d orbital is available for bonding. Even for coordinatively saturated compounds, the validity of such an hypothesis must seriously be questioned. Thus, the existing data from NMR spectroscopy on rotational barriers in metal carbenes, while interesting, do not necessarily provide information on the $\pi$-bond strengths in these compounds. Alternative criteria need to be adopted.

Calculated Mulliken $\pi$-overlap populations[13] for planar dihydridomethylidenetitanium, **1a**, and dihydridomethylidenezirconium, **5a**, are of comparable magnitude to that in isobutene and significantly larger than values for main-group isobutene analogues, i.e., 1,1-dimethylsilaethylene, 1,1-dimethylgermaethylene, and 1,1-dimethylstannaethylene.[14] This suggests that the $\pi$-bond strengths in both the eight-electron titanium and zirconium methylidene complexes may be comparable to those in normal olefins, e.g., 65 kcal $mol^{-1}$ in ethylene,[15] and considerably larger than those in the main-group olefin analogues, ca., 30–45 kcal $mol^{-1}$.[16] Increased coordination of the metal leads to a marked decrease in $\pi$-overlap population and presumably to a decrease in $\pi$-bond strength.

The present results are qualitative and must await better theoretical treatments and/or experimental thermochemical measurements. Both are in progress in our laboratory. They do suggest, however, that $\pi$-bonds between carbon and transition metals are likely to be much stronger than those in analogous main-group compounds. This is entirely consistent with the multitude and diversity of known transition-metal carbenes, compared to the scarcity of stable compounds incorporating double bonds between carbon and heavier main-group elements.

**Registry No.** **1a**, 78499-81-7; **2a**, 85028-89-3; **3a**, 85028-90-6; **4a**, 79899-81-3; **5a**, 85028-91-7.

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[13] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

[14] W. J. Pietro, M. M. Francl and W. J. Hehre, unpublished calculations.

[15] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

[16] W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, **104**, 4329 (1982), and references therein.

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# Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. 3. Hydroformylation Catalyzed by the Products of the Interaction of $Co_2(CO)_8$ with 1,1′-Ferrocenylenephenylphosphine Oligomers and Polymers

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Reactions of $Co_2(CO)_8$ with ferrocenylphosphine oligomers of the type $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (I, $x = 1$–4) and $Ph_2P[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (III, $x = 1$, 2) or polymers of the type $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xOH$ (II, $\bar{M}_w$ 8900–161 000 amu) have been studied. Detailed IR and $^{31}P$ NMR spectroscopic investigations revealed that the polymeric ligands chelate Co in a tridentate fashion, similar to I ($x = 3$), when a high P/Co ratio is used. Use of such Co catalysts at 170–190 °C for the hydroformylation of 1-hexene revealed reactivity and selectivity similar to those of $PPh_3$ for ligands of type I and type III, while Co complexes of the polymers, II, demonstrated a $\bar{M}_w$-dependent activity and a lower selectivity to alcohols. It is felt that the observed tendency for tridentate chelation in these complexes inhibits the aldehyde-to-alcohol reduction step. A $^{31}P$ NMR study of the cobalt complex of the trimer I ($x = 3$) provided evidence for the presence of two enantiomeric isomers and selective quadrupolar broadening in the equatorial direction.

## Introduction

We have recently reported[1] that the reaction of (1,1′-ferrocenediyl)phenylphosphine with 1 molar equivalent of 1-lithio-1′-(diphenylphosphino)ferrocene in THF resulted in the formation of oligomers. After hydrolysis, species of type I were obtained ($x = 1$–5) which were separated by preparative-scale high-performance liquid chromatography. In a similar fashion, reaction of 1 or 2 molar equivalents of 1-lithio-1′-(diphenylphosphino)ferrocene with two of diphenylchlorophosphine or one of phenyldichlorophosphine resulted in the isolation of symmetrical dimer III ($x = 1$) or trimer III ($x = 2$), respectively. Under appropriate conditions (temperature, mode of addition, solvent), the reaction of 1,1′-dilithioferrocene tetra-

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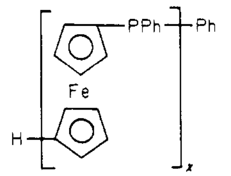
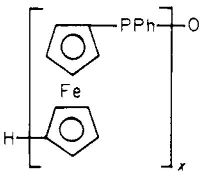
[1] Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrou, P. E.; Martin, S. *Organometallics* **1982**, *1*, 1283.

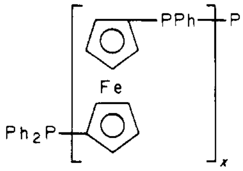
0276-7333/83/2302-0818$01.50/0



I



II



III

methylethylenediamine with phenyldichlorophosphine gave high molecular weight ($\bar{M}_w$) polymers (IIA, 8900; IIB, 47000, IIC, 55000, IID, 161000). Both the oligomers and polymers were found to be thermally stable ≥350 °C in air.

These polymers (and oligomers), unlike those isolated previously,[2] contain tertiary phosphines with the ability to coordinate to transition metals. The preparation of immobilized transition-metal complexes on organic supports has attracted widespread attention over the past decade.[4] It is important for such materials to be inert to the reaction mixture and able to withstand the required reaction conditions (temperature, pressure, etc.).

Our studies[5] and those of others[6,7] have revealed that the phosphinated polystyrene analogue of the Shell Co/$PR_3$ catalyst system cannot endure the vigorous (>185 °C) reaction temperatures necessary to generate the desired alcoholic products from hydroformylation reactions.

It was of interest, therefore, to examine I and II as supports for $Co_2(CO)_8$ and to investigate the catalytic activity of such species in the hydroformylation reaction. In addition, the solubility of the highly linear polymers, II, in solvents such as $CH_2Cl_2$ allows $^{31}P\{^1H\}$ NMR study of the interaction of II with $Co_2(CO)_8$ in solution.[9] Attempts thus can be made to correlate the solution IR and NMR data with the concentration of the various cobalt species present before and after the hydroformylation reaction.

## Results and Discussion

**Reaction of $Co_2(CO)_8$ with $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (I) and $Ph_2P[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (III).** The initial products of the reactions of monotertiary phosphines with $Co_2(CO)_8$ are the ionic complexes *trans*-$[L_2Co(CO)_3][Co(CO)_4]$ that are, depending on solvent and temperature, readily transformed into covalent $[(L)Co(CO)_3]_2$ derivatives.[11,12] The reaction of $Co_2(CO)_8$ with $R_2M(CH_2)_nMR_2$ (R = alkyl, aryl, M = P or As, $n > 1$) is known to give various products, depending on R, M, and $n$.[13] Kotz et al.[14] have studied the reaction of I ($x = 1$) with $Co_2(CO)_8$ in $CH_2Cl_2$ and isolated and characterized ($\nu$(CO) 2064 (w), 1987 (s), 1870 (vs) $cm^{-1}$) $[(L)_2Co(CO)_3][Co(CO)_4]$, IV. Our data verify that this is the isolated product, whether the solvent is $CH_2Cl_2$ or toluene. The $^{31}P\{^1H\}$ NMR spectrum of IV showed a singlet at 49.4 ppm. When left standing in solution, IV converts to a covalent dimer having a single $^{31}P\{^1H\}$ NMR resonance at 56.4 ppm.

