Organometallics **2004,** *23,* 2701−2707

In Situ High-Pressure NMR Studies of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ in Supercritical Carbon Dioxide: Ligand Substitution, Hydrogenation, and Hydroformylation Reactions[†]

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Received September 15, 2003

The dimeric cobalt complex $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (**1**) reacts reversibly with hydrogen to produce $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ (**4**). The carbonyl and the phosphine ligands of both **1** and **4** are very labile. Compound **1** reacts with CO to give $Co_2(CO)_7[P(p\text{-}CF_3C_6H_4)_3]$ (**2**), and compound **4** reacts with CO and $P(p\text{-}CF_3C_6H_4)_3$ (**L**) to give $HCo(CO)_4$ (**5**) and $HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3]_2$ (**6**), respectively. The ^{31}P NMR studies show that, in the presence of **1**, the line width of the ^{31}P resonance of **L** is temperature dependent, and at constant temperature, its broadening is proportional to the square root of the concentration of **1**. This broadening is attributed to its exchange reaction with the mononuclear cobalt radical $(CO)_3LCo^\bullet$ (**3**), which is generated by the homolysis of **1**. Compound **1** catalyzes the hydroformylation of olefins in supercritical carbon dioxide. In contrast to the unsubstituted $Co_2(CO)_8$, the phosphine-modified catalyst system is stable under low CO pressures and the hydroformylation reactions can be carried out at low pressures. In situ monitoring of ^{31}P and ^{59}Co NMR spectra of the solution shows that the phosphine-containing hydrido cobalt complexes **4** and **6** are the only hydrido cobalt complexes present in detectable concentrations in **1**-catalyzed hydroformylation reactions; nevertheless, the possibility that the observed activity for **1** comes primarily from the more active $HCo(CO)_4$, present in concentrations below detectable limits, has not been rigorously excluded.

Introduction

Dicobalt octacarbonyl was the first catalyst used in the hydroformylation of olefins. This catalytic reaction, also known as the oxo reaction, converts olefins to aldehydes and alcohols by their reaction with hydrogen and carbon monoxide.[1,2] With the exception of the Ruhrchemie/Rhone-Poulenc process,[3−5] which uses rhodium catalysts in aqueous solutions, all other oxo processes are carried out in organic solvents. There is growing interest in developing alternatives to conventional organic solvents that are used in such large-scale industrial processes. The main driving force for this activity is the reduction of the environmental burden associated with disposal of organic solvents. Among the various alternatives are the use of water,[6] supercritical CO_2 ($scCO_2$),[7] and low-melting ionic liquids[8,9] as the reaction media. Supercritical CO_2 is particularly ideal for conducting catalytic reactions that involve gaseous reactants, such as H_2 and CO. The presence of a single homogeneous phase eliminates the gas−liquid mixing problems, which complicate the reactor design. It also eliminates the problem in processes in which slow gas/liquid mixing may limit the process rate and adversely affect product selectivity and catalyst stability.

Following our demonstration of the catalytic hydroformylation of propylene by $Co_2(CO)_8$ in $scCO_2$,[10] we have extended the study to the phosphine-modified cobalt catalysts. Our initial attempts to employ the conventional Shell-type catalyst, e.g., $Co_2(CO)_6(PBu_3)_2$, in supercritical fluids proved to be problematic because of the formation of insoluble salts. Further studies showed that CO induced the disproportionation of $Co_2(CO)_6(PBu_3)_2$ to yield the insoluble cobalt(I)/cobalt(−I)

[†] Work supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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10.1021/om030600h CCC: $27.50

salt $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$, as depicted in eq 1.[11,12]

$$Co_2(CO)_6(PBu_3)_2 + CO \rightleftharpoons [Co(CO)_3(PBu_3)_2][Co(CO)_4] \quad (1)$$

This cobalt(I)/cobalt(−I) salt precipitates out of $scCO_2$ and $scCO_2$/toluene mixtures, preventing use of the tri-*n*-butylphosphine-modified catalyst in these solvent systems. However, cobalt complexes synthesized from less basic and more CO_2-philic ligands, such as tris(*p*-(trifluoromethyl)phenyl)phosphine, $P(p\text{-}CF_3C_6H_4)_3$, work well in $scCO_2$. Enhanced solubilities of fluorinated phosphines and their metal complexes are well documented in the literature.[7,13−15] We found that $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ reacts with hydrogen to produce $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$, and it catalyzes the hydroformylation of olefins in $scCO_2$. Reported here is in situ high-pressure NMR evidence for the involvement of odd-electron radical species in some of the ligand substitution reactions in this system. In addition, the hydrogenation of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ was investigated. We have also examined the use of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ as a catalyst for the hydroformylation of olefins in $scCO_2$.

