Supplemental Information

Table 4. Equilibrium Constants[a]

Solvent	Ligand	Temp	ln $K_{p'}$	ln K_p
Benzene	n-Bu$_3$P	75	-9.00	-5.65
Benzene	n-Bu$_3$P	100	-8.49	-5.07
Benzene	n-Bu$_3$P	125	-8.00	-4.51
Benzene	n-Bu$_3$P	150	-7.00	-3.45
Benzene	n-Bu$_3$P	175	-6.92	-3.32
Dioxane	n-Bu$_3$P	100	-8.53	-5.11
Dioxane	n-Bu$_3$P	112	-8.07	-4.62
Dioxane	n-Bu$_3$P	125	-7.87	-4.38
Dioxane	n-Bu$_3$P	137	-7.63	-4.11
i-butanol	n-Bu$_3$P	90	-9.13	-5.74
i-butanol	n-Bu$_3$P	100	-9.03	-5.61
i-butanol	n-Bu$_3$P	120	-8.48	-5.01
i-butanol	n-Bu$_3$P	130	-8.41	-4.91
i-butanol	n-Bu$_3$P	140	-8.20	-4.68
scCO$_2$	(p-CF$_3$C$_6$H$_4$)$_3$P	70	-9.27	-5.93
scCO$_2$	(p-CF$_3$C$_6$H$_4$)$_3$P	80	-8.97	-5.60
scCO$_2$	(p-CF$_3$C$_6$H$_4$)$_3$P	90	-8.76	-5.37

$scCO_2$	$(p\text{-}CF_3C_6H_4)_3P$	100	-8.71	-5.29
$scCO_2$	$(p\text{-}CF_3C_6H_4)_3P$	110	-8.60	-5.15

[a]For the reaction in eq 8. The $K_{p'}$ values are defined with the choice of standard states such that the activity of the CO is in atm with the dimer and hydride expresed in concentrations, M. For the K_p values, the activity of all of the species are in units of atm using the conversion $K_p = (RT) K_{p'}$ as described in the text. The NMR measurments in $scCO_2$ yield K_p values directly.

Kinetics for HCo(CO)$_4$ Formation. The approach to equilibrium data[5] that was obtained under pseudo first-order reaction conditions employing excess H_2 was plotted using the integrated form of the rate law for the case of a pseudo first-order forward reaction in conjunction with an apposing second-order reverse process in Figure 4. The resultant effective first-order rate constants, k_1, were converted to second-order rate constants by dividing by the H_2 and plotted versus temperature along with the available data from the literature in Figure 5.
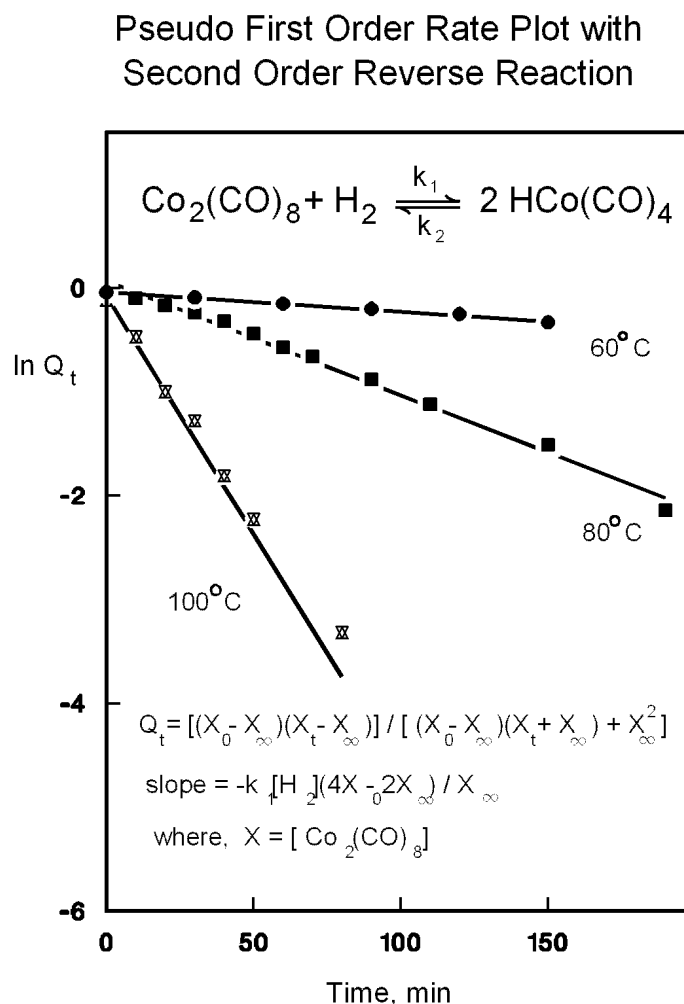

Figure 4. Integrated rate law for the case of a pseudo first order forward reaction in conjunction with an

apposing second order reverse process in the hydrogenation of $Co_2(CO)_8$.