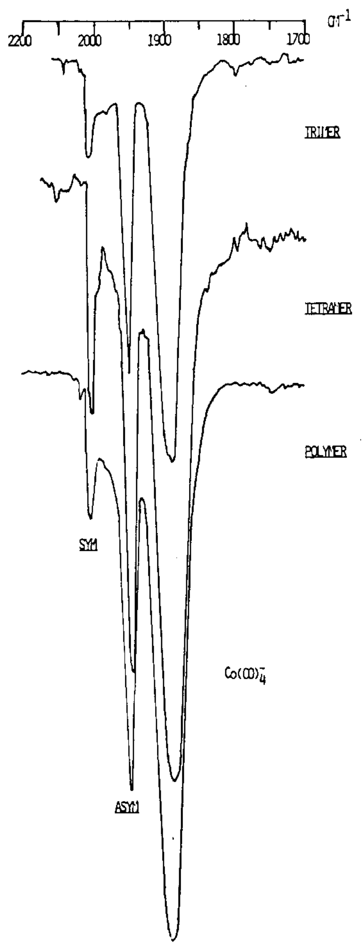


**Figure 1.** IR spectra of the products from the interaction of $Co_2(CO)_8$ with trimer VII, tetramer VIII, and polymer IIB (in $CH_2Cl_2$).

$Co_2(CO)_8$ reacts with III ($x = 1$) at 0 °C in THF, in 1:1 or 2:3 molar ratios, to produce a mixture of products that we identified as $[Co(CO)_3(L\sim L)][Co(CO)_4]$, Va, and $[Co_2(CO)_4(L\sim L)_3][Co(CO)_4]_2$, Vb, by their overlapping $\nu$(CO) absorptions at 2005 and 1885 $cm^{-1}$ and at 1995, 1955, and 1885 $cm^{-1}$, respectively.[15] No effort was made to

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[2] Polymers of the type $H[-\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh(O))-]_x OH$ have been prepared[3] by the Lewis acid catalyzed polycondensation of ferrocene with phenyldichlorophosphine. No polymer was obtained with $\bar{M}_w$ greater than 6000 and no effort was made to isolate unoxidized phosphine polymers.

[3] (a) Neuse, E. W.; Chris, G. J. *J. Macromol. Sci., Chem.* **1967**, *A1* (3), 371. (b) Pittman, C. U. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2927.

[4] (a) Whitehurst, D. D. *CHEMTECH* **1980**, 44. (b) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109.

[5] Wood, C. D.; Garrou, P. E., submitted for publication.

[6] Trevillyan, A. E. U.S. Patent 4045493, 1977.

[7] Although an early publication[8] indicated recycling of such Co/polystyrene/phosphine catalysts was achieved, close examination of the data reveals substantial losses of both Co and P (see polymer discussion section).

[8] Evans, G. O.; Pittman, C. U.; McMillian, R.; Beach, R. T.; Jones, R. *J. Organomet. Chem.* **1974**, *67*, 295.

[9] Earlier studies[8] on the interaction of $Co_2(CO)_8$ with phosphinated polystyrene were effected using only IR spectroscopy. Immobilized homogeneous catalysts also can be examined by high-resolution $^{31}P\{^1H\}$ solid-state NMR using magic-angle-spinning techniques.[10]

[10] Bemi, L.; Clark, H. C.; Davies, J. A.; Drexler, D.; Fyfe, C. A.; Wasylishen, R. *J. Am. Chem. Soc.* **1982**, *104*, 438.

[11] Heck, R. F. *J. Am. Chem. Soc.* **1975**, *85*, 657.

[12] Manning, A. R. *J. Chem. Soc. A* **1968**, 1135.

[13] Thornhill, D. J.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2086.

[14] Kotz, J. C.; Nivert, C. L. *J. Organomet. Chem.* **1973**, *52*, 387.

[15] Thornhill and Manning[13] have isolated and identified $Co(CO)_3(L\sim L)^+$ ($L\sim L = Ph_2P(CH_2)_4PPh_2$) and $Co_2(CO)_4(L\sim L)_3^{2+}$ ($L\sim L = Ph_2P(CH_2)_2PPh_2$) with $\nu$(CO) at 2001 $cm^{-1}$ and at 2007 and 1955 $cm^{-1}$, respectively. The notations $L\sim L'\sim L$ etc. that follow are meant to be a shorthand dipiction of the ferrocenyl phosphine oligomers of type I or III which are symmetric or asymmetric respectively.

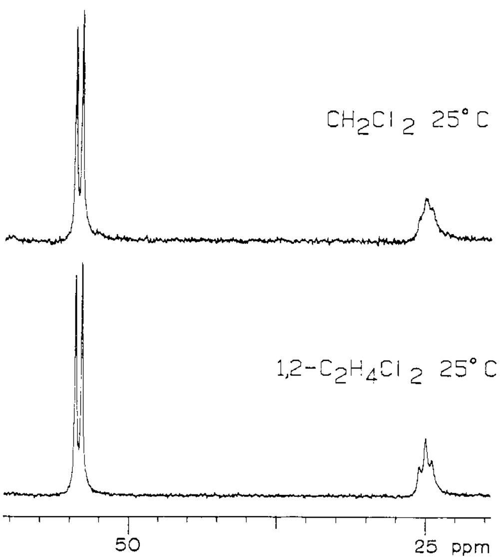


**Figure 2.** 36.2-MHz $^{31}P\{^1H\}$ NMR spectra of III ($x = 2$) in (A) $CH_2Cl_2$ and (B) 1,2-$C_2H_4Cl_2$.

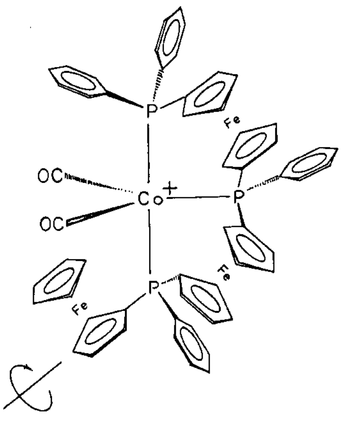


**Figure 3.** Proposed stereochemistry for one possible isomer of VII.

separate or isolate these materials in pure form. As we changed the reactant molar ratio from 1:1 to 2:3, the quantity of Va produced increased relative to Vb. When the mixture was left standing in solution, an insoluble precipitate formed (Vc, $\nu$(CO) 2023 (vw), 1979 (sh), 1945 (s) cm$^{-1}$) which is probably similar to the insoluble $[-(CH_2)_4PPh_2-Co_2(CO)_6-Ph_2P(CH_2)_4-]_x$ ($\nu$(CO) 1946 (s), 1973 (sh), 2026 (vw).[13] Reactions of $Co_2(CO)_8$ with the asymmetrical dimer I ($x = 2$) appear to be similar and were not investigated further.