Results

$Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1). The dark brown compound was synthesized by the stoichiometric reaction between $Co_2(CO)_8$ and $P(p\text{-}CF_3C_6H_4)_3$ (**L**) in toluene,[16] as depicted in eq 2. In contrast to the PBu_3-substituted

$$Co_2(CO)_8 + 2P(p\text{-}CF_3C_6H_4)_3 \rightleftharpoons Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2 + 2CO \quad (2)$$

cobalt complex $Co_2(CO)_6(PBu_3)_2$, which disproportionates to form $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$ (eq 1) in toluene under high pressures of CO,[11,12] no salt formation was observed in toluene solutions of **1** under CO. The absence of salt formation is attributed to the lower basicity of the fluorinated phosphine, since formation of the Co(I) cation is less favored with a less basic phosphine. Substitution of the para hydrogens of triphenylphosphine with the CF_3 groups also increases the solubility of the phosphine-modified Co−Co-bonded dimer in $scCO_2$. Figure 1 shows the solubility of **1** in $scCO_2$ in the temperature range of 80−130 °C. Excess phosphine is added in this experiment for calibration and for suppressing its dissociation from **1**. The low basicity of the fluorinated phosphine makes it necessary to add excess ligand to suppress its displacement by CO, a necessary reactant in hydroformylation reactions. In the absence of added phosphine ligand, 10% of **1** (^{31}P, δ 68.6 ppm) reacts with CO to give $Co_2(CO)_7[P(p\text{-}CF_3C_6H_4)_3]$ (**2**; δ 64.6 ppm) and $P(p\text{-}CF_3C_6H_4)_3$ (δ −5.8 ppm) at 100 °C under 8.0 atm of CO, as depicted in eq 3.

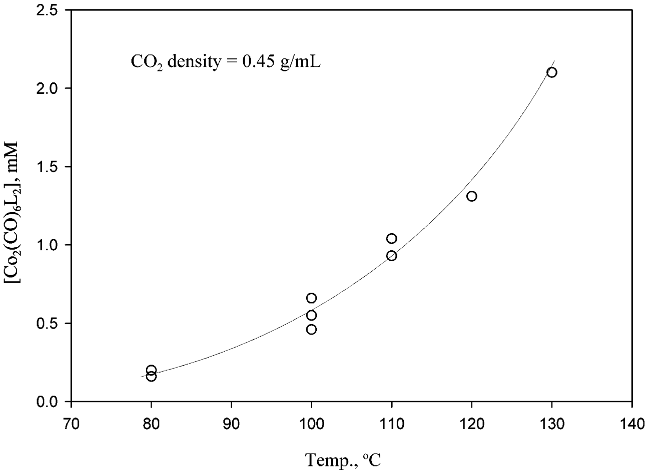

Figure 1. Solubility of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ in $scCO_2$ at a density of 0.45 g/mL.

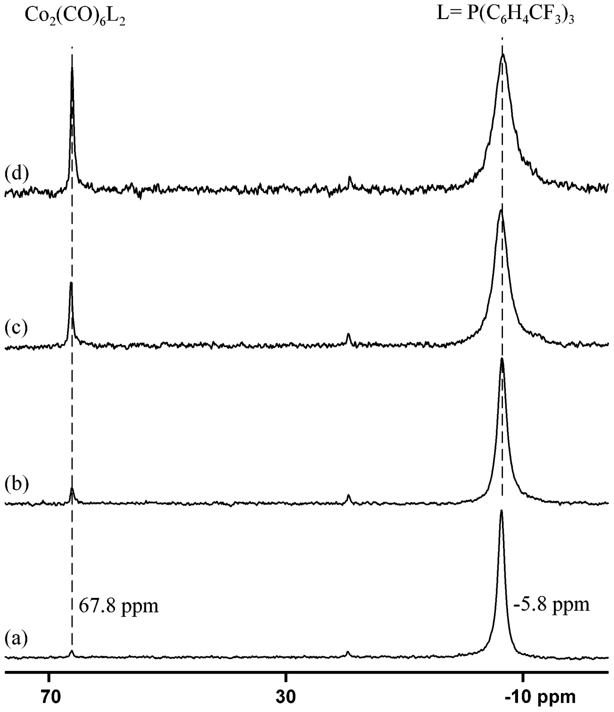

Figure 2. Effect of the concentration of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (**1**) on the line width of the ^{31}P resonance of $P(p\text{-}CF_3C_6H_4)_3$ (**L**) at 100 °C in $scCO_2$. [**L**] = 33.0 mM and [**1**] = (a) 0.29 mM, (b) 0.73 mM, (c) 1.81 mM, and (d) 3.28 mM. P_{CO} = 6.8 atm, and P_{total} = 306 atm.

$$Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2 + CO \rightleftharpoons Co_2(CO)_7[P(p\text{-}CF_3C_6H_4)_3] + P(p\text{-}CF_3C_6H_4)_3 \quad (3)$$

Dependence of the Line Width of the ^{31}P Resonance of $P(p\text{-}CF_3C_6H_4)_3$ on the Concentration of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1). We have observed that the line width of the ^{31}P resonance of **L** changes with temperature and with the concentration of **1**. Figure 2 shows the ^{31}P NMR spectra of solutions containing 33.0 mM of **L** and variable concentrations of **1** in $scCO_2$ at 100 °C under 8.5 atm of CO and a total pressure of 306 atm. These spectra show that the line width of **L** increases with the concentration of **1**, while that of **1**

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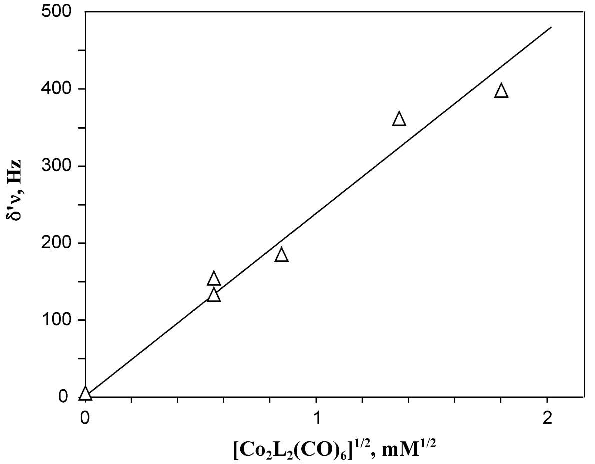

Figure 3. Correlation of the line width of the ^{31}P resonance of $P(p\text{-}CF_3C_6H_4)_3$ with the concentration of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ in $scCO_2$ at 100 °C. $P_{CO} = 6.8$ atm, and $P_{total} = 306$ atm.

itself remains fairly constant, the line width being 57, 52, 55, and 56 Hz in spectra a–d, respectively.

