An Examination of the Reductive-Elimination Reaction. Chemistry of XYCo[P(OR)$_3$]$_z$$^+$ Complexes[1]
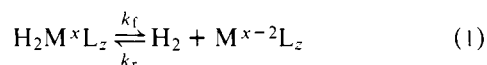
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Abstract: Protonation of HCo[P(OR)$_3$]$_4$ yielded the cationic dihydride complexes, H$_2$Co[P(OR)$_3$]$_4$$^+$, which were isolated as hexafluorophosphate salts. All had cis octahedral geometry in solution. Exchange of D$_2$ with the dihydrides gave only D$_2$Co[P(OR)$_3$]$_4$$^+$; no HD was formed. Reductive elimination of hydrogen from these complexes decreased in the order P(O-*i*-C$_3$H$_7$)$_3$ > P(OCH$_3$)$_3$ > P(OC$_2$H$_5$)$_3$. This elimination step proceeded without deuterium incorporation in the presence of deuterated solvents. At 30 °C, the unimolecular rate constant for the elimination reaction in H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$ was 4.2 × 10^{-5} s^{-1}. Reductive elimination of methane from the presumed H(CH$_3$)Co[P(OCH$_3$)$_3$]$_4$$^+$, obtained by protonation of CH$_3$Co[P(OCH$_3$)$_3$]$_4$ and by methylation of HCo[P(OCH$_3$)$_3$]$_4$, was at least three orders of magnitude greater than reductive elimination of hydrogen from the corresponding dihydride complex. Attempts to isolate (CH$_3$)$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$, presumably generated by the methylation of CH$_3$Co[P(OCH$_3$)$_3$]$_4$, were unsuccessful because of facile elimination of methane. Key intermediates in the reductive elimination of hydrogen and of methane in the H$_2$Co$^+$ and H(CH$_3$)Co$^+$ complexes were the tetrahedral Co[P(OR)$_3$]$_4$$^+$ species. Salts of these intermediates were obtained by an indirect procedure, and a series of relatively stable five-coordinate adducts LCo[P(OR)$_3$]$_4$ with L = NH$_3$, CH$_3$CN, ethylene, propylene, and diphenylacetylene were obtained from the coordinately unsaturated complexes. All Co[P(OR)$_3$]$_4$$^+$ complexes were very active catalysts for olefin isomerization. In these catalytic reactions, the key intermediates were of the form H(allyl)Co[P(OR)$_3$]$_3$$^+$.
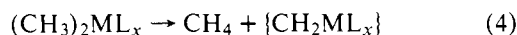
Introduction

Important in the reaction schemes of coordination complexes, organometallic compounds, and even metal surfaces is the reductive-elimination reaction

$$H_2M^xL_z \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2 + M^{x-2}L_z \qquad (1)$$

which is the complementary or reverse reaction to the oxidative-addition reaction. In the forward reductive-elimination step, there is a formal decrease of two in the oxidation state of the metal atom. The thermodynamic factors reflected in the k_f/k_r ratio of a reaction like (1) have not been systematically evaluated in coordination chemistry, although the typical M–H bond strengths[2] in low-valent and neutral coordination complexes are generally sufficient to counter the 105 kcal/mol bond energy gain generated in the hydrogen molecule in (1). Electron density on the metal atom is a key factor in stabilizing the M–H bond, and accordingly, the equilibrium in (1) will tend to lie to the left with ligands that are strong σ donors and weak π acceptors.

Other general classes of the reductive-elimination reaction are illustrated in the equations

$$R(H)ML_x \rightarrow RH + ML_x \qquad (2)$$

$$R_2ML_x \rightarrow RR + ML_x \qquad (3)$$

$$(CH_3)_2ML_x \rightarrow CH_4 + \{CH_2ML_x\} \qquad (4)$$

$$(RC{=}O)(H)ML_x \rightleftharpoons RCHO + ML_x \qquad (5)$$

All are important established or implicated steps in stoichiometric or catalytic reaction schemes. Reaction 2 is a terminal step in the hydrogenation of alkanes and is only rarely a reversible step. Alkane elimination via reaction 3 is largely observed[3] for platinum(IV) and gold(III) complexes and is presently known only as an irreversible reaction. Methane elimination from a dimethyl transition metal complex, eq 4, is well established[4] and the possible methylene (carbene) complex is implicated as a catalyst precursor in the olefin metathesis reaction.[5] Aldehyde elimination from the acylmetal hydride, eq 5, is a key step in the hydroformylation reaction; the reverse reaction is a step in decarbonylation reactions.

Although reductive-elimination reactions are well known,[6] the mechanistic details are not. We describe here the first of our studies of the reductive-elimination reaction wherein qualitative and quantitative (kinetic) aspects provide some insight to mechanistic features of classes 1, 2, and 4 of the elimination reaction. This study is based on the chemistry of complexes of the form XYCo[P(OR)$_3$]$_z$$^+$ derived from protonation and alkylation reactions of HCo[P(OR)$_3$]$_4$, CH$_3$Co[P(OR)$_3$]$_4$, and η^3-C$_3$H$_5$Co[P(OR)$_3$]$_3$. Also described is the utilization of the alkyl- and allylcobalt complexes protonation reaction for the synthesis of species like Co[P(OCH$_3$)$_3$]$_4$L$^+$, Co[P(OCH$_3$)$_3$]$_4$(olefin)$^+$, Co[P(OCH$_3$)$_3$]$_4$$^+$, and Co[P(OCH$_3$)$_3$]$_3$(diene)$^+$ and the catalytic properties of Co[P(OCH$_3$)$_3$]$_4$$^+$.

Results and Discussion

Synthesis and Chemistry of H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$. Protonation of HCo[P(OCH$_3$)$_3$]$_4$[7] with trifluoroacetic acid quantitatively yielded H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$ (1), which was isolated in crystalline form as the PF$_6$$^-$ salt. The ^{1}H NMR spectrum of the cationic dihydride consisted at 27 °C of a binomial quintet for the OCH$_3$ protons (virtual coupling of all four phosphorus nuclei) and a broad hydride resonance. The latter resonance sharpened on temperature decrease and at −36 °C was a complex multiplet similar to cis-H$_2$Ru(PR$_3$)$_4$ complexes.[8] Line-shape changes over the 30 to −36 °C temperature interval were characteristic of a mutual intramolecular exchange process; thus, this complex is analogous to the isoelectronic and stereochemically nonrigid iron and ruthenium H$_2$ML$_4$ complexes. A very slight asymmetry in the hydride resonance of this cobalt complex suggested the presence of small amounts of the trans stereoisomer.

The triethyl phosphite analogue, H$_2$Co[P(OC$_2$H$_5$)$_3$]$_4$$^+$ (2), was prepared in an identical fashion and was spectrally analogous to the trimethyl phosphite derivative except that the alkoxy proton resonance consisted of a CH$_3$ triplet and a methylene quartet of quintets (virtual coupling of all four phosphorus nuclei). H$_2$Co[P(O-*i*-C$_3$H$_7$)$_3$]$_4$$^+$ (3) was prepared by protonation of the corresponding hydride with HPF$_6$ in diethyl ether and by oxidative addition of hydrogen to Co[P(O-*i*-C$_3$H$_7$)$_3$]$_4$$^+$. This dihydride, difficult to obtain pure, had a hydride NMR resonance similar to those of the above two dihydrides.
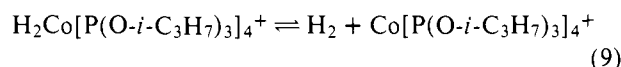
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All three six-coordinate hydrides showed a hydride NMR resonance at about 2 ppm downfield from the parent five-coordinate HCo[P(OR)$_3$]$_4$ hydride resonances. The expected A$_2$B$_2$ ^{31}P{^{1}H} spectra were not observed even at low temperatures; a single broad (150–200 Hz minimum line width) resonance was observed down to −130 °C. The broad resonances are ascribed to the adverse effect of an interaction of the cobalt nucleus with the ^{31}P nucleus.

The crystalline hexafluorophosphate salts of **1–3** were indefinitely stable in an inert atmosphere and for several days in air. In solution, **1** and **2** slowly and irreversibly decomposed (several weeks at 20 °C and hours at 80 °C) to form hydrogen, the very stable Co[P(OR)$_3$]$_5$$^+$ cations,[9] cobalt metal, and Co[P(OR)$_3$]$_6$$^{3+}$. This decomposition proceeded through the reaction sequence

$$H_2Co[P(OR)_3]_4^+ \rightleftharpoons H_2 + Co[P(OR)_3]_4^+ \quad (6)$$

$$S(\text{solvent}) + Co[P(OR)_3]_4^+ \rightleftharpoons SCo[P(OR)_3]_4^+ \quad (7)$$

$$9SCo[P(OR)_3]_4^+ \xrightarrow[\text{steps}]{\text{several}} 6Co[P(OR)_3]_5^+$$
$$+ Co[P(OR)_3]_6^{3+} + 2Co + 9S \quad (8)$$
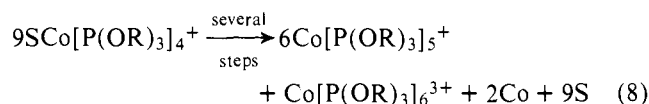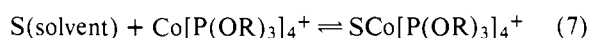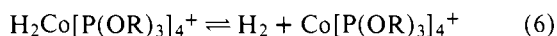
In contrast, the isopropyl derivative, **3**, decomposed in solution at 20 °C within 1 day to form hydrogen and Co[P(O-*i*-C$_3$H$_7$)$_3$]$_4$$^+$.[10]

$$H_2Co[P(O-i-C_3H_7)_3]_4^+ \rightleftharpoons H_2 + Co[P(O-i-C_3H_7)_3]_4^+ \quad (9)$$

The latter cation, unlike the trimethyl and triethyl phosphite analogues (see later discussion), was stable in solution, and underwent no detectable disproportionation (eq 8).

By taking advantage of the equilibrium reactions 6 and 9, the dideuteride complexes D$_2$Co[P(OR)$_3$]$_4$$^+$ were prepared in a dichloromethane solution. Analysis of the residual gases by mass spectrometry showed only H$_2$ and D$_2$ present; HD was not detected. An analogous displacement was observed between H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$ and D$_2$ in acetonitrile solution, although about 10% HD was produced presumably due to a deprotonation step that occurred slowly in weak donor solvents:
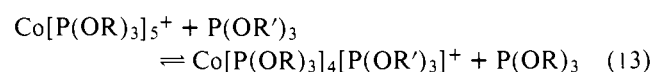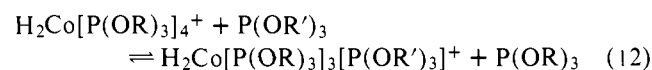
$$S + H_2Co[P(OR)_3]_4^+ \rightleftharpoons SH^+ + HCo[P(OR)_3]_4 \quad (10)$$

In stronger donor or basic solvents, complete deprotonation was effected. Deprotonation of H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$ to HCo[P(OCH$_3$)$_3$]$_4$ was complete in less than 2 h through reaction with a methanol solution of sodium methoxide and with the nitrogen base 1,1,3,3-tetramethylguanidine. The role of solvents was also demonstrated by the moderately fast proton exchange between HCo[P(OR)$_3$]$_4$ and H$_2$Co[P(OR)$_3$]$_4$$^+$ in donor solvents (NMR time scale).
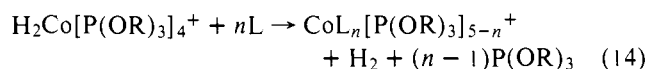
Reductive Elimination of Hydrogen from H$_2$Co[P(OCH$_3$)$_3$]$_4$PF$_6$. Reaction of donor ligands such as carbon monoxide or phosphites with the cobalt(III) dihydride cations, H$_2$Co[P(OR)$_3$]$_4$$^+$, gave pentacoordinate cobalt(I) cations and hydrogen:

$$H_2Co[P(OR)_3]_4^+ + L \rightleftharpoons CoL[P(OR)_3]_4^+ + H_2 \quad (11)$$
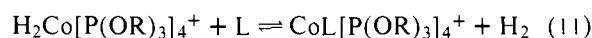
The equilibrium constants for eq 11 lie far to the right for L = CO or P(OR)$_3$; the reactions were not detectably reversible under 1 atm of hydrogen. Stoichiometry of the Co(I) complexes obtained was dependent on ligand exchange equilibria in both product and reactant complexes:

H$_2$Co[P(OR)$_3$]$_4$$^+$ + P(OR′)$_3$
$$\rightleftharpoons H_2Co[P(OR)_3]_3[P(OR')_3]^+ + P(OR)_3 \quad (12)$$

Co[P(OR)$_3$]$_5$$^+$ + P(OR′)$_3$
$$\rightleftharpoons Co[P(OR)_3]_4[P(OR')_3]^+ + P(OR)_3 \quad (13)$$

Carbon monoxide reacted with H$_2$Co[P(OCH$_3$)$_3$]$_4$PF$_6$ to give mainly Co(CO)$_2$[P(OCH$_3$)$_3$]$_3$PF$_6$ and Co(CO)[P(OCH$_3$)$_3$]$_4$PF$_6$,[11] whereas the products obtained from the reaction of H$_2$Co[P(OCH$_3$)$_3$]$_4$PF$_6$ with P(OCH$_2$CH$_3$)$_3$, L, gave a near random mixture of ethyl and methyl phosphite complexes which could be only partially fractionated on an alumina chromatography column:

$$H_2Co[P(OR)_3]_4^+ + nL \rightarrow CoL_n[P(OR)_3]_{5-n}^+$$
$$+ H_2 + (n-1)P(OR)_3 \quad (14)$$

The facile reductive elimination of hydrogen from the d^6 cobalt(III) dihydride cations contrasted sharply with the neutral isoelectronic H$_2$Fe[P(OCH$_3$)$_3$]$_4$ complex which showed no evidence of reaction with excess trimethyl phosphite at temperatures up to 120 °C. Actually Fe[P(OCH$_3$)$_3$]$_5$ reacted with hydrogen at 25 °C

$$Fe[P(OCH_3)_3]_5 + H_2 \rightarrow P(OR)_3 + H_2Fe[P(OR)_3]_4 \quad (15)$$

to form the dihydride with displacement of a phosphite ligand.[12] This dramatic shift in the equilibrium constant for these reactions of isoelectronic complexes may be ascribed to the higher electron density in the iron complex which can lead to greater stabilization of the iron hydride complex and to a lower stability of the M–P bond in the pentakis phosphite iron derivative. The complexes H$_2$Fe[P(O-*i*-C$_3$H$_7$)$_3$]$_4$ and H$_2$Fe[P(OC$_6$H$_5$)$_3$]$_4$ underwent exchange reactions[13a] with deuterium gas at 25 and 80 °C, respectively, but equilibrium amounts of H$_2$, HD, and D$_2$ were observed in the product gases suggesting that a clean unimolecular dissociation of H$_2$ was not the initial step in the exchange.