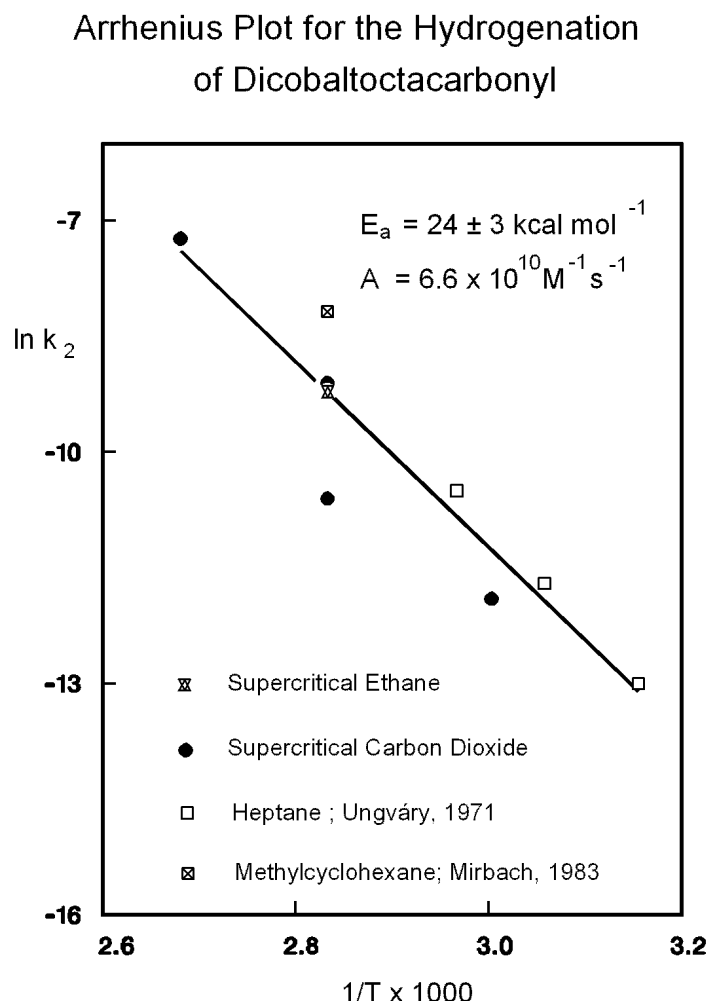## Arrhenius Plot for the Hydrogenation
of Dicobaltoctacarbonyl

Figure 5. Plot of $ln(k_2)$ versus $1/T$ for the hydrogenation of $Co_2(CO)_8$.

Heterolytic Co-Co Bond Cleavage. The phosphine-modified cobalt hydroformylation system employing n-Bu$_3$P, is often referred to as the Shell process.[22,36-39] This system has been extensively investigated by high-pressure IR spectroscopy.[49-52] These IR investigations have suggested that the phosphine ligand is displaced by CO according to the equilibrium in eq 5. In contrast to the IR investigations, the *in-situ* NMR method found no detectable amount of $Co_2(CO)_7(Bu_3P)$ formation under steady-state conditions with its unique chemical shift of 56.0 ppm even at 350 atm of CO pressure unless the Co/L ratio was less than unity. Alternatively, carbon monoxide reacts reversibly to effect the heterolytic Co-Co bond cleavage to yield the well known mixed valence salt, eq 4, which can be

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independently synthesized to confirm its chemical shift of 52.4 ppm. The process in eq 4 is reversible and the thermodynamics have been determined.[48] The kinetics for the reverse of the reaction in eq 7 have been extensively investigated by Kochi and found to proceed by electron transfer producing $Co(CO)_3L_2$ and $Co(CO)_4$ radical intermediates.[69] Interestingly, we have found that transient quantities of $Co_2(CO)_7L$ are produced after rapidly decreasing the temperature. The transient $Co_2(CO)_7L$ intermediate subsequently decays to undetectably low concentrations levels as the system returns to equilibrium at the lower temperature. This observation fits in nicely with the work and mechanisms from the Kochi group.[69] Furthermore, the fact that a separate resonance for $Co_2(CO)_7L$ is observable as a sharp NMR resonance indicates that $Co_2(CO)_7L$ is not in fast exchange with free phosphine at these temperatures.