It is shown in Figure 3 that the plot of $\delta'\nu$, the broadening of the resonance of **L** at half-height, vs $[\mathbf{1}]^{1/2}$ gives a linear plot through the origin with a slope of 240 Hz $mM^{-1/2}$. For a first-order rate process, the lifetime τ correlates with $\delta'\nu$ by eq 4, and eq 5 follows.

$$\tau^{-1} = \pi\delta'\nu \tag{4}$$

$$\tau^{-1} = \pi \times 240[\mathbf{1}]^{1/2}\ s^{-1} = 7.5 \times 10^{2}[\mathbf{1}]^{1/2}\ s^{-1} \tag{5}$$

The linear plot in Figure 3 indicates that broadening of the resonance of the free ligand is not caused by the exchange of the free ligand with **1** but with a compound that has a square-root dependence on the concentration of **1**. Consistently, the ^{31}P resonance for **1** does not broaden under these conditions. It is, therefore, suggested that broadening of the resonance of **L** is due to its exchange reaction (eq 6) with the paramagnetic radical complex $(CO)_3LC^{\bullet}$ (**3**), which is generated by the homolysis of **1** in eq 7.

$$(CO)_3LCo^{\bullet} + {}^{*}L \rightleftharpoons (CO)_3{}^{*}LCo^{\bullet} + L \tag{6}$$

$$Co_2(CO)_6L_2 \rightleftharpoons 2(CO)_3LCo^{\bullet} \tag{7}$$

For such a mechanism and under conditions that the equilibrium in eq 7 lies far to the left, the mean lifetime for **L**, τ, may be expressed as

$$\tau = [\mathbf{L}]/k_6[\mathbf{3}][\mathbf{L}] = 1/k_6K_7^{1/2}[\mathbf{1}]^{1/2} \tag{8}$$

It follows from eqs 5 and 8 that $k_6K_7^{1/2} = 7.5 \times 10^2$ $mM^{-1/2}\ s^{-1}$ or $k_6K_7^{1/2} = 2.4 \times 10^4$ $M^{-1/2}\ s^{-1}$.

Hydrogenation of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1) in $scCO_2$. $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ reacts with hydrogen reversibly to give $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ (**4**), as shown in eq 9.

$$Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2 + H_2 \rightleftharpoons 2HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3] \tag{9}$$

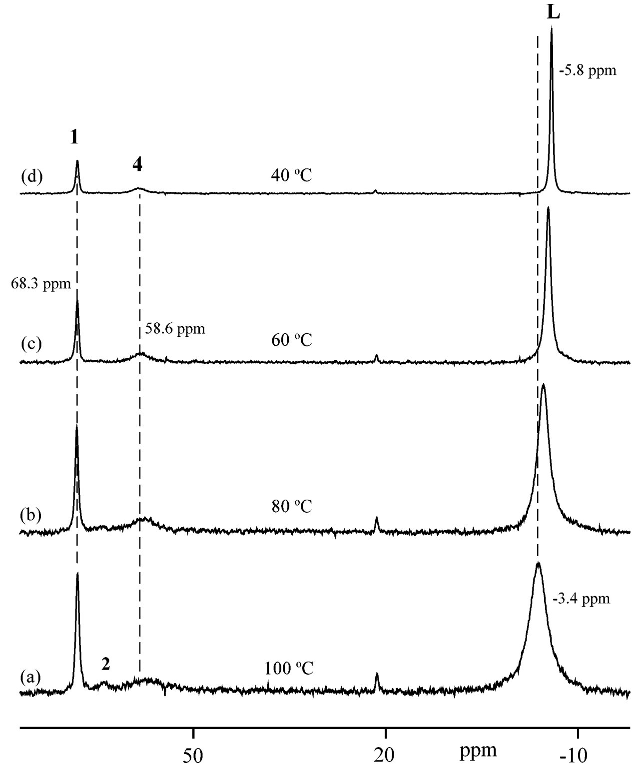

Figure 4. ^{31}P NMR spectra of the product solution of the reaction of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (**1**) with H_2 in $scCO_2$: (a) 100 °C; (b) 80 °C; (c) 60 °C; (d) 40 °C. Initial composition: 17.2 μmol of **1** and 80.4 μmol of $P(p\text{-}CF_3C_6H_4)_3$. Initial pressures at 35 °C: $P_{H_2} = 8.2$ atm, $P_{CO} = 7.9$ atm, and $P_{total} = 168$ atm.