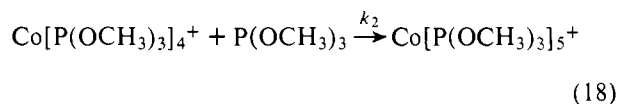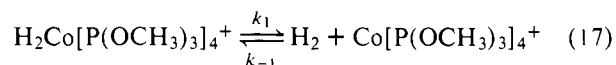The hydrogen elimination reaction, 11, is similar in concept to the hydrogen exchange reaction

$$H_2Co[P(OR)_3]_4^+ + D_2 \rightleftharpoons D_2Co[P(OR)_3]_4^+ + H_2 \quad (16)$$
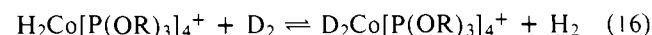
for which a bimolecular mechanism involving a 20-electron intermediate or transition state H$_2$D$_2$Co[P(OR)$_3$]$_4$$^+$ or a mechanism involving initial dissociation of phosphite followed by addition of H$_2$ to give H$_2$D$_2$Co[P(OR)$_3$]$_4$$^+$ are both quite implausible because no HD was detected in the products of eq 16 and because of the formal oxidation state of five for such species. A bimolecular process for the ligand displacement of hydrogen, eq 11, is less improbable than for reaction 16; however, a much more attractive intermediate for both reactions 11 and 16 would be Co[P(OR)$_3$]$_4$$^+$ derived from a dissociative reaction mode.

When monitored by NMR, the rates of both substitution reactions 12 and 13 were essentially independent of the concentration of the excess ligand. Preliminary observations of the trimethyl phosphite ligand displacement of hydrogen in H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$ (eq 11) under pseudo-first-order conditions by monitoring the visible absorption of the product Co[P(OCH$_3$)$_3$]$_5$$^+$ also showed the rate not to be dependent on concentration of trimethyl phosphite, suggesting preliminary unimolecular ligand dissociation as the rate-limiting step. Kinetic parameters were obtained for the latter reaction both spectrophotometrically and by following evolution of hydrogen in a vacuum system. The rate constant for the analogous reaction, 11, with triethyl phosphite and H$_2$Co[P(OC$_2$H$_5$)$_3$]$_4$$^+$ was also obtained by following hydrogen evolution. The exchange equilibria prohibited facile analysis of the reductive elimination reaction for mixed ligand systems; relative rate constants for H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$ and Co[P(OCH$_3$)$_3$]$_5$$^+$ in reactions 11 (L = P(OCH$_3$)$_3$), 12 (L = P(OC$_2$H$_5$)$_3$), and 13 (L = P(OC$_2$H$_5$)$_3$) were 1, 5, and 10, respectively.

From a spectrophotometry-based kinetic analysis of the trimethyl phosphite displacement of hydrogen from H$_2$Co[P(OCH$_3$)$_3$]$_4$$^+$, eq 11, the apparent rate constants, k(obsd) = observed rate/[H$_2$Co[P(OCH$_3$)$_4$]$_4$$^+$], showed little de-

pendence on the concentration of $P(OCH_3)_3$. A dissociative (reductive elimination) model based on the reactions

$$H_2Co[P(OCH_3)_3]_4^+ \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} H_2 + Co[P(OCH_3)_3]_4^+ \quad (17)$$

$$Co[P(OCH_3)_3]_4^+ + P(OCH_3)_3 \overset{k_2}{\rightarrow} Co[P(OCH_3)_3]_5^+$$

$$(18)$$

provided the best data fit with a "steady-state" concentration of the intermediate $Co[P(OCH_3)_3]_4^+$ and the rate equations:

$$\text{initial rate} \simeq k(\text{obsd})[H_2Co[P(OCH_3)_3]_4^+]_{\text{initial}}$$

$$\simeq \frac{-d[H_2Co[P(OCH_3)_3]_4PF_6]}{dt}$$

$$= \frac{k_1 k_2 [H_2Co[P(OCH_3)_3]_4PF_6][P(OCH_3)_3]}{k_{-1}[H_2] + k_2[P(OCH_3)_3]} \quad (19)$$

$$\frac{1}{k(\text{obsd})} = \frac{[H_2Co[P(OCH_3)_3]_4PF_6]_{\text{initial}}}{\text{initial rate}}$$

$$= \frac{1}{k_1} + \frac{k_{-1}[H_2]}{k_1 k_2 [P(OCH_3)_3]} \quad (20)$$

Least-squares analysis of the data established a linear relationship between $1/k(\text{obsd})$ and $1/[P(OCH_3)_3]$ with values for $k_1 = 4.2 \times 10^{-5} \text{ s}^{-1}$ at 30 °C and $k_{-1}[H_2]/k_2 = 4.82 \times 10^{-4}$ M. The value of $k_{-1}[H_2]/k_2 = 4.82 \times 10^{-4}$ M only set a *lower bound* for the ratio k_{-1}/k_2. During the measurement time, $[H_2]$ varied from approximately 0–6% of 1.3×10^{-3} M, i.e., reached a maximum of 7.8×10^{-4} M in the sealed UV cell. Therefore $k_{-1}/k_2 > 4.86 \times 10^{-4}/7.8 \times 10^{-4} = 0.6$. It may be concluded that trapping of $Co[P(OCH_3)_3]_4^+$ by H_2 or $P(OCH_3)_3$ was quite competitive, which is not to say that the products $H_2Co[P(OCH_3)_3]_4^+$ and $Co[P(OCH_3)_3]_5^+$ are equally favored thermodynamically. Only by observing the reaction under conditions of low hydrogen concentration were kinetic ambiguities due to the back reaction (k_{-1}, eq 17) avoided.

The reductive elimination reaction occurred faster in acetonitrile than in methylene chloride solution, and ligand redistribution forming $Co[P(OCH_3)_3]_5^+$ was evident even in the absence of added $P(OCH_3)_3$. Polarity effects may have accounted for the rate difference in reductive elimination from $H_2Co[P(OCH_3)_3]_4^+$, perhaps augmented by reductive elimination from species such as $H_2Co(CH_3CN)[P(OCH_3)_3]_3^+$.

Kinetic data for the trimethyl phosphite reaction with $H_2Co[P(OCH_3)_3]_4^+$ obtained by direct tensimetric measurement of the hydrogen evolution rate showed an invariance in rate with changes in the concentration of the trimethyl phosphite as it should be for the approximation of $k_2[P(OCH_3)_3] \gg k_{-1}[H_2]$. The average observed rate constant at 23 °C of $1.45 \times 10^{-5} \text{ s}^{-1}$ when corrected to 30 °C became $\sim 3 \times 10^{-5} \text{ s}^{-1}$. This was in fair agreement with the 4.2×10^{-5} value at 30 °C determined by the spectrophotometric method. Deuterium evolution from the $D_2Co[P(OCH_3)_3]_4^+$ and $P(OCH_3)_3$ reaction was followed to obtain a rate $k(\text{obsd})$ of $0.93 \times 10^{-5} \text{ s}^{-1}$ at 23 °C. The kinetic isotope ratio of $K^H(\text{obsd}):k^D(\text{obsd})$ was 1.51:1. A rough measure of the activation parameters for the hydrogen elimination reaction was obtained for the temperature range of 23–40 °C with $\Delta H^{\ddagger} = 21 \pm 1.0$ kcal.

Hydrogen displacement rate in the triethyl phosphite reaction system

$$H_2Co[P(OC_2H_5)_3]_4^+ + P(OC_2H_5)_3 \rightarrow H_2$$
$$+ Co[P(OC_2H_5)_3]_5^+ \quad (21)$$
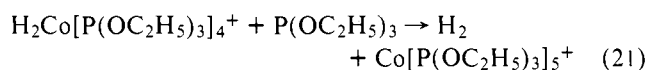
was followed by measuring the hydrogen evolution rate. The observed rate at 23 °C fell from $0.23 \times 10^{-5} \text{ s}^{-1}$ to 0.18×10^{-5} s^{-1} at 23 °C as the molar ratio of ligand to complex fell from 16.4 to 10.6 but plots of $-\ln [H_2(\text{total}) - H_2(\text{at a time } t)]$ vs. time were linear over 2 half-lives. Hence, this reaction is presumed to be mechanistically analogous to the trimethyl phosphite system. The observed rate of hydrogen elimination for the triethyl phosphite system was $\sim$ seven times lower than that observed in the trimethyl phosphite system. The much more sterically congested triisopropyl phosphite analogue was by far the least stable of the set of three complexes; hydrogen evolution from the solution state of this complex, eq 9, was complete within 1 day *in the absence of additional phosphite ligands*.

All the kinetic data for the phosphite displacement of hydrogen from the $H_2Co[P(OR)_3]_4^+$ complexes point to a dissociative (reductive elimination) reaction but a distinction between a dissociative and an interchange (I_d) reaction cannot be made with the kinetic data alone. However, the isolation of the specific intermediate, $Co[P(OCH_3)_3]_4^+$, as a crystalline hexafluorophosphate salt (vide infra) and the demonstration that this species, in fact, reacts with hydrogen and with trimethyl phosphite to form $H_2Co[P(OCH_3)_3]_4^+$ and $Co[P(OCH_3)_3]_5^+$, respectively, are strong evidence that the phosphite reaction with $H_2Co[P(OR)_3]_4^+$ is largely a dissociative (reductive elimination) reaction, rather than an interchange (I_d) reaction. Furthermore, the sterically congested $H_2Co[P(O-i-C_3H_7)_3]_4^+$ complex slowly evolved hydrogen and yielded the isolable $Co[P(O-i-C_3H_7)_3]_4^+$ cation. Solution reactivities (disproportionation reactions) of the $Co[P(OCH_3)_3]_4^+$ and $Co[P(OC_2H_5)_3]_4^+$ intermediates were too great to allow quantitative studies of these coordinately unsaturated complexes.

Protonation of $CH_3Co[P(OCH_3)_3]_4$—Reductive Elimination of Methane. Protonation of $CH_3Co[P(OCH_3)_3]_4$ with CF_3COOH or $HO(C_2H_5)_2PF_6$ in methanol or acetone led to immediate methane formation. The reaction was essentially complete within the time of mixing at −20 °C and in less than 45 min at −45 °C. At −70 °C, about 31% reaction occurred after ten min. Protonation of $CD_3Co[P(OCH_3)_3]_4$ in CH_2Cl_2 led to only CD_3H formation and protonation of $CH_3Co[P(OCH_3)_3]_4$ in CD_2Cl_2 to only CH_4 formation. Clearly this experiment eliminates methane generation by a methyl radical scavenging process operating on solvent, P–O–CH_3, or other Co–CH_3 protons. All attempts to detect the presumed intermediate, cis-$CH_3(H)Co[P(OCH_3)_3]_4^+$, were unsuccessful. Postulation of the cis-methylhydridocobalt intermediate seems eminently reasonable in the light of the above-discussed protonation of $HCo[P(OCH_3)_3]_4$. Methane elimination from cis-methylhydridometal complexes is typically an irreversible reaction and generally a more rapid reaction than hydrogen elimination from the analogous cis-dihydridometal complex.

In the presumed two-step sequence leading to methane elimination

$$CH_3Co[P(OCH_3)_3]_4 + H^+ \rightarrow \{CH_3(H)Co[P(OCH_3)_3]_4^+\}$$
$$(22)$$

$$\{CH_3(H)Co[P(OCH_3)_3]_4^+\} \rightarrow Co[P(OCH_3)_3]_4^+ + CH_4$$
$$(23)$$
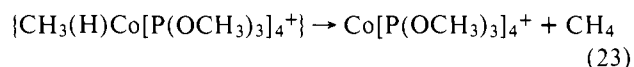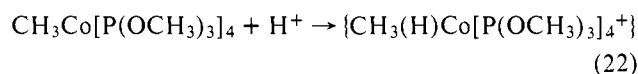
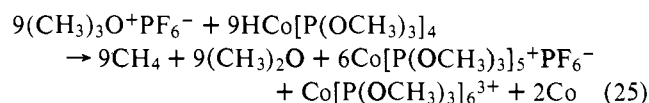the $Co[P(OCH_3)_3]_4^+$ intermediate could not be directly isolated because in the absence of donor solvent there was a rapid production of $Co[P(OCH_3)_3]_5^+$, which was isolated as the PF_6^- salt. However, the putative tetracoordinate cation intermediate was trapped as a derivative. For example, the protonation of the methyl derivative with $NH_4^+PF_6^-$ gave methane and $(H_3N)Co[P(OCH_3)_3]_4^+$:

$$NH_4^+PF_6^- + CH_3Co[P(OCH_3)_3]_4 \rightarrow CH_4$$
$$+ (H_3N)Co[P(OCH_3)_3]_4^+PF_6^- \quad (24)$$
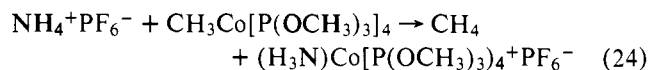
Also, in a separate experiment, the solid $Co[P(OCH_3)_3]_4^+$-PF_6^- salt was isolated and fully characterized (see below).

These results, especially the reaction of the labeled reagents, established a very fast and clean reductive elimination of methane from the postulated intermediate $CH_3(H)Co[P(OCH_3)_3]_4^+$ in the protonation of the methylcobalt complex. An alternative mechanism of direct protic cleavage of the methyl group, however, cannot be ruled out.

