Chemistry of the Transition Metal-Hydrogen Bond.[1] II. HCo[P(OR)3]4

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Abstract: The 18-electron $HCo[P(OR)_3]_4$ complexes exhibit a high barrier to ligand dissociation with the barriers decreasing in the series $P(OCH_3)_3 > P(OC_2H_5)_3 > P(OC_6H_5)_3$ as sensed by the reaction $HCo[P(OR)_3]_4 + P(OR')_3 \rightleftharpoons HCo[P(OR)_3]_3P(OR')_3 + P(OR)_3$. In a nonpolar solvent, exchange equilibrium is attained only after 4-6 weeks at 100° and the rate is not detectably affected by large changes in phosphite concentration. Ligand exchange with carbon monoxide is orders of magnitude more rapid. Ligand substitution rates are substantially increased in polar media like alcohols and nitriles. This finding appears to have broad application to coordination complexes and may facilitate the synthesis of a variety of organometallic complexes. Protonation of $HCo[P(OCH_3)_3]_4$ occurs with strong acids to give $H_2Co[P(OCH_3)_3]_4^+$ which is present in solution primarily as the cis stereoisomer. The metal-hydrogen bond in $HCo[P(OR)_3]_4$ is not especially protonic as evidenced by the lack of reaction with strong bases like OH^- or OR^-. Hydrogen abstraction was effected with alkali metal hydrides to form $M^+Co[P(OR)_3]_4^-$. These salts are versatile reagents for the synthesis of a wide variety of new organometallic compounds that include $RCo[P(OR)_3]_4$, η^3-$RCo[P(OR)_3]_3$, $Co_2[P(OR)_3]_8$, and $Hg\{Co[P(OR)_3]_4\}_2$.

Metal-hydrogen and metal-carbon bonds are ubiquitous elements in transition metal complex catalysis of organic reactions.[3-6] We have initiated a broad chemical study[1,7,8] of various classes of metal hydrides to develop more fully the chemical principles and systematics[9] in this important metal hydride area.

Results and Discussion

A. Structure of HCo[P(OR)3]4 Complexes. All hydrides of the type $HM[P \lessdot]_4$, structurally defined[10-13] to date, have near C_{3v} microsymmetry ($HCoP_4$) with the MP_4 skeleton a nearly regular tetrahedron. The hydrogen atom position, established in one of the X-ray studies,[13] is on a face of the tetrahedron. Since the set of structurally defined hydrides includes $HCo(PF_3)_4$[12] and $HCo[C_6H_5P(OC_2H_5)_2]_4$,[13] it is unlikely that the $HCo[P(OR_3)_4$ complexes have any structure but the quasi-tetrahedral form. A pervasive feature of these quasi-tetrahedral hydrides is a high degree of stereochemical nonrigidity,[1,14] and we find that the $HCo[P(OR_3]_4$ class possesses this dynamic characteristic. A limiting slow exchange nmr spectrum (^1H, ^{13}C, and ^{31}P) was not detected even at *ca.* $-140°$ for $HCo[P(OR)_3]_4$ with $R = CH_3$, C_2H_5, i-C_3H_7, and C_6H_5. The only $HCoL_4$ complex for which a limiting spectrum has been observed[14] is $HCo(PF_3)_4$.

B. Ligand Dissociation in HCo[P(OR)3]4. Phosphite ligand lability in $HCo[P(OR)_3]_4$ complexes is very low. Nmr studies showed that there is no ligand exchange process, fast with respect to the nmr time scale, for any of these hydrides, alone or in admixture with free phosphite ligand, to temperatures of 100°. Consonant with this feature, $HCo[P(OCH_3)_3]_4$ was found to have a very low activity as a catalyst for the hydrogenation of 1-hexene.

In nonpolar solvents like benzene, ligand dissociation in $HCo[P(OR)_3]_4$ does proceed but at relatively low rates even at temperatures of 100°. This dissociation was detected by nmr monitoring of the reaction

$$HCo[P(OR)_3]_4 + xP(OR')_3 \rightleftharpoons$$
$$HCo[P(OR)_3]_{4-x}[P(OR')_3]_x + xP(OR)_3$$
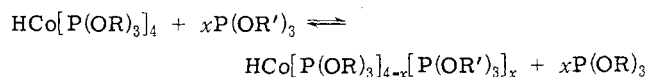
For $HCo[P(OC_6H_5)_3]_4$ and triethyl phosphite in about a 1:5 molar ratio, the reaction was complete with $HCo[P(OC_2H_5)_3]_4$ the only hydride complex detectable after about 4 weeks at 100°. Reaction rate was unaffected by an

eightfold increase in triethyl phosphite concentration establishing the rate determining reaction step to be primarily ligand dissociation as might be anticipated for an 18-electron complex. The stepwise character of the reaction was incisively clear from the character of the nmr spectrum of the reaction mixture as a function of time. In the preliminary stages of the reaction, the only hydride detected by nmr other than the reactant hydride was $HCo[P(OC_6H_5)_3]_3[P(OC_2H_5)_3]$. At progressively later stages, $HCo[P(OC_6H_5)_3]_2[P(OC_2H_5)_3]_2$, $HCo[P(OC_6H_5)_3][P(OC_2H_5)_3]_3$, and $HCo[P(OC_2H_5)_3]_4$ appeared in order, and were readily identified by their ^1H nmr spectra. Each of the mixed phosphite complexes was isolated and characterized[15] but the 2:2 complex was never obtained in analytically pure form. Triphenyl phosphite did not displace phosphite in $HCo[P(OC_2H_5)_3]_4$ at 100°.

The alkyl phosphite complexes, $HCo[P(OCH_3)_3]_4$ and $HCo[P(OC_2H_5)_3]_4$, also undergo exchange with triethyl phosphite and trimethyl phosphite, respectively, although a 5-6 weeks reaction time was required for equilibrium to be attained at 100° in benzene. The nmr spectra for the two reaction systems were nearly identical at equilibrium where the hydride and ligand concentrations were in a 1:4 molar ratio in both systems.[16] A slightly longer time was required for equilibration with the $HCo[P(OCH_3)_3]_4$-$P(OC_2H_5)_3$ system than with the alternative one. This suggests that the ligand dissociation step becomes more facile with increasing steric bulk (or larger cone angle[17]) of the ligands.

No exchange of alkoxy groups was observed within 1 day between $HCo[P(OCH_3)_3]_4$ and ethanol or potassium ethoxide nor between $HCo[P(OC_2H_5)_3]_4$ and methanol or potassium methoxide. This is a further documentation of the resistance of $HCo[P(OR)_3]_4$ to ligand dissociation since transesterification between $P(OCH_3)_3$ and C_2H_5OH is rapid at 25°.[8] An analogous resistance to transesterification has been reported for a closely related, six-coordinate class of hydrides, $H_2Fe[P(OR)_3]_4$.[8]

Carbon monoxide reacts with $HCo[P(OC_2H_3)_3]_4$ to form successively $HCo[P(OCH_3)_3]_3CO$ and $HCo[P(OCH_3)_3]_2(CO)_2$ at rates that are far in excess (at least 10-10^2) of those for phosphite ligand exchange. This suggests a rate equation for the carbon monoxide reaction of the type k[complex][CO] since dissociative or interchange[18] reactions are not especially rate sensitive to the nature of the entering group. In fact, the substitution rate was not detecta-

bly different with CO pressures of 1 and 3 atm; however, CO solution activity may not have been substantially altered over this pressure range.

Ligand substitution rates in $HCo[P(OCH_3)_3]_4$ were very sensitive to reaction medium. For example, rate of ligand exchange in $HCo[P(OCH_3)_3]_4$-$P(OC_2H_5)_3$ is increased by more than two orders of magnitude in reaction medium change from benzene to acetonitrile (methanol is intermediate in effect). Rate enhancement by acetonitrile is not catalytic. We suggest that acetonitrile solvation effects render a dissociative intermediate $HCo[P(OCH_3)_3]_3$ more similar in energy to $HCo[P(OCH_3)_3]_4$. Detailed kinetic studies are in progress because we consider this phenomenon to be of great value in chemical synthesis; an analogous solvent effect has been demonstrated for substitution reactions in $Fe[P((OCH_3)_3]_5$.[19]

The reaction

$$HCo[P(OCH_3)_3]_4 + CO \longrightarrow$$

$$HCo[P(OCH_3)_3]_3CO + P(OCH_3)_3$$
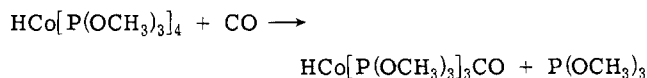
appears to be irreversible; the monocarbonyl did not react with excess phosphite at elevated temperatures and with a variety of solvents.

