Separation of the Diastereoisomers a and b of the Complexes (η^3-RC_3H_4)Fe(CO)(NO)($(C_6H_5)_2$PN(R′)CH(CH_3)(C_6H_5)(1–4). Fractional Crystallization. A 4-g (8.7-mmol) sample of **1a,b** was dissolved in a mixture of 45 mL of petroleum ether and 15 mL of ether. The red solution, cooled to −30 °C for 3 days, gave a crystalline precipitate. This procedure, repeated 10 times with the crystalline fraction using reduced solvent quantities, yielded the less soluble diastereomer **1a** in 100% optical purity.

The more soluble diastereomer was obtained from the mother liquor of the first crystallization. The mother liquor was concentrated and cooled to −30 °C, whereby part of the remaining less soluble diastereomer crystallized. After five repetitions of this operation followed by evaporation of the resulting mother liquor, the solution gave an oil in which the more soluble diastereomer **1b** was enriched to 80% optical purity.

The diastereomer mixtures of **2a,b** were separated similarly; the optical purities obtained are given in Table I.

The diastereoisomers of **3a,b** cannot be separated in the same way because the less soluble did not crystalline at −30 °C. When the mixture was cooled to −60 °C, an oil precipitated that cannot be solidified. This operation led only to an enrichment of 20% for **3a** in the oil and **3b** in the resulting solution (Table I).

Diastereomer Separation by Preparative Liquid Chromatography. The chromatography was carried out with Merck Lobar columns type B filled with LiChroprep Si 60 (40–63 μm): eluent petroleum ether/benzene (8:1), pressure 1–2 bar, substrate between 500 mg and 1 g, dissolved in 5 mL eluent (if necessary with some additional benzene). For the complexes **2a,b** and **4a,b** twofold passage through the two-column setup, described previously,[10,13] gave two completely separated zones in approximately 6 h, containing the diastereomers **a** (second zone) and **b** (first zone), respectively, in optically pure form. For complexes **1a,b** the bands overlapped appreciably after the same passage through four columns. Diastereomer **1a** can be obtained optically pure from the front part and diastereomer **1b** from the back part of the zone. The overlap area was discarded.

Compounds **3a,b** were passed three times through the two-column system which resulted only in a broadening of the red zone. Four equal fractions were collected. The first, enriched in **3a**, and the last, enriched in **3b**, were chromatographed through another two columns, the bands being cut into three fractions, respectively. The best enrichments obtained are given in Table I.

X-ray Intensity Data Collection and Structure Solution. Intensity measurements were carried out with an Enraf-Nonius CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing are given in table III.

All data processing and calculations were carried out by using the SHELX-76 system of programs.[33] The structure were both solved by the Patterson method. Since there was no reason to expect any distortions of the phenyl rings, these were refined as rigid bodies (with the carbon–carbon bonds being 1.395 Å) with idealized hydrogens (C–H = 0.97 Å). The methyl groups were also treated as rigid bodies. The remaining non-hydrogen atoms were refined anisotropically.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG. This study was supported in part by the Robert A. Welch Foundation. I.B. thanks the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award for the summer of 1982, spent at the University of Regensburg.

Registry No. **1a**, 87555-33-7; **1b**, 87585-10-2; **2a**, 87555-34-8; **2b**, 87585-11-3; **3a**, 87555-35-9; **3b**, 87585-12-4; **4a**, 87555-36-0; **4b**, 87585-13-5; (η^3-C_3H_5)Fe$(CO)_2$NO, 12071-54-4; (η^3-$CH_3C_3H_5$)Fe$(CO)_2$NO, 34664-02-3.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and atomic coordinates and temperature factors for compounds **1a** and **2b** (Tables IV and V) (24 pages). Ordering information is given on any current masthead page.

Formate Formation during $Co_2(CO)_8/PR_3$-Catalyzed Hydroformylation

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Received August 9, 1983

Careful examination of phosphine-modified cobalt hydroformylation (2000 psig, CO/H_2 = 1:2, 190 °C, Co/P = 1:1) as a function of PR_3 reveals that moderate selectivity to formates can be achieved depending on the cone angle of the PR_3 ligand chosen. These results are rationalized in terms of a stabilization or destabilization of a carboalkoxycobalt intermediate. Formate yields as high as 46% have been achieved with PEt_3 at 4000 psig. The organometallic species present in the reaction are examined in detail for $Co_2(CO)_8/PR_3$ (PR_3 = PCy_3, PEt_3, and PPh_3) by ^{31}P NMR and IR spectroscopy.