The mirror reaction, methylation of the $HCo[P(OCH_3)_3]_4$ complex, did, in fact, form the same products: methane (100%), $Co[P(OCH_3)_3]_5^+$ isolated in 65-70% yield, and cobalt metal isolated in 10-20% yield as based on the idealized reaction

$$9(CH_3)_3O^+PF_6^- + 9HCo[P(OCH_3)_3]_4$$
$$\rightarrow 9CH_4 + 9(CH_3)_2O + 6Co[P(OCH_3)_3]_5^+PF_6^-$$
$$+ Co[P(OCH_3)_3]_6^{3+} + 2Co \quad (25)$$

where the yields of the pentacoordinate $Co[P(OCH_3)_3]_5^+PF_6^-$ salt and cobalt metal should be 67 and 22%, respectively. Little deuterium incorporation (0–3%) into the product methane was detected for reactions effected in CD_2Cl_2. Reaction rate was substantially lower than for the protonation of the methylcobalt complex; methane evolution was complete only after 1–2 h for 1-2-mmol scale reactions. The rate difference is ascribed to steric factors due to (1) the much larger size of the methylating reagent compared to the proton and (2) the more uniform envelope of phosphite groups around the metal in the quasi-tetrahedral $HCo[P(OCH_3)_3]_4$ hydride than in the methylcobalt analogue.

A further comment regarding the cobalt complexes isolated from the methylation of the cobalt hydride is in order. The initially isolated $Co[P(OR)_3]_5^+PF_6^-$ salt was green-yellow rather than yellow because $Co[P(OCH_3)_3]_4^+PF_6^-$ (blue) was present (~10%). Another aqua-blue cobalt complex that analyzed for $HCo[P(OCH_3)_3]_4^+PF_6^-$ was isolated in 3–5% yield from this reaction.[13b] This complex, which was paramagnetic and exhibited a sharp infrared absorption at 1925 cm⁻¹ which could be ascribed to a Co–H stretching frequency, ostensibly was formed in a redox reaction during the methylation reaction.

Methylation of CH₃Co[P(OCH₃)₃]₄—Reductive Elimination of Methane. All attempts to isolate $(CH_3)_2Co[P(OCH_3)_3]_4^+$ from reactions of $CH_3Co[P(OCH_3)_3]_4$ with $CH_3SO_3CF_3$ or $(CH_3)_3O^+PF_6^-$ in dichloromethane or dimethyl carbonate were unsuccessful owing to facile elimination of methane. Because paramagnetic species were produced in this reaction, an NMR monitoring of the reaction was not feasible.

Methane was the major gaseous product (90–95%) from this methylation reaction with small amounts of ethylene (2–5%) and ethane (2–5%). When the methylation was effected in deuteriodichloromethane, CH_3D and CH_4 were obtained with the former 6–9% of the total methanes (vide infra). The alkylation reaction was slow; reaction in dichloromethane was largely heterogeneous owing to the relative insolubility of the oxonium salt. The reaction at 25 °C was about 80% complete within ~12 h as judged by methane evolution. Total yields of hydrocarbons based on the reaction

$$(CH_3)_3O^+ + CH_3Co[P(OCH_3)_3]_4 \rightarrow CH_4$$
$$+ (CH_3)_2O + \{CH_2Co[P(OCH_3)_3]_4^+\} \quad (26)$$
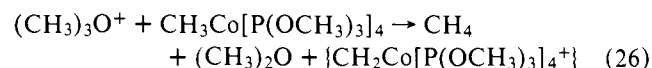
were in the range of 55–75%; with a 100% excess of the oxonium salt the yields rose to 75–85%. Complications in a quantitative assessment of the methylation reaction arose from reaction of oxonium salt with free trimethyl phosphite liberated

in the reaction sequence leading to methane formation. Separate experiments established that methane was not formed when the oxonium salt alone was contacted with the dichloromethane solvent over a 24-h period. Reaction of $CD_3Co[P(OCH_3)_3]_4$ with $CF_3SO_3CH_3$ yielded approximately equivalent amounts of CD_4, CD_3H, CDH_3, and CH_4.

A dimethylcobalt cation formed from methylation of the methylcobalt complex could decompose to give methane by an α-hydrogen elimination, a characteristic common to polymethyl derivatives of transition metals; however, all attempts to detect a $(CH_3)_2Co^+$ intermediate and to characterize the ultimate fate of the cobalt complex were unsuccessful. Alternatively, $CF_3SO_3CH_3$ could react with $CH_3Co[P(OCH_3)_3]_4$ to give the CH_3 radical and $CH_3Co[P(OCH_3)_3]_4^+$, but the very small amount of solvent involvement (CD_2Cl_2 experiment) does not *seem* consistent with a radical reaction. The mechanistic features of this methylation reaction are unresolved.

Tetrahedral Co[P(OCH₃)₃]₄⁺. The primary product or intermediate in the decomposition of $H_2Co[P(OCH_3)_3]_4^+$, the methylation of $HCo[P(OCH_3)_3]_4$, and the protonation of $CH_3Co[P(OCH_3)_3]_4$ was postulated as $Co[P(OCH_3)_3]_4^+$. This species was trapped as $LCo[P(OCH_3)_3]_4^+$ complexes by the protonation of $CH_3Co[P(OCH_3)_3]_4$ in the presence of the free ligand, L, and these derivatives were isolated and characterized as hexafluorophosphate salts. $Co[P(OCH_3)_3]_4^+$ derivatives prepared in this fashion were L = ethylene, diphenylacetylene, ammonia, acetonitrile, acetone, and methanol; $H_3NCo[P(OC_2H_5)_3]_4^+$ was prepared analogously. $Co[P(OCH_3)_3]_4^+PF_6^-$ itself was indirectly prepared from the thermal decomposition (25 °C) of the crystalline propene and 1-hexene complexes, η^2-olefin $Co[P(OCH_3)_3]_4^+PF_6^-$, which were isolated at −80 °C from the reaction of $HO(C_2H_5)_2PF_6$, $CH_3Co[P(OCH_3)_3]_5$, and the olefin and then warmed to 25 °C in a vacuum (dynamic) system.

$Co[P(OCH_3)_3]_4^+PF_6^-$, a deep blue solid, dissolved in noncoordinating solvents such as CH_2Cl_2 and $CHClF_2$ to give deep blue, paramagnetic solutions. Because of the steric bulk of the phosphite ligand, a tetrahedral structure was anticipated for this tetracoordinate d^8 complex, an anticipation consistent with its color and paramagnetic character. This tetracoordinate complex decomposed in solution at 25 °C to form $Co[P(OCH_3)_3]_5^+$, cobalt metal, and $Co[P(OCH_3)_3]_6^{3+}$. Even in the solid state, this coordinately unsaturated complex displayed a high reactivity toward oxidative-addition and ligand-complexation reactions. Thus hydrogen addition to the crystalline salt was immediate, evidenced by a blue to white color change to give $H_2Co[P(OCH_3)_3]_4^+PF_6^-$, as was ammonia addition to form the red $H_3NCo[P(OCH_3)_3]_4^+PF_6^-$ complex. Ethylene addition required several minutes to quantitatively form yellow η^2-$C_2H_4Co[P(OCH_3)_3]_4^+PF_6^-$.

A solution state susceptibility measurement (Evans NMR method[14]) for $Co[P(OCH_3)_3]_4^+PF_6^-$ gave $\mu_{eff} = 2.7$ μ_B at −10 °C, a value slightly lower than the spin only value of 2.83 μ_B and reported values for similar tetrahedral complexes of 3.0–3.3 μ_B, indicating a lesser orbital contribution. An analogous complex $Co[P(O-i-C_3H_7)_3]_3Cl$ had a value of $\mu_{eff} = 2.9$ μ_B.[10]

The blue, crystalline $Co[P(OC_2H_5)_3]_4^+PF_6^-$ salt was isolated by the same procedure as for the trimethyl phosphite analogue and this salt showed the same addition reaction with hydrogen and with ammonia, although rates were slightly lower than for $Co[P(OCH_3)_3]_4^+PF_6^-$.

Properties of CH₃Co[P(OR)₃]₄ and LCo[P(OCH₃)₃]₄⁺ Complexes. Both $CH_3Co[P(OCH_3)_3]_4$ and $CH_3Co[P(OC_2H_5)_3]_4$ are stereochemically nonrigid molecules. As reported earlier,[7] the trimethyl phosphite derivative did not show evidence of a limiting slow exchange ³¹P NMR spectrum to ~−150 °C; a single broad resonance was observed even at

the lowest temperatures. In contrast, the more sterically congested triethyl phosphite complex displayed a limiting AB_3 $^{31}P\{^1H\}$ spectrum at -83 °C. This was consistent with the

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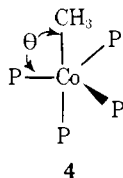
expected stereoisomeric form, **4,** in near trigonal bipyramidal geometry; the angle θ is expected to be less than 90° because of the interligand nonbonding repulsions between axial and equatorial phosphite ligands. Similar stereochemistry has been reported for the analogous d^8 complexes, $CH_3Co[P(CH_3)_3]_4$[15] and $CH_3Ni[P(CH_3)_3]_4^+$.[16]

The $H_3NCo[P(OR)_3]_4^+PF_6^-$ complexes prepared from NH_4PF_6 and $CH_3Co[P(OR)_3]_4$ were stereochemically nonrigid in solution and exhibited a parallel spectral behavior to the methyl derivatives discussed above. A single $^{31}P\{^1H\}$ resonance (half-height width of ~130 Hz) was observed for the trimethyl phosphite derivative down to -150 °C ($CHClF_2$ solution) whereas the triethyl phosphite derivative showed a complex resonance at -100 °C. A definitive distinction between an AB_3 and an AB_2C spectrum was not achieved for the latter complex; the former would be consistent with a form and a stereochemistry analogous to the methyl derivatives, **4.** For the trigonal bipyramidal form, steric and electronic considerations would favor an axial NH_3 substituent for a d^8 complex.[17]

The observed single $^{31}P\{^1H\}$ resonances of $CH_3Co[P(OCH_3)_3]_4$ and $NH_3Co[P(OCH_3)_3]_4PF_6$ were almost certainly due to true fluxional processes and were not the results of accidental degeneracy of $P_{equatorial}$ and P_{axial} chemical shifts over wide temperature ranges. Firstly, temperature variation usually caused independent changes in chemical shifts on the order of several parts per million for different ^{31}P nuclei in compounds cited here, so that accidental degeneracy was unlikely to be maintained over the 100 °C range studied. Further, the difference between P_{axial} and $P_{equatorial}$ chemical shifts in $CH_3Co[P(OCH_2CH_3)_3]_4$ was 21 ppm and several parts per million for $Co(NH_3)[P(OCH_2CH_3)_3]_4^+$; a similar situation would be expected for the limiting cases of the $P(OCH_3)_3$ derivatives.

Jesson and Meakin[18] observed higher activation energies with increased steric bulk of phosphite ligands for intramolecular rearrangements in ML_5 species ($M = Rh^+, Ir^+, Pt^{2+}$, Pd^{2+}; $L = P(OR)_3$) and reasonably suggested that the main factor in determining barrier height was relative destabilization of the transition state, compared to the ground state, by steric crowding. This rationale would seem to apply to the $CoL'L_4^+$ complexes.

The acetonitrile derivative $CH_3CNCo[P(OCH_3)_3]_4^+$, obtained by direct reaction of $Co[P(OCH_3)_3]_4^+PF_6^-$ with acetonitrile, was also a stereochemically nonrigid structure which only at low temperatures, -108 °C, yielded a limiting AB_3 $^{31}P\{^1H\}$ spectrum which again placed the unique ligand at the axial site of a trigonal bipyramid, as in **4.**

In the olefin and diphenylacetylene derivatives, η^2-$LCo[P(OR)_3]_4^+$, prepared by the protonation of $CH_3Co[P(OCH_3)_3]_4$ in the presence of the olefin or acetylene, the expected[17] trigonal bipyramidal form with the unsaturated ligand at an equatorial site, **5,** was evident from the near first-order A_2B_2 $^{31}P\{^1H\}$ spectra at -30 °C for the ethylene and diphenylacetylene derivatives. Similar structures and stereochemistry have been established by X-ray studies of several olefin $Fe(CO)_4$ complexes[17,19] which are isoelectronic to the d^8 cobalt complexes. The 1-hexene and propylene analogues showed an apparent $ABCD$ $^{31}P\{^1H\}$ spectrum at -30

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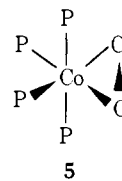
°C as expected for the stereoisomeric form **5.** In all cases, the spectra broadened above -30 °C but, because the complexes underwent dissociation at elevated temperatures, the origin of the initial broadening could not be established.

All the $LCo[P(OCH_3)_3]_4^+$ complexes displayed facile displacement reactions. *Based on the displacement reaction*, the ligand–cobalt interaction decreased in the series L = CO $> P(OCH_3)_3 > H_2 > NH_3 \sim CH_3CN >$ ethylene $\sim$ diphenylacetylene $\gg$ propylene $\sim$ 1-hexene $>$ methanol $\sim$ acetone. Thus for example, hydrogen "displaced" NH_3 from $H_3NCo[P(OCH_3)_3]_4^+$ to give $H_2Co[P(OCH_3)_3]_4^+$. However, these displacements are less likely associative displacement reactions than ligand competition reactions for an active intermediate $Co[P(OCH_3)_3]_4^+$ usually present in finite concentrations in solutions of the complexes:
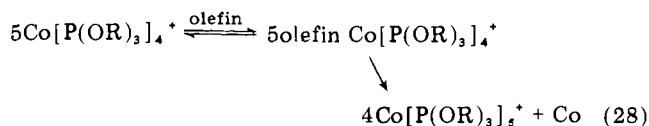
$$LCo[P(OCH_3)_3]_4^+ \rightleftharpoons L + Co[P(OCH_3)_3]_4^+ \quad (27)$$
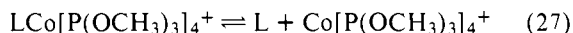
Protonation of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ and "Diene" Complexes. Reaction of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ with $H[O(C_2H_5)_2]^+PF_6^-$ in methanol at -50 °C in the presence of conjugated dienes (butadiene and 1,3-cyclohexadiene) produced insoluble diene-$Co[P(OCH_3)_3]_3^+PF_6^-$ salts. 1,3- and 1,5-cyclooctadienes both yielded the same diene cobalt complex. With the former reactant, the diene complex salt separated out as yellow crystals almost immediately upon mixing of the reactants whereas with 1,5-cyclooctadiene the reaction solution was initially green and slowly turned yellow to give crystals of the diene cobalt salt. No tractable complex could be isolated with the unconjugated diene bicyclo[2.2.1]-hepta-2,5-diene. Only the conjugated dienes have appropriate symmetries to nicely interact with d^8-ML_3 fragments. However, the structures of these diene complexes cannot be uniquely determined from the NMR spectra. Spectral details are consistent with η^4-diene complexes and with a hooked allyl formulation, Co-η^3-$C_3H_4CH_2$.