By far the most interesting results, and those most pertinent to the catalytic studies using type II polymeric ligands, were obtained from the reaction of the trimers I ($x = 3$ and III ($x = 2$) and tetramer I ($x = 4$) with $Co_2(CO)_8$. $Co_2(CO)_8$ reacted with III ($x = 2$) to give $[Co(CO)_2(L{\sim}L{\sim}L)][Co(CO)_4]$, VI ($\nu$(CO) 2012, 1950, 1884 cm$^{-1}$; Figure 1), consistent with the structural assignment for $[Co(L{\sim}L'{\sim}L)(CO)_2][BF_4]$ ($L{\sim}L'{\sim}L = Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$), $\nu$(CO) 2007, 1953 cm$^{-1}$).[16] The $^{31}P\{^1H\}$ NMR spectrum of VI at −70 °C in $CD_2Cl_2$ revealed an $A_2B$ pattern with $^2J_{P-P'} = 20.1$ Hz. When the solution was warmed up, no fluxional processes were observed. At 25 °C, broadening of the high-field (bridging P) resonance occurred while the low-field signal was sharp and still maintained its 20.1-Hz coupling. Changing the solvent to 1,2-dichloroethane (viscosity change from 0.49 to 0.76 cP) returned much of the triplet structure to the high-field resonance (Figure 2). We believe this is an example of a directional quadrupolar effect, i.e., partial decoupling of the $^{31}P-^{59}Co$ spin–spin coupling resulting from the rapid quadrupolar relaxation of the $^{59}Co$ nucleus with spin $I = {}^7/_2$. At low temperatures (−70 °C) the quadrupolar relaxation is very effective (the rotational correlation times are long because of the relatively higher viscosity and lower temperature). As the temperature is raised or the viscosity of the solvent decreased, the line-shape effects due to quadrupolar relaxation become more pronounced. Such effects have been noted before[17] for complexes of the type $Co[P(OR)_3]_5^+$. We propose the structure shown below for VI since the bridging P, upfield resonance, is broadened

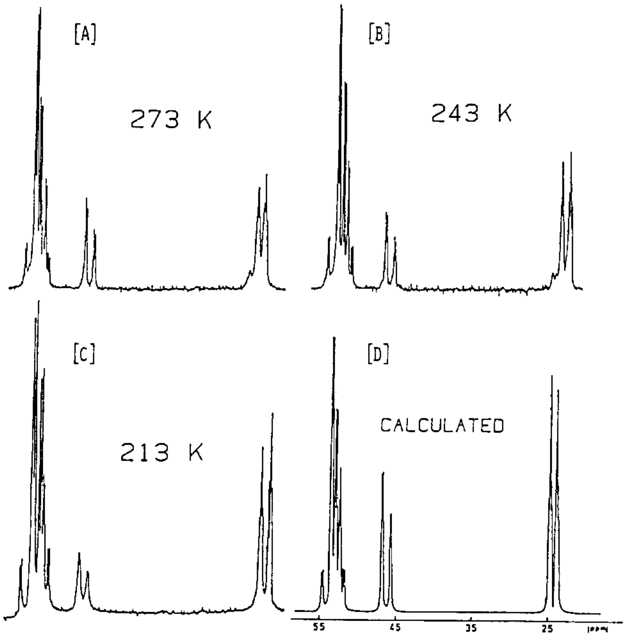
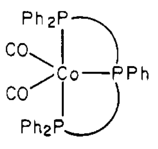


**Figure 4.** 101.3-MHz $^{31}P\{^1H\}$ NMR spectra for VIIa and VIIb at (A) 273 K, (B) 243 K, (C) 213 K, and (D) simulated.



VI

and it is known that $J_{P_B-Co} > J_{P_A-Co}$.[17] This proposed structure is also consistent with the $\nu$(CO) values previously described[16] and the $^2J_{P-P'}$ value of 20 Hz,[18] indicating cis phosphine stereochemistry.

Reaction of $Co_2(CO)_8$ with I ($x = 3$) also resulted in the isolation of $[Co(CO)_2(L''{\sim}L'{\sim}L)][Co(CO)_4]$, VII. The relative intensities of the symmetric (high-frequency) and antisymmetric (low-frequency) stretching vibrations can be used to calculate a C–Co–C bond angle of 115°.[20] Thus

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[16] Dubois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076.

[17] Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5760.

[18] Our reported $^2J_{P_{ax}-P_{eq}}$ of 20 Hz at first appears out of line with Meek's[16] report of 74 Hz for $Co(CO)_2(L{\sim}L'{\sim}L)^+$ ($L{\sim}L'{\sim}L = Ph_2P(CH_2)_3PPh(CH_2)_3-PPh_2$). However, $^2J_{P_{ax}-P_{eq}}$ for $L{\sim}L'{\sim}L = PPh_2(CH_2)_2PPh(CH_2)_2PPh_2$ is reported[16] to be 33 Hz. Since the nature of P–P coupling in such chelating phosphine systems is presently unclear,[19] it is not surprising that the angular changes around phosphorus caused by the different bite angles of these various ligands cause drastic changes in $^2J_{P_{ax}-P_{eq}}$.

[19] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 244.

[20] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience, New York, 1972; p 697.

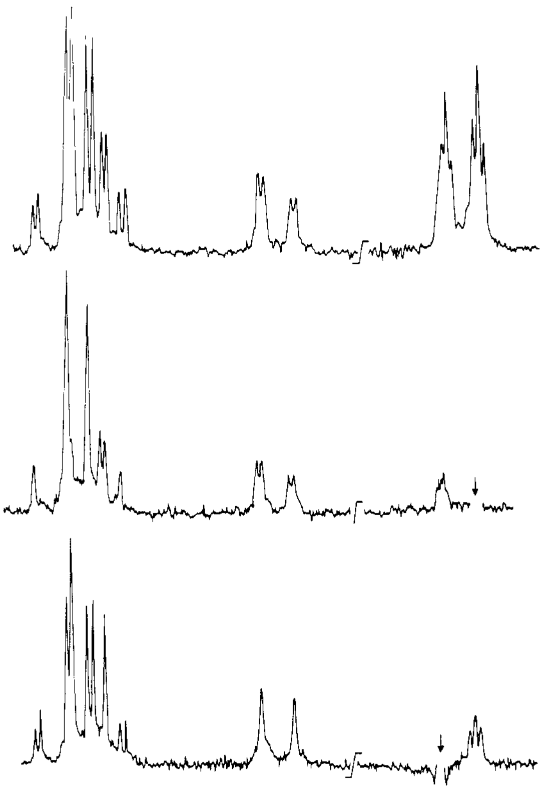


**Figure 5.** 109.3-MHz $^{31}P\{^1H\}$ homonuclear phosphorus-decoupled spectrum of VIIa and VIIb at 0 °C.

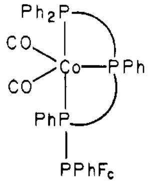
we can again assign a trigonal-bipyramidal structure with equatorial CO's similar to VI as shown in Figure 3.

$^{31}P\{^1H\}$ NMR spectra recorded at 101.3 MHz (Figure 4) are consistent with the presence of two isomers VIIa and VIIb in a 10:7 ratio which appear as two overlapping ABX spin systems. Complete line assignments were made possible by homonuclear phosphorus decoupling experiments (Figure 5). Arrows indicate site of irradiation. Note saturation can be observed in the nearby X portion of the ABX spin system of the other isomer due to its proximity to the irradiating signal. Isomeric ratios were calculated from a computer-simulated spectrum (Figure 4). The fit agrees nicely except for the broadening observed at higher temperatures for the high-field, bridging phosphorus resonance. Again this is explained by the aforementioned quadropolar effects of Co which are larger in the equatorial direction, since $J_{Co-P_e} < J_{Co-P_a}$.