Introduction

Recent observations concerning synthesis gas reactions in general and the hydroformylation reaction in particular[1–3] have led us to examine the formation of formates during $Co_2(CO)_8/PR_3$-catalyzed hydroformylation reactions. Hydroformylation has been the topic of scores of research publications and review articles.[4–7] The reaction is known to proceed via aldehydes to alcoholic products

(1) Wood, C. D.; Garrou, P. E. In "Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals"; Herman, R. G., ED.; Plenum Press: New York, in press.
(2) Dubois, R. A.; Garrou, P. E. *J. Organomet. Chem.* **1983**, *141*, 69.
(3) Fellmann, J. D.; Garrou, P. E.; Seyferth, D.; Withers, H. P.; Traficante, D. D. *Organometallics* **1983**, *2*, 818.
(4) Paulik, F. E. *Catal. Rev.* **1972**, *6*, 49.
(5) Heck, R. F. "Organotransitionmetal Chemistry"; Academic Press: New York, 1974.
(6) Wender, I.; Pino, P. "Organic Synthesis Via Metal Carbonyls"; Wiley-Interscience: New York, 1977; Vol. 2.
(7) Pruett, R. L. In "Advances in Organometallic Chemistry"; West, R., Stone, F. G. A.; Eds.; Academic Press: New York, 1979.

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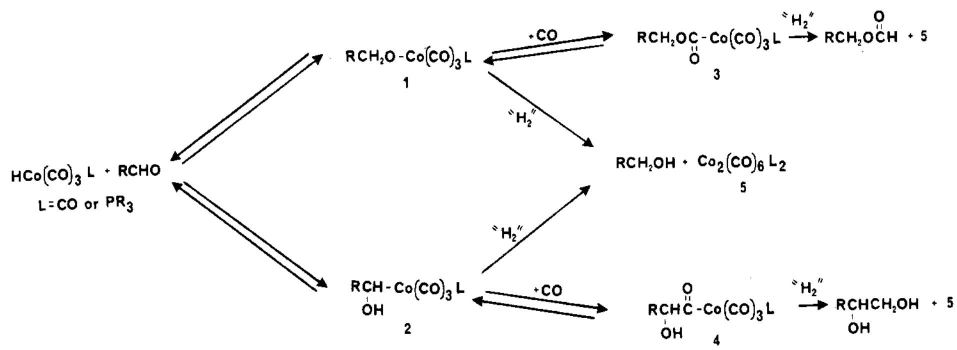
Scheme I. Possible Pathways for Aldehyde Addition and Subsequent Carboxylation



at high pressures (3500–5000 psig) and temperatures (175–200 °C) for unmodified $Co_2(CO)_8$ or at lower pressures (~500 psig) for tertiary phosphine modified systems. The early mechanistic studies of Heck,[8] Orchin,[9] and Marko[10] all proposed that such aldehyde reduction occurred via aldehyde addition to $HCo(CO)_4$ or $HCo(CO)_3L$ (for the PR_3-modified systems) to generate an alkoxy intermediate, **1**, which can then undergo hydrogenolysis to alcoholic products (Scheme I). The appearance of formates (a byproduct observed in <5% yields during most hydroformylation reactions) was rationalized as due to further CO insertion into **1** and subsequent hydrogenolysis.[11] The products expected from carbonylation and hydrogenolysis of the possible cobalt–carbon bonded intermediate **2**, α-hydroxy aldehydes or 1,2-diols, have not been reported as hydroformylation byproducts. This should not be interpreted as evidence against the formation of such intermediates, but rather only that such intermediates, if present, do not undergo further carbonylation and hydrogenolysis under "normal" conditions.

Marko[13] has shown that 35% formate selectivity can be achieved with $HCo(CO)_4$ under 4500 psig of synthesis gas. To our knowledge no studies have examined the effect of ancilliary tertiary phosphine ligands on formate selectivity during the hydroformylation reaction. We wish herein to describe our studies concerning such subject matter.