The butadiene complex was substantially more stable than the 1,3-cyclooctadiene complex, which slowly decomposed at 20 °C. Reactivity patterns also followed this order since the butadiene complex did not react with hydrogen at 25 °C and was only slowly converted (several days time) to $Co[P(OCH_3)_3]_5^+$ at 25 °C by reaction with trimethyl phosphite. Hydrogen converted the 1,3-cyclooctadiene complex largely to $Co[P(OCH_3)_3]_5^+$ at 25 °C.

Both the butadiene and 1,3-cyclooctadiene complexes had AB_2 $^{31}P\{^1H\}$ spectra at -100 °C. The diene-cobalt complexes were stereochemically nonrigid and the AB_2 spectra collapsed to a broad resonance at 10 °C. No detailed analysis of line-shape changes was made. The ^1H NMR spectra were fully consistent with a simple η^4-diene complex; however, the recent studies by Ittel et al.[20] show a protonated diene $Fe[P(OR)_3]_3$ complex to have an unusual allyl–iron interaction, and a similar protonated butadiene $Fe[P(CH_3)_3]_3$ is believed[12] to be structurally analogous. An X-ray study of the cobalt complex would be necessary to unequivocally distinguish between an η^4-diene form and, for example, a hooked allyl, Co-η^3-$C_3H_4CH_2$ structure.

Catalysis of Olefin Isomerization with $Co[P(OR)_3]_4^+$, $LCo[P(OR)_3]_4^+$, and $H_2Co[P(OR)_3]_4^+$ Complexes. Olefins were very rapidly isomerized by $Co[P(OCH_3)_3]_4^+PF_6^-$ in acetone or methylene chloride solution at 0–22 °C. At catalyst to 1-hexene ratios of $\sim1:140$, the turnover rates were 1.5 and 5.5 mol of olefin per mol catalyst per second at 0 and 22 °C, re-

spectively. However, catalyst lifetime was short, 1–2 min, owing to the decomposition sequence

$$5Co[P(OR)_3]_4^{+} \xrightarrow{\text{olefin}} 5olefin\ Co[P(OR)_3]_4^{+}$$

$$\searrow$$

$$4Co[P(OR)_3]_5^{+} + Co \quad (28)$$

The $C_2H_4Co[P(OCH_3)_3]_4^+$ and $(C_8H_{12})Co[P(OCH_3)_3]_3^+$ complexes which readily undergo olefin or diene dissociation displayed comparable catalytic activities but the stable "butadiene" cobalt derivative was inactive.

The isomerization products revealed a lack of specificity in the catalytic reaction, and were close to equilibrium mixtures. For example, 1-hexene was isomerized at 0 °C by Co-$[P(OCH_3)_3]_4^+$ (1-hexene:catalyst = 100:1) within 3 min to a mixture of 1-hexene (3.6%), *cis*- and *trans*-3-hexene (8.4%), *cis*-2-hexene (44.6%), and *trans*-2-hexene (43.4%). However, competitive reactions showed that 1-hexene was isomerized at least 20 times faster than *trans*-2- and *trans*-3-hexenes and about 6 times faster than *cis*-2-hexene. Equilibrium could thus not be reached before catalyst death occurred (also within 3 min), assuming one hydrogen transfer per association/dissociation of hexene with catalyst. The very high activity of the catalyst makes plausible the assumption of at least several catalytic events during the association of one hexene molecule and catalyst complex. This is supported by the observation that the ratio of isomerized products (specifically including 3-hexenes) varied little during the time course of the reaction, including those reactions with olefin completely isomerized and active catalyst still present and those with excess 1-hexene still present when catalyst activity ceased.

Olefin isomerization by $Co[P(OCH_3)_3]_4^+$ is proposed to occur by formation of a π-allylcobalt hydride intermediate as outlined in Scheme I. This system would be fully analogous to that of $Fe_3(CO)_{12}$-catalyzed olefin isomerizations where olefin $Fe(CO)_4 \rightleftharpoons$ olefin $Fe(CO)_3$ was the rate-determining step as elegantly established by Casey and Cyr.[21]

Isomerization of 1-hexene to *cis*- and *trans*-2-hexene catalyzed by $Co[P(O-i-C_3H_7)_3]_4PF_6$ was slower and more selective than for the trimethyl phosphite analogue. In addition, catalyst activity was maintained over the entire course of the reaction at 20 °C when the ratio of olefin:catalyst was 600:1 and with acetone or methylene chloride as solvent. Activity was still evident when tested after 20 h. The difference in catalyst lifetime is directly attributable to the steric bulk of the triisopropyl phosphite ligands which causes complete destabilization of $Co[P(O-i-C_3H_7)_3]_5^+$ relative to the four-coordinate complex. $Co[P(O-i-C_3H_7)_3]_4PF_6$ was recovered completely unchanged from these catalytic solutions. Initial turnover rates during the first 1 min of the reaction were 2.5 mol 1-hexene $(mol\ [P(O-i-C_3H_7)_3]_4^+)^{-1}\ s^{-1}$, that is, about one-half lower than for the trimethyl phosphite catalyst. Since the electronic properties of the phosphite complexes are quite similar the difference in rate is probably also steric in origin; the forward rate constant for adduct formation, and probably the equilibrium constants also, would be lowered owing to the steric bulk of the triisopropyl phosphite complex. A higher value for the reverse rate constants for the same steric reasons would account for the higher selectivity of the catalyst since fewer catalytic events (hydride transfers) during each association of hexene and $Co[P-i-C_3H_7)_3]_4^+$ could occur. No 3-hexenes were formed from 1-hexene and initially about two times as much *cis*-2-hexenes as *trans*-2-hexene was formed. Over several hours slow conversion of *cis*-2-hexene to *trans*-2-hexene occurred.

Excess triisopropyl phosphite inhibited the isomerization reaction catalyzed by $Co[P(O-i-C_3H_7)_3]_4^+$. At a 1-hexene:catalyst ratio of 50:1 in dichloromethane solution and P(O-$i-C_3H_7)_3$:catalyst ratios of 5:1, 30:1, and 70:1, the approximate

Scheme I
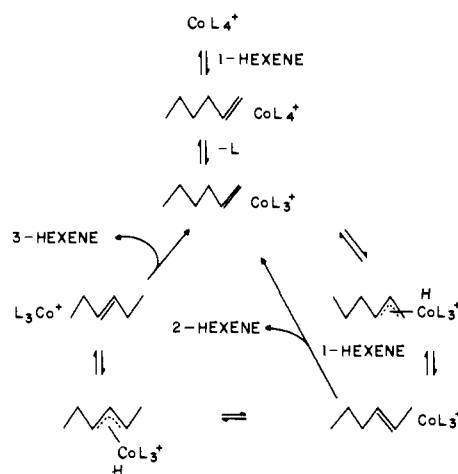
rates of olefin isomerization were respectively 20, 8, and 5% of the rate in the absence of triisopropyl phosphite. This inhibition clearly indicates a key dissociative step (see Scheme I) which is required for the formation of the π-allylcobalt hydride intermediate. Preferred formation of *cis*-2-hexene over *trans*-2-hexene implies faster formation of the anti-substituted allyl than of the syn isomer (assuming π-allyl intermediates), although the latter is usually thermodynamically more stable.

$H_2Co[P(OCH_3)_3]_4^+$ in the presence of excess trifluoroacetic acid was a catalyst, albeit of low activity, for the isomerization of terminal olefins such as 1-hexene or 1-pentene to a mixture of internal olefin isomers. The catalytic system, generated by addition of trifluoroacetic acid to $HCo[P(OCH_3)_3]_4$ in polar solvents such as acetone or methylene chloride, was shown within the limits of NMR detection to contain only the dihydride cation. The neutral monohydride, $HCo[P(OCH_3)_3]_4$, was inactive as a catalyst for either hydrogenation or isomerization, consistent with its dissociative inertness.

Surprisingly, the pure salt, $H_2Co[P(OCH_3)_3]_4^+PF_6^-$, was not a catalyst for olefin isomerization even in the presence of excess trifluoroacetic acid. Addition of $NaPF_6$ to normally catalytically active solutions containing 1-hexene, $HCo[P(OCH_3)_3]_4$, and CF_3COOH led to inhibition of isomerization rate with a nearly linear (inverse) relationship between $[PF_6^-]$ and rate. Greater than 1:1 ratios of $NaPF_6$ to cobalt complex completely blocked the isomerization. The isomerization of 1-pentene with CF_3COOD and $DCo[P(OCH_3)_3]_4$ in acetone-d_6 gave 1- and 2-pentenes that contained no deuterium. Finally, the addition of H_2 to the reaction system completely blocked the isomerization of olefins. The data are consistent with $Co[P(OCH_3)_3]_4^+$ as the catalyst precursor being derived from the equilibria

$$H_2Co[P(OCH_3)_3]_4^{+} \rightleftharpoons H_2 + Co[P(OCH_3)_3]_4^{+}$$

$$\Big\Downarrow \text{olefin} \qquad (29)$$
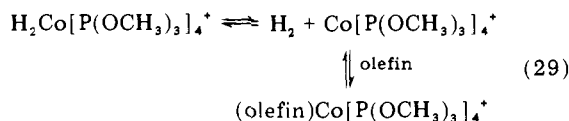
$$(olefin)Co[P(OCH_3)_3]_4^{+}$$

The curious effect of the PF_6^- ion on these catalytic reactions is not fully understood, although the counterion might affect the equilibrium in eq 29 sufficiently to greatly alter the concentration of the $(olefin)Co[P(OCH_3)_3]_4^+$ catalyst precursor.

Experimental Section

Procedure, Reagents, and Techniques. Routine manipulations of air-sensitive organometallic compounds were performed under an inert atmosphere (argon and occasionally prepurified nitrogen), or in a conventional vacuum line. A Vacuum Atmospheres HE-43 Dri-Lab was used for operations such as weighing, chromatography, and initial

preparation of samples for NMR and analysis. Schlenk techniques using a double manifold system supplemented the Dri-Lab for manipulations at temperatures other than ambient.

All solvents and reagent liquids were routinely purified and/or dried by refluxing with and distilling from the following drying agents under nitrogen: acetonitrile, P_2O_5; acetone, K_2CO_3 then 4 Å molecular sieves; ethers, CaH_2 (stored over alumina); hydrocarbons, Na/benzophenone; methanol, CaH_2; methylene chloride, P_2O_5; olefins, $LiAlH_4$; and tetrahydrofuran, Na/benzophenone (stored over alumina).

Solution ^1H NMR spectra were measured either with a Varian Associates A-60A (plus temperature control unit V-4343) or Bruker HX-90 spectrometer (with NMR-4 Digilab data system, FTS/NMR Pulser 400-2, and type B-ST 100/700 temperature controller) at ambient temperature unless otherwise noted, and were internally referenced to tetramethylsilane (or to benzene, and then corrected to tetramethylsilane). Spectra (90 MHz) were recorded in either Fourier transform (FT) or continuous wave (CW) mode, using either ^2H or ^{19}F internal lock. Solution ^{31}P NMR spectra were measured at 36.43 MHz on a Bruker HX-90 spectrometer (as above) with ^2H or ^{19}F internal lock and were completely ^1H decoupled unless noted differently. ^{31}P spectra were referenced to $P(OCH_3)_3$ which was contained in a sealed capillary within the NMR tube. All samples were prepared in the drybox using dry, deoxygenated solvent, and evacuated and sealed on the vacuum line.

Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer as halocarbon or Nujol mulls between KBr disks, using polystyrene as reference.

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Samples were contained in ampules which were sealed off under vacuum. Melting points were in most cases decomposition points and were reproducible (±2 °C) when recorded in sealed capillaries on a Mel-Temp melting-point apparatus at 70-80 V. Recorded temperatures were uncorrected.

Gas chromatographic separations were performed using a Perkin-Elmer 990 gas chromatograph. Mass spectra were determined by the direct inlet method on an Associated Industries MS-902 spectrometer and by coupled gas chromatography–mass spectrometry on a Finnigan 3300 mass spectrometer. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer for routine spectra and on a Gilford 2220 UV–vis spectrophotometer adapted to a Beckman monochrometer for kinetic measurements, in matched quartz cells of 10-mm path length.

Woelm neutral alumina, dried in vacuo at 200 °C for 24 h, then deactivated by storing under pentane-containing $P(OCH_3)_3$, was used for column chromatographic purifications. Columns were washed with two bed volumes of eluting solvent prior to application of the organometallic species.

$HCo[P(O-i-C_3H_7)_3]_4$. A solution of $NaBH_4$ (3.0 g, 0.079 mol) and $P(O-i-C_3H_7)_3$ (50 mL, 0.22 mol) in 1,2-dimethoxyethane (250 mL) was thoroughly purged with argon and maintained at 0 °C. $CoCl_2$ (5.2 g, 0.04 mol) in ethanol (200 mL) was added dropwise over 1 h. The reaction mixture was stirred at 0 °C for a further 1 h. Pentane (200 mL) was added and then the solution was filtered. After most of the solvent was removed from the filtrate under vacuum at room temperature, methanol or acetonitrile (100 mL) was added to precipitate the product. Filtration gave a cream solid which was dried under vacuum: yield 23.4 g (66%); mp 166 °C; ^1H NMR (C_6D_6, 300 K) δ −4.83 (m, 1 H, OCH), −1.36 (d, 6 H, OCH(CH_3)$_2$), and 16.72 (quintet, CoH) (J_{HH} = 6, J_{PH} = 24 Hz); 36.43-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (toluene-d_8, 195 K) δ −25.35 (s); (C_6D_6, 300 K) δ −21.7 (s); IR (Nujol mull) ν_{Co-H} 1945 cm^{-1}. Anal. Calcd for $H_{85}C_{36}O_{12}P_4Co$: H, 9.59; C, 48.42; Co, 6.60. Found: H, 9.61; C, 48.37; Co, 6.41.