Figure 4a shows the ^{31}P NMR spectrum of the product solution from the hydrogenation of **1** in the presence of **L** in $scCO_2$ after it was heated to 100 °C with 8.2 atm of H_2, 7.9 atm of CO, and a total pressure of 168 atm at 35 °C. In addition to the resonances for **1** (δ 68.3 ppm), **2** (δ 62.2 ppm), and **L** (δ −5.8 ppm), there is a broad resonance at δ 58 ppm, which is in the region for hydrido cobalt complexes[17] and is assigned to **4**. The weak resonance at δ 22 ppm is not assigned; it does not appear to affect the results of this and other experiments in this study. The ^1H resonance of **4** appears as a broad resonance at δ −11.3 ppm (HHW = 60 Hz). The fact that **2** was observed as a minor species in the reaction suggests that, in addition to **4**, the unsubstituted hydrido complex $HCo(CO)_4$ (**5**), which is cogenerated with **4** in the hydrogenation of **2** in eq 10, is likely to be present as a minor species.

$$Co_2(CO)_7[P(p\text{-}CF_3C_6H_4)_3] + H_2 \rightleftharpoons HCo(CO)_4 + HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3] \tag{10}$$

Parts b–d of Figure 4 show the ^{31}P NMR spectra of the product solution after the temperature was dropped to 80, 60, and 40 °C, respectively. These spectra show that the line widths of **4** and **L** change with temperature, but not that of **1**. We have shown in Figure 2 that the ^{31}P resonance of **L** is broadened by **1** in the absence of hydrogen. The broadening of **L** has been attributed to the cobalt radical **3** generated in eq 7. The system becomes much more complex when hydrogen is added. It is possible that **3** also contributes to the broadening

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[17] Wood, C. D.; Garrou, P. E. *Organometallics* **1984**, *3*, 170.

of **4** through the hydrogen atom abstraction reaction in eq 11, similar to that reported for $(CO)_4Co^\bullet$.[18]

$$H^*Co(CO)_3[P(p\text{-}CF_3C_6H_4)_3] + (CO)_3[P(p\text{-}CF_3C_6H_4)_3]Co^\bullet \rightleftharpoons HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3] + (CO)_3[P(p\text{-}CF_3C_6H_4)_3]^*Co^\bullet \tag{11}$$

In addition, the reversible ligand dissociation reactions, depicted in eqs 12 and 13, may also contribute to the broadening of **4**.

$$HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3] \rightleftharpoons HCo(CO)_3 + P(p\text{-}CF_3C_6H_4)_3 \tag{12}$$

$$HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3] \rightleftharpoons HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3] + CO \tag{13}$$

The reverse of the process in eq 12 could contribute to the broadening of **L** in the presence of hydrogen. Future work will focus on resolving the complex array of ligand exchange reactions in this system in the presence of hydrogen.

The resonance of **L** shifted upfield from δ −3.4 to −5.8 ppm as the temperature was lowered from 100 to 40 °C, corresponding to a temperature coefficient of 0.04 ppm/K for the resonance. This temperature coefficient is well within the reported temperature coefficients for the ^{31}P resonance, for which values as high as 0.065 ppm/K have been reported.[19]

The ^{59}Co spectrum corresponding to the ^{31}P spectrum of Figure 4a is shown in Figure 5a. It should be noted that the quadrupolar cobalt nucleus very often makes the ^{59}Co resonance too broad to be observed, if the electric field gradient generated by its orbital electrons deviates very much from the spherical symmetry. Compound **1** appears to fall into this category. The broad non-Lorentzian resonance at δ −3010 ppm (δ 0 ppm for saturated aqueous $K_3Co(CN)_6$) is quite close to the reported resonance of δ −3030 ppm for $HCo(CO)_4$ (**5**),[10] The ^{59}Co resonance is known to be very sensitive to its oxidation state,[20] and the observed resonance can be safely assigned to a Co(I) resonance or overlapping Co(I) resonances.

The ^{59}Co spectrum in Figure 5b, recorded of a product solution obtained under similar reaction conditions except that CO was not added, shows two partially resolved, broad resonances of comparable intensities at δ −2890 and −3010 ppm. The corresponding ^1H and ^{31}P spectra of the solution exhibit a broad singlet at δ −11.3 and 56.5 ppm, respectively. When the solution was cooled to 35 °C, well-resolved ^1H and ^{31}P NMR resonances were obtained and the two ^1H resonances exhibited their hyperfine structures. The ^1H NMR spectrum (Figure 5, inset A), which shows a doublet at δ −11.1 ppm ($J_{P-H} = 36$ Hz) and a triplet at δ −11.6 ppm ($J_{P-H} = 42$ Hz), indicates the presence of two hydrido cobalt complexes, with one and two phosphine ligands, respectively. These resonances are, therefore, assigned to $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ (**4**) and $HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3]_2$ (**6**). The ^{31}P NMR spectrum (Figure 5, inset B) exhibits two partially resolved resonances at δ 57.8 and 54.8 ppm. These two ^{31}P resonances are assigned to **4** and **6**, on the basis of the shifting of their equilibrium with CO pressure. It is fortunate that the interconversion between **4** and **6**, as shown in eq 14, is so slow at 35 °C that their ^1H and ^{31}P resonances are resolved.

