogen, preventing a solution of CO2 and oxygen. The reaction mixture was pressurized with CO/H<sub>2</sub> (1:1) to reach 100 bar at 100 °C. The reaction mixture was cooled to the desired temperature (e.g., 75 °C) after 2 h stirring under 100 bar of syngas. A sample was taken to determine the initial Co concentration in the organic phase. Then the pressure was decreased to 10 bar. The stirring was stopped for 2 min to allow phase separation in the reactor, and a 50  $\mu$ L sample was taken from the lower aqueous phase of the reaction mixture by a deep leg. The sample was diluted to 10 mL with MeOH/HCl (9:1). The parallel calibration of AAS was performed by using solutions of either Co(NO<sub>3</sub>)<sub>2</sub> or Co<sub>2</sub>(CO)<sub>8</sub> in MeOH/HCl in the concentration range 12.5-50 ppb. A 20 µL sample was used for the AAS measurement.

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#### Notes

The authors declare no competing financial interest.

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