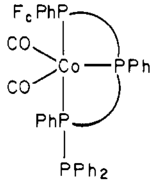
$|^2J_{P-P}|$ for isomer VIIa ($J_{AB}$ = 112 Hz, $J_{AX}$ = 17.9 Hz, $J_{BX}$ = 20.8 Hz) are consistent with the $J_{P-P'}$ data for VI. No fluxional behavior is observed between −90 and 25 °C. The chemical shifts for the AB portion of VIIb give evidence for an unusual chemical shift anisotropy, since the "B" portion is found ~5 ppm upfield from its chemical shift in VIIa. A possible explanation is that either the phenyl or ferrocenyl moiety (denoted by the rotation axis in Figure 3) is in position to sterically interact with the Co. Consistent with this is the fact that at −70 °C, the "B" portion begins to broaden without loss of coupling to the A or X portions (Figure 4). Examination of models indicates that restricted rotation about the ferrocenyl–phosphorus axis could be responsible for this broadening. Except for this behavior, VIIa is similar to isomer VIIb, i.e., $J_{AB}$ = 113 Hz and $J_{BX}$ = $J_{AX}$ = 16.4 Hz.

Since we have previously shown[1] that the high-field $^{31}P\{^1H\}$ NMR spectrum reveals chemical shift differences for the two enantiomeric pairs of I ($x$ = 3), it is reasonable to assume that VIIa and VIIb are the chiral cobalt phosphine species derived from these.

$Co_2(CO)_8$ reacted with I ($x$ = 4) to give complex VIII with $\nu$(CO) similar to that observed for the trimer (see Figure 1). The 101.3-MHz $^{31}P\{^1H\}$ NMR spectrum of VIII is extremely complex, revealing a 3:1 ratio of bound to free phosphorus, but in general is consistent with that observed for VIIa and VIIb. It is interesting to note that the $Ph_2P$ terminus of I ($x$ = 4) appears to bind preferentially compared to the $F_cPhP$ end as observed by a 1:4 ratio of the respective free ligand resonances. The complexity of the spectrum is again expected since there are now four enantiomeric pairs and either end of the ligand can dangle free (VIIIa vs. VIIIb).



VIIIa



VIIIb

**Interaction of $Co_2(CO)_8$ with Type II Polymeric Ligands.** The main impetus for new polymeric supports for the Co/phosphine catalyzed hydroformylation reaction is thermal stability. Trevillyan[6] has pointed out that conventional polystyrene polymers have poor thermal stability at the elevated temperatures required for hydroformylation. To overcome this, the diphenylphosphino substrate was bound to polyphenylene backbones. Such materials had excellent thermal stability, allowing reaction temperatures of 195 °C to be conveniently achieved in the hydroformylation reaction. In contrast, Pittman,[8] using the cobalt catalysts obtained by reaction of $Co_2(CO)_8$ with polystyrene-bound diphenylphosphino groups of various phosphorus coverages and percent cross-linkings, presented data that revealed a 42% loss of Co and a 20% loss of *phosphorus* after only 6 h at 172 °C. This *phosphorus* loss obviously is due to thermal degradation of the carrier resin.

The Co complexes that form from the interaction of $Co_2(CO)_8$ with phosphinated supports should be dependent on the proximity of the phosphorus atoms and the P/Co ratio. In previous studies using phosphinated polystyrene,[8] in which the P loading varied from 1.76 to 4.95%, these resins were treated with large molar excesses of $Co_2(CO)_8$. In all cases the IR spectra of the resin-bound Co complexes ($\nu$(CO) 2045 (m), 1992 (s), 1886 (s)) were consistent with the formation of $[Co(CO)_3(L)_2][Co(CO)_4]$.

We have found that the polymers of type II react with $Co_2(CO)_8$ in methylene chloride with a Co/P ratio of 1:3.7 to give brown, homogeneous solutions whose IR absorptions (Figure 6) indicated coordination similar to that observed for the trimer and tetramer, i.e., $[Co(CO)_2(L''{\sim}L'{\sim}L)][Co(CO)_4]$, VII. The $^{31}P\{^1H\}$ NMR spectra of such materials, IX (Figure 7), can be analyzed similarly to the trimer and tetramer spectra, i.e., resonances at ~26.2 ppm for the equatorial phosphines and axial resonances at ~51.3 and ~45 ppm for isomer IXa and 21.2 and 48.7 ppm for the equatorial and axial phosphines of isomer IXb. Free ligand was observed at −32.5 ppm, indicating that all of the phosphorus has not been coordinated. A small resonance also was observed at 52.8 ppm. This increased in intensity when the polymers were treated with $Co_2(CO)_8$ at a Co/P ratio of 1:1.9 (Figures 6 and 7). We believe that this is due to *trans*-$[Co(CO)_3(L)_2][Co(CO)_4]$ since the infrared spectrum reveals $\nu$(CO) bands at 2075, 1998, 1985, and 1950 cm$^{-1}$ (increasing in intensity vs. 2002 and 1890 cm$^{-1}$). We feel that these data are consistent with the following interpretation. At low Co/P ratios, $Co_2(CO)_8$

Table I. Hydroformylation of 1-Hexene Using $Co_2(CO)_8$/Ferrocenylphosphine Catalysts

| cat.[a] | $M_w$ of polymer | time, h | temp, °C | solv | conversn[c] | selectivity, % alcohols | aldehydes | alkanes | formates | L/B (alcohols)[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| IV | monomer | 3 | 170 | toluene[b] | 100 | 61.0 | 7.0 | 4.0 | 2.0 | 1.9 |
| Va and Vb | dimer | 3 | 170 | toluene[b] | 100 | 51.0 | 16.0 | 3.0 | 4.0 | 1.7 |
| VIIa and VIIb | trimer | 3 | 170 | toluene[b] | 100 | 57.0 | 5.0 | 3.0 | 5.0 | 2.5 |
| IXA | 8900 | 3 | 170 | toluene[b] | 100 | 10.0 | 54.0 | 3.0 | 4.0 | 2.0 |
| $PPh_3$ |  | 3 | 170 | toluene[b] | 100 | 50.0 | 10.0 | 4.0 | 6.0 | 2.1 |
| IX | 8900 | 10 | 190 | THF | 100 | 77.0 | 8.4 | 4.6 | 1.6 | 1.8 |
| IX | 47000 | 10 | 190 | THF | 100 | 52.3 | 26.7 | 6.7 | 0.4 | 1.5 |
| IX | 161000 | 10 | 190 | THF | 92 | 34.7 | 39.9 | 7.9 |  | 1.4 |

[a] All reactions under 2000 psig, 1:2 $CO/H_2$. [b] Solubility low (see text). [c] Unaccounted for material thought to be in the form of aldol-condensation products. [d] L/B = linear/branched.