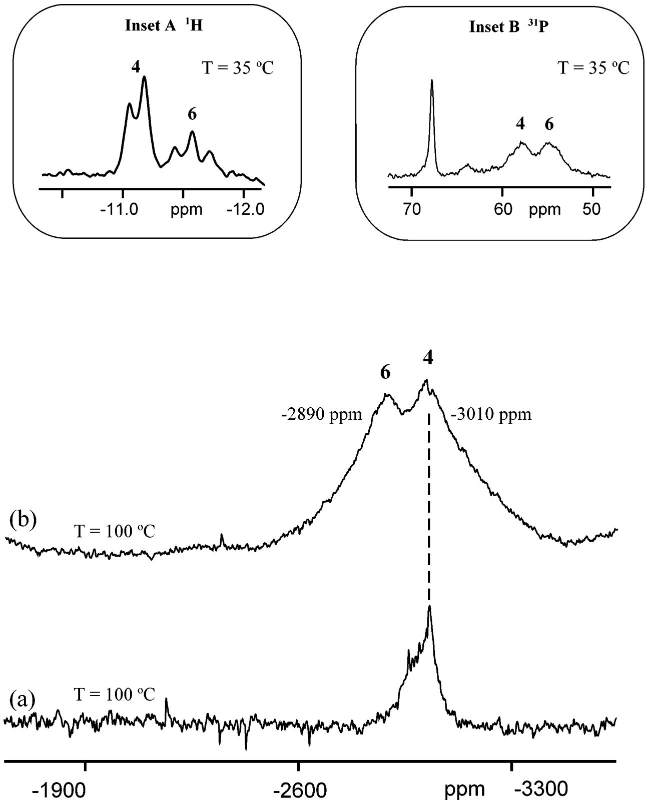

Figure 5. ^{59}Co NMR spectra of hydrido cobalt(I) complexes in $scCO_2$ at 100 °C. Initial compositions and gas pressures at 35 °C: (a) same as Figure 4a; (b) 19 μmol of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$, 52 μmol of $P(p\text{-}CF_3C_6H_4)_3$, $P_{H_2} = 21$ atm, and $P_{total} = 179$ atm. Insets A and B: ^1H and ^{31}P NMR spectra of the solution of (b) at 35 °C.

$$HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3] + P(p\text{-}CF_3C_6H_4)_3 \rightleftharpoons HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3]_2 + CO \tag{14}$$

Following the assignments of the ^1H and ^{31}P resonances, the two ^{59}Co resonances at δ −2890 and −3010 ppm in Figure 5b are assigned to **6** and **4**, since the resonance at δ −2890 ppm was observed only when CO was absent in the solution. The resonance in Figure 5a can now be assigned to **4**, with possible minor contribution from **5** and **6**.

Hydroformylation of Olefins Catalyzed by $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1) in $scCO_2$. The hydroformylation of ethylene catalyzed by **1** can be carried out with preformed **1** or with **1** generated in situ by the reaction of $Co_2(CO)_8$ with $P(p\text{-}CF_3C_6H_4)_3$. Curve I in Figure 6 shows the rate of consumption of H_2, as followed by ^1H NMR, for the hydroformylation of ethylene at 100 °C in a $scCO_2$ solution containing 33 μmol of **1**, 590 μmol of $P(p\text{-}CF_3C_6H_4)_3$, 8.2 mmol of H_2, 8.7 mmol of CO, and 16.1 mmol of C_2H_4. The ^1H NMR spectra show that the consumption of H_2 was accompanied by the consumption

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[18] Rathke, J. W.; Klingler, R. J.; Krause, T. R. *Organometallics* **1992**, *11*, 585.

[19] Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978; p 101.

[20] Reference 19, p 225.

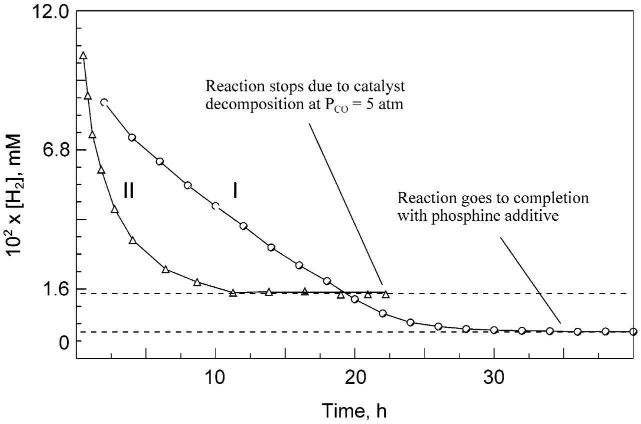

Figure 6. Hydroformylation of ethylene with $Co_2(CO)_8$ and with $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ in $scCO_2$. Initial conditions for curve I (○): 33 μmol of **1**, 590 μmol of **L**, 8.2 mmol of H_2, 8.7 mmol of CO, 16.1 mmol of C_2H_4, and $P_{total} = 178$ atm at 35 °C. Initial conditions for curve II (△): 39 μmol of $Co_2(CO)_8$, 8.6 mmol of H_2, 8.6 mmol of CO, 16.6 mmol of C_2H_4, and $P_{total} = 181$ atm at 35 °C.

Table 1. Hydroformylation of Propylene

expt	catalyst; amt, μmol	T, °C	amt of C_3H_6, mmol	amt of H_2, mmol	amt of CO, mmol	P_{total},[a] atm	n-C_4H_8O,[b] mol %
1	$Co_2(CO)_6L_2$; 9.9[c]	100	5.3	9.0	9.0	360	80
2	$Co_2(CO)_8$; 11.7	100	5.2	9.2	9.2	369	81
3	$Co_2(CO)_8$; 91	70	5.7	44	44	384	86

[a] Initial pressure at reaction temperature. [b] n-Butyl aldehyde. [c] $P(p\text{-}CF_3C_6H_4)_3$, 590 μmol, added.

of ethylene and the production of propionaldehyde in a mole ratio of 1:1:1. The ^1H and the ^{13}C NMR spectra of the product solution indicate that propionaldehyde is the sole product. No hydrogenation to produce propane was observed. For comparison, the rate of H_2 consumption for $Co_2(CO)_8$-catalyzed hydroformylation of ethylene under similar conditions is shown in curve II. It is clear from these two rate plots that the unmodified cobalt catalyst is more active. However, the phosphine-modified cobalt catalyst is more stable, and the reaction proceeded until all of the CO, which is equimolar to H_2, was consumed. For the unmodified catalyst, the catalytic reaction stopped when the CO pressure dropped down to 5 atm.