C. Character of the Co-H Bond. The $HCo[P(OR)_3]_4$ class of hydrides in a marked, but explicable, contrast to the analogous hydrides, $HCo[CO]_4$ and $HCo[PF_3]_4$, has a relatively inert H-Co bond as shown by the resistance of the hydrogen atom to abstraction as a proton by alkali metals or bases such as $OC_2H_5^-$, OCH_3^-, or OH^-. Abstraction requires a very strong base like potassium or sodium hydride. These react quantitatively with $HCo[P(OCH_3)_3]_4$ to form $MCo[P(OCH_3)_3]_4$.[7] The corresponding reaction with $HCo[P(OC_2H_5)_3]_4$ is slower, requiring an approximate threefold increase in time to reach completion, and $HCo[P(O-i-C_3H_7)_3]_4$ does not react. Since the electronic properties of the alkyl phosphite ligands vary little, the decrease in the subsequent lack of reactivity in the series CH_3, C_2H_5, and i-C_3H_7, may be reasonably ascribed to increasing protective envelopment of the Co-H bond by the alkoxy groups. Ligand dissociation in the hydrides is not the first step in the reaction with potassium hydride because dissociation is orders of magnitude too slow[20] to account for the $HCo[P(OR)_3]_4$ (R = CH_3 or C_2H_5) reaction rate with potassium hydride. $HCo[P(OC_6H_5)_3]_4$ also reacts with potassium hydride but intramolecular oxidative-addition of an ortho carbon-hydrogen bond to the metal atom occurs to give a complex reaction mixture.

Since the conjugate base, $Co[P(OR)_3]_4^-$, reacts with water, methanol, and ethanol to give the hydride, the acid dissociation constant of the Co-H bond in the hydrides must be low.[21] The relatively "hydridic" character of the cobalt-hydrogen bond is directly assignable to the strong σ-donating properties of the phosphite ligands to the metal atom, which donor effect inhibits loss of the hydrogen atom as a proton. With the less basic and stronger π-acceptor ligands PF_3 and CO, loss of H as a proton is promoted in $HCo(PF_3)_4$ and $HCo(CO)_4$, respectively, where these two hydrides have acid dissociation constants comparable to hydrogen chloride.[22]

Water does not react with the $HCo[P(OR)_3]_4$ complexes (water-acetone media). In slightly acidified D_2O-acetone solutions, hydrogen-deuterium exchange occurs to give $DCo[P(OR)_3]_4$. This exchange proceeds through deuteration of the hydride

$$HCo[P(OR)_3]_4 + D^+ \rightleftharpoons HDCo[P(OR)_3]_4^+$$

$$HDCo[P(OR)_3]_4^+ \rightleftharpoons DCo[P(OR)_3]_4 + H^+$$
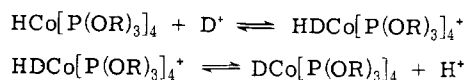
The cationic dihydride intermediate, isoelectronic with $H_2Fe[P(OCH_3)_3]_4$,[19] is relatively unstable in the crystalline state or in the presence of mineral acids. Characterization of the dihydride as predominantly the cis stereoisomer was achieved through nmr analysis. In the proton nmr spectrum, the phosphite methyl multiplet is nearly identical with that for $H_2Fe[P(OCH_3)_3]_4$[19] and the complex Co-H multiplet ($-35°$) is analogous to those for cis ruthenium(II) dihydrides with four phosphite, phosphonite, or phosphine ligands.[23,24] Separation of the two sharp inner lines is 71 Hz which is equal to the absolute sum of $J_{H_5P_1}$ + $J_{H_5P_2}$ + $J_{H_5P_3}$ and $J_{H_5P_4}$.[23] A fast exchange process is evident in the changes of the Co-H dihydride resonance as a function of temperature with the multiplet broadening to a featureless resonance at 25°. This process is not proton exchange between the cationic dihydride and traces of $HCo[P(OCH_3)_3]_4$ because solutions that contain comparable concentrations of the di- and monohydrides show the characteristic line-shape change for the Co-H resonance of the dihydride and no change in the characteristic quintet Co-H resonance for the monohydride over the -35 to $+40°$ range. Fast dissociative exchange of the type
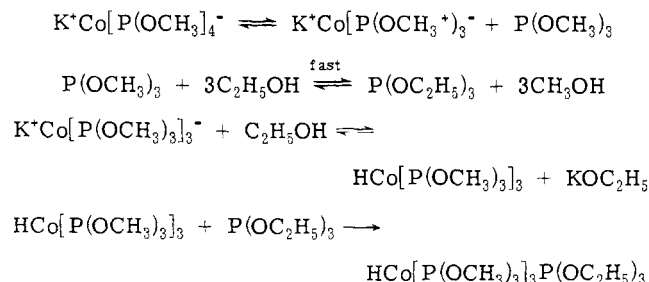
$$H_2Co[P(OCH_3)_3]_4^+ \rightleftharpoons H_2Co[P(OCH_3)_3]_3^+ + P(OCH_3)_3$$
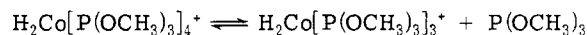
is not operative since the ^1H nmr resonance of a mixture of $H_2Co[P(OCH_3)_3]_4^+$ and $P(OCH_3)_3$ is simply a sum of the two individual pure species from -35 to $+40°$. A mutual exchange, intramolecular rearrangement process can be eliminated as the sole, rapid exchange process because the two sharp inner lines broaden at a rate comparable to the other components of the Co-H dihydride multiplet.[23] We suggest that a small amount of $trans$-$H_2Co[P(OCH_3)_3]_4^+$ is present in solution and that nonmutual, intramolecular exchange (cis $\rightleftharpoons$ trans) is rapidly occurring in the -20 to $+40°$ range. A slight asymmetry in the Co-H multiplet of the dihydride may be accounted for by the overlap of the resonance for the trans isomer ($ca.$ 10%) and the major cis multiplet resonance.

Solutions of $HCo[P(OR)_3]_4$ discolor (oxidize) on exposure to air. Reaction rate with oxygen is too fast to be based solely on a ligand predissociation step; direct attack of the metal atom by O_2 is the assumed reaction sequence.

D. Chemistry of $K\{Co[P(OR)_3]_4\}$. Hydrogen chloride reacts virtually instantaneously with $KCo[P(OR)_3]_4$ to quantitatively form the hydride and potassium chloride. Water also reacts to form the hydride but at a slightly reduced rate and with minor decomposition of the cobalt complex. Alcohols convert the salt to the hydride but at a rate that is about three orders of magnitude lower than that of water. Protonation of the $Co[P(OR)_3]_4^-$ anion might be a substantially activated process because the phosphite ligands rather effectively envelop and shield the cobalt atom. This feature alone is insufficient to account for the "protonation" rate differential for water and alcohol. The character of the "salt" may be substantially different in aqueous and alcoholic media, a thesis that is supported by exchange features ($vide\ infra$) that were probed for the alcohol reaction. Attempts to directly define stereochemistry for $KCo[P(OCH_3)_3]_4$ dissolved in methanol and methanol-fluorodichloromethane solutions were not successful; the ^{31}P nmr {H} spectra of these solutions consisted of a structureless $KCo[P(OCH_3)_3]_4$ resonance (25 to $-100°$) along with the characteristic $HCo[P(OCH_3)_3]_4$ (alcoholysis product) resonance.