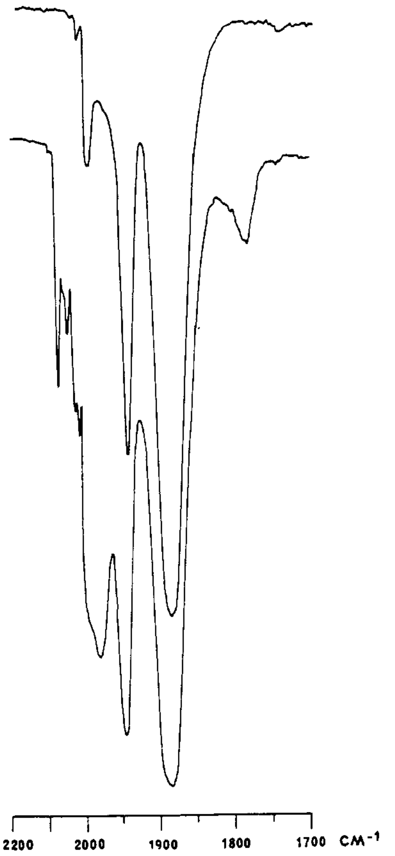


**Figure 6.** $Co_2(CO)_8$ loaded onto IIB (in $CH_2Cl_2$): (A) Co/P = 1:3.7; (B) Co/P = 1:1.9.

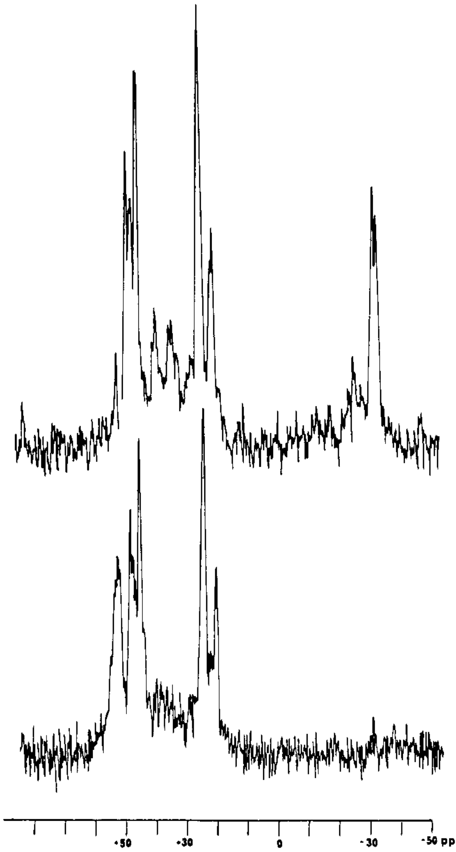


**Figure 7.** 36.2-MHz $^{31}P\{^1H\}$ NMR spectrum of $Co_2(CO)_8$ loaded onto IIB: (A) Co/P = 1:3.7; (B) Co/P = 1:1.9.

reacts to form mostly species in which the polymers are acting like a tridentate chelate to the metal. At higher Co/P ratios, $Co_2(CO)_8$, finding less available phosphorus, produces more bidentate-type complexes in a fashion similar to the previous results with polystyrene.[8]

Infrared and $^{31}P\{^1H\}$ NMR spectral characterizations also were conducted on polymer solutions after exposure to 2000 psig of 1:2 $CO/H_2$ at 190 °C for 30 min to see if any irreversible structural changes were induced. Selective $^1H$ decoupling NMR experiments at −20 °C (aromatic and Cp proton resonances only) on IIB loaded with $Co_2(Co)_8$ (Co/P = 1:3.5) revealed no hydride resonances.[21] The $^{31}P\{^1H\}$ NMR spectra were virtually identical with the spectra of solutions before exposure to syn gas, the only difference being the slight growth of unidentified resonances at ~35 ppm.

Reaction of IIC loaded with $Co_2Co_8$ (Co/P = 1:3.5) with 2000 psig of 1:2 $CO/H_2$ for 10 h at 190 °C resulted in black, homogeneous solutions that failed to give NMR signals. We presume that paramagnetic decomposition products (which could not be removed by filtering) or paramagnetic reaction products were obtained. Infrared spectra of these solutions were complex (ν(CO) 2045 (w), 2020 (sh), 1998 (s), 1970 (w), 1935 (s), 1885 (vs) $cm^{-1}$) but indicated the presence of species not present before this prolonged reaction with syn gas (Figure 8).

**Hydroformylation.** Results of the hydroformylation of 1-hexene using cobalt complexes of the ferrocenylphosphine monomer, dimer, oligomers, and polymers and a comparative $Ph_3P$ case are presented in Table I. The cobalt complexes of the monomer, dimer, and trimer were prepared in toluene and gave results comparable to those obtained with $Ph_3P$.[22] After the catalytic reactions were

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(21) The solution was held at 180 °C for 1 h, then cooled rapidly, and vented. The samples then were transferred quickly in a drybox to an NMR tube for analysis. Similar experiments using $P\text{-}c\text{-}Hx_3$ as the phosphine have resulted in the observation of $HCo(CO)_3(P\text{-}c\text{-}Hx_3)$.[5] We can, therefore, surmise that the hydride that forms from the Co complexes of these polymers (II) under the reaction conditions must be less stable, after the $CO/H_2$ atmosphere is vented, than its $P\text{-}c\text{-}Hx_3$ analogue.

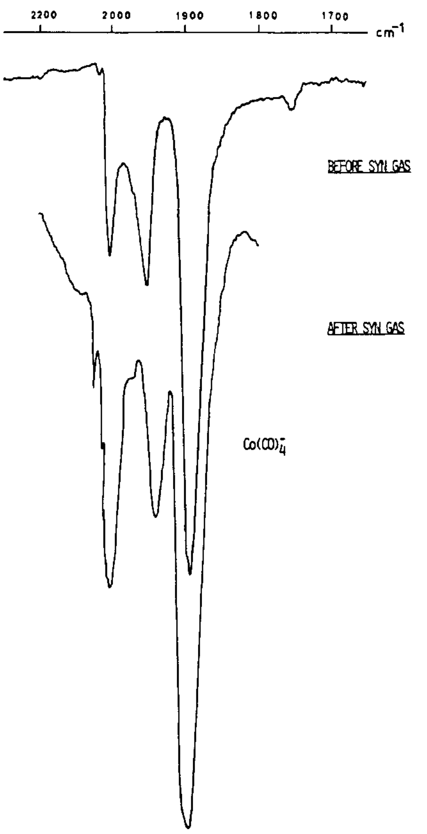
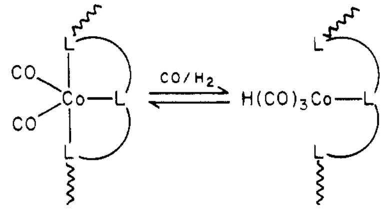


**Figure 8.** IR spectra of $Co_2(CO)_8$ on IIC (Co/P = 1:3.5) in THF before and after exposure to 2000 psig of $CO/H_2$, 190 °C for 30 min.