Results and Discussion

Observation of higher than normal selectivity to formates during the $Co_2(CO)_8/PR_3$-catalyzed hydroformylation of dicyclopentadiene[1] led us to more closely examine formate formation during the hydroformylation of 1-hexene. The results of such studies are given in Table I. Four hours was chosen as a standard reaction time to ensure that complete conversion of the 1-hexene and complete aldehyde reduction had occurred. In several reactions we monitored product composition vs. time and found that formates did not decompose under these conditions and thus the selectivities shown are truely a measure of the kinetic product distribution. Reaction mass balance, obtained by gas chromatography, was in the 73–97% range. The balance of the unaccounted for material appears to be in the form of aldol condensation products and derivatives thereof which were characterized by higher retention time GC peaks and their mass spectra which indicated dimeric molecularity. The reactions, as observed previously,[1] are very dependent on the peroxide content of the 1-hexene. We found that commercial 1-hexene, on standing (months–years) formed quantities of peroxides that could not be removed by passage down a column of activated alumina. Such contaminated olefin needed treatment with ferrous sulfate and subsequent distillation prior to use. The use of contaminated olefin resulted in low formate selectivity (<10% for all PR_3 ligands examined).

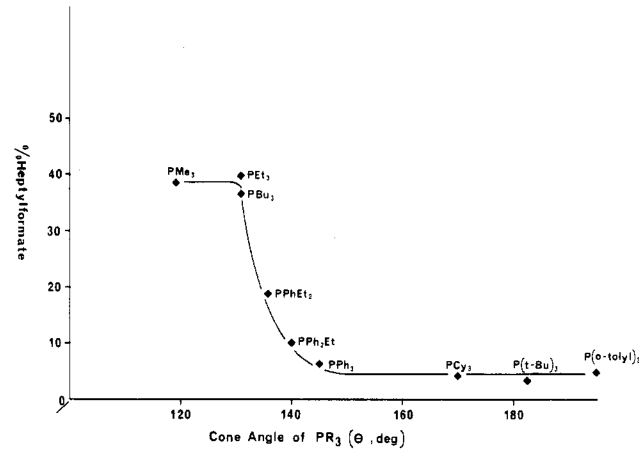


Figure 1. Dependence of formate selectivity on PR_3 cone angle.

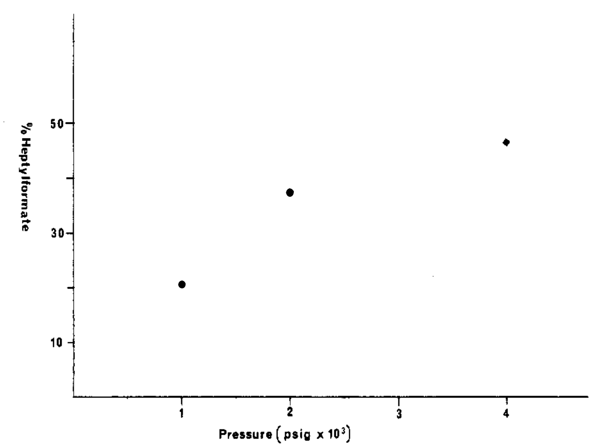


Figure 2. Dependence of formate selectivity on CO/H_2 pressure.

Formate Selectivity. Figures 1 and 2 reveal that the selectivity to formates is directly dependent on the steric nature of the organophosphine (cone angle) and the reaction pressure, respectively. Thus the relative percentage of formates observed decreases as the cone angle of the organophosphine increases and/or as the pressure decreases. These relationships should be examined in light

(8) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097.
(9) Goetz, R. W.; Orchin, M. *J. Org. Chem.* **1962**, *27*, 3698.
(10) Marko, L. *Proc. Chem. Soc.* **1962**, 67.
(11) Alkoxycobalt and carboalkoxycobalt species such as **1** and **3** have been isolated from the reaction of tetracarbonylcobaltate anion with *tert*-butyl hypochlorite followed by treatment with PPh_3.[12a] Recently the preparation of $MeOC(O)Co(CO)_4$ from the reaction of methyl oxalyl-chloride with tetracaronylcobaltate anion has been described.[12b]
(12) (a) Heck, R. F. *J. Organomet. Chem.* **1964**, *2*, 195. (b) Milstein, D.; Huckoby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.
(13) Marko, L.; Szabo, P. *Chem. Tech. (Leipzig)* **1961**, *13*, 482.