Reaction of $KCo[P(OCH_3)_3]_4$ with C_2H_5OH yielded $HCo[P(OCH_3)_3]_4$ as well as hydrides with ethyl and methyl phosphite substituents. Chromatographic separation of the complex hydride species was not achieved so it was not

established whether they were of the $HCo[P(OCH_3)_3]_x$-$[P(OC_2H_5)_3]_{4-x}$ or $HCo[P(OCH_3)_x(OC_2H_5)_{3-x}]_4$ class. Since C_2H_5OH was present in large excess, the former class is the more likely product. In any case, the formation of ethyl phosphite complexes placed certain constraints on the nature of the alcoholysis reaction. Transesterification of the product hydride has been established to be immeasurably slow even in strongly basic media, *vide supra*. In fact, transesterification rates should be very low for any bound phosphite. Therefore, the "protonation" reactions, at least in alcohol solution, must involve a ligand predissociation step as speculatively outlined below

$$K^+Co[P(OCH_3)_3]_4^- \rightleftharpoons K^+Co[P(OCH_3^+)_3]_3^- + P(OCH_3)_3$$

$$P(OCH_3)_3 + 3C_2H_5OH \overset{fast}{\rightleftharpoons} P(OC_2H_5)_3 + 3CH_3OH$$

$$K^+Co[P(OCH_3)_3]_3^- + C_2H_5OH \rightleftharpoons$$
$$HCo[P(OCH_3)_3]_3 + KOC_2H_5$$

$$HCo[P(OCH_3)_3]_3 + P(OC_2H_5)_3 \longrightarrow$$
$$HCo[P(OCH_3)_3]_3P(OC_2H_5)_3$$

These reaction features are in accord with experimental observation. Protonation in aqueous media is probably distinguished by the dissolution of the salt into solvated potassium and $Co[P(OCH_3)_3]_4^-$ ions rather than ion pairs or ion multiples. Direct reaction of the anion with water or a more facile ligand dissociation for the discrete, relatively electron-rich anion

$$\{Co[P(OCH_3)_3]_4\}^- \rightleftharpoons Co[P(OCH_3)_3]_3^- + P(OCH_3)_3$$
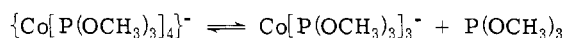
could account for the higher protonation rate in water. Nevertheless some ligand dissociation must occur as evidenced by the formation of trimethyl phosphite.

The $KCo[P(OR)_3]_4$ derivatives react quickly and often spectacularly with the ambient atmosphere. This reactivity is in sharp contrast to that of the parent hydrides. Inorganic or organic halides undergo simple metathetical reactions[1,7] with $KCo[P(OR)_3]_4$ and these reactions provided a practical route to new compounds of the type η^1-$RCo[P(OR)_3]_4$, η^3-$RCo[P(OR)_3]_3$, and $M\{Co[P(OR)_3]_4\}_x$ as well as a sequential route to $Co_2[P(OR)_3]_8$. Reaction rates follow an order of R_3M-X > allyl-X > R-X $\gg$ aryl-X and X = I > Br > Cl, which is *consistent* with a dominant S_N2 reaction mechanism. Through this conventional substitution scheme, $KCo[P(OR)_3]_4$ has proven to be a versatile organometallic reagent.

E. Chemistry of η^1- and η^3-$RCo[P(OCH_3)_3]_x$. Structurally, $CH_3Co[P(OCH_3)_3]_4$ should be analogous to the parent hydride. The expected, limiting AB_3 $^{31}P\{H\}$ spectrum is observed below $-80°$ for the CH_3 and CD_3 derivatives and this AB_3 pattern goes to an A_4 spectrum above $-80°$. This presumably reflects a very high degree of fluxionality in the methyl derivative. Construction of a model, using established or reasonable distances for the bonds in this molecule, shows that the methyl derivative cannot have the C_{3v} quasi-tetrahedral structure because of CH_3 proton interactions with the methoxy groups of the phosphite ligands. Rather the equatorial P-Co-P angles should be about midway between $109.5°$ for the quasi-tetrahedral form and $120°$ for an idealized C_{3v} trigonal bipyramidal form. An X-ray structural test of this formulation is in progress. This assumed departure from the quasi-tetrahedral structure of the hydride is probably a primary factor contributing to the larger barrier to intramolecular exchange in the methyl derivative as compared to the hydride.

There is a relatively small number of σ-alkyl derivatives of transition metals although the number is rapidly growing as more effective synthesis procedures are developed. The small number is not due to an intrinsic instability of the M-C bond. $CH_3Co[P(OCH_3)_3]_4$ has high thermal stability and low reactivity with no evidence of decomposition below 120 and $150°$ for the solution and solid states, respectively. In contrast, $CH_3Co(CO)_4$ has high thermal reactivity; decomposition is fast below $0°$. Reactivity in the carbonyl derivative appears to be due to an equilibrium with an acyl form through which acetone and polynuclear cobalt carbonyls are sequentially formed.[25]

$$CH_3COCo(CO)_3 + CH_3Co(CO)_4 \rightleftharpoons$$

$$CH_3-Co(CO)_3Co(CO)_4 \longrightarrow CH_3COCH_3 + [Co_2(CO)_7]$$
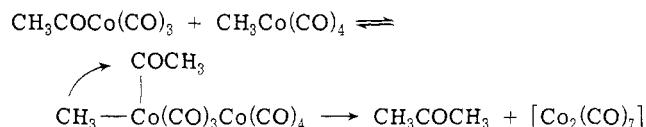
Ligand dissociation rate in $CH_3Co[P(OCH_3)_3]_4$ is comparable to that in the parent hydride. Carbon monoxide reacts at $100°$ over a 1-week period to give $CH_3Co[P(OCH_3)_3]_3CO$. There was no evidence of disubstitution under these conditions nor of carbonyl insertion to give an acyl derivative. The latter process is probably inhibited by the strong σ-donor properties of the three phosphite ligands; carbonyl insertion is favored by increasing positive charge on the metal atom. The CH_3-Co bond is rapidly cleaved by hydrogen chloride and is not attacked by water. Trifluoroacetic acid protonates the cobalt atom to give *cis*-$CH_3(H)Co[P(OCH_3)_3]_4$.[26]
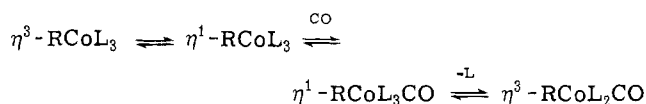
Ethyl chloride reacts with $KCo[P(OCH_3)_3]_4$ to ostensibly give the σ-ethyl derivative, but reactivity through β-hydrogen elimination is so high that the only products detected were ethylene and $HCo[P(OCH_3)_3]_4$.

Allyl- and 1-methylallylcobalt tris(trimethyl phosphite) obtained in high yield from the allyl halides and $KCo[P(OCH_3)_3]_4$ are crystalline, thermally stable compounds. Formulation as η^3 derivatives is fully supported by the ^1H and ^{31}P nmr spectra with intrinsic spectral (^1H nmr) features similar to the carbonyl analogs.[27] These allyl derivatives are fluxional molecules as shown by their temperature-dependent $^{31}P\{H\}$ nmr spectra in which there is a transition from A_3 to AB_2 and ABC patterns for the allyl and 1-methylallyl derivatives, respectively, below $-120°$. No unique structural or intramolecular rearrangement mechanism can be derived from these data.[1] Nevertheless a simple, idealistic view is that the $Co[P(OCH_3)_3]_3$ substructure is pyramidal with a near C_{3v} CoP_3 skeleton and a coplanar allyl group sitting over the pyramid only slightly out of a plane normal to the pseudo-C_3 axis.[28] In this structural view, the slightly activated rearrangement process reflected in the $AB_2 \rightarrow A_3$ or ABC $\rightarrow A_3$ transition in the $^{31}P\{H\}$ spectra could be most simply viewed as the rotation (helical in form) of the allyl group about the pseudo-C_3 axis.[29] The benzyl derivative, $C_6H_5CH_2Co[P(OCH_3)_3]_3$ is also formulated as a η^3 derivative although the requisite inequivalence of ortho and meta carbon atoms and of methylene protons is not evident at $-130°$ by ^{13}C nmr. In the "limiting" exchange region of *ca.* $-150°$ accessible with our equipment, the $^{31}P\{H\}$ spectrum is an AB_2 not an ABC pattern. Accordingly, it is proposed that a bond shift of the translational form
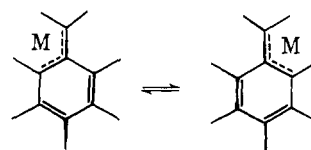
is rapid on the nmr time scale to temperatures below $-150°$, while bond rotation about the Co–C$_3$ centroid is fast above ca. $-120°$.[29]