$H_2Co[P(OCH_3)_3]_4PF_6$. CF_3COOH (3.04 mL, 0.041 mol) was added to a stirred solution of $HCo[P(OCH_3)_3]_4$ (22.2 g, 0.04 mol) and $NaPF_6$ (6.12 g, 0.04 mol) in methanol (120 mL) and diethyl ether (40 mL). The reaction mixture was then concentrated to 80 mL under vacuum using a rotary evaporator. Filtration gave microcrystalline, white solids which were washed with diethyl ether (10 mL) and dried under vacuum: yield 22.7 g (81%); mp 203 °C dec; ^1H NMR (acetone-d_6, 270 K) δ −3.68 (quintet, methoxy protons, (J_{PH} = 2.88 Hz) and 13.1 (m, Co–H); 36.43-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (acetone-d_6, 205 K) δ −13.31 (single broad resonance); IR (Nujol mull) ν_{Co-H} 2032, 1962 cm^{-1}; (methanol solution) 1970 cm^{-1}. Anal. Calcd for $H_{38}C_{12}O_{12}F_6P_5Co$: H, 5.46; C, 20.53; F, 16.23; P, 22.06; Co, 8.39. Found: H, 5.46; C, 20.45, F, 15.59; P. 22.46; Co, 8.03.

$H_2Co[P(OCH_2CH_3)_3]_4PF_6$. HPF_6–diethyl ether complex (0.825 mL, 0.005 mol) was added via glass-only syringe to a solution of $HCo[P(OCH_2CH_3)_3]_4$[22] (3.64 g, 0.005 mol) in ethanol (50 mL). Tetrahydrofuran (30 mL) was added, and the solution was concentrated by rotary evaporation to 15 mL. Filtration gave microcrystalline white solids: yield 3.1 g (71.2%); mp 222-223 °C dec; ^1H NMR (acetone-d_6, 240 K) δ −1.3 (triplet, CH_3 of ethoxy group), −4.12 (quartet of quintets, methylene of ethoxy group) (J_{HH} = 7, J_{PH} = 1.5 Hz), and 13.2 (m, CoH); 36.43-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (acetone-d_6, 205 K) δ −8.44 ppm (s); IR (halocarbon mull) ν_{Co-H} 1975 cm^{-1}. Anal. Calcd for $H_{62}C_{24}O_{12}F_6P_5Co$: H, 7.18; C, 33.11; Co, 6.77. Found: H, 7.18; C, 33.04; Co, 6.60.

$H_2Co[P(O-i-C_3H_7)_4]PF_6$. Crystalline blue $Co[P(O-i-C_3H_7)_3]_4PF_6$ (0.5 g, 0.0048 mol) was evacuated in a sealable tube. H_2 (0.9 atm, 0.05 mol) was admitted. Over 3–4 h the color of the solid changed to a pale cream. (In CH_2Cl_2 solution the compound reacted over 5–10 min.) The solid was left under H_2 overnight and no further change in color occurred; mp 170 °C (with rapid heating the compound turned progressively more blue after about 120 °C and was probably losing hydrogen); ^1H NMR (CD_2Cl_2, −10 °C) δ −4.57 (m), −1.21 (d), and 14.46 (m); IR (Nujol mull) ν_{Co-H} 1995 cm^{-1} (assigned by lack of this band in the IR spectra of both $Co[P(O-i-C_3H_7)_3]_4PF_6$ and $D_2Co[P(O-i-C_3H_7)_3]_4PF_6$) ν_{P-F} 840 cm^{-1}. Anal. Calcd for $H_{86}C_{36}O_{12}P_5F_6Co$: H, 8.34; C, 41.62; Co, 5.67. Found: H, 8.32; C, 41.61; Co, 5.53.

$D_2Co[P(OCH_3)_3]_4PF_6$. A solution of $H_2Co[P(OCH_3)_3]_3PF_6$ (5 g, 0.0071 mol) in CH_2Cl_2 (20 mL) was stirred in a 500-mL flask under D_2 (~0.02 mol) for 3 days. Noncondensable gases were removed at −196 °C and then replaced with pure D_2 (~0.02 mol). Again the solution was stirred for 3 days. Solvent was removed under vacuum to give white solids: yield 5 g; mp 202 °C dec; ^1H NMR (acetone-d_6, 300 K) δ −3.68 (quintet, methoxy protons); IR (Nujol mull) ν_{Co-D} 1410 cm^{-1} (possible accompanying band masked by phosphite absorptions); Raman (4880-Å exciting line) (solid) ν_{Co-D} 1464, 1413 cm^{-1}.

$D_2Co[P(OCH_2CH_3)_3]_4PF_6$. $H_2Co[P(OCH_2CH_3)_3]_4PF_6$ (3 g, 0.0034 mol) in tetrahydrofuran (30 mL) was stirred under D_2 (0,6 atm, 0.025 mol) at 50 °C in a 1000-mL round-bottom flask for 7 days. The solution was cooled to −196 °C, the flask was evacuated, and pure D_2 (0.025 mol) was admitted. The solution was again stirred for 7 days at 50°C. The solution was stripped to dryness, then diethyl ether (30 mL) was added. White, crystalline solids formed, which were collected by filtration and dried under vacuum: yield 2.5 g; mp 230 °C dec; IR (Nujol mull). The band at 1980 cm^{-1} assigned to the Co–H stretch in the infrared spectrum of $H_2Co[P(OCH_2CH_3)_3]_4PF_6$ was completely absent from the spectrum.

Deprotonation of $H_2Co[P(OCH_3)_3]_4PF_6$. A. $H_2Co[P(OCH_3)_3]_3PF_6$ (2.16 g, 0.003 mol) was added to a solution of 1,1,3,3-tetramethylguanidine (0.35 mL, 0.003 mol) in nitromethane (10 mL). Hexane (50 mL) was added and the two-phase system stirred for 2 h. The hexane layer was separated and concentrated to yield $HCo[P(OCH_3)_3]_4$, identified by ^1H NMR (1.45 g, 87%).
B. $H_2Co[P(OCH_3)_3]_4PF_6$ (0.14 g, 0.0002 mol) and CH_3ONa (0.04 g, 0.0074 mol) were shaken in an NMR tube in acetonitrile-d_3 (0.2 mL) and methanol-d_4 (0.2 mL). After 2 h the ^1H NMR spectrum showed only $HCo[P(OCH_3)_3]_4$.

Effect of Donor Solvent on $H_2Co[P(OCH_3)_3]_4PF_6$. A solution of $H_2Co[P(OCH_3)_3]_4PF_6$ (1 g, 0.0014 mol) in CH_2Cl_2 (10 mL) under vacuum in a 60-mL tube at 20 °C for 10 days evolved 0.000 16 mol of H_2 whereas a solution of $H_2Co[P(OCH_3)_3]_4PF_6$ (1.4 g, 0.002 mol) in CH_3CN under vacuum in a 60-mL tube at 20 °C for 10 days evolved 0.0013 mol of H_2.

Molecularity of H_2–D_2 Exchange in $H_2Co[P(OCH_3)_3]_4^+$. $H_2Co[P(OCH_3)_3]_4PF_6$ (1.72 g, 0.002 45 mol) in CH_2Cl_2 (25 mL) was stirred under D_2 (0.0031 mol) for 40 h at 20 °C. Noncondensable gases (at −196 °C) were removed (sample A). $P(OCH_3)_3$ (0.8 mL, 0.0064 mol) was added to the solution. After the solution was stirred at 20 °C for 35 h the evolved gases were collected (0.0025 mol, sample B). Mass spectral analysis showed [D_2]/[H_2] in sample A = 1.19 and in sample B = 1.34. The amount of HD formed was less than 2% in both samples.

$H_2Co[P(OCH_3)_3]_4PF_6$ (1.72 g, 0.002 45 mol) in acetonitrile (25 mL) was stirred under D_2 (0.003 mol) for 40 h at 20 °C. Noncondensable gases were removed and analyzed by mass spectrometry: 42% H_2, 9.5% HD, 48.5% D_2.

H_2/D_2 Exchange in $H_2Co[P(OCH_2CH_3)_3]_4PF_6$. $H_2Co[P(OCH_2CH_3)_3]_4PF_6$ (1.31 g, 0.0015 mol) in CH_2Cl_2 (3 mL) was

stirred under D_2 (0.82 atm, 0.001 89 mol) at 24 °C for 50 h. After the solution was cooled to −196 °C, noncondensable gases were removed for analysis by mass spectrometry: 93% D_2, 0% HD, 7% H_2. H_2Co-[P(OCH$_2$CH$_3$)$_3$]$_4$PF$_6$ (1.31 g, 0.0015 mol) in CH_2Cl_2 (3 mL) was stirred under D_2 (0.8 atm, 0.001 84 mol) at 24 °C for 7 days. Gases analyzed as above showed 79% D_2, 0% HD, 21% H_2.

Kinetics: $H_2CoL_4^+ + L \rightarrow CoL_5^+ + H_2$. A Gilford 2220 UV–visible spectrometer (adapted to a Beckman monochromator) was used to monitor the visible absorption (3800 Å) of the yellow product Co-[P(OCH$_3$)$_3$]$_5^+$. Beer's law was checked for CH_2Cl_2 solutions of Co-[P(OCH$_3$)$_3$]$_5$PF$_6$ by plotting absorption vs. concentration for nine solutions over the concentration range used in the study, i.e., 4×10^{-5} to 1×10^{-3} M. The slope of the linear plot gave the molar extinction coefficient at 3800 Å: 1.12×10^3 M^{-1} cm^{-1}. Since the molar extinction coefficient of the reactant H_2Co[P(OCH$_3$)$_3$]$_4$PF$_6$ at 3800 Å was estimated to be 10 M^{-1} cm^{-1}, the absorption measurements were not corrected for decrease in reactants.

Preliminary observation of the system was made using a Cary-14 UV–visible spectrometer. Under pseudo-first-order conditions (P(OCH$_3$)$_3$/H_2Co[P(OCH$_3$)$_3$]$_4^+$ = 6:1, 9:1, 20:1) the rate of formation of Co[P(OCH$_3$)$_3$]$_5^+$ was first order in H_2Co[P(OCH$_3$)$_3$]$_4^+$ but insensitive to P(OCH$_3$)$_3$ concentration. Observed pseudo-first-order rate constants for five approximately 1×10^{-3} M solutions of H_2Co[P(OCH$_3$)$_3$]$_4^+$ in acetonitrile were 3.7 (±0.3) × 10^{-3} s^{-1} and in CH_2Cl_2 were 1.3 (±0.08) × 10^{-5} s^{-1}. In CH$_3$CN, Co[P(O-CH$_3$)$_3$]$_5^+$ was formed in the absence of P(OCH$_3$)$_3$ at a rate about 20% of that in the presence of P(OCH$_3$)$_3$. In CH_2Cl_2, formation of Co-[P(OCH$_3$)$_3$]$_5^+$ in the absence of P(OCH$_3$)$_3$ occurred with an apparent rate constant of ~4 × 10^{-7} s^{-1}.

The *method of initial rates* was used to assess dependence of the reaction on [P(OCH$_3$)$_3$]$_3$. The Gilford spectrometer was used to record absorbance changes as a function of time over the range 0–0.2 A, which corresponded to the first 12–14% of the reaction. Samples of approximately 0.2 g of H_2Co[P(OCH$_3$)$_3$]$_4$PF$_6$ were weighed accurately (±0.0005) on a Mettler balance in vials under an argon atmosphere. Dilution with CH_2Cl_2, together with mixing of an aliquot of a standard 2.13×10^{-2} M solution of P(OCH$_3$) in CH_2Cl_2, gave reaction mixtures of composition between 0.9×10^{-3} and 1.3×10^{-3} M in H_2Co[P(OCH$_3$)$_3$]$_4$PF$_6$, and between 8.5×10^{-4} and 7.8×10^{-2} M in P(OCH$_3$)$_3$. The ratio P(OCH$_3$)$_3$/H_2Co[P(OCH$_3$)$_3$]$_4^+$ thus varied from 0.5 to 77. The mixtures were thoroughly shaken and transferred to a 1-cm quartz cell which was capped with a Teflon plug and sealed with paraffin wax. All solutions to this stage were handled in a drybox with argon atmosphere. The cell was then removed from the drybox and held in a 30 °C constant temperature bath for 30 s to equilibrate, then placed in the cell holder of the spectrometer which was maintained at 30 ± 0.1 °C. Total time from initial dilution of H_2Co[P(OCH$_3$)$_3$]$_4$PF$_6$ to start of data collection was about 15 min, during which time less than 1–2% of reaction had occurred. In order to avoid errors due to cell differences, a single quartz cell was used for all sample observations and similarly the same reference cell was always used. In the absence of P(OCH$_3$)$_3$, solutions of H_2Co-[P(OCH$_3$)$_3$]$_4$PF$_6$ in CH_2Cl_2 showed an increase in absorption with time at 3800 Å. However, the rate of this process was at least 30 times smaller than the rate when P(OCH$_3$)$_3$ was added to the system. The origins of this process were not firmly established and the data on rates in the presence of P(OCH$_3$)$_3$ were not corrected for this base rate. both because of its relatively small magnitude and because it may, in fact, be the same reaction via the equilibrium

$$H_2Co[P(OCH_3)_3]_4^+ \rightleftharpoons H_2Co[P(OCH_3)_3]_3^+ + P(OCH_3)_3$$

In order to obtain apparent rate constants closely corresponding to the initial reaction rate, slopes were estimated between 2 and 6% of reaction progress. Although one could assume no interference by reaction products at this stage in the reaction, the kinetics were also first order when followed over several half-lives at P(OCH$_3$)$_3$/H_2Co[P(OCH$_3$)$_3$]$_4^+$ = 6:1, 18:1. A linear plot of $1/k$(obsd) vs. 1/[P(OCH$_3$)$_3$] was obtained from a computer-assisted least-squares analysis of the data (43 points). Experimental errors (Δx and Δy) of 2% were assumed for values of [P(OCH$_3$)$_3$] = x and k(obsd) = y. Uncertainties $\sigma_x = \Delta(1/x)$ and $\sigma_y = \Delta(1/y)$ of the reciprocal data points $1/x$ and $1/y$ were estimated as $\sigma_x = [d(1/x)/dx] \Delta x \cong (1/x^2) \Delta x$. Since the uncertainties σ_x and σ_y in the reciprocal plot data tended to overemphasize uncertainties in lower values of x (higher values of $1/x$), the data set was compensated by (a) taking more points at lower values of x and (b) giving less emphasis to each point at lower values of x by applying a weighting factor $(\sigma_v)^2/(\sigma_x)^2$ to each point
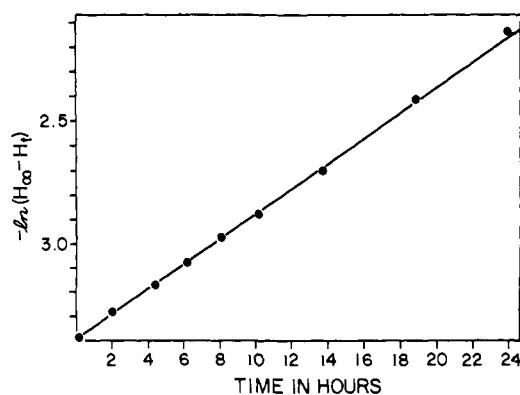

Figure 1. Plot of $-\ln (H_\infty - H_t)$ against time for H_2Co[P(OCH$_3$)$_3$]$_4^+$ (0.14 M) + P(OCH$_3$)$_3$ (2.4 M) → Co[P(OCH$_3$)$_3$]$_5^+$ + H_2. Rate determined by measurement of hydrogen evolution.

in the data (where σ_v was arbitrarily the lowest value in the data set for $1/x$). The data for $1/y$ were similarly weighted.