Table I. Formate Formation for $Co_2(CO)_8/PR_3$-Catalyzed Hydroformylations

run	phosphine modifier[a]	P/Co	temp, °C	press, psig	selectivity[b] hexane	heptanol	heptyl formate	mass balance[c]	% linear alcohol[d]	pK_a[i] of PR_3	cone angle,[j] deg
1	PPh_3	1	190	2000	9	70	7	86	64.3	2.7	145
2		4	190	2000	11	65	7	83	72.9		
3	$P(p\text{-}ClC_6H_4)_3$	1	190	2000	6	62	5	73	64.3	1.03	145
4	$P(p\text{-}MeOC_6H_4)_3$	1	190	2000	6	68	5	79	65.5	4.57	145
5	PPh_2Et	1	190	2000	10	70	10	90	74.4	4.92	140
6	$PPhEt_2$	1	190	2000	20	31	18	76[e]	82.8	6.25	136
7	P(*n*-butyl)$_3$	1	175	2000	13	14	40	80[f]		8.43	132
8		1	190	2000	15	48	30	93	79.1		
9	PMe_3	1	190	2000	9	52	32	93	76.7	8.65	118
10		1	190	2000	10	46	36	92	76.2		
11		1	190	3600	9	48	40	97	76.2		
12		3	190	2000	11	50	23	84	87.0		
13	PEt_3	1	190	1000	23	43	21	87	86.3	8.69	132
14		1	190	2000	13	33	37	83	76.7		
15		1	190	4000	19	18	46	83	83.3		
16		4	190	2000	18	44	24	87	89.2		
17	PCy_3	1	190	2000	13	62	4	87[g]	68.8	9.70	170
18		1	200	2000	14	65	6	85	67.5		
19	P(*tert*-butyl)$_3$	1	190	2000	6	72	3	81	69.7	11.40	182
20	$P(o\text{-}MeC_6H_4)_3$	1	190	2000	3	60	5	68	71.4	3.08	194
21			175	2800	2	52	15	69[h]	73.7		
22			200	3600	4	49	21	74[h]	70.6		

[a] $Co_2(CO)_8 + PR_3$ catalyst system. All reactions run on 1-hexene (4.0 g, 4.8×10^{-2} mmol) + $Co_2(CO)_8$ (0.08 g, 2.3×10^{-4} mmol) in 20 mL of toluene at $H_2/CO = 2$ for 4 h. [b] Based on 100% conversion unless otherwise noted, determined by GC using the internal standard method. [c] Most of the unaccounted for material in form of aldol condensation products. [d] At 100% conversion of 1-hexene. [e] 7% isomerized hexenes observed. [f] 9% isomerized hexenes; 4% heptanal observed. [g] 8% heptanal observed. [h] Some decomposition of the $Co_2(CO)_8$ was noted. [i] Taken from ref 28. [j] Taken from ref 29.

of the equilibria known to be involved[4,5,8,12] during the Co-catalyzed hydroformylation reaction (eq 1–10).[14]

$$[Co(CO)_3PR_3]_2 + H_2 \rightleftharpoons 2HCo(CO)_3PR_3 \quad (1)$$

$$HCo(CO)_3 + PR_3 \rightleftharpoons HCo(CO)_2PR_3 + CO \quad (2)$$

$$HCo(CO)_3PR_3 + RCH{=}CH_2 \rightleftharpoons RCH_2CH_2Co(CO)_3PR_3 \quad (3)$$

$$RCH_2CH_2Co(CO)_3PR_3 + CO \rightleftharpoons RCH_2CH_2C({=}O)Co(CO)_3PR_3 \quad (4)$$

$$RCH_2CH_2C({=}O)Co(CO)_3PR_3 \rightleftharpoons RCH_2CH_2C({=}O)Co(CO)_2PR_3 + CO \quad (5)$$

$$RCH_2CH_2C({=}O)Co(CO)_2PR_3 \overset{\text{"H"}}{\rightleftharpoons} RCH_2CH_2C({=}O)H + HCo(CO)_2PR_3 \quad (6)$$

$$RCH_2CH_2CHO + HCo(CO)_2PR_3 \rightleftharpoons RCH_2CH_2CH_2OCo(CO)_2PR_3 \quad (7)$$

$$RCH_2CH_2CH_2OCo(CO)_2PR_3 \overset{\text{"H"}}{\rightleftharpoons} RCH_2CH_2CH_2OH + HCo(CO)_2PR_3 \quad (8)$$

$$RCH_2CH_2CH_2OCo(CO)_2PR_3 + CO \rightleftharpoons RCH_2CH_2CH_2OC({=}O)Co(CO)_2PR_3 \quad (9)$$

$$RCH_2CH_2CH_2OC({=}O)Co(CO)_2PR_3 \overset{\text{"H"}}{\rightleftharpoons} RCH_2CH_2CH_2OC({=}O)H + HCo(CO)_2PR_3 \quad (10)$$