η^3-RCo[P(OCH$_3$)$_3$]$_3$ complexes readily absorbed carbon monoxide to yield crystalline products of the form η^3-RCo-[P(OCH$_3$)$_3$]$_2$[CO], η^3-RCo[P(OCH$_3$)$_3$](CO)$_2$, as well as η^3-RCo(CO)$_3$. This substitution reaction is orders of magnitude faster than carbon monoxide substitution in CH$_3$Co-[P(OR)$_3$]$_4$, with monosubstitution reaching completion in 6 hr at 25°. The relatively high reactivity of these compounds as compared to the methyl and hydride derivatives is ascribable to facile production of a coordinately unsaturated intermediate. Since phosphite dissociation has been shown to be slow, it is unlikely that the coordinately unsaturated species would be produced by ligand dissociation. A $\eta^3 \rightleftharpoons \eta^1$ process probably produces the requisite 16-electron complex.

$$\eta^3\text{-RCoL}_3 \;\rightleftharpoons\; \eta^1\text{-RCoL}_3 \;\overset{CO}{\rightleftharpoons}\;$$

$$\eta^1\text{-RCoL}_3CO \;\overset{-L}{\rightleftharpoons}\; \eta^3\text{-RCoL}_2CO$$

Although this postulated $\eta^3 \rightleftharpoons \eta^1$ transition which would equilibrate the "syn" and "anti" protons of the allyl group is slow with respect to the nmr time scale below 110°, it could still be sufficiently rapid in terms of the time scale of the carbon monoxide reaction to account for the experimental results.[30]

Chemistry of Co$_2$[P(OR)$_3$]$_8$ and M{Co[P(OR)$_3$]$_4$}$_x$. Chlorotrimethylgermane reacts with KCo[P(OR)$_3$]$_4$ in an apparent sequential fashion that passes initially through (CH$_3$)$_3$GeCo[P(OR)$_3$]$_4$ to hexamethyldigermane and Co$_2$[P(OR)$_3$]$_8$. Models indicate that in (CH$_3$)$_3$Ge-[P(OR)$_3$]$_4$ there would be severe nonbonding interactions between the methyl groups on germainum and the alkyl groups of the phosphite ligands. Hence a radical dissociation of the germyl derivative is a plausible process. Chlorotrimethylsilane and trifluoroacetyl chloride yield the same cobalt derivative but the fate of the silicon and carbon halides is not similar to germanium with the silyl chloride forming primarily hexamethyldisiloxane. It appears that radical processes predominate after formation of these particular XCo[P(OR)$_3$]$_4$ derivatives.

Co$_2$[P(OR)$_3$]$_8$ is not structurally analogous to Co$_2$(CO)$_8$.[31] Phosphites are not especially attractive bridging ligands and in fact are not known to bridge bonds between metal atoms. The ^{1}H nmr spectrum shows two types of R environments with a 3:1 population ratio and the ^{31}P{H} spectrum is an AB$_3$ pattern. These data are only consistent with a bi(trigonal bipyramidal) structure in which each cobalt has axial cobalt and phosphorus bonds and three equatorial phosphorus bonds. An accurate scale model was constructed, and substantial H–H and O–H repulsions were found in the bi(trigonal bipyramidal) form even with the Co–Co distances in the 3.0–3.2 Å range. So crowded is the coordination sphere that a low barrier for homolytic dissociation to ·Co[P(OR)$_3$]$_4$ might be anticipated; however, neither the methyl nor ethyl derivatives gives evidence of dissociation below 100°. Relief of interligand repulsion of methoxy groups in the dimer requires that the coplanar equatorial phosphorus atoms and the axial phosphorus atom all lie on one side of the cobalt atom to which they are bonded. In this structural form, the tetrahedral jump rearrangement mechanism is no longer applicable and any other plausible intramolecular rearrangement should face a rather formidable energy barrier because of the congested environment about the cobalt atom. In fact,

this molecule is rigid on the ^{1}H nmr time scale to 120° above which irreversible decomposition ensues.

The dimers, Co$_2$[P(OR)$_3$]$_8$, react rapidly with air and are thermally unstable both in solution and as solids above 100°. Water and exposure to a neutral alumina column effected a transformation of the dimers to the corresponding hydrides. The cobalt–cobalt bond is cleaved by HCl to give an intractable oil and HCo[P(OR)$_3$]$_4$. The dimer showed no reactivity toward hydrogen at 25° and 2 atm of pressure.

The mercurial Hg{Co[P(OCH$_3$)$_3$]$_4$}$_2$ consists of mercury linked, trigonal bipyramids of C_{3v} CoL$_3$L units; the ^{31}P{H} nmr spectrum at $-80°$ is an AB$_3$ pattern. Thermal decomposition of the mercurial is measurably fast at 80° with the formation of mercury and paramagnetic material.

Experimental Section

Reagents and Procedure. All operations involving air-sensitive materials were effected either in a drybox (Vacuum/Atmospheres Dri Lab with a Model HE-493 Dri Train) or a conventional vacuum system. Tetrahydrofuran was purified by the sequential steps of (1) reflux over sodium hydroxide for 24 hr, (2) distillation into a flask containing lithium aluminum hydride, (3) reflux for 48 hr, and (4) distillation into a flask for vacuum storage over sodium. Pentane was refluxed over lithium aluminum hydride for 48 hr. All other reagents were purchased in their purest commercially available form and used as obtained.

HCo[P(OC$_2$H$_5$)$_3$]$_4$, HCo[P(O-i-C$_3$H$_7$)$_3$]$_4$, and HCo-[P(OC$_6$H$_5$)$_3$]$_4$ were prepared by literature procedures.[10]

Solution ^{1}H nmr spectra were measured either with a Varian Associates HA-100 D or a Varian Associates HR-220 spectrometer at ambient temperature unless noted differently and are internally referenced to tetramethylsilane. Samples were prepared in the drybox using dry, deoxygenated solvent and evacuated and sealed on the vacuum line.

Solution ^{31}P and ^{13}C nmr spectra were measured at 36.43 and 22.63 MHz, respectively, on a Bruker HFX-90 spectrometer with a Digilab Fourier accessory. Temperatures were measured with a copper–constantan thermocouple located immediately below the spinning sample tube in the probe. This thermocouple was calibrated using a similar thermocouple held coaxially inside a spinning nmr sample tube partially filled with solvent. Samples were prepared in the drybox using dry deoxygenated solvents. Solution ^{31}P nmr spectra are internally referenced to trimethyl phosphite and are proton noise decoupled.

HCo[P(OCH$_3$)$_3$]$_4$. To a stirred solution of CoCl$_2$ (9.40 g, 0.073 mol) and P(OCH$_3$)$_3$ (60.00 g, 4.80 mol) in 1,2-dimethoxyethane (400 ml) that was maintained at 0°, NaBH$_4$ (6.00 g, 0.158 mol) was slowly added over a period of 20 min. After 2 hr, the solvent was removed under vacuum and the residue was extracted with hexane. The hexane extracts were concentrated and eluted with hexane through a chromatographic column, 2.5 × 60 cm, of neutral alumina. The eluate was collected and the solvent was removed under vacuum. The solid product was recrystallized from hexane at $-78°$ to give yellow crystals: mp 212.0 dec; ^{1}H nmr, δ 15.09 (quintet) (J_{PH} = 19.0 Hz) and -3.57 (m); 36.43-MHz ^{31}P nmr ($-80°$), δ -35 ppm (s). Anal. Calcd for C$_{12}$H$_{37}$O$_{12}$P$_4$Co: C, 25.91; H, 6.70; Co, 10.59. Found: C, 26.22; H, 6.75; Co, 10.20.