We have also examined **1**-catalyzed and $Co_2(CO)_8$-catalyzed hydroformylation of propylene in $scCO_2$, with the hope that different n-butyl aldehyde/isobutyl aldehyde selectivities are obtained with these two catalysts. We found that the selectivities for n-butylaldehyde are essentially the same for the two catalysts, 80 and 81%, under similar conditions (Table 1, experiments 1 and 2). For the unmodified $Co_2(CO)_8$, we found that the selectivity for n-butyl aldehyde increased from 81 to 86% when the temperature was lowered from 100 to 70 °C with higher CO and H_2 pressures. We have previously obtained a 88% selectivity for n-butylaldehyde in $scCO_2$ at 80 °C with $P_{H_2} = P_{CO} = 42$ atm.[10] In another study in benzene solution, a selectivity of 83% was reported at 80 °C with $P_{H_2} = P_{CO} = 80$ atm.[21]

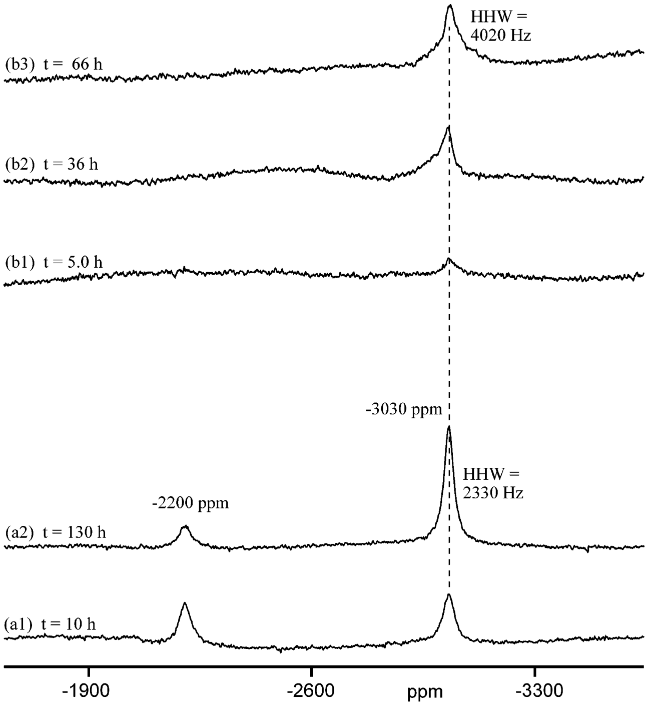

Figure 7. ^{59}Co NMR spectra from two separate experiments in the hydroformylation of propylene with $Co_2(CO)_8$ and with $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (**1**) at 100 °C in $scCO_2$. For a1 and a2: $Co_2(CO)_8$, 11.7 μmol; H_2, 9.2 mmol; CO, 9.2 mmol; C_3H_6, 5.2 mmol; $P_{total} = 185$ atm at 35 °C. For b1–b3: **1**, 9.9 μmol; **L**, 590 μmol; H_2, 8.8 mmol; CO, 9.2 mmol; C_3H_6, 5.3 mmol; $P_{total} = 181$ atm at 35 °C.

In Figure 7, the ^{59}Co NMR spectra recorded during the hydroformylation reaction in experiments 1 and 2 of Table 1 are shown. For the unsubstituted $Co_2(CO)_8$ system, the spectra (a1 and a2 in Figure 7) reveal that both $Co_2(CO)_8$ (δ −2200 ppm) and $HCo(CO)_4$ (δ −3030 ppm) were present. These resonances, which show the steady-state concentrations of these complexes, are quite Lorentzian. In contrast, the ^{59}Co NMR spectra for the $P(p\text{-}CF_3C_6H_4)_3$-modified system (b1−b3 in Figure 7) show only one resonance in the hydrido cobalt region. These resonances, which are broader and more distorted, are assigned to the unresolved resonances of $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ (**4**) and $HCo(CO)_2[P(p\text{-}CF_3C_6H_4)_3]_2$ (**6**). The presence of a small amount of $HCo(CO)_4$ (**5**) cannot be ruled out. These assignments are supported by the ^{31}P NMR spectrum of the solution, which shows a resonance at δ 67.2 ppm for **1** and a broad resonance centered at δ 58 ppm in the ratio of 58:42. The resonance at δ 58 ppm is assigned to the unresolved resonances of **4** and **6**.

Discussion

As mentioned earlier, we did not find the ^{59}Co resonance that can be assigned to **1** in the hydrogenation of **1** (Figure 5), even though the corresponding ^{31}P spectrum (Figure 4) shows that **1** is at equilibrium with **4**. Similarly, we did not find a ^{59}Co resonance for **1** in the hydroformylation of olefins (b1−b3 in Figure 7), even though the ^{31}P NMR spectra show that **1** accounts for 58% of the cobalt complexes in the solution. In contrast, in the hydroformylation with $Co_2(CO)_8$, the ^{59}Co resonances for both $Co_2(CO)_8$ and $HCo(CO)_4$ were observed (a1 and a2 in Figure 7). The failure of **1** to give an observable ^{59}Co resonance might be attributed to the

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[21] Pino, P.; Piacenti, F.; Bianchi, M.; Lazzaroni, R. *Chim. Ind. (Milan)* **1968**, *50*, 106.

higher distortion from the spheric symmetry of the electric field gradient generated by its orbital electrons. In our previous work, we were not able to observe the ^{59}Co NMR spectrum of $Co_2(CO)_6[P(n\text{-}C_4H_9)_3]_2$ either.