It has been shown that the overall hydroformylation reaction rate decreases with an increase in PR_3 basicity.[4] The fact that $HCo(CO)_4$ produces the fastest rate while $HCo(CO)_n(PR_3)_{4-n}$ give slower rates can be rationalized in terms of the position of equilibrium 2. In other words, the further to the left the equilibrium lies, the faster the reaction due to the greater proportion of the reaction that proceeded via the unligated $HCo(CO)_3$ intermediate. Such speculation was supported by studies that revealed increasing the PPh_3 concentration in Co/PR_3 catalyst systems slowed down the rate, presumably by shifting the equilibrium further to the right while increasing the concentration of PBu_3 had no effect on the rate, since it was surmised, equilibrium 2 lies far to the right already. One must compare the aforementioned results with the high-pressure IR studies of Whyman[15] and Penniger[16,17] which revealed that although complex mixtures of Co/PBu_3 species exist under CO/H_2 at low temperatures and pressures, the major species at 190 °C and 600 psig is $HCo(CO)_3(PBu_3)$. Penniger[18] also showed, in a series of very revealing kinetic studies, that under normal agitation conditions, CO mass transfer is rate limiting at 190 °C and thus eq 2 is usually forced to the right by lack of reactant CO.

Such arguments concerning equilibrium 2 clearly do not explain our formate selectivity. If the weakly basic ligands (runs 1–4, 20) give rise to a higher concentration of unligated $HCo(CO)_4$, the formate selectivity resulting from those reactions should fall somewhere between the unmodified results (runs 21–22) and the results obtained with the more basic PR_3 ligands. In fact, unmodified $Co_2(CO)_8$ results in 15–20% formate, whereas $Co_2(CO)_8$ modified by weakly basic tertiary phosphine reveal <5% formates.

As an alternative explanation, we propose stabilization of one or more of the possible stereochemical isomers of **3** (Scheme I). In other words, equilibrium 9 lies further

(14) At this point we do not wish to enter the controversy over whether hydrogenolysis ("H") occurs via an H_2 oxidative addition/reductive elimination sequence or via intermolecular reaction of $RC(O)Co(CO)_3L$ with $HCo(CO)_3L$[4-8]

(15) Whyman, R. *J. Organomet. Chem.* **1974**, *66*, C23.
(16) vanBoven, M.; Alemdaroglu, N. H.; Penninger, J. M. L. *Ind. Eng. Chem., Prod. Res. Dev.* **1975**, *14*, 259.
(17) We were limited in our experiments to 4000 psig.
(18) (a) Fahey, D. H. *J. Am. Chem. Soc.* **1980**, *103*, 136. (b) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. (c) Keim, W.; Berger, M.; Eisenbeis, A.; Kadelka, J.; Schlupp, J. *J. Mol. Catal.* **1981**, *13*, 95.

Table II. NMR and IR Data for Selected $Co_2(CO)_8/PR_3$ Complexes

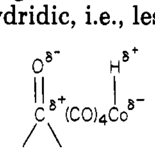
complex	^1H NMR, ppm	^{31}P NMR, ppm	IR ν(CO), cm^{-1}
$HCo(CO)_4$	10.0[a]		
$Co_2(CO)_7PPh_3$		82.4[b]	2079 (m), 2025 (m), 1995 (s), 1962 (m)
$[Co(CO)_3(PPh_3)]_2$		71.65[b]	1960 (s)
$[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-$			1995 (s), 1978 (m), 1890 (s)
$HCo(CO)_3PPh_3$	10.7 ($^2J_{P-H}$ = 51 Hz)		2041 (m), 1952 (s)
$Co_2(CO)_7PCy_3$		81.9	2079 (m), 2020 (m), 1987 (s), 1955 (m)
$[Co(CO)_3PCy_3]_2$		79.2	1963 (m), 1943 (s)
$[Co(CO)_3(PCy_3)_2]^+[Co(CO)_4]^-$		75.9	1955 (m), 1980 (m), 1890 (s)
$HCo(CO)_3PCy_3$	10.1 ($^2J_{P-H}$ = 51 Hz)	70.5	2038 (m), 1953 (s)
$Co_2(CO)_7PEt_3$		65.7	2079 (m), 2020 (m), 1990 (m), 1955 (m)
$[Co(CO)_3PEt_3]_2$		61.2	1945 (s)
$[Co(CO)_3(PEt_3)_2]^+[Co(CO)_4]^-$		59.5	1992 (s), 1890 (s)
$HCo(CO)_3PEt_3$	9.7 ($^2J_{P-H}$ = 51 Hz)	51.3	2042 (m), 1950 (s)

[a] From ref 26. [b] Assigned by analogy; standard complexes not made by independent synthesis.

to the right for PR_3 ligands with a small cone angle and further to the left for larger PR_3 ligands (all vs. unligated $HCo(CO)_3$). If one assumes the hydrogenolysis rates for **1** and **3** are comparable, this should lead to an increase or decrease in the formate selectivity respectively (eq 8 vs. eq 10).