KCo[P(OCH$_3$)$_3$]$_4$. HCo[P(OCH$_3$)$_3$]$_4$ (5.32 g, 0.009 mol) and KH (0.3836 g, 0.009 mol) were stirred in tetrahydrofuran (200 ml) at 65° for 36 hr under vacuum. After the hydrogen evolution had ceased, the reaction mixture was filtered. The insoluble product was collected and washed with tetrahydrofuran. The resulting white solid was insoluble in all common organic solvents with which it did not react (mp 245.0° dec). Anal. Calcd for KC$_{12}$H$_{36}$O$_{12}$P$_4$Co: C, 24.25; H, 6.11; Co, 9.92; K, 6.58. Found: C, 23.94, 23.86; H, 6.02, 5.92; Co, 9.75, 9.77; K, 6.29, 6.70.

KCo[P(OV$_2$H$_5$)$_3$]$_4$ was prepared in a similar fashion to KCo-[P(OCH$_3$)$_3$]$_4$. The reaction was complete after 80 hr at 70°. The white solid was insoluble in all common organic solvents with which it did not react (mp 218° dec). Anal. Calcd for KC$_{24}$H$_{60}$O$_{12}$P$_4$Co: C, 37.79; H, 7.93; Co, 7.72; K, 5.13. Found: C, 37.82; H, 7.81; Co, 7.83; K, 4.91.

HCo[POC$_2$H$_5$)$_3$]$_4$ and NaH. A slurry of HCo[POC$_2$H$_5$)$_3$]$_4$ (7.245 g, 0.010 mol) and NaH (0.240 g, 0.010 mol) was stirred in

tetrahydrofuran (100 ml) at 70° for 5 days after which time the hydrogen evolution ceased (0.002 g, 0.010 mol). The reaction mixture was then filtered and the insoluble product was washed with tetrahydrofuran. The resulting white product was insoluble in all common organic solvents with which it did not react (mp 215.0 dec).

$CH_3Co[P(OCH_3)_3]_4$. A slurry of $KCo[P(OCH_3)_3]_4$ (1.070 g, 0.002 mol) and CH_3I (0.2555 g, 0.0018 mol) in tetrahydrofuran (25 ml) was stirred for 10 hr at ambient temperature. The volatile materials were then removed under vacuum, and the soluble solid product was extracted from the residue with pentane (25 ml). The product was recrystallized from the pentane solution at −78° to give yellow crystals: mp 143.3° dec; ^1H nmr, δ −0.20 (quintet) (J_{PH} = 8.38 Hz) and −3.68 (m); 36.43-MHz ^{31}P nmr (−80°), δ −27.00 (s). Anal. Calcd for $C_{13}H_{39}O_{12}P_4Co$: C, 27.38; H, 6.84; Co, 10.33. Found: C, 27.01, 27.51; H, 6.88, 6.85; Co, 10.35, 10.37.

$C_6H_5Co[P(OCH_3)_3]_4$. $C_6H_5N_2BF_4$ (0.899 g, 0.0050 mol) was added to a slurry of $KCo[P(OCH_3)_3]_4$ (2.997 g, 0.0050 mol) in tetrahydrofuran (200 ml) that was maintained at −64°. Nitrogen evolution (0.0051 mol) was immediate upon addition. After 20 min, the volatile materials were removed under vacuum, and the solid product was extracted from the residue with pentane: ^1H nmr, δ −3.56 (m, 7.4) and −6.96 (m, 1.0); 36.43-MHz ^{31}P nmr (−80°), δ −20 ppm (m).

{$Co[P(OCH_3)_3]_4$}$_2$. $(CH_3)_3GeCl$ (0.672 g, 0.004 mol) was slowly added to a slurry of $KCo[P(OCH_3)_3]_4$ (2.500 g, 0.004 mol) in pentane (30 ml) that was maintained at −45°. After 20 min, the volatile materials were removed under vacuum and found to contain [$(CH_3)_3Ge$]$_2$: mol wt (vapor density) calcd 235.37, found 234. The product was extracted from the residue with pentane. The crude product was recrystallized from pentane at −78° to give brown crystals (mp 131.4° dec). The same solid product was obtained when $(CH_3)_3SiCl$, CF_3COCl, or CH_3COCl were used in place of $(CH_3)_3GeCl$: cryoscopic mol wt (benzene) calcd 1110.48, found 1100; ^1H nmr, δ −3.15 (d, 3) (J_{PH} = 12 Hz) and −3.90 (d, 1) (J_{PH} = 12 Hz); 36.43-MHz ^{31}P nmr (−80°), δ −50 (d, 3) (J_{PP} = 73 Hz) and −128 (q, 1) (J_{PP} = 73 Hz). Anal. Calcd for $C_{24}H_{72}O_{24}P_8Co$: C, 25.96; H, 6.54; Co, 10.61. Found: C, 25.79; H, 6.55; Co, 10.59.

{$Co[P(OC_2H_5)_3]_4$}$_2$ was prepared in a similar manner to {$Co[P(OCH_3)_3]_4$}$_2$: ^1H nmr, δ −1.19 (t, 1) (J_{H-H} = 7 Hz); −1.25 (t, 3) (J_{H-H} = 7 Hz), −4.04 (doublet of quartets, 3) (J_{PH} = 7, J_{HH} = 7 Hz), and −4.31 (doublet of quartets, 1) (J_{PH} = 7, J_{HH} = 7 Hz).

Hg{$Co[P(OCH_3)_3]_4$}$_2$. A solution of $HgCl_2$ (1.35 g, 0.010 mol) in tetrahydrofuran (10 ml) was added to a slurry of $KCo[P(OCH_3)_3]_4$ (5.94 g, 0.010 mol) in tetrahydrofuran that was maintained at −63°. After 20 min, the solvent was removed under vacuum and the crude product extracted from the residue with pentane (20 ml): ^1H nmr, δ −3.60 (m); 36.43-MHz ^{31}P nmr (−80°), δ −26 (d, 3) (J_{PP} = 71 Hz) and −44 (q, 1) (J_{P-P} = 71 Hz).

η^3-$CH_2CHCH_2Co[P(OCH_3)_3]_3$. A slurry of $KCo[P(OCH_3)_3]_4$ (4.80 g, 0.0081 mol) and CH_2CHCH_2I (1.29 g, 0.0078 mol) in tetrahydrofuran (50 ml) was stirred at ambient temperatures for 9 hr. The solvent was then removed under vacuum and the solid product was extracted from the residue with pentane (30 ml). The product was recrystallized from pentane at −78° to give orange crystals: mp 154.0° dec; ^1H nmr, δ −1.425 (doublet of quartets, 2) ($J_{H_{anti}-P}$ = 7.2, $J_{H_{anti}-H}$ = 9.2 Hz), −2.335 (doublet of quartets, 2) ($J_{H_{syn}-P}$ = 3.0, $J_{H_{syn}-H}$ = 6.0 Hz), −4.865 (m, 1) (J_{H-P} = 2.0 Hz), and −3.495 (m, 27); 36.43-MHz ^{31}P nmr (−80°), δ −30 (m) (J = 60 Hz). Anal. Calcd for $C_{12}H_{32}O_9P_3Co$: C, 30.51; H, 6.83; Co, 12.48; P, 19.70. Found: C, 30.27; H, 6.10; Co, 12.71; P, 19.95.

η^3-$(CH_3)CHCHCH_2Co[P(OCH_3)_3]_3$ was prepared and characterized in the same manner as η^3-$CH_2CHCH_2Co[P(OCH_3)_3]_3$: mp 150.5° dec; ^1H nmr, (anti isomer) δ −0.87 (doublet of quartets, 1) ($J_{P-H_{anti}}$ = 8.0, $J_{H_{anti}-H}$ = 8.0 Hz), −1.21 (doublet of quartets, 3) (J_{P-CH_3} = 8.0, J_{CH_3-H} = 8.0 Hz), −2.22 (m, 2), −3.50 (m, 27), and −4.54 (m, 1), (syn isomer) δ −1.30 (doublet of quartets, 2) ($J_{P-H_{anti}}$ = 4.0, $J_{H_{anti}-H}$ = 8.0 Hz), −1.59 (doublet of quartets, 3) (J_{P-CH_3} = 4.0, J_{CH_3-H} = 8.0 Hz), −2.16 (doublet of quartets, 1) ($J_{P-H_{syn}}$ = 4.0, $J_{H-H_{syn}}$ = 4.0 Hz), −3.50 (m, 27), and −4.54 (m, 1). Anal. Calcd for $C_{13}H_{34}O_9P_3Co$: C, 32.10; H, 7.05; Co, 12.12; P, 19.14. Found: C, 32.40; H, 7.77; Co, 12.00; P, 18.88.