complete, the solutions remained homogeneous. IX ($\bar{M}_w$ 8900) revealed lower activity for the aldehyde to alcohol reduction step as evidenced by the greater amount of aldehyde observed. It should be noted that these polymers are not very soluble in toluene, and thus the reaction proceeds similarly to those with other heterogenized catalysts which typically reveal rates slower than their homogeneous counterparts.[4b] The polymers are soluble in THF, where one observes the $\bar{M}_w$ of the polymer has a pronounced effect on the selectivity. As the $\bar{M}_w$ increases, less alcohol and more aldehyde are observed. Again, since ~100% conversion of the 1-hexene is achieved in all cases, it must be assumed that the aldehyde-to-alcohol reduction is the slow step in this overall sequence. Two explanations are possible. It is known that basicity of $PR_3$ has a pronounced effect on the rate of aldehyde reduction, as does the concentration of $HCo(CO)_3PR_3$, the species thought to be responsible for the reduction.[23] Since it is unlikely that the basicity of the phosphines is changing as the molecular weight of the polymers increases, one must assume that the concentration of $HCo(CO)_3L$, the monophosphine-substituted hydride, is responsible for the difference in rate. If $HCo(CO)_3L$ is truely the active aldehyde-to-alcohol reduction catalyst, in our cases the initially tridentate chelation must dissociate to give monodentate coordination before catalytic activity can be achieved. This is probably an equilibrium reaction as shown below and in our case, the equilibrium does not lie as far to the right as we require because of the entropy of chelation and the steric contraints imposed by the entangled, though linear, polymers.



In addition it should be recalled that although ionic species of type VII are formed from reaction of $Co_2(CO)_8$ and polymer under ambient conditions, under hydroformylation conditions $HCo(CO)_4$ could be initially formed from reaction of $CO/H_2$ with the $Co(CO)_4$ anion. $HCo(CO)_4$ would be expected to equilibrate with the phosphine present to form $HCo(CO)_x(L)_x$ species, but its presence early on in the reaction may be responsible for the observed ~100% conversion of olefin to aldehyde in all cases. The $\bar{M}_w$ vs. reactivity dependence is only observed in the aldehyde to alcohol conversion step which is known to be $PR_3$ dependent.

In conclusion, it appears that Co complexes of these ferrocenylphosphine polymers desire tridentate coordination of the ligand to Co. Such chelation in the midst of such a polymeric network inhibits the specific activity of these catalysts for aldehyde to alcohol reduction. It is clear from molecular models that the phosphorus atoms in such polymeric systems need to be spaced further apart in order to avoid the strong tendencies for chelation and thus to make use of the excellent thermal stability imparted by such ligand systems.

## Experimental Section

**General Comments.** All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Air- and/or moisture-sensitive compounds were handled in a Vacuum Atmospheres HE-43 drybox. All solvents were of reagent grade, dried over activated 4A molecular sieves and deaerated. $Co_2(CO)_8$ was obtained from Strem Chemicals and recrystallized from hexane. The diphosphine III ($x = 1$) was obtained courtesy of Strem Chemicals and used without purification. The remaining oligomeric and polymeric phosphines were prepared and purified as previously described.[1] Infrared spectra were recorded on a Beckman IR 4240 spectrometer. Routine $^{31}P$ NMR analysis were carried out on a JEOL FX-90Q spectrometer operating at 36.2 MHz. High-field $^{31}P$ NMR experiments were performed on a Bruker WP-250 spectrometer operating at 101.3 MHz. Homonuclear $^{31}P\{^1H\}$ experiments were performed on a Bruker HX-270 spectrometer operating at 109.3 MHz.

For the homonuclear phosphorus decoupling experiments, the proton decoupling coil in a Bruker HX-270 probe was modified so that it could be tuned to 109.3 MHz. The modification consisted of the simple addition of a small coil wired in series with the proton coil. Altering the decoupling channel in this way was considered preferable to modifying the phosphorus observation channel through the insertion of the decoupling frequency directly into the receiver coil. The latter method had a reasonable possibility of degrading the signal-to-noise ratio.

To ensure the proper pulsing synchronization between the decoupling and observation channels, the DC pulses normally generated in the spectrometer for homonuclear proton decoupling were used to gate a standard mixer through the IF (or X) port. The output from a frequency synthesizer set to the exact decoupling frequency was connected to the LO port, and the output at the RF port fed to a 20-W ENI broad-band amplifier. A 109.3-MHz band-pass filter was used at the amplifier output to attenuate noise at other frequencies. After the filter two pairs

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(22) A reviewer points out that conclusions about relative rates of reactions based on charging a reactor and only analyzing for product formation after a fixed time are tenuous. We agree, however, product formation vs time data for the hexene hydroformylations described in this study are not available. On the basis of other proprietary hydroformylation studies, we can conclude that no induction period is observed except the normal one due to reactor heat up which was identical in all cases.

(23) Paulik, F. E. *Catal. Rev.* **1972**, *6*, 49.

of crossed diodes were employed to prevent any radio frequency (rf) output whenever the gating pulses were off. A variable attenuator placed between the frequency synthesizer and the LO port of the mixer provided suitable control of the power delivered to the decoupling coil.

The elemental analysis of the tetraphenylborate salts were performed by Schwartzkopf and were found to be consistently off, even after repeated crystallizations. Presumably, these compounds either do not combust well or there are impurities present that are interfering with the analysis but are not observable by NMR or IR spectroscopy.

**Reaction of $Co_2(CO)_8$ with Ferrocenylphosphines To Give Cobalt Carbonyl Phosphine Complexes. General Procedure.** In a typical experiment the ferrocenylphosphine was dissolved in ~10 mL of solvent and cooled to $-30$ °C. The appropriate amount of $Co_2(CO)_8$ was added, with stirring, as the solid to the cold solution, and the reaction temperature was allowed to rise to room temperature after all CO evolution had stopped (~30 min). At this point, either the reaction mixture was examined by NMR spectroscopy or the solvent was removed in vacuo to leave the crude reaction product. Purified samples could be obtained by precipitation from methylene chloride solutions containing the crude product with either hexane or toluene. The tetraphenylborate salts were prepared from the partially purified tetracarbonylcobaltate(I) salts by using a fourfold excess of $NaBPh_4$ in acetone. Addition of an excess of water precipitated the $BPh_4^-$ salt which was recrystallized from 1-propanol/acetone solution.

**(1) Reaction of $Co_2(CO)_8$ with $PPh_2Fc$, I ($x$ = 1).** $Co_2(CO)_8$ (0.23 g, 0.675 mmol) was treated with $PPh_2Fc$ (0.5 g, 1.35 mmol) in methylene chloride according to the general method. $[Co(CO)_3(PPh_2Fc)_2][Co(CO)_4]$ could be observed at this point by IR and NMR spectroscopy. When the solution was left standing overnight in a THF/$Et_2O$ solution at $-30$ °C, 0.65 g of red crystals of $[Co(CO)_3L]_2$ precipitated.

$[Co(CO)_3(PPh_2Fc)_2][Co(CO)_4]$: $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, $\delta$) 49.4 (s); IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2064 (w), 1987 (s), 1870 (vs).

$[Co(CO)_3(PPh_2Fc)]_2$: $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, $\delta$) 56.4 (s); IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 1974 (sh), 1955 (s), 1938 (sh). Elemental Anal. Calcd for $C_{50}H_{38}O_6Fe_2P_2Co_2$: C, 58.51; H, 3.73; Co, 11.48. Found: C, 56.28; H, 3.89; Co, 11.20.