The absence of a ^{59}Co resonance at δ −2200 ppm in Figure 5 and in Figure b1−b3 in Figure 7 clearly indicates the absence of $Co_2(CO)_8$ in these solutions. It follows then that $HCo(CO)_4$ (**5**) is also absent, or is a very minor species, in these solutions, since $Co_2(CO)_8$ and **5** are in equilibrium under these reaction conditions. These results support our assignment of the ^{59}Co resonance at δ −3010 ppm in Figure 5a to **4** rather than **5**. Compounds **4** and **5** happen to have nearly identical chemical shifts.

$Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ was found to catalyze the hydroformylation of ethylene and propylene. In a solution containing a large excess of $P(p\text{-}CF_3C_6H_4)_3$ (62 mM), the compound has a catalytic activity which is about 1/10 of that of $Co_2(CO)_8$. However, it is more stable under low CO pressures, and it allows the hydroformylation reaction to be carried out to the complete depletion of CO. The ^{31}P and ^{59}Co NMR spectra of the solutions clearly indicate that $HCo(CO)_3[P(p\text{-}CF_3C_6H_4)_3]$ (**4**) is the predominant, if not the only, cobalt complex present under the reaction conditions. However, due to the lability of all of these cobalt complexes, it is not possible to rule out a contribution from the more reactive $HCo(CO)_4$ simply because it was not observed. Our attempts to establish the case for **4** as the catalyst for the hydroformylation of propylene by the altered selectivity of *n*-butyl aldehyde/isobutyl aldehyde turned out to be negative. The *n*-butyl aldehyde/isobutyl aldehyde ratio for **1** is similar to that obtained for $Co_2(CO)_8$. It is possible that the unsubstituted and the phosphine-substituted catalyst systems have similar product selectivities, but it is also possible that the main effect of the addition of the phosphine ligand is simply the reduction of the concentration of the more active $HCo(CO)_4$.

Experimental Section

General Considerations. A General Electric GN300/89 NMR spectrometer was used for the in situ NMR studies. The high-pressure probe used in this study has been described previously.[10] Carbon monoxide, hydrogen, ethylene, propylene, and carbon dioxide were of research grades from AGA Specialty Gases and Equipment, and were used as received. Dicobalt octacarbonyl and tris(*p*-(trifluoromethyl)phenyl)phosphine from Strem Chemicals were used without further purification.

$Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1). The compound was synthesized by the reaction of $Co_2(CO)_8$ with the stoichiometric amount of $P(p\text{-}CF_3C_6H_4)_3$ in toluene.[16] To a flask containing 210 mg (0.61 mmol) of $Co_2(CO)_8$ and 569 mg (1.22 mmol) of $P(p\text{-}CF_3C_6H_4)_3$ under a nitrogen atmosphere was added 12.0 mL of deaerated toluene at ambient temperature. Stirring of the solution caused immediate gas evolution, and a dark brown solution was obtained. Dark brown precipitate gradually fell out of the solution during the following 1 h. The solution was heated at 60 °C for 1 h and then cooled for the product to crystallize out of the solution. The precipitate was collected on a sintered-glass filter, washed with petroleum ether, and dried. Yield: 350 mg. The crude product was further purified by recrystallization from toluene. It is important to filter the solution to remove any metallic cobalt produced in the process. Anal. Found: C, 47.89; H, 2.36; F, 27.82; P, 5.00; Co, 9.30. Calcd for $C_{48}H_{24}F_{18}P_2O_6Co_2$: C, 47.31; H, 1.99; F, 28.06; P, 5.08; Co, 9.67; O, 7.88. The compound exhibits a ^{31}P resonance at δ 68.6 ppm (in toluene, 85% aqueous H_3PO_4 at 0 ppm). Note on the elemental analysis: incomplete liberation of fluorine was encountered in the initial analysis by oxygen flask combustion. The correct fluorine analysis was obtained by a more vigorous decomposition technique, pyrolysis at 1100 °C. The analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Solubility of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ in $scCO_2$. This experiment was carried out to assess the density of $scCO_2$ needed to dissolve a sufficient amount of **1** at ~100 °C to study the hydroformylation reaction. Preliminary experiments indicated that **1** has limited solubility in $scCO_2$ at a low density of CO_2. The high-pressure cell, 9.5 mL in volume, was loaded with 40 mg (33 μmol) of **1** and 275 mg (330 μmol) of $P(p\text{-}CF_3C_6H_4)_3$ (**L**), the latter being added for calibration and for suppression of its dissociation from **1**. The cell was charged with 7.5 atm of CO and 7.5 atm of CH_4 at 35 °C, followed by the addition of CO_2 to bring the total pressure to 86.3 atm. Methane was added for use in shimming the magnet. The solubilities of the cobalt dimer at 80−130 °C were obtained by comparing its integrated areas against that of free **L** after equilibrium was reached. The results are shown in Figure 1.