η^3-$C_6H_5CH_2Co[P(OCH_3)_3]_3$. A slurry of $KCo[P(OCH_3)_3]_4$

(5.94 g, 0.010 mol) and $C_6H_5CH_2I$ (1.96 g, 0.0080 mol) in tetrahydrofuran was stirred for 2 hr at ambient temperatures. The volatile materials were removed under vacuum, and the crude product was extracted from the residue with pentane. The product was recrystallized from pentane at −78° to give brown crystals: mp 137.3° dec; ^1H nmr, δ −1.80 (quartet, 2) (J_{PH} = 6.32 Hz), −3.44 (m, 27), −6.54$_{(meta)}$ (d, 2) (J_{H-H} = 7.5 Hz), −6.96$_{(ortho)}$ (t, 2) (J_{H-H} = 7.5 Hz), and −7.50$_{(para)}$ (t, 1) (J_{H-H} = 7.5 Hz); 36.43-MHz ^{31}P (−80°), δ −22 (d, 2) (J_{PP} = 64.5 Hz) and −51 (t, 1) (J_{PP} = 64.5 Hz). Anal. Calcd for $C_{16}H_{34}O_9P_3Co$: C, 36.78; H, 6.56; Co, 11.28; P, 17.82. Found: C, 36.00; H, 6.95; Co, 10.91; P, 18.75.

$HCo[P(OC_6H_5)_3]_4$ and $P(OC_2H_5)_3$—Exchange Reaction. A solution of triethyl phosphite (33.7 g, 0.199 mol) and HCo-[$P(OC_6H_5)_3$]$_4$ (3.26 g, 0.025 mol) in benzene (200 ml) was heated at 100°. After 1 week, the high field solution ^1H nmr spectrum of the reaction mixture showed that the major product was $HCo[P(OC_6H_5)_3]_3[P(OC_2H_5)_3]$. After 2 weeks reaction, all the substituted products were present in approximately the same concentration and when 3 weeks had elapsed only $HCo[P(OC_6$-$H_5)_3][P(OC_2H_5)_3]_3$ and $HCo[P(OC_2H_5)_3]_4$ were present. Consequently, by quenching the reaction at appropriate intervals, mixtures rich in the desired component could be produced. The products of these mixtures were separated by column chromatography (a neutral alumina column, 50.0 cm long and 2 cm wide, was eluted with a 10% acetone–90% hexane mixture). By this procedure, analytically pure samples of $HCo[P$-$(OC_6H_5)_3]_3[P(OC_2H_5)_3]$ and $HCo[P(OC_6H_5)_3][P(OC_2H_5)_3]_3$ were isolated, but a method for obtaining analytically pure HCo-[$P(OC_6H_5)_3]_2[P(OC_2H_5)_3]_2$ was not devised. These hydrides, white solids, were recrystallized from hexane until their melting points did not vary: mp 186.0 dec; ^1H nmr, δ 13.27 (doublet of quartets) (J_{P_1H} = 63.8, J_{P_2H} = 49.5 Hz). (Anal. Calcd for $C_{60}H_{61}O_{12}P_4C_6$: C, 62.24; H, 5.31; P, 10.70. Found: C, 62.63; H, 5.79; P, 9.55.) mp 177.0 dec; ^1H nmr, δ 14.74 (doublet of quartets) (J_{P_1H} = 8.0 Hz) (Anal. Calcd for $C_{36}H_{61}O_{12}P_4Co$: C, 49.78; H, 7.08; P, 14.26. Found: C, 49.00; H, 7.23; P, 13.89).

$HCo[P(OC_6H_5)_3]_2[P(OC_2H_5)_3]_2$. ^1H nmr, δ 13.99 (triplet of triplets) (J_{P_1H} = 53.6, J_{P_2H} = 11.0 Hz).

$HCo[P(OCH_3)_3]_4$ and $P(OC_2H_5)_3$ and $HCo[P(OC_2H_5)_3]_4$ and $P(OCH_3)_3$ Exchange Reactions. Solutions of triethyl phosphite (16.66 g, 0.100 mol) and $HCo[P(OCH_3)_3]_4$ (5.32 g, 0.009 mol) in benzene (50 ml) and trimethyl phosphite (12.40 g, 0.100 mol) and $HCo[P(OC_2H_5)_3]_4$ (7.27 g, 0.010 mol) in benzene (50 ml) were heated at 100°. Initially, the ^1H nmr spectra (δ 0.0 to −2.0 ppm) of the reaction mixture was the triplet of the methyl resonance of $HCo[P(OC_2H_5)_3]_4$. As reaction proceeded and increasing amounts of $P(OCH_3)_3$ became coordinated, new triplets developed for species of the type $HCo[P(OCH_3)_3]_{4-x}[P(OC_2H_5)_3]_x$ and free $P(OC_2H_5)_3$. After 5 weeks, no further change in either the number or intensity of these resonances was seen. Other areas of the ^1H nmr spectr of the reaction mixture were too complex to afford a ready measure of the equilibrium. When equimolar amounts of ligand were present in these reaction mixtures, their equilibrium solution ^1H nmr spectra were identical. Under similar conditions, $HCo[P(OC_2H_5)_3]_4$ evidenced no ligand exchange with free triphenyl phosphite.

$HCo[P(OCH_3)_3]_4$ and CO Reaction. In a closed vessel (164 ml) that was pressurized with CO (3 atm, 0.02 mol), a solution of $HCo[P(OCH_3)_3]_4$ (1.33 g, 0.002 mol) in C_6H_6 (5 ml) was stirred for 1 week at ambient temperatures. The solution ^1H nmr spectra of the product showed that $HCo[P(OCH_3)_3]_4$, $HCo[P(O$-$CH_3)_3]_3[CO]$, and $HCo[P(OCH_3)_3]_2[CO]_2$ were present in approximate molar ratios of 90:7:3. The reaction was also effected in methanol under identical conditions and the solid product that was isolated after 1 week by recrystallization from pentane at −40° was $HCo[P(OCH_3)_3]_3[CO]$. No unreacted starting material was detected: 60-MHz ^1H nmr, δ 14.34 (quartet) (J_{PH} = 39.24 Hz) and −3.50 (m). After 2 weeks of reaction the ratio of $HCo[P(O$-$CH_3)_3]_3[CO]$ to $HCo[P(OCH_3)_3]_2[CO]_2$ in the product was 3.5: 1: 60-MHz ^1H nmr, δ 13.29 (triplet) (J_{PH} = 11 Hz).

After 3 weeks at 75°, concentrated solutions of $HCo[P(O$-$CH_3)_3]_3[CO]$ in benzene and methanol showed no signs of exchange of CO for free $P(OCH_3)_3$ at molar ratios of 20:1 of phosphite to complex.

Transesterification and Deprotonation Reaction Attempts. A so-

lution of HCo[P(OC$_2$H$_5$)$_3$]$_4$ (7.2 g, 0.010 mol) in methanol (32.04 g, 1.00 mol) was stirred for 2 hr, after which time the HCo-[P(OC$_2$H$_5$)$_3$]$_4$ was recovered unchanged. Under similar reaction conditions, HCo[P(OC$_2$H$_5$)$_3$]$_4$ (7.27 g, 0.010 mol) in THF (15 ml) did not react with H$_2$O (0.180 g, 0.010 mol) nor did HCo-[P(OC$_2$H$_5$)$_3$]$_4$ (7.27 g, 0.010 mol) in methanol (20 ml) react with potassium methoxide (0.701 g, 0.010 mol). Similarly, HCo-[P(OCH$_3$)$_3$]$_4$ was quantitatively recovered from its solutions in C$_2$H$_5$OH, C$_2$H$_5$OH and KOC$_2$H$_5$, THF, and H$_2$O and a slurry of THF and KOH after a 2-hr period.