**(2) Reaction of $Co_2(CO)_8$ with $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$, III ($x$ = 1).** In two experiments the ratio of $Co_2(CO)_8$ to $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ was varied from 1:1 to 2:3. For both experiments, 0.17 g (0.3 mmol) of $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ was treated with $Co_2(CO)_8$ (0.1 and 0.07 g, respectively) in THF according to the general method. After 5 min at 25 °C, the IR and NMR spectra revealed the formation of $[Co(L{\sim}L)(CO)_3][Co(CO)_4]$, Va, and $[Co_2(L{\sim}L)_3(CO)_4][Co(CO)_4]_2$, Vb. After 1–2 h, an orange precipitate of ($[-LCo(CO)_3){\cdot}Co(CO)_3L-]_n$) formed and was filtered. The red filtrate contained an unidentifiable specie(s) (by IR).

$[Co(L{\sim}L)(CO)_3][Co(CO)_4]$, Va: $^{31}P\{^1H\}$ NMR (THF, $\delta$) 53.1 (s); IR (THF, $\nu$(CO) ($cm^{-1}$)) 1995 (s), 1885 (vs).

$[-LCo(CO)_3{\cdot}Co(CO)_3L-]_n$, Vc: IR (Nujol mull, $\nu$(CO) ($cm^{-1}$)) 2023 (vw), 1979 (sh), 1945 (s). Elemental Anal. Calcd for $C_{40}H_{28}O_6FeP_2Co_2$: C, 57.17; H, 3.36; Co, 14.03. Found: C, 54.68; H, 3.42; Co, 13.15.

$[Co_2(L{\sim}L)_3(CO)_4][Co(CO)_4]_2$, Vb: $^{31}P\{^1H\}$ NMR (THF, $\delta$) 52.6 (s); IR (THF, $\nu$(CO) ($cm^{-1}$)) 2000 (s), 1955 (ms), 1895 (vs).

Soluble filtrate: IR (THF, $\nu$(CO) ($cm^{-1}$)) 1985 (ms), 1957 (s), 1930 (w).

**(3) Reaction of $Co_2(CO)_8$ with $Ph_2P[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$, III ($x$ = 2; L~L′~L).** III ($x$ = 2; 0.1 g) was treated with $Co_2(CO)_8$ (0.04 g) in $CH_2Cl_2$ according to the general method. IR and NMR analyses showed that the reaction was complete after 30 min. Solutions of the product remained unchanged after 1 week at 25 °C under nitrogen. The tetraphenylborate salt of the cation was prepared by reaction of the product with a fourfold excess of $NaBPh_4$ in acetone.

$[Co(CO)_2(L{\sim}L'{\sim}L)][Co(CO)_4]$, VI: $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, $\delta$, $-70$ °C) 55.02 (d, $J_{pp'}$ = 20.1 Hz), 24.98 (t, $J_{pp'}$ = 20.1 Hz); IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2012 (ms), 1950 (s), 1884 (vs); $I_{sym}/I_{asym}$ = 0.692.

$[Co(CO)_2(L{\sim}L'{\sim}L)][BPh_4]$: $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, $\delta$, 25 °C) 54.9 (d, $J_{pp'}$ = 17.1 Hz), 25.2 (br t); IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2006 (ms), 1952 (s). Elemental Anal. Calcd for $C_{76}H_{61}O_2Fe_2P_3CoB$: Co, 4.82; Fe, 9.14; P, 7.61. Found: Co, 4.75; Fe, 9.70; P, 7.06.

**(4) Reaction of $Co_2(CO)_8$ with $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$, I ($x$ = 3; L″~L′~L).** I ($x$ = 3; 0.33 g) was treated with $Co_2(CO)_8$ (0.11 g) in methylene chloride according to the general method. IR and NMR analyses showed the reaction was complete after 30 min. Solutions of the product remained unchanged after 1 week at 25 °C under nitrogen. The tetraphenylborate salt was prepared by using a fourfold excess of $NaBPh_4$ in acetone.

$[Co(CO)_2(L''{\sim}L'{\sim}L)][Co(CO)_4]$, VII: IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2010 (m), 1950 (s), 1890 (vs); $I_{sym}/I_{asym}$ = 0.4; $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, $\delta$, $-50$ °C) isomer VIIa (major isomer; ABX spin system) 53.07 (A, dd, $|J_{AB}|$ = 111.7 Hz), 51.84 (B, dd, $|J_{BA}|$ = 111.7 Hz), 24.15 (X, t, $|J_{AX}|$ = 17.9 Hz, $|J_{BX}|$ = 20.8 Hz), isomer VIIb (minor isomer; ABX spin system) 52.15 (A, dd, $|J_{AB}|$ = 113.1 Hz), 45.74 (B, dd, $|J_{BA}|$ = 113.1 Hz), 24.98 (X, t, $|J_{AX}| = |J_{BX}|$ = 16.4 Hz) (note: $A_{ax} = PPh_2Fc-$; $B_{ax} = PPhFc_2-$; $X_{eq} = -PPhFc_2-$).

$[Co(CO)_2(L''{\sim}L'{\sim}L)][BPh_4]$: IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2006 (m), 1952 (s). Elemental Anal. Calcd for $C_{80}H_{65}O_2Fe_3P_3CoB$: C, 69.74; H, 4.76; Co, 4.06; Fe, 12.16. Found: C, 68.37; H, 5.12; Co, 4.17; Fe, 13.60.

**(5) Reaction of $Co_2(CO)_8$ with $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4Ph)-]_xPh$, I ($x$ = 4; L‴~L″~L′~L).** I ($x$ = 4; 0.45 g, 0.36 mmol) was treated with $Co_2(CO)_8$ (0.12 g, 0.36 mmol) in methylene chloride according to the general procedure. IR analysis of the solution showed the reaction was complete after 30 min, and the spectrum remained unchanged for at least 1 week at 25 °C under nitrogen. The tetraphenylborate salt was prepared by using a fourfold excess (0.5 g) of $NaBPh_4$ in acetone; isolated yield 0.34 g.

$[Co(CO)_2(L'''{\sim}L''{\sim}L'{\sim}L)][Co(CO)_4]$, VIII: IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2010 (m), 1948 (s), 1890 (vs).

$[Co(CO)_2(L'''{\sim}L''{\sim}L'{\sim}L)][BPh_4]$: IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2002 (m), 1948 (s). Elemental Anal. Calcd for $C_{96}H_{78}O_2Fe_4P_4CoB$: Co, 3.51; Fe, 13.29; P, 7.37. Found: Co, 2.99; Fe, 13.25; P, 6.96.

**(6) Reaction of $Co_2(CO)_8$ with $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xOH$, II.** In a series of reactions, several polymers were treated with $Co_2(CO)_8$ ($\bar{M}_w$ range 8900–161 000 g/mol). In all cases the same results were obtained as determined by IR and NMR spectroscopy. Below are described the reactions for a polymer of molecular weight 47000 g/mol (IIB).