The competition between the processes in eq 4 and 5 is highly dependent on the basicity of the phosphine. Thus, the process in eq 4 dominates for the highly basic $n\text{-}Bu_3P$ ligand. However, there is no evidence for salt formation, eq 4, for the weakly basic $(p\text{-}CF_3C_6H_4)_3P$ phosphine and excess ligand that needs to be added to suppress the ligand dissociation process in eq 5 during the hydroformylation of ethylene and propylene.[8]

Unknown Species at -19 ppm. In addition to the mixed valent salt in eq 7, the reaction of $Co_2(CO)_6L_2$ with CO results in the production of another species that is readily apparent in the ^{31}P NMR spectra. The chemical shift of the new species is approximately -19 ppm.[7] The exact value of the chemical shift depends on the phosphine and CO loading due to facile ligand exchange reactions. The addition of excess phosphine enhances the formation of this new species. With an L/Co ratio of 3.0, more than 90% of the cobalt is converted to this species at -19 ppm. The salt and dimer represent less than 10% of the cobalt at a L/Co ratio of 3.0 and modest CO pressure. The species at -19 ppm is extraordinarily labile toward phosphine exchange. Furthermore, the degree of phosphine lability depends on the phosphine loading. Thus, at an L/Co ratio of 1.0, separate resonances for the new

complex at -19 ppm and free phosphine, -31 ppm, are resolvable at temperatures below 50 ^{o}C. However, at an L/Co ratio of 3.0, separate resonances for the species at -19 ppm and free n-Bu$_3$P phosphine at -31 ppm are resolvable only at temperatures below -50 C^o. This is a difference of 100 ^{o}C in the coalescence temperature. In marked contrast, neither Co$_2$(CO)$_6$L$_2$ nor [Co(CO)$_3$L$_2$]$^+$ exhibit evidence for phosphine exchange on the NMR time scale at temperatures below 50 ^{o}C. Not even HCo(CO)$_3$L is anywhere near as labile as this new species. The complex at -19 ppm is not only the most labile species in the phosphine-modified system, it is also the dominant cobalt-containing species at the L/Co ratio and temperature/pressure conditions under which the Shell process is conducted.[22,36-39] Furthermore, this species has never been mentioned in the considerable literature that exists for the phosphine-modified cobalt hydroformylation reaction.[22,49-52]

When the species at -19 ppm is prepared at L/Co = 1.0, the resultant complex is too unstable at 1 atm pressure to allow its isolation. However, the analog that is generated at L/Co = 3.0 is sufficiently stable that it can be removed from the high-pressure reactor and separated from the residual dimer and salt. It exhibits xenophilic properties[70] with a four-band IR spectrum in the carbonyl region that is characteristic of a neutral species in toluene and methylcyclohexane solvent, while in methylene chloride the only IR band of any significance is that for [Co(CO)$_4$]$^-$. The presence of the anion in methylene chloride solution was confirmed by the ^{59}Co spectrum, which exhibits the correct chemical shift and ^{13}C coupling to four equivalent carbonyls. This latter point was confirmed by synthesizing the compound under enriched ^{13}CO and transfering it to methylene chloride, where the observed coupling pattern changed, consistent with four equivalent carbonyls with the higher ^{13}C content. Notably, there is no IR resonance near 1890 cm^{-1} for this species in nonpolar solvents, indicating that the neutral form of this xenophilic complex does not contain free [Co(CO)$_4$]$^-$ anion. This species is under further characterization, the results of which will be reported separately.

Additional References

69. Kochi, J. K. *In Organometallic Radical Processes*; Trogler, W. C. Ed,; Elsevier, Amsterdam, 1990, Chapter 7.

70. Whittlesey, C. *Coord. Chem. Rev.* **2000**, *206-207*, 395-418.