HCo[P(OCH$_3$)$_3$]$_4$ and CF$_3$COOH. CF$_3$COOH (0.0103 g, 0.0009 mol) was slowly added to a solution of HCo[P(OCH$_3$)$_3$]$_4$ (0.532 g, 0.0009 mol) in acetone-d_6 (1 ml). The solution immediately became colorless, and the ^{1}H nmr spectra at low fields were virtually indistinguishable from that of H$_2$Fe[P(OCH$_3$)$_3$]$_4$: 60-MHz ^{1}H nmr, δ −3.864 (quintet) (J_{PH} = 2.88 Hz) and +13.02 (broad). The ^{1}H nmr spectra at high fields is broad at room temperature presumably due to quadrupolar relaxation effects of the Co (I = $^7\!/_2$) nucleus.

The protonation reaction proceeded with C$_6$D$_6$, C$_7$D$_8$, (C$_2$H$_5$)$_2$O, CH$_3$OH, THF, or CH$_2$Cl$_2$ as solvents. Use of stronger acids such as H$_2$SO$_4$ resulted only in decomposition of the hydride to an intractable oil.

KCo[P(OC$_2$H$_5$)$_3$]$_4$ Reactions. A slurry of KCo[P(OC$_2$H$_5$)$_3$]$_4$ (2.017 g, 0.0026 mol) in THF (25 ml) was stirred at ambient temperatures under vacuum. Hydrogen chloride (0.100 g, 0.0030 mol) was slowly added to the slurry and the mixture immediately became yellow and all the solids appeared to dissolve. The volatile materials were then removed under vacuum, and pentane (10 ml) was used to extract the product from the solids. HCo-[P(OC$_2$H$_5$)$_3$]$_4$ (1.739 g, 0.0024 mol) was recovered in a 90.9% yield.

All operations were similar to the above except that an equimolar amount of H$_2$O (0.054 g, 0.0030 mol) was distilled into the reaction vessel under vacuum. HCo[P(OC$_2$H$_5$)$_3$]$_4$ (1.565 g, 0.00216 mol) was recovered in an 81.9% yield. Triethyl phosphite was detected in the reaction mixture.

A slurry of KCo[P(OC$_2$H$_5$)$_3$]$_4$ (4.037 g, 0.0056 mol) in methanol (25.00 g, 0.781 mol) was stirred at ambient temperatures for 2 hr, during which time the solids slowly dissolved. After the volatile materials were removed under vacuum, the solid product was extracted with pentane (20 ml). The solution ^{1}H spectra of this product showed that both HCo[P(OCH$_3$)$_3$]$_4$ and HCo[P(OC$_2$H$_5$)$_3$]$_4$ were present plus some species with mixed phosphite ligands. The solids insoluble in pentane were unreacted potassium salt (mp 212.0 dec).

With all operations similar to the methanol reactions, ethanol was allowed to react. The only solid pentane-soluble product was HCo[P(OC$_2$H$_5$)$_3$]$_4$ and the pentane insoluble product was unreacted potassium salt (mp 212.0 dec).

HCo[P(O-i-C$_3$H$_7$)$_3$]$_4$ and KH Interaction. A slurry of HCo[P(O-i-C$_3$H$_7$)$_3$]$_4$ (0.892 g, 0.001 mol) and KH (0.040 g, 0.001 mol) in THF (20 ml) was stirred at 80° for 2 weeks during which time no hydrogen evolution, as monitored by a Toepler pump, was evident.

CH$_3$Co[P(OCH$_3$)$_3$]$_4$ and HCl. HCl (0.3648 g, 0.010 mol) was distilled into a solution of CH$_3$Co[P(OCH$_3$)$_3$]$_4$ (5.707 g, 0.010 mol) in tetrahydrofuran (24 ml). The yellow solution was stirred for 2 hr during which time it slowly became blue. One-hundredth of a mole of methane (mol wt 16.25, theory 16.043 g/mol) was evolved.

η^3-CH$_2$CHCH$_2$Co[P(OCH$_3$)$_3$]$_3$ and CO. (1) A solution of η^3-CH$_2$CHCH$_2$Co[P(OCH$_3$)$_3$]$_3$ (0.472 g, 0.001 mol) in toluene (5 ml) was stirred at ambient temperatures under a 1 atm pressure of CO. A decrease in CO pressure, attributable to an approximate uptake of an equimolar (0.001 mol) amount of CO, was observed over the course of 6 hr. No further uptake of CO was seen as stirring was continued for 12 hr. The solution was filtered. Integration of the ^{1}H nmr spectra showed that 1 mol of P(OCH$_3$)$_3$ had been liberated per mole of complex. A single C–O stretch (ν_{CO} = 1956 cm^{-1}) was evident in the infrared spectrum. After the volatile materials were removed under vacuum, the solid product was recrystallized from pentane at −78°: 100-MHz nmr ((CH$_3$)$_4$Si = 0), δ −1.070 (doublet of triplets, 2) ($J_{H_{anti}P}$ = 9.52, JH$_{anti}$H = 9.52 Hz), −2.020 (triplet, 2) ($J_{H_{syn}H}$ = 5.51 Hz), −2.955 (m, 18), and −4.211 (m, 1) ($J_{H-H_{syn}}$ = 5.51, $J_{H-H_{anti}}$ = 9.52 Hz).

(2) A solution of η^3-CH$_2$CHCH$_2$Co[P(OCH$_3$)$_3$]$_3$ (0.472 g,

0.001 mol) in methanol (5 ml) was stirred at ambient temperatures under an approximate CO pressure of 3 atm, which corresponded to a 10:1 molar ratio of CO to complex. After 2 weeks the reaction vessel was opened, and the volatile products were separated by vacuum distillation. A yellow volatile product that reacts with P(OCH$_3$)$_3$ to evolve CO and give η^3-CH$_2$CHCH$_2$Co[P(O-CH$_3$)$_3$][CO]$_2$ is recovered; this volatile product is η^3-CH$_2$CHCH$_2$Co(CO)$_3$. The solid products were recrystallized from pentane at −40° to give the yellow crystalline product η^3-CH$_2$CHCH$_2$Co[P(OCH$_3$)$_3$][CO]$_2$: 100-MHz ^{1}H nmr ((CH$_3$)$_4$Si = 0), δ −1.303 (doublet of doublets, 2) ($J_{H_{anti}P}$ = 10.62, JH$_{anti-H}$ = 2.07 Hz), −2.105 (doublet of doublets, 2) ($J_{H_{syn}-P}$ = 2.90, $J_{H_{syn}H}$ = 5.82 Hz), −2.826 (doublet, 9) (J_{P-H} = 12.00 Hz), and −3.98 (m, 1).

η^3-C$_6$H$_5$CH$_2$Co[P(OCH$_3$)$_3$]$_3$ and CO. Under conditions similar to those in the reaction of η^3-CH$_2$CHCH$_2$Co[P(OCH$_3$)$_3$]$_3$ and CO, a solution of η^3-C$_6$H$_5$CH$_2$Co[P(OCH$_3$)$_3$]$_3$ was stirred in contact with an atmosphere of CO. Again uptake of CO was approximately equimolar; however, in this reaction, the uptake ceased after 4 hr. One mole of P(OCH$_3$)$_3$ had been replaced and the infrared spectrum of the product showed a single C–O (ν_{CO} = 1966 cm^{-1}) stretch: 100-MHz ^{1}H nmr [(CH$_3$)$_4$Si = 0], δ −3.30 (triplet, 2) (J_{P-H} = 3.0 Hz), −3.05 (m, 18), and −6.95 (m, 5).

Deuteration of HCo[P(OCH$_3$)$_3$]$_4$. A solution of HCo-[P(OCH$_3$)$_3$]$_4$ (0.532 g, 0.0009 mol) and D$_2$O (0.180 g, 0.009 mol) in acetone-d_6 (3 ml) was stirred for 24 hr after which time no change in the ^{1}H nmr spectrum of the solution was evident (δ 15.09 (quintet) (J_{PH} = 19.0 Hz) and −3.57 (m)). Upon addition of CF$_3$COOD (0.0103 g, 0.0009 mol), the solution ^{1}H nmr spectrum changed markedly (δ 13.02 (broad) and −3.864 (quintet) (J_{PH} = 2.88 Hz)). After 2 hr the high field ^{1}H resonance became vanishingly small with no concomitant change in the low field resonances. The solution was then evaporated to dryness, and H$_2$O (0.162 g, 0.009 mol) and acetone-d_6 (3 ml) were then added to the solid. After 2 hr, the high field ^{1}H resonance reappeared while no change in the low field resonance was evident.