The CO pressure should affect the position of equilibrium 9, and Figure 2 reveals this is indeed the case. Formate selectivity can be increased from 21–46% by increasing the pressure from 1000 to 4000 psig. At some point, however, the CO pressure should force equilibrium 2 to the left and no PR_3 effect should be observed.[17] We believe this has been observed during the CO hydrogenation studies of Fahey[18a] wherein he reports no difference in selectivity whether $Co_2(CO)_8$ or $Co_2(CO)_6(PEt_3)_2$ were used as catalyst at 20 000 psig and 230 °C.

Further comparisons can be made to the recent studies on homogeneous CO hydrogenation. If one assumes formaldehyde is the key intermediate,[18a] the mechanistic pathways should be the same as that shown in Scheme I. The work of Fahey,[18a] Keim,[18b,c] and others has shown that pathway II only starts to occur at pressures significantly above the 4500 psig we were limited to. We nevertheless carefully examined our reaction solutions for traces of 1,2-octanediol and found none. It has been suggested that the direction of the metal hydride addition to the aldehyde bond should be influenced by the polarity of the metal–hydrogen bond.[18a] It was therefore hoped that metal–carbon bond formation would be favored by $HCo(CO)_3(PR_3)$ when the PR_3 ligand was very basic since it would make the H more hydridic, i.e., less protonic.



As we pointed out before, **2** may be forming, but product analysis indicates that carboxylation and hydrogenolysis are not occurring under our conditions.

Effects of P/Co Ratio. Table I reveals that in the few examples examined (runs 2, 12, 16) formate selectivity is not affected by the P/Co ratio for the larger PR_3 ligands while a decrease in percent of formates is observed for the smaller ligands. It is not obvious why this is occurring. Blank reactions have shown that heptyl formate is stable in the presence of PPh_3 or PEt_3 under reaction conditions. Rationalization of this excess ligand effect should await a broader examination of PR_3 ligands, but one should mention at this point that the normal $Co_2(CO)_8/PBu_3$ hydroformylation conditions in addition to being at lower pressures than we have examined are generally at much higher PR_3–Co ratios, i.e., large excess of PR_3. Consistent with this fact is our observation that at $Co_2(CO)_8/PEt_3$ of 1:1 at 500 psig CO/H_2 we observed metal plating from solution.

Catalyst Characterization. Organophosphines are known to react with $Co_2(CO)_8$ to give yellow $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$ and red $[Co(CO)_3PR_3]_2$.[19] The concentrations of these species in solution are known to be solvent and temperature dependent. High-pressure IR studies of a solution of $Co_2(CO)_8$ + PBu_3 have identified $HCo(CO)_4$, $Co_2(CO)_7PBu_3$, and $HCo(CO)_3PBu_3$.[15,16] We find that the $^{31}P\{^1H\}$ NMR and IR spectra of a $Co_2(CO)_8$ + $2PR_3$ catalyzed hydroformylation reaction, which has been cooled, vented to atmospheric pressure, and carefully transferred under argon, reveals four products regardless of the catalyst precursor: $Co_2(CO)_8$ + $2PR_3$ in situ, $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$, or $[Co(CO)_3PR_3]_2$. The spectra were analyzed in detail for three representative tertiary phosphines, PCy_3, PEt_3, and PPh_3 (Table II).

The $^{31}P\{^1H\}$ NMR spectrum (−50 °C) of the 1-hexene hydroformylation catalyzed by $Co_2(CO)_8/2PCy_3$ reveals $Co_2(CO)_7(PCy_3)$,[20] $[Co(CO)_3(PCy_3)]_2$,[22] and $HCo(CO)_3(PCy_3)$.[24] Although the latter species have not been isolated, we assign the +72.8 ppm resonance to this structure based on selective decoupling experiments which reveal hydride coupling and ^1H NMR which reveals $^2J_{P-H}$ = 49 Hz.[25] This value is in agreement with Hieber's report[26] of 51 Hz for $HCo(CO)_3(PPh_3)$. IR ν(CO) absorptions fit nicely with ν(CO) values given for similar species.[23] In a similar fashion, ^{31}P and ^1H NMR and IR spectra were used to identify analogous species in the $Co_2(CO)_8$ + 2L (L = PPh_3 or PEt_3) systems. (See Table II for data.)[27]

(19) (a) Hieber, W.; Freyer, W. *Chem. Ber.* **1958**, *91*, 1230. (b) Vohler, O. *Chem. Ber.* **1958**, *91*, 1235.