**Low-Loaded Polymers (Co/P = 1:3.7).** $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_x\mathit{OH}$, II (0.2 g), was treated with $Co_2(CO)_8$ (0.03 g) in methylene chloride according to the general method. IR and NMR spectra were recorded. A similar reaction was performed in THF and gave the same results as determined by IR and NMR spectroscopy.

**High-Loaded Polymer (Co/P = 1:1.9).** To the above reaction mixture was added 0.03 g of $Co_2(CO)_8$, and the mixture was stirred for 15 min. The IR and NMR data were recorded and are summarized below.

$[Co(CO)_2(-L''{\sim}L'{\sim}L-)][Co(CO)_4]$, IX ($\bar{M}_w$ 47 000): $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, $\delta$) isomer a 51.3 (br d, $J_{pp'} \approx$ 110 Hz), 45 (br d, $J_{pp'} \approx$ 110 Hz), 26.2 (br m), isomer b 48.7 (br m), 21.2 (br m); IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) isomers a and b 2002 (sh), 1950 (s), 1890 (vs).

Trans diphosphine: $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, $\delta$) 52.8 (br m); IR ($CH_2Cl_2$, $\nu$(CO) ($cm^{-1}$)) 2075 (m), 1998 (sh), 1985 (sh), 1950 (s), 1890.

**Reaction of $Co_2(CO)_8$ Loaded on $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xOH$, II, with $CO/H_2$.** Polymer IIB (0.3 g) was treated with 0.05 g of $Co_2(CO)_8$ in approximately 15 mL of THF. IR and NMR analysis showed that the predominant species present was $[Co(CO)_2(-L''{\sim}L'{\sim}L-)][Co(CO)_4]$, IX. The reaction mixture was placed in a stirring autoclave and pressurized to 1500 psig of syn gas ($CO/H_2$ = 1:2). The reactor was slowly heated to 190 °C (~1.5 h) where it remained for 30 min. The autoclave was quickly cooled to $-10$ °C under pressure, and a sample was withdrawn for NMR analysis at low temperature.

$^{31}P$ NMR analysis showed no major changes except for a slight increase in intensity of the unidentified resonance at ~35 ppm. IR analysis was consistent with the NMR results.

In similar fashion, polymer IIC (0.3 g) was treated with $Co_2(CO)_8$ (0.05 g) in THF and then exposed to syn gas according to the above conditions for 10 h at 190 °C. The resulting solution gave no NMR resonances, presumably due to paramagnetic species present.

Similar results were obtained for a reaction mixture prepared by treating 0.17 g of polymer IIB with 0.025 g of $Co_2(CO)_8$ at 180 °C. In both cases the IR spectra were nearly identical: IR (THF, $\nu$(CO) ($cm^{-1}$)) 2045 (w), 2020 (sh), 1998 (s), 1970 (vw), 1935 (m), 1885 (vs).

**(7) Hydroformylation of 1-Hexene. Polymers.** The following reaction conditions were used in all of the catalytic runs involving the polymers. $Co_2(CO)_8$ (0.04 g) was placed in 20 mL of THF, and the polymer (0.04 g) was added. 1-Hexene (4.0 g) and 1.0 g of *n*-decane were added, causing the homogeneous catalyst to precipitate. The reaction mixture was placed in a stirring autoclave, purged twice with argon, and then pressurized to 1500 psig of CO and $H_2$ (1:2). The reactor was heated to 190 °C, and the mixture was stirred for 10 h and then slowly cooled. The homogeneous red solution was sampled for GLC analysis. See Table I for GLC results.

**Oligomers.** $Co_2(CO)_8$ (0.04 g) was dissolved in 20 mL of toluene. The appropriate amount of oligomer then was added. 1-Hexene (4.0 g) and 1.0 g of *n*-decane were added, and the reaction mixture was placed in a stirring autoclave, flushed with argon, and pressurized to 1500 psig of CO and $H_2$ (1:2). The reactor was heated to 170 °C and kept at that temperature for 3 h. The homogeneous red solution was sampled for GLC analysis. See Table I for GLC results.

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**Registry No.** I (x = 1), 12098-17-8; I (x = 2), 82311-92-0; I (x = 3), 82311-93-1; I (x = 4), 82322-77-8; III (x = 1), 12150-46-8; III (x = 2), 82311-96-4; IV, 85267-29-4; Va, 85250-09-5; Vb, 85250-11-9; VI, 85250-13-1; VII, 85250-16-4; VIII, 85250-19-7; $[Co(CO)_3(PPh_2Fc)]_2$, 85250-07-3; $[Co(CO)_2(L \sim L' \sim L)][BPh_4]$, 85250-14-2; $[Co(CO)_2(L'' \sim L' \sim L)][BPh_4]$, 85250-17-5; $[Co(CO)_2(L''' \sim L'' \sim L' \sim L)][BPh_4]$, 85250-20-0; $Co_2(CO)_8$, 10210-68-1; 1-hexene, 592-41-6.

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# Crystal, Geometrical, and Electronic Structure of $HFe_4(CO)_{12}BH_2$. A Boron Analogue of a Protonated Carbido Cluster

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The new ferraborane $HFe_4(CO)_{12}BH_2$ has been prepared and structurally characterized by a single-crystal, X-ray diffraction study. This compound, which is a $HFe_4(CO)_{12}$ "butterfly" fragment with a $BH_2$ fragment bridging the "wing-tips", is isoelectronic as well as structurally related to $HFe_4(CO)_{12}CH$ an iron cluster containing a Fe–H–C interaction. The geometrical and electronic structure of this ferraborane is analyzed in terms of electron-counting rules as well as with a fragment analysis utilizing the Fenske–Hall approach. This analysis demonstrates that the ferraborane is most properly described either as an arachno, four-atom cluster with an interstitial boron atom or as a saturated, 62-electron complex with the $BH_2$ ligand contributing five electrons. The orientation of the $BH_2$ fragment with respect to the iron butterfly is explained in terms of the special properties of the frontier orbitals of the tetrametal fragment. The interaction of a filled cluster orbital with an empty B–H antibonding orbital of free $BH_2$ provides a logical explanation for the strong Fe–H–B three-center interaction in $HFe_4(CO)_{12}BH_2$ and a justification for considering the ferraborane a hydrogenated iron boride cluster. Crystals of $HFe_4(CO)_{12}BH_2$ form in the monoclinic space group $P2_1/c$ with the following unit-cell parameters: $a$ = 16.429 (5) Å, $b$ = 8.740 (3) Å, $c$ = 13.237 (3) Å, $\beta$ = 94.32 (1)°, $V$ = 1896 Å$^3$, $Z$ = 4. The X-ray structure was solved as described in the text and refined to $R_1$ = 0.044 and $R_2$ = 0.045 for 2817 independent reflections.

In the past few years there has been a substantial number of homonuclear four-metal cluster compounds in which the metal atoms are arranged in a so-called "butterfly" array (Figure 1a) reported.[1-7] Usually in these compounds there is an atom or group of atoms (X) bridging the "wing-tip" metals; however, recently an example of an unsupported osmium butterfly complex was reported.[8] The structural parameters of a variety of tetrairon complexes have been compared previously,[1] and it appears that the two most sensitive to variation in X are the dihedral

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