References and Notes

(1) Paper I, E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, **95**, 5419 (1973).
(2) (a) Cornell University. (b) University of Pennsylvania.
(3) J. Halpern, *Advan. Chem. Ser.*, **No. 70**, 1 (1969).
(4) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).
(5) R. Ugo, *Chim. Ind. (Milan)*, **51**, 1319 (1969).
(6) E. L. Muetterties, Ed., "Transition Metal Hydrides," Marcel Dekker, New York, N.Y., 1971.
(7) E. L. Muetterties and F. J. Hirsekorn, *J. Chem. Soc., Chem. Commun.*, 683 (1973).
(8) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 4545 (1972).
(9) See ref 6 for a general review of structure and systematics.
(10) R. W. Baker and P. Pauling, *Chem. Commun.*, 322 (1971).
(11) R. W. Baker, B. Ilmaier, P. J. Pauling, and R. S. Nyholm, *Chem. Commun.*, 1077 (1970).
(12) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970).
(13) D. D. Titus, A. A. Orid, R. E. Marsh, and H. B. Gray, *Chem. Commun.*, 322 (1971).
(14) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).
(15) Like the parent hydrides, these "mixed" phosphitocobalt hydrides are stereochemically nonrigid.
(16) Because the chemical shifts of the individual hydrides were so similar, an unequivocal nmr characterization of individual hydrides in the reaction mixture was not feasible.
(17) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
(18) Ligand substitution in Mo(CO)$_5$(NR$_3$) is of the interchange type, k = {k_1 + k_2[CO]}[complex]. Sensitivity of rate to ligand character was not found to be significant. W. D. Covey and T. L. Brown, *Inorg. Chem.*, **12**, 2820 (1973).
(19) E. L. Muetterties and J. W. Rathke, to be submitted for publication.
(20) This point was specifically checked with respect to the solvent medium, tetrahydrofuran, for the ligand dissociation process.
(21) Acetonitrile did not react with the potassium salt but this does not necessarily place a limit on the pK_a of the acid since kinetic effects may be operative in this potential solvolysis reaction.

(22) Reference 6, p 238.
(23) (a) Cf. P. Meakin, E. L. Muetterties, and J. P. Jesson, J. Amer. Chem. Soc., 95, 75 (1973). (b) It should be noted that an alternative rationale of the line-shape changes is in quadrupolar relaxation effects.
(24) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, J. Amer. Chem. Soc., 92, 3482 (1970).
(25) R. F. Heck, Advan. Organometal. Chem., 4, 243 (1966).
(26) E. L. Muetterties and F. J. Hirsekorn, to be submitted for publication.
(27) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, J. Amer. Chem. Soc., 83, 1601 (1961).
(28) Plausible structural alternatives are a "bidentate" allyl ligand bridging two equatorial sites or an equatorial and an axial site in an idealized trigonal bipyramid, provided there is fast rotation of the allyl group in the C_3 plane, and bridging an apical and basal site (free allyl group rotation) or two basal sites of an idealized square pyramid. In the last case, there would be the possibility of two diastereomers unless allyl group rotation

in the C_3 plane is fast. Geometric distinctions among all alternatives are small. A crystallographic study of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ is planned.
(29) An alternative based on trigonal bipyramidal or square pyramidal structural forms[27] comprises some type, e.g., a Berry process, of five-coordinate rearrangement. In these alternative idealized structural forms, rotation of the allyl ligand about some CoP_3 axis will not lead to environmental equivalence of phosphorus atoms. Assuming solution state structure emulates closely the solid state structure, the planned[27] crystallographic study may resolve this point if the solid state structure is very close to either of these two[27] idealized structures.
(30) The $\eta^3 \rightleftharpoons \eta^1$ conversion is postulated as a first step in the catalytic function of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ in aromatic hydrocarbon hydrogenations, E. L. Muetterties and F. J. Hirsekorn, J. Amer. Chem. Soc., 96, 4063 (1974).
(31) $CO_2(CO)_8$ has bridging CO groups for the solid state, but it is claimed that a nonbridged isomer coexists with the bridged isomer in solution: K. Noack, Helv. Chim. Acta, 47, 1555 (1964).

Carbon-13 Nuclear Magnetic Resonance Study of the Fluxional Behavior of Cyclooctatetraenetricarbonylchromium, -molybdenum, and -tungsten and Tetramethylcyclooctatetraenetricarbonylchromium

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Abstract: The fluxional behavior of 1,3,5,7-tetramethylcyclooctatetraenetricarbonylchromium, (TMCOT)Cr(CO)$_3$, previously shown by ^{1}H nmr to be based on a single, reversible type of 1,2-shift has been reexamined with ^{13}C nmr. The previous conclusions are confirmed. For the cyclooctatetraenetricarbonyl metal compounds, (COT)M(CO)$_3$, M = Cr, Mo, or W, for which no pathway had previously been established, ^{13}C nmr shows conclusively that 1,2-shifts are not the pathway and that only 1,3-shifts or a process resulting in random shifts are admissible. While 1,3-shifts cannot be ruled out rigorously, it is argued that a process in which the metal atom moves to a position over the midpoint of a virtually flat octagonal ring whence it can pass with equal probability to any of the eight equilibrium positions is more likely. On this basis the qualitatively different behavior of the (TMCOT)M(CO)$_3$ and (COT)M(CO)$_3$ compounds can be understood as arising from the different energies required to flatten the rings.

For almost a decade now there has been much interest in stereochemically nonrigid molecules. Conjugated cyclopolyenemetal compounds such as (COT)M(CO)$_3$, where COT = cyclooctatetraene and M = (Fe, Ru, Os), **1**, and (Cr, Mo, and W), **2**, have been studied in much detail.[1-8] The bonding of the group VIII and group VI metals to the cyclooctatetraene ring differs[1,9] making a direct comparison of the spectra and dynamical behavior of the two groups inappropriate. Earlier work has been reviewed[2,10] previously in detail. The rearrangement process for the group VIII metals has been shown directly from the fitting of simulated spectra to have an omnidirectional 1,2-shift mechanism. Because of the extensive spin–spin coupling, the spectra of the group VI metals were too complex for a dynamical analysis. The mechanism was thus inferred after a study[11] of the isostructural[9,12] (TMCOT)M(CO)$_3$, where TMCOT = 1,3,5,7-tetramethylcyclooctatetraene and M = Cr, Mo, and W, which indicated that a 1,2-shift was operative as the low energy process in the substituted complexes.

Little if anything more could be done to elucidate the mechanism of the site exchange in compounds of type **2** until Fourier transform carbon-13 spectrometers became available. Carbon-13 offers several advantages over proton nmr for the study of fluxional molecules.[13] Of particular relevance here is the fact that the low natural abundance of carbon-13 eliminates complications due to spin–spin coupling when broad-band proton decoupling is employed. Thus in the present case, compounds **2** should have simple spectra consisting of four discrete lines in the slow exchange limit. As the temperature is raised, the mode of collapse of these peaks, *i.e.*, uniform or selective, can easily be discerned.

The 1,2-shift originally discovered for (COT)Ru(CO)$_3$[4] has been confirmed *via* carbon-13 for (COT)Fe(CO)$_3$.[14] In a preliminary communication[15] we have reported that (COT)Mo(CO)$_3$ does *not* undergo a 1,2-shift as the four ring signals broaden uniformly. We have now completed a carbon-13 nmr study of the compounds **2** as well as (TMCOT)Cr(CO)$_3$ and report the results in detail here.

Experimental Section

The compounds were all prepared by methods described previously.[6,11,16-18] All samples were handled under nitrogen. Solvents were dried over Na–K benzophenone and distilled just prior to use.

Instrumental Measurements. The proton nmr spectra were measured on a Varian Associates HA-100 spectrometer. Temperature calibrations for the variable temperature spectra were obtained from either methanol or ethylene glycol standards and are expected to be accurate to ±3°.

Carbon-13 nmr spectra were recorded on a Jeol PFT-100/Nicolet 1080 Fourier transform spectrometer at 25.035 MHz. The