(20) By comparison to an authentic sample prepared by the method of Marko[21] wherein $Co_2(CO)_8$ is treated with $[Co(CO)_3PCy_3]_2$ under CO.

(21) Szabo, P.; Fekete, L.; Bor, G.; Nagy-Magos, Z.; Marko, L. *J. Organomet. Chem.* **1968**, *12*, 245.

(22) By comparison to authentic $[Co(CO)_3PCy_3]_2$ prepared by the method of Manning or Slaugh.[23]

(23) (a) Manning, A. R. *J. Chem. Soc. A* **1968**, 1135. (b) Thornhill, D. S.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2086. (c) Slaugh, L. H.; Mullineaux, R. D. *J. Organomet. Chem.* **1968**, *13*, 469.

(24) We feel the ionic species $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$ is not observed by NMR due to its insolubility. At −50 °C a precipitate is observed on the bottom of the NMR tube which redissolves on warming.

(25) The reported value of 49 Hz was obtained from the ^1H NMR hydride signal (Cy decoupled).

(26) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 2933.

(27) We should note that Whyman[15] reports in his high-pressure IR work that the hydride $HCo(CO)_3(PBu_3)$ converts to $Co_2(CO)_6(PBu_3)_2$ on releasing excess Co/H_2 pressure. In all our examples we find the hydrides stable enough to observe their ^{31}P and ^1H NMR spectra after venting excess pressure from the solution. One does observe reversal to nonhydride complexes is occurring with time.

Conclusions

At a 1:1 ratio of $Co_2(CO)_8$ to PR_3, product selectivity in the hydroformylation reaction reveals a strong dependence on the cone angle of PR_3 and the CO pressure. Increased formate selectivity is explained by a stabilization of carboalkoxycobalt intermediates by organophosphines of small cone angles and a destabilization by organophosphines having large cone angles. No 1,2-diol products are observed.

Experimental Section

All operations were conducted under purified argon or nitrogen, using standard inert-atmosphere techniques. The cobalt octacarbonyl (Strem Chemical) was either sublimed or recrystallized from hexane prior to use. The 1-hexene (Aldrich, Gold Label) was checked for peroxides and purified, if needed, by extraction with aqueous ferrous sulfate. The 1-hexene and toluene were flushed with argon and stored over 4A molecular series. The trialkylphosphine cocatalysts were purchased from Strem Chemical and checked by ^{31}P NMR prior to use. The hydrogen (UHP) and carbon monoxide (UHP) were obtained from Matheson and used as received.

Infrared spectra were determined on a Beckman IR4240 spectrometer. NMR spectra were recorded on a JEOL FX90-Q spectrometer equipped with a broad-band, tunable probe. Phosphorus-31 chemical shifts were referenced to external 85% H_3PO_4.

1-Hexene Hydroformylation. In a typical reaction, a mixture of 4.0 g of 1-hexene, 1.0 g of decane (internal standard), 0.08 g of $Co_2(CO)_8$, 1 or 2 equiv of PR_3, and 20 mL of toluene was loaded into a glass reactor vessel in an inert atmosphere drybox. The vessel was placed into a 300 cm^3 stirring reactor (Autoclave Engineers), and the system was purged with argon. The reactor was pressurized to 1600 psig of syn-gas and heated to 195-200 °C in about 20 min. At that temperature, the reactor pressure was ~2000 psig. Reaction times were 4 h. The reactor was then cooled to room temperature and depressurized to give a red solution which was analyzed.

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Product Analysis. The hydroformylation products were determined by GLC analysis that were performed on a Hewlett-Packard 5730A gas chromatograph using a 30-m SE30 capillary column. These products were characterized by GC/MS (Hewlett-Packard 5985) and ^{13}C NMR/JEOL (FX90-Q) comparison with authentic samples obtained from Aldrich. The heptyl formate was prepared by esterification of heptanol with formic acid. Yields were determined vs. an internal standard with experimentally determined response factors.

Preparation of $[Co(CO)_3(PR_3)_2]^+ [Co(CO)_4]^-$. These compounds were prepared as described in the literature.[23] For example, a toluene solution containing 0.50 g of $Co_2(CO)_8$ was treated with 0.82 g of $P(C_6H_{11})_3$ and stirred for 1 h. Filtering the mixture gave 0.90 g of yellow $\{Co(CO)_3[P(C_6H_{11})_3]_2\}^+[Co(CO)_4]^-$ (70% yield).