Values obtained from the plot of $1/k$(obsd) vs. 1/[P(OCH$_3$)$_3$] were slope = 11.49 s M (standard deviation = 0.78, i.e., 7%) and intercept = 2.378×10^4 s (standard deviation = 3.6×10^2, i.e., less than 2%). Thus, $k_1 = 1/2.378 \times 10^4$ s^{-1} = 4.20×10^{-5} s^{-1}, and $k_{-1}[H_2]/k_2$ = (11.49) (4.20 × 10^{-5}) = 4.8 × 10^{-4} M.

In the hydrogen evolution method, L = P(OCH$_3$)$_3$, the reaction was monitored by following hydrogen evolution as a function of time. The temperature was maintained at 23 ± 0.5 °C by means of a water bath around the reaction vessel, and the contents of the reaction vessel was stirred with a magnetic follower. Noncondensable gases were periodically removed from the 100·mL vessel containing the reaction solution by cooling the solution to −196 °C and removing H_2 using a Toepler pump. After the measurement the solution was quickly raised to room temperature and time taken for the measurement was discounted from total reaction time. Since the half-life of the reaction was 13.2 h at 23 °C, temperature fluctuations over the several minutes of cooling and rewarming had no observable effect on the data and straight-line plots were obtained consistently for $-\ln (H_\infty - H_t)$ vs. time (where H_t = hydrogen evolved at time t and H_∞ = total hydrogen evolved at completion of the reaction). Measurements were taken at 1.5- or 2-h intervals over 16 h to obtain each value of k(obsd). See Figure 1 for a typical data set. Values of H_∞ were obtained by heating the solution at 80 °C, after data collection, until no further hydrogen was evolved. The amount of gas was measured and added to the amount generated during data collection to get the total value, H_∞. Solutions were typically 0.1 M in H_2Co[P(OCH$_3$)$_3$]$_4^+$ and 0.8–2.4 M in P(OCH$_3$)$_3$ in CH_2Cl_2. Total volume of the solutions was 10 mL. H_2 was identified as a product of the reaction by mass spectrometry.

For the reaction

$$D_2Co[P(OCH_2CH_3)_3]_4^+ + P(OCH_2CH_3)_3$$
$$\rightarrow Co[P(OCH_2CH_3)_3]_5^+ + D_2$$
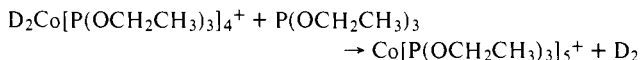
the procedure described for the analogous trimethyl phosphite system was followed. In this case, the half-life of the reaction was approximately 60 h and straight-line plots of $-\ln (H_\infty - H_t)$ vs. time were obtained when the reaction was monitored until 60–70% of the total hydrogen had been evolved (Figure 2). H_2 was identified as a product of the reaction by mass spectrometry. Co[P(OCH$_2$CH$_3$)$_3$]$_5$PF$_6$ was isolated as microcrystalline, yellow solids: mp 255 °C dec; ^{1}H NMR (acetone-d_6, 30 °C) δ −1.3 (triplet) and −4.13 (broad quartet). Anal. Calcd for H$_{75}$C$_{30}$O$_{15}$P$_6$F$_6$Co: H, 7.03; C, 34.92; Co, 5.71. Found: H, 7.40; C, 34.86; Co, 5.64.

The activation energy for the reaction

$$H_2CoL_4^+ + L \rightarrow CoL_5^+ + H_2$$
$$[L = P(OCH_3)_3]$$
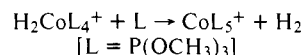
was determined by hydrogen evolution procedure maintaining the solutions at temperatures between 20 and 50 °C. Error in the temperature measurement above 40 °C was within ±1° so that the accuracy of $\Delta H^{\ddagger}$ was limited to ±5% using data collected at these temperatures. Using only the data from the temperatures at and below 40 °C, the error was ±2.5% (when empirically evaluated from the plot shown in Figure 3).
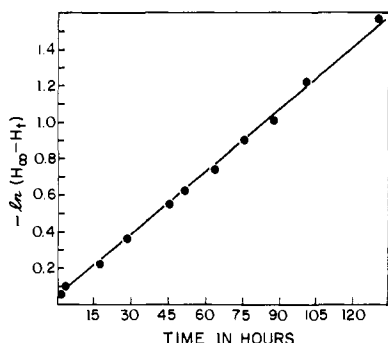
Figure 2. Plot of hydrogen evolution rate against time for reaction $H_2Co[P(OC_2H_5)_3]_4^+$ (0.2 M) + $P(OC_2H_3)_3$ (0.33 M) → $Co[P(O-C_2H_5)_3]_5^+$ + H_2.

Figure 3. Arrhenius plot for data obtained for $H_2Co[P(OCH_3)_3]_4^+$ (0.3–0.32 M) + $P(OCH_3)_3$ (2.1–3.8 M) at 23–49 °C. Rate data obtained by measuring hydrogen evolution. Rates at temperatures above 40 °C were relatively imprecise because of the necessity of cooling the solutions rapidly and more frequently in order to measure the hydrogen by the Toepler method.

Protonation of $CH_3Co[P(OCH_3)_3]_4$ and Methylation of $HCo-[P(OCH_3)_3]_4$. One to five millimoles of HPF_6, CF_3COOH, and NH_4PF_6 were added to a stirred solution of $CH_3Co[P(OCH_3)_3]_4^7$ (same number of millimoles) in solvents (3–30 mL) that included CH_3OH, CD_2Cl_2, and CD_3CN and reaction temperatures that ranged from −70 °C to 24 °C. Reaction was effected on a vacuum line and noncondensable gases were collected and measured with a Toepler pump and then analyzed by mass spectrometry. Yields of CH_4 were essentially quantitative. Reaction of $CD_3Co[P(OCH_3)_3]_4$ with NH_4PF_6 in CH_2Cl_2 was similarly monitored at 24 °C; a quantitative yield of CD_3H was obtained in 20 min.

In the methylation of $HCo[P(OCH_3)_3]_4$, the cobalt complex and $(CH_3)_3O^+PF_6^-$ (1 or 2 mmol of each) were placed in a reaction vessel which was then attached to a vacuum line and evacuated. Solvents (dichloromethane, acrylonitrile, dimethyl carbonate, and acetonitrile) were then added through a dropping funnel or by vacuum distillation. All reactions were run at 25 °C. Noncondensable gas collection, measurement, and analysis was as described above. Methane formation was quantitative in dichloromethane and dimethyl carbonate, ~70% in acrylonitrile, and zero in acetonitrile. In CD_2Cl_2, the methane was 98% CH_4 and 2% CH_3D.

Methylation of $CH_3Co[P(OCH_3)_3]_4$. Methylation of $CH_3Co-[P(OCH_3)_3]_4$ and of $CD_3Co[P(OCH_3)_3]_4$ with $(CH_3)_3O^+PF_6^-$ in CH_2Cl_2 and CD_2Cl_2 (5–25 mL) was run at 1-, 2-, and 4-mmol scales. Reaction conditions and analysis were as described above for dichloromethane solution (vacuum solvent transfer). Methane and alkane total yields were 70–90% at 24 °C assuming one hydrocarbon carbon atom produced per cobalt complex for reactant ratios of 1:1, 1:2, and 2:1 cobalt complex to oxonium salt.

Methylation was also followed by adding a solution of $CH_3SO_3CF_3$ in CH_2Cl_2 to a CH_2Cl_2 solution of $CH_3Co[P(OCH_3)_3]_4$ and of $CD_3Co[P(OCH_3)_3]_4$. The reaction system was also examined in CD_2Cl_2.

$Co[P(OCH_3)_3]_4PF_6$. A solution of $CH_3Co[P(OCH_3)_3]_4$ (2.28 g, 0.004 mol) in methanol (15 mL) was maintained at −100 °C. Propene (4–5 mL) was condensed into the solution. After a solution of HPF_6–diethyl ether complex (0.66 mL, 0.004 mol) in methanol (4 mL) was added, the reaction mixture was stirred for 1 h, then filtered at −80 °C. The resulting yellow solid η^2-$(C_3H_6)Co[P(OCH_3)_3]_4PF_6$ was washed with diethyl ether (10 mL) and pentane (2 × 10 mL) and dried at −80 °C under vacuum for several hours. The adduct was then allowed to warm to 25 °C under dynamic vacuum for 4 h during which propene was removed leaving the pale blue product, yield 2.7 g (96%), mp 192 °C dec. Anal. Calcd for $H_{36}C_{12}O_{12}P_5F_6Co$: H, 5.18; C, 20.58; Co, 8.42. Found: H, 5.13; C, 20.41; Co, 8.09. An identical procedure was followed using 1-hexene in place of propene with the same results.

$CH_3Co[P(OCH_2CH_3)_3]_4$. $KCo[P(OCH_2CH_3)_3]_4$ (1.53 g, 0.002 mol), CH_3I (0.002 mol), and 18-crown-6 ether (0.023 g, 0.0002 mol) were stirred in tetrahydrofuran (30 mL) for 20 h at 20 °C. The reaction mixture was filtered and the solvent was removed from the filtrate under vacuum. Residues from the filtrate were redissolved in pentane and eluted with pentane through a phosphite-deactivated alumina column (8 × 2 cm). Yellow solids were obtained: yield 1.07 g (74%); mp 110 °C dec; ^1H NMR (C_6H_6, 310 K) δ −3.89 (quartet of multiplets, 24 H, OCH_2CH_3), −1.24 (triplet, 36 H, OCH_2CH_3), and +0.11 (quintet, 3 H, $CoCH_3$) (J_{PH} = 8.4 Hz); 36.43-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (acetone-d_6, 310 K) δ −38.12 (quartet, 1 P, axial)

and −17.34 ppm (doublet, 3 P, equatorial) (J_{PP} = 91.4 Hz). Anal. Calcd for $H_{63}C_{25}O_{12}P_4Co$: H, 8.60; C, 40.65; Co, 7.98. Found: H, 8.44; C, 40.11; Co, 7.76.

$Co[P(OCH_2CH_3)_3]_4PF_6$. $CH_3Co[P(OCH_2CH_3)_3]_4$ (1.4 g, 0.001 89 mol) and 1-hexene (2 mL, 0.016 mol) in ethanol (20 mL) were cooled to −50 °C under argon, HPF_6–diethyl ether complex (0.33 mL, 0.002 mol) in ethanol (10 mL) was added and the solution was stirred at −50 °C for 1 h. Pentane (30 mL) was added and the yellow solid product was collected by filtration at −66 °C. The yellow solids η^2-(1-hexene)$Co[P(OCH_2CH_3)_3]_4PF_6$ were washed with cold diethyl ether (2 × 10 mL) at −66 °C and dried under vacuum at −50 °C for 2 h. Blue $Co[P(OCH_2CH_3)_3]_4PF_6$ was obtained by removal of 1-hexene from the adduct at 25 °C under vacuum over 4 h (Note: other solvent systems tried in this reaction all produced oils), yield 1.04 g (64%), mp 223–224 °C. Anal. Calcd for $H_{60}C_{24}O_{12}P_5F_6Co$: H, 6.96; C, 33.18; Co, 6.78. Found: H, 7.30; C, 32.50; Co, 6.37.

$H_3NCo[P(OCH_3)_3]_4PF_6$. To a stirred solution of $CH_3Co-[P(OCH_3)_3]_4$ (5.0 g, 0.0088 mol) in methanol (20 mL) maintained at 0 °C was added a solution of NH_4PF_6 (1.42 g, 0.0088 mol) in methanol (20 mL) in three portions over 0.5 h. After 4 h, CH_4 evolution had ceased and some orange-red crystals had precipitated. The solution was cooled to −66 °C, and the solids were then collected by filtration. The product was dried thoroughly under vacuum: yield 5 g (80%); mp 202 °C dec; ^1H NMR (acetone-d_6, 270 K) δ −3.66 (m, 36 H, methoxy protons) and −1.2 (m, 3 H, NH); 36.43-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (acetone-d_6, 200 K) δ −5.78 ppm (s); IR (halocarbon mull) ν_{N-H} 3370, 3295 (sh) cm^{-1}. Anal. Calcd for $H_{39}C_{12}NO_{12}F_6P_5Co$: H, 5.44; C, 20.08; N, 2.37; P, 21.61. Found: H, 5.29; C, 20.18; N, 2.21; P, 21.39.

$H_3NCo[P(OCH_2CH_3)_3]_4PF_6$. A solution of NH_4PF_6 (0.16 g, 0.001 mol) in ethanol (4 mL) was added to a solution of $CH_3Co-[P(OCH_2CH_3)_3]_4$ (0.74 g, 0.001 mol) in diethyl ether. After stirring for 10 min the solution turned red. Pentane (10 mL) was added and the solution was concentrated under vacuum until crystals formed, using a rotary evaporator. The red solid product was isolated by filtration: yield 0.89 g (100%); mp 204–205 °C dec; ^1H NMR (CD_2Cl_2, 300 K) δ −4.57 (m, 3 H, NH_3), −3.92 (broad quartet, 24 H, OCH_2CH_3), and −1.17 (triplet, 36 H, OCH_2CH_3); 36.45-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (CD_2Cl_2, 180 K) δ −4.76 (complex multiplet); IR (Nujol mull) ν_{N-H} 3370 (m), 3280 cm^{-1} (weak). Anal. Calcd for $H_{63}C_{24}O_2P_5F_6NCo$: H, 7.17; C, 32.55; N, 1.58; Co, 6.66. Found: H, 7.20; C, 32.37; N, 1.71; Co, 6.27.