Line Width of the ^{31}P Resonance of $P(p\text{-}CF_3C_6H_4)_3$. Early experiments indicated that the line width of the ^{31}P resonance of **L** changed with the concentration of **1**. A set of four experiments were carried out to correlate the line width of the ^{31}P resonance of **L** with the concentration of **1**. The cell (10.0 mL) was loaded with 154 ± 1 mg (33.0 mM) of **L** and the desired amounts of **1**, which were 3.5 mg (0.29 mM), 8.9 mg (0.73 mM), 22.0 mg (1.81 mM), and 40.0 mg (3.28 mM), respectively. Carbon monoxide and methane were introduced at room temperature to give each a pressure of about 6.8 atm. Carbon dioxide was then added to give a total pressure of ~120 atm. The pressure was adjusted to 306 atm by the addition of more CO_2 after the cell was equilibrated at 100 °C. As a background check, we have shown that, in the absence of **1**, the line width of the ^{31}P resonance of **L** is 20 ± 1 Hz, independent of the temperature and the density of CO_2.

Hydrogenation of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1) in $scCO_2$. The high-pressure cell containing 21 mg of $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ and 37.5 mg of $P(p\text{-}CF_3C_6H_4)_3$ was charged with 7.9 atm of CO and 8.2 atm of H_2 at 35 °C; CO_2 was then added to bring the pressure to 168 atm. The temperature was then raised to 100 °C, at which point the pressure reached 470 atm. The ^{31}P NMR spectra of the solution at 100, 80, 60, and 40 °C, shown in Figure 4, were recorded after the solution was allowed to reach equilibrium at the respective temperatures.

The ^{59}Co NMR spectrum was also recorded at 100 °C. For comparison, a ^{59}Co NMR spectrum was recorded for a reaction carried out under different reaction conditions without added CO. These spectra are shown in Figure 5.

Hydroformylation of Ethylene and Propylene Catalyzed by $Co_2(CO)_6[P(p\text{-}CF_3C_6H_4)_3]_2$ (1) in $scCO_2$. A high-pressure cell containing 40 mg (33 μmol) of **1** and 275 mg (590 μmol) of $P(p\text{-}CF_3C_6H_4)_3$ was charged with 21.7 atm of H_2, 23.1 atm of CO, and 20.5 atm of C_2H_4 at 35 °C in the order listed, followed by the addition of CO_2 to give a total pressure of 178 atm. The cell was then heated to 100 °C and the reaction followed by recording one ^{31}P and one ^{1}H spectrum every 2 h. Integration of the ^{1}H resonances of H_2 and C_2H_4 gives the initial mole ratio of $C_2H_4/H_2 = 1.85$. This higher ratio, as compared to that calculated from the pressure increments in the loadings, is due to the compressibility of C_2H_4. A ^{13}C NMR spectrum was recorded at the end of the reaction.

The hydroformylation of propylene was carried out in a similar fashion. The high-pressure cell containing 12 mg (9.9 μmol) of **1** and 275 mg (590 μmol) of $P(p\text{-}CF_3C_6H_4)_3$ was charged with 9.9 atm of C_3H_6 and 47.8 atm of a 1:1 H_2/CO mixture at 35 °C in the order listed, followed by the addition of the addition of CO_2 to bring the total pressure to 181.3 atm. The cell was then heated to 100 °C and the reaction followed by recording one ^{59}Co and one ^{1}H spectrum every 2 h. Integration of the ^{1}H resonances of H_2 and C_3H_6 gave an initial mole ratio of $C_3H_6/H_2 = 0.60$.

Hydroformylation of Ethylene and Propylene Catalyzed by $Co_2(CO)_8$ in $scCO_2$. For the hydroformylation of ethylene, the high-pressure cell was loaded with 13.3 mg (39 μmol) of $Co_2(CO)_8$ and was then pressurized with 23.2 atm of CO, 21.2 atm of H_2, and 21.2 atm of C_2H_4 at 35 °C in the order listed, followed by the addition of CO_2 to bring the total pressure to 181 atm. The cell was then heated to 100 °C and the reaction followed by ^{1}H spectroscopy. Integration of the ^{1}H resonances of H_2 and C_2H_4 gave the initial mole ratio of $C_2H_4/H_2 = 1.86$.

For the hydroformylation of propylene, the high-pressure cell was loaded with 4.0 mg (11.7 μmol) of $Co_2(CO)_8$ and was pressurized with 9.8 atm of C_3H_6 and 49.0 atm of a 1:1 CO/H_2 mixture at 24 °C. The temperature was raised to 35 °C, and CO_2 was then added to increase the pressure from 62.3 to 185 atm. The cell was then heated to 100 °C, and the reaction was followed by ^{31}P and ^{1}H spectroscopy every 1 h. Integration of the ^{1}H resonances of H_2 and C_3H_6 gave the initial mole ratio of $C_3H_6/H_2 = 0.40$.

In another experiment, 31 mg (91 μmol) of $Co_2(CO)_8$ was used. The cell was charged with 10.7 atm of C_3H_6 at 23 °C. The temperature was raised to 40 °C, and a 1:1 mixture of CO and H_2 was added to raise the pressure to 255 atm, followed by the addition of CO_2 to bring the total pressure to 328 atm. The temperature was then raised to 70 °C and the reaction was followed by ^{59}Co and ^{1}H spectroscopy every 1 h. Integration of the ^{1}H resonances of H_2 and C_3H_6 gave the initial mole ratio of $C_3H_6/H_2 = 0.117$.

Acknowledgment. Support for this work was provided by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

OM030600H