Preparation of $[Co(CO)_3PR_3]_2$. These products were prepared as described in the literature.[23] For example, a toluene solution of 0.50 g of $Co_2(CO)_8$ and 0.82 g of $P(C_6H_{11})_3$ was heated to reflux under nitrogen for 2 h. The toluene was concentrated in vacuo, and 1.1 g of red $[Co(CO)_3P(C_6H_{11})_3]_2$ was isolated by filtration (90% yield).

Preparation of $Co_2(CO)_7PR_3$. For example, a mixture of 0.10 g of $[Co(CO)_3P(C_6H_{11})_3]_2$ and 0.6 g of $Co_2(CO)_8$ in 10 mL of toluene was heated to 60 °C for 4 h under CO. A red solution was isolated, and IR analysis confirmed the presence of $Co_2(CO)_7P(C_6H_{11})_3$.[21]

Characterization of $HCo(CO)_3PR_3$. A mixture of 0.20 g of $Co_2(CO)_8$ and 0.32 g of $P(C_6H_{11})_3$ in 20 mL of toluene was heated in the stirring autoclave at 200 °C for 0.5 h under 2000 psig syn-gas. The reactor was cooled to 0 °C via an ice bath, and the contents were isolated. The toluene was removed in vacuo at -78 °C to remove the dimer and salt products. The solution was then analyzed by ^1H and ^{31}P NMR spectroscopy at -50 °C.

Registry No. 1-Hexene, 592-41-6; heptyl formate, 112-23-2; PPh_3, 603-35-0; $P(4\text{-}ClC_6H_4)_3$, 1159-54-2; $P(4\text{-}MeOC_6H_4)_3$, 855-38-9; PPh_2Et, 607-01-2; $PPhEt_2$, 1605-53-4; $P(n\text{-}C_4H_9)_3$, 998-40-3; PMe_3, 594-09-2; PEt_3, 554-70-1; PCy_3, 2622-14-2; $P(t\text{-}C_4H_9)_3$, 13716-12-6; $P(o\text{-}CH_3C_6H_4)_3$, 6163-58-2; $Co_2(CO)_8$, 10210-68-1; $Co_2(CO)_7PPh_3$, 15906-55-5; $[Co(CO)_3PPh_3]_2$, 10170-27-1; $HCo(CO)_3PPh_3$, 19537-79-2; $Co_2(CO)_7PCy_3$, 18947-76-7; $[Co(CO)_3PCy_3]_2$, 32875-65-3; $[Co(CO)_3(PCy_3)_2^+[Co(CO)_4]^-$, 22900-17-0; $HCo(CO)_3PCy_3$, 87615-25-6; $Co_2(CO)_7PEt_3$, 16456-69-2; $[Co(CO)_3PEt]_2$, 16456-70-5; $[Co(CO)_3(PEt_3)_2]^+[Co(CO)_4]^-$, 54438-20-9; $HCo(CO)_3PEt_3$, 87615-26-7; $[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-$, 55397-73-4.

Communications

Photochemistry of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and Related Complexes in Rigid Matrices at Low Temperature: Loss of Carbon Monoxide from the Trans Isomer To Yield Triply CO-Bridged Species

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Received September 23, 1983

Summary: Near-UV irradiation of $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_4$ (R = H, Me, Bz) in an organic matrix at 77 K yields formation of $(\eta^5\text{-}C_5R_5)_2Fe_2(CO)_3$ having a symmetrical triply CO-bridged structure. Interestingly, only the trans isomer of the starting species undergoes efficient photoreaction.

Metal complexes having a two-electron metal-metal bond are known to be generally reactive upon photoexcitation to give metal-centered radicals.[1] Recently, results in this laboratory have shown that photoexcitation of $Mn_2(CO)_{10}$ in rigid matrices at low temperature yields only net loss of CO, not $Mn(CO)_5$ radicals found to dominate the photoproducts in fluid solution at 298 K.[2] Presumably, the cage effect associated with the rigid matrix contributes to the dramatic change in the net photoreaction. Thus, even though extrusion of a small two-electron donor ligand has a low quantum efficiency, it is possible to bring about clean formation of coordinatively unsaturated dinuclear molecules.

We now report that *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and related complexes lose CO upon photoexcitation in rigid media at low temperature to yield triply CO-bridged

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