η^2-$C_2H_4Co[P(OCH_3)_3]_4PF_6$. A solution of $CH_3Co[P(OCH_3)_3]_4$ (2.28 g, 0.004 mol) in methanol (25 mL) was slowly purged with ethylene introduced through a sintered glass gas inlet tube, and was cooled to −78 °C. HPF_6–diethyl ether complex (0.66 mL, 0.004 mol) in methanol (2 mL) was added. After the solution was stirred for 45 min at −78 °C, diethyl ether (10 mL) was added and the product was filtered at −78 °C. The pale yellow solids were washed with diethyl ether (10 mL) and dried under vacuum: yield 2.1 g (72%); mp 188–194 °C (slow melt, dec); ^1H NMR (CD_2Cl_2, 247 K) δ −3.50 (m, methoxy protons) and −2.51 (m, olefinic protons); 36.43-MHz ^{31}P NMR [$P(OCH_3)_3$ = 0] (CD_2Cl_2, 222 K) δ 2.1 (triplet) and −13.34 ppm (triplet) (J_{PP} = 128 Hz); IR (halocarbon mull) ν (olefinic C–H) 3005 cm^{-1}. Anal. Calcd for $H_{40}C_{14}O_{12}F_6P_5Co$: H, 5.54; C, 23.09; Co, 8.09. Found: H, 5.63; C, 22.85; Co, 7.92.

η^2-$(C_6H_5C≡CC_6H_5)Co[P(OCH_3)_3]_4PF_6$. A solution of CH_3Co-

[P(OCH$_3$)$_3$]$_4$ (1.14 g, 0.002 mol) and 1,2-diphenylacetylene (0.5 g, 0.0028 mol) in methanol (10 mL) and diethyl ether (5 mL) was cooled to −50 °C. HPF$_6$-diethyl ether complex (0.33 mL, 0.002 mol) in methanol (4 mL) was added. The reaction mixture was stirred for 1 h during which the solution color changed from green to purple and a yellow solid precipitated. The solids were collected by filtration at −70 °C, washed with cold diethyl ether (2 × 15 mL), and dried under vacuum: yield 1.4 g (79%); mp 184 °C dec; ¹H NMR (CD$_2$Cl$_2$, 0 °C) δ −3.65 (m, methoxy protons) and −7.43 (m, phenyl protons); 36.43-MHz ³¹P NMR [P(OCH$_3$)$_3$ = 0] (acetone-d_6–Freon 22, 222 K) δ −12.0 (triplet, 2 P) and +12.8 (triplet, 2 P) (J_{PP} = 115 Hz). Anal. Calcd for H$_{46}$C$_{26}$O$_{12}$C$_5$C$_6$Co: H, 5.28; C, 35.55; Co, 6.71. Found: H, 5.3; C, 31.13; Co, 6.74 (the compound was not obtained pure; ∼10–15% Co[P(OCH$_3$)$_3$]$_5$PF$_6$ was always minimally present by ³¹P NMR).

(CH$_3$CN)Co[P(COH)$_3$]$_4$PF$_6$. CH$_3$CN was added dropwise to a slurry of Co[P(OCH$_3$)$_3$]$_4$PF$_6$ (0.7 g, 0.001 mol) in pentane/diethyl ether (40/60, 5 mL). The blue cobalt reactant immediately formed a deep red oil which subsequently solidified. The red solids were collected by filtration and dried under vacuum: yield 0.68 g (91%); mp 180 °C dec; ¹H NMR (CD$_2$Cl$_2$, −35 °C) δ −3.56 (broad s, methoxy protons) and −2.15 (m, CH$_3$CN); 36.43-MHz ³¹P NMR [P(OCH$_3$)$_3$ = 0] (acetone-d_6, 220 K) δ −8.35 (s), (acetone-d_6–Freon 22, 145 K) complex multiplet, δ −8.0; IR (halocarbon mull) $\nu_{C\equiv N}$ 2250, 2280 cm⁻¹ (very weak). Anal. Calcd for H$_{39}$C$_{14}$O$_{12}$P$_5$F$_6$NCo: H, 5.30; C, 22.68; N, 1.89; Co, 7.95. Found: H, 5.35; C, 22.30; N, 1.56; Co, 7.81.

C$_4$H$_6$Co[P(OCH$_3$)$_3$]$_3$PF$_6$. η³-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$ (1.88 g, 0.004 mol) in methanol (15 mL) was cooled to −100 °C under argon. 1,3-Butadiene was bubbled through a sintered glass gas inlet into the solution until about 4 mL had condensed. HPF$_6$-diethyl ether (0.66 mL, 0.004 mol) in methanol (5 mL) was added via syringe. A slow purge of argon was maintained over the solution while it was stirred at −100 °C for 2 h, during which time a color change from dark brown to green occurred. After addition of diethyl ether (10 mL) the solution was filtered at −78 °C. The pale green solids were washed with diethyl ether (10 mL) and pentane (2 × 10 mL) at −78 °C, then dried under vacuum: yield 1.75 g (70%); mp 204 °C dec; ¹H NMR (CD$_2$Cl$_2$, 300 K) δ −5.44 (m, 2 H, butadiene C$_2$, C$_3$ protons), −3.6 (m, 27 H, methoxy protons), −2.13 (m, 2 H, syn protons), −0.37 (m, 2 H, anti protons); 36.43-MHz ³¹P NMR [P(OCH$_3$)$_3$ = 0] (acetone-d_6–toluene, 180 K) δ −4.53 (doublet, 2 basal), −27.45 ppm (triplet, 1, apical) (J_{PP} = 22.5 Hz); IR (halocarbon mull) ν (olefinic C–H) 3015 cm⁻¹. Anal. Calcd for H$_{33}$C$_{13}$O$_9$F$_6$P$_4$Co: H, 5.28; C, 24.77; P, 19.66; Co, 9.35. Found: H, 5.25; C, 24.49; P, 19.71; Co, 9.22.

(1,3-Cyclooctadiene)Co[P(OCH$_3$)$_3$]$_3$PF$_6$. To a solution of η³-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$[7] (0.94 g, 0.002 mol) and 1,5-cyclooctadiene (1 mL, 0.008 mol) in methanol (10 mL) and diethyl ether (10 mL) maintained at −70 °C was added HPF$_6$-diethyl ether complex (0.33 mL, 0.002 mol) in methanol (4 mL). The temperature was raised to −50 °C and the solution was stirred for 1 h. The yellow solids which slowly formed were collected by filtration at −70 °C, washed with cold diethyl ether (2 × 15 mL), and dried under vacuum: yield 1.3 g (95%); mp 194-195 °C dec; ¹H NMR (CD$_2$Cl$_2$, −30 °C) δ −5.09 (m, C$_2$ and C$_3$ diene protons), −3.56 (broad s, methoxy protons), −1.73 and −1.10 (m, C$_1$ and C$_4$ protons and aliphatic protons of diene); 36.45-MHz ³¹P NMR [P(OCH$_3$)$_3$ = 0] (acetone-d_6–Freon 22, 180 K) δ −7.26 (doublet, area 2) and −23.16 (triplet, area 1) (J_{PP} = 30.2 Hz). Anal. Calcd for H$_{39}$C$_{17}$O$_9$P$_4$F$_6$Co: H, 5.74; C, 29.83; P, 18.11; Co, 8.61. Found: H, 5.85; C, 29.69; P, 18.40; Co, 8.45.

η³-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$ (0.94 g, 0.002 mol) and 1,3-cyclooctadiene (3 mL) in methanol (15 mL) were cooled to −60 °C. HPF$_6$-diethyl ether (0.33 mL, 0.002 mol) in methanol (3 mL) was added. A yellow precipitate formed immediately. The mixture was stirred for 15 min at −50 °C, then filtered at −70 °C. The yellow solids obtained were dried thoroughly under vacuum, yield 1.3 g (95%), mp 198-200 °C dec. All spectral properties were identical with those described above for the product obtained starting with 1,5-cyclooctadiene. In both cases the ¹H NMR spectra were consistent with coordinated 1,3- rather than 1,5-cyclooctadiene. At ambient temperature in solution (CD$_2$Cl$_2$, acetone-d_6, etc.) the compound decomposed leaving a supernatant containing Co[P(OCH$_3$)$_3$]$_5^+$ and uncoordinated 1,3-cyclooctadiene.

Addition Reactions to Co[P(OCH$_3$)$_3$]$_4^+$. Co[P(OCH$_3$)$_3$]$_4$PF$_6$ (0.35 g, 0.005 mol) was placed in a reaction tube attached to the vacuum line, evacuated, and closed off. The vacuum line was filled with NH$_3$

at 0.6 atm pressure. On admission of NH$_3$ to the reactant, the blue solid immediately turned bright orange. An infrared spectrum of the product was characteristic of NH$_3$Co[P(OCH$_3$)$_3$]$_4^+$: ν_{N-H} 3370 cm⁻¹.

Co[P(OCH$_3$)$_3$]$_4$PF$_6$ (0.35 g, 0.0005 mol) was attached to the vacuum line as above. On admission of 0.85 atm H$_2$, the blue solid immediately turned white. The ¹H NMR spectrum of the product was identical with that of H$_2$Co[P(OCH$_3$)$_3$]$_4^+$: δ −3.7 (quintet, J_{P-H} = 2.9 Hz).

Co[P(OCH$_3$)$_3$]$_4$PF$_6$ (0.2 g, 0.000 28 mol) was placed in an NMR tube, attached to the vacuum line, and evacuated. As ethylene (0.8 atm) was admitted to the sample the blue solid turned yellow over a period of about 5 min. CD$_2$Cl$_2$ (0.3 mL) with several drops of C$_6$H$_6$ as reference was condensed onto the NMR tube which was then sealed off. ¹H NMR showed free ethylene at δ −5.25 and resonances consistent with the spectrum of η²-C$_2$H$_4$Co[P(OCH$_3$)$_3$]$_4^+$: δ −3.51 and −2.50.

Ligand Metathesis Reactions for LCo[P(OCH$_3$)$_3$]$_4^+$. The ethylene complex (0.15 g, 0.002 mol) was placed in an NMR tube attached to the vacuum line. CD$_2$Cl$_2$ (0.3 mL) was distilled into the tube which was then sealed off under 0.8 atm NH$_3$. On warming the contents of the tube to 0 °C, the color of the solution changed from yellow to red over 10–15 min. The ¹H NMR spectrum was consistent with a solution of NH$_3$Co[P(OCH$_3$)$_3$]$_4^+$ and free ethylene at 0 °C.

The above procedure was repeated using H$_2$ in place of NH$_3$. On warming to 20 °C the color of the solution quickly faded and ¹H NMR revealed the spectrum of H$_2$Co[P(OCH$_3$)$_3$]$_4^+$.

P(OCH$_3$)$_3$ (2 mL, 0.017 mol, i.e., excess) was added under vacuum to solid NH$_3$Co[P(OCH$_3$)$_3$]$_4$PF$_6$ (0.52 g, 0.000 73 mol) and stirred for 30 min at 24 °C. The system was cooled to −66 °C and evolved gases were collected using a Toepler pump. During the next 30 min no further gas was evolved from the system. In total, 0.000 72 mol of gas was collected and shown to be NH$_3$ by infrared. Yellow solids from the reaction were collected by filtration and identified as Co[P(OCH$_3$)$_3$]$_5$PF$_6$ by melting point and ¹H NMR.

NH$_3$Co[P(OCH$_3$)$_3$]$_4$PF$_6$ in acetone-d_6 was shaken in a sealed NMR tube under an atmosphere of H$_2$. The red solution faded to pale cream during 15 min and ¹H NMR showed a spectrum characteristic of H$_2$Co[P(OCH$_3$)$_3$]$_4^+$. This product (as PF$_6^-$ salt) was confirmed by melting point and infrared analysis.

A solution of NH$_3$Co[P(OCH$_3$)$_3$]$_4$PF$_6$ (1.4 g, 0.001 95 mol) in CH$_2$Cl$_2$ (2 mL) was stirred under CO (0.0033 mol, at 0.75 atm) at 24 °C. The color changed from red to yellow over 20 min. Yellow solid isolated from the reaction showed carbonyl stretching in the infrared at 2040, 1980, and 1970 cm⁻¹. Literature values[11] for Co(CO)$_2$[P(OCH$_3$)$_3$]$_3^+$, 2037, 1982 cm⁻¹; for Co(CO)[P(OCH$_3$)$_3$]$_4^+$, 1970 cm⁻¹.

Olefin Isomerization by H$_2$Co[P(OCH$_3$)$_3$]$_4^+$. The catalytic system of H$_2$Co[P(OCH$_3$)$_3$]$_4^+$CF$_3$COO⁻ and CF$_3$COOH was prepared in situ from HCo[P(OCH$_3$)$_3$]$_4$ and CF$_3$COOH using acetone as solvent. ¹H NMR was used to monitor the progress of the reactions, using the integrated olefinic resonances to estimate the relative amounts of primary and internal olefins. Reactant ratios commonly used were olefin/cobalt species = 10–15 and CF$_3$COOH/cobalt species = 4–10. Typical turnover rates in an active system were 0.2-0.3 mol substrate (mol catalyst)⁻¹ min⁻¹. The catalysis of isomerization of 1-hexene was *qualitatively* examined for the effects of the CF$_3$COOH, CF$_3$COO⁻, PF$_6^-$, and H$_2$ concentrations. For the study of trifluoroacetic acid concentration effects on rate, acetone-d_6 solutions (0.23 mL) containing 0.08 mmol of HCo[P(OCH$_3$)$_3$]$_4$ and 1.08 mmol of 1-hexene were treated with 0.38, 0.76, and 1.14 mmol of CF$_6$COOH; the times for essentially complete (equilibrium mixture of isomers) isomerization of the olefin were 2.5-3, 1, and 0.5 h, respectively. Addition of CF$_3$COOH to solutions of H$_2$Co[P(OCH$_3$)$_3$]$_4^+$PF$_6^-$ and 1-hexene led to no isomerization (after 7 h), Similar experiments with addition of NaOCOCF$_3$ to acetone solutions of H$_2$Co[P(O-CH$_3$)$_3$]$_4^+$PF$_6^-$ and 1-hexene (1:1 and 1:5 ratios of cobalt complex to NaOCOCF$_3$) led to no isomerization after 4 h. Also addition of CF$_3$COOH to such mixtures of H$_2$Co[P(OCH$_3$)$_3$]$_4^+$PF$_6^-$ and NaOCOCF$_3$ led to no olefin isomerization. A 1:1.3 molar mixture of HCo[P(OCH$_3$)$_3$]$_4$ and NaOCOCF$_3$ with a fourfold excess of CF$_3$COOH (acetone solution) gave a 30% isomerization of 1-hexene (100:1 olefin to cobalt ratio).

Inhibition of the olefin isomerization reaction by PF$_6^-$ was examined for acetone-d_6 solutions (0.07 mL) of HCo[P(OCH$_3$)$_3$]$_4$ (0.075 mmol), trifluoroacetic acid (0.4 mmol), and 1-hexene (1.08 mmol).
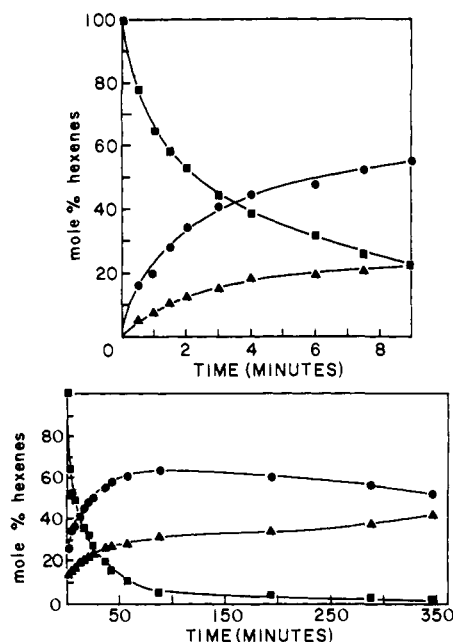
Figure 4. Plot of the rate of 1-hexene isomerization as a function of time at 20 °C for the Co[P(O-*i*-C₃H₇)₃]₄PF₆ catalyzed reaction in acetone (1.5 mL). The graph codes follow: ●, 1-hexene; ■, *cis*-2-hexene; ▲, *trans*-2-hexene concentrations. In the top plot the catalyst amount, 1-hexene amount, catalyst to 1-hexene ratio, and the number of turnovers in the first minute were (0.07 g, 0.067 mmol), (4 mL, 32 mmol), 478, and 140 mol of 1-hexene per mol of catalyst per min, respectively. In the bottom plot, these values were (0.05 g, 0.056 mmol), (4 mL, 32 mmol), 570, and 160, respectively.

Samples with 0.05, 0.02, 0.01, and 0.005 mmol of added NaPF₆ were followed by NMR for the 1-hexene isomerization; the percent isomerization was 75 (4 h), 100 (4 h), 100 (4 h), and 100% (1 h), respectively. With 0.12 mmol of added NaPF₆, there was no isomerization after 7 h. The sodium salts of B(C₆H₅)₄⁻ and BF₄⁻ as well as NH₄⁺PF₆⁻ also retarded the isomerization.

Inhibition by hydrogen gas was examined for pairs of samples made up by condensing volatile reactants on HCo[P(OCH₃)₃]₄ in NMR tubes attached to the vacuum line, which were then sealed off either under vacuum or under approximately 0.8 atm H₂. The samples were warmed to 20 °C and observed by NMR.

1. HCo[P(OCH₃)₃]₄ (0.05 g, 0.09 mmol), 1-hexene (0.2 mL, 1.6 mmol), CF₃COOH (0.03 mL, 4 mmol), and acetone-*d₆* (0.2 mL). Under vacuum: after 18 h, 30% isomerization; after 2 days, 50% isomerization. Under H₂: after 18 h, 4% isomerization; after 2 days, 5–7% isomerization.

2. HCo[P(OCH₃)₃]₄ (0.05 g, 0.09 mmol), 1-hexene (0.2 mL, 1.6 mmol), CF₃COOH (0.14 mL, 1.8 mmol), acetone-*d₆* (0.2 mL). Under vacuum: after 6 h, 71% isomerization. Under H₂: after 6 h, 1–2% isomerization.

3. HCo[P(OCH₃)₃]₄ (0.15 g, 0.27 mmol), 1-pentene (0.4 mL, 3.8 mmol), CF₃COOH (0.2 mL, 0.25 mmol), acetone-*d₆* (0.1 mL). Under vacuum: after 3 days, 100% isomerization. Under H₂: after 3 days, 40% isomerization.

Deuterium incorporation into isomerized olefins was examined for the following reaction mixture prepared in an NMR tube: DCo-[P(OCH₃)₃]₄ (0.15 mL, 0.27 mmol), 1-pentene (0.4 mL, 3.8 mmol), CF₃COOD (0.2 mL, 25 mmol), and acetone-*d₆* (0.1 mL). After the isomerization was approximately 50% complete the pentenes were examined by combined gas chromatography/mass spectrometry (20% ethyl-*N*,*N*-dimethyl oxamate, 6 ft, with squalane, 6 ft). *No* deuterium incorporation was detected in 1-pentene (50%), *trans*-2-pentene (22.2%), or *cis*-2-pentene (27.8%) from the reaction mixture. The experiment was repeated, analyzing the olefins at later stages in the reaction: 1-pentene (0%), *trans*-2-pentene (72.5%), *cis*-2-pentene (27.5%). In the latter experiment 1-pentene was fully converted to internal olefin and the two 2-pentenes had further equilibrated, yet *no* deuterium-containing products were detected. The extent of deuteration in the catalyst system was checked by heating DCo-[P(OCH₃)₃]₄ (0.57 g, 0.001 mmol), CF₃COOD (0.1 mL, 0.012 mol), and P(OCH₃)₃ (1 mL) in diethyl ether (1 mL) at 50 °C for 2 h;

0.000 98 mol of gas was evolved; D₂, HD = 40.3:9.2, no H₂, i.e., overall 90.8% D, 9.2% H, from H or D₂Co[P(OCH₃)₃]₄ species. CF₃COOD was Aldrich 99% D, opened and handled only in an inert atmosphere.

Olefin Isomerization by Co[P(OCH₃)₃]₄PF₆. Isomerizations of 1-, 2-, and 3-hexenes catalyzed by Co[P(OCH₃)₃]₄PF₆ were carried out using olefin:catalyst ratios between 140 and 700. A slurry of catalyst and hexene was placed in a 15-mL round-bottom flask fitted with septum-sealed side arm and slow bypass of argon, and cooled to 0 °C. Addition of acetone solubilized the catalyst and initiated the reaction (the slurry of blue solids changed to a yellow, homogeneous solution). Aliquots of 0.1 mL were withdrawn at intervals, quenched with 0.3 mL of pentane in air, and analyzed by gas chromatography using a 6 ft × ⅛ in. 20% ethyl-*N*,*N*-dimethyl oxamate on Chromosorb P (AW 60/80 mesh) column coupled to a 6 ft × ⅛ in. squalane on Chromosorb P column with helium flow rate of 35 mL/min, injection port at 150 °C, manifold at 150 °C, hot-wire detector at 200 °C with 150-A current. Compositions were calculated from relative peak areas (height × width at half-height). For 1-hexene and 2-hexene, equilibrium was nearly achieved within about 30 s. After about 2 min, there was no further change.

Isomerization of 1-hexene catalyzed by η⁴-(1,3-cyclooctadiene)Co[P(OCH₃)₃]₃PF₆ complex was carried out using a procedure identical with that described above. The results were very similar to those obtained for Co[P(OCH₃)₃]₄⁺PF₆.

Olefin Isomerization by Co[P(O-*i*-C₃H₇)₃]₄PF₆. Co[P(O-*i*-C₃H₇)₃]₄PF₆ and 1-hexene were placed in a 15-mL round-bottom flask with septum-covered side arm and stopcock for argon bypass. Exact quantities are given under the graphed results (Figure 4). Acetone was added through the side arm to solubilize the catalyst, giving a blue solution. Aliquots (0.1 mL) were withdrawn at intervals, quenched, and analyzed by gas chromatography (as for experiments using Co[P(OCH₃)₃]₄PF₆ as catalyst). Aliquots (0.2 mL) of a 0.05 M solution of Co[P(O-*i*-C₃H₇)₃]₄PF₆ in CD₂Cl₂ were added to NMR tubes containing 1-hexene (0.45 mL, 0.0005 mol) and (1) no P(O-*i*-C₃H₇)₃, (2) P(O-*i*-C₃H₇)₃ (0.05 mL, 0.003 mol), and (3) P(O-*i*-C₃H₇)₃ (0.12 mL, 0.000 72 mol). The olefinic resonances were monitored by ¹H NMR. After 15 min (1) was completely isomerized to 2-hexenes. After 1 h (2) contained ~10% 2-hexenes and (3) contained ~5% 2-hexenes.

Attempted Hydrogenation of Olefins with H₂Co[P(O-*i*-C₃H₇)₃]₄PF₆. A slurry of H₂Co[P(O-*i*-C₃H₇)₃]₄PF₆ (0.08 g, 0.001 mmol) and 1-hexene (4 mL, 32 mmol) was purged with hydrogen for 15 min. Acetone (1.5 mL) was added and the solution was stirred. Hydrogen pressure was maintained at 1 atm. Aliquots of 0.1 mL were periodically removed for analysis by gas chromatography. After 12 h, no hexane was detected in the reaction mixture; isomerization proceeded at a rate ~15–20% that of the reactions catalyzed by a comparable amount of Co[P(O-*i*-C₃H₇)₃]₄PF₆ in the absence of hydrogen.

References and Notes

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The Octahedral Hexasilver Molecule. Seven Crystal Structures of Variously Vacuum-Dehydrated Fully Ag+-Exchanged Zeolite A

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Abstract: The structures of seven differently vacuum-dehydrated fully Ag+-exchanged zeolite A crystals have been determined by single-crystal X-ray diffraction techniques. Their structures were solved and refined in the cubic space group $Pm3m$ at 24 (1) °C. All crystals were ion exchanged in flowing streams of aqueous $AgNO_3$, followed by dehydration at constant temperatures ranging from 395 to 475 °C for from 2 to 10 days. In two of these structures with an approximate unit-cell composition of $Ag^+_8Ag^0_4H^+_{2x} Si_{12}Al_{12}O_{46+x}$, $x \simeq 1$, eight equivalent Ag+ ions lie at sites of near trigonal planar coordination on threefold axes very near the centers of the 6-oxygen rings. Two-thirds of the sodalite units contain octahedral Ag_6 molecules at their centers, while the remaining one-third of the sodalite units are empty of silver species. (Alternatively, contrary to the tendency of metal atoms to form clusters, and with molecular symmetry less than the site symmetry, molecules of Ag_5 or Ag_4 with an octahedral structure in which one or any two vertices are missing may exist.) The probable six-atom cluster, which is stabilized by coordination to eight Ag+ ions, is closest packed and is a unit of the structure of silver metal. It is the smallest possible fully developed single crystal of silver, whose natural form is {111}. The Ag–Ag distance in the cluster, ca. 2.92 Å, is near the 2.89 Å bond length in silver metal. Two oxide ions per unit cell, approximately one from a position which links the sodalite units together and the other from an H_2O molecule, have been lost as O_2 as a result of decomposition to preserve charge balance. By comparison with partially hydrated fully Ag+-exchanged zeolite A, it is observed that the populations of Ag+ ions at 4-ring and 8-ring sites are the first to be depleted as some Ag+ ions are reduced to Ag^0. It is also observed that the hexasilver molecule is stable within the zeolite only when it is stabilized by coordination to at least six Ag+ ions at 25 °C or eight at ca. 450 °C.

Introduction

The structures of small clusters of some metals, notably platinum, palladium, and nickel, are of interest because of their pronounced catalytic activity. These three metals, and several others including gold, rhodium, iridium, and aluminum, are isostructural with silver.

Catalysts containing both Ag^0 and Ag^+ are important in partial oxidation processes such as the formation of ethylene oxide from ethylene and oxygen.[1] A vacuum-dehydrated sample of zeolite A, containing H^+ ions and Ag_6 clusters complexed to eight Ag^+ ions, after exposure to oxygen, partially oxidized NH_3 to form the saturated hydronitrogens N_3H_5 (triazane) and N_3H_3 (cyclotriazane).[2] These processes are indicative of a unique chemistry which is inadequately understood at present.

Metal ions in zeolites can be readily reduced. For example, Ni^{2+} ions in zeolite Y can be reduced to Ni^+ by sodium vapor, and to the metallic state by hydrogen.[3] Cu^{2+} ions in CuNa–Y were reduced to Cu^+ after treatment with carbon monoxide at elevated temperatures, while reduction of these ions by hydrogen gas gave Cu^0.[4] The dipositive cations of the relatively volatile elements Hg, Cd, and Zn can be removed as atoms from zeolite X by heating in hydrogen.[5]

Silver ions can also be reduced intrazeolitically. Tsutsumi and Takahashi[6] reported that Ag^+ ions in zeolite Y could be

reduced to bulk clusters of Ag^0 after treatment with alcohols and alkylbenzene. Ag^+ ions in Ag–X and Ag–Y were also reduced after treatment with carbon monoxide at 350 °C.[7] Matsumoto et al.[8] found that Ag^+-exchanged zeolite A is thermally unstable and loses its crystal structure at a lower temperature than Na_{12}-A does.[9] According to them, the more Ag^+ ions exchanged to zeolite A, the less its thermal stability. Beyer[10] also found that about 70% of the Ag^+ ions in zeolite A were reducible by hydrogen after dehydration at 150 °C, and that about 92% of the Ag^+ ions were reducible at 330 °C. Beyer, Jacobs, and Uytterhoeven[11] reported that polynuclear cations of mean or approximate composition Ag_3^+ form upon partial reduction of dehydrated fully Ag^+-exchanged zeolite Y.

The crystal structures of vacuum-hydrated fully Ag^+-exchanged zeolite A samples were determined in order to learn the structure of fully dehydrated Ag_{12}-A for comparison with that of partially hydrated Ag_{12}-A,[9,12] whose three residual water molecules bridge between three Ag^+ ions inside the sodalite unit.[13] It was hoped that complete dehydration could be achieved and that a near zero coordinate[14-17] or zero coordinate[18-21] Ag^+ ion would be found. Decomposition of the zeolite framework or of water molecules, and the concomitant production of silver atoms, was not anticipated when this work was initiated.

The structures reported herein are those of seven differently