gression analysis of the experimental data. The assumption here is that eq 18 together with the experimental data provide a legitimate basis for a statistical determination of the nongeometrical constants.

(34) An initial regression analysis of all the ketones in Table VI with $\theta \sim 120°$ revealed that 2,2,6,6-tetramethylcyclohexanone (32) and cis-3,5-di-tert-butylcyclohexanone (39) differed by more than 2.9 standard deviations from the experimental values. There is also reason to suspect[35,36] that the assumed chair geometries used in calculating the geometrical parameters for these compounds may deviate in an important way from the actual geometries. Hence these compounds and the closely related 2,2,6,6-tetraethylcyclohexanone (33) and 3-tert-butylcyclohexanone (35) were omitted from the analysis. Also omitted were the cyclohexanones with bulky γ substituents, 36, 40, and 41, where conformational stabilization is known to affect B values significantly.[9] A further justification for the omissions just noted is given in ref 37, which is best read at the end of this section.

(35) J. B. Stothers and C. T. Tan, Can. J. Chem., 52, 308 (1974).

(36) S. Wolfe and J. R. Campbell, Chem. Commun., 872 (1967).

(37) In the Theory C.3 section it is noted that different sets of nongeometric constants in eq 18 are necessary for the idealized cyclohexanones, cyclopentanones, and cyclobutanones because of the strong θ dependence of B. Stothers and Tan find evidence[35] from ^{13}C NMR measurements that 2,2,6,6-tetramethylcyclohexanone (32) has a flattened chair geometry, and hence there is a concomitant change in θ here from its value in the idealized chair cyclohexanones. Such strained, flattened chairs can best be treated as a separate class of ketones, with their own set of nongeometrical constants. Unfortunately, the paucity of data for such systems

at this time precludes determination of the constants. If one can extrapolate from the very limited data at hand, it can be seen by comparing $B(n\pi^*,65)$ = 82×10^{-8} with $B(n\pi^*,61)$ = -20×10^{-8} that the contribution from forward out-of-plane α-substituent carbons becomes increasingly negative with increasing θ. If one can extrapolate further to 2,2,6,6-tetramethylcyclohexanone (32), then a flattened chair geometry with four forward out-of-plane methyl groups would be consonant with the strongly negative observed $B(n\pi^*,32)$ = -176×10^{-8}. There is also evidence[31] for chair flattening in the case of cis-3,5-di-tert-butylcyclohexanone (39). However, here the affected α substituents are hydrogens, and an analogous extrapolation would lead one to expect a strong positive increment in the B value, in accord with $B(n\pi^*,39)$ = 193×10^{-8}. For the γ-substituted cyclohexanones 35, 40, and 41, independent evidence for conformational stabilization can be found in their Raman spectra. Table VIII gives the relative intensities of the Raman band of this series which Fuhrer et al.[21] find to be most clearly associated with the out-of-plane bend ($\nu \sim 655$ cm^{-1}, PE 32%).[21] The dramatic drop in the intensity of the 655-cm^{-1} band with increasing bulk of the γ substituent shows clearly that the nature of the out-of-plane bending motion is significantly and monotonically modified by bulky γ substituents. Such modifications had been inferred previously[9] from the MCD data and their important role in MCD analysis noted.[9]

(38) NOTE ADDED IN PROOF. Recent ab initio energy calculations (M. Askari, N. S. Ostland, and L. Schäfer, J. Am. Chem. Soc., submitted for publication) indicate that the relative populations of the chair-chair conformers of 5 and 6 are >99 and ~75%, respectively. Thus the anomalous MCD behavior noted for 6 may well reflect the presence of a significant population of nonchair forms in that compound.

Low Valent Cobalt Triisopropyl Phosphite Complexes. Characterization of a Catalyst for the Hydrogenation of α,β-Unsaturated Ketones

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Abstract: A group of new low valent cobalt complexes with triisopropyl phosphite ligands (L) has been prepared. Chemically and catalytically, the group was largely distinguished from analogous groups derived from less bulky phosphite ligands. In the cobalt(0) and -(1) classes, all species were tetrahedral and paramagnetic as in CoL_4, CoL_4^+, and CoL_3X; the cobalt(1) class tended to be diamagnetic and five-coordinate at low temperature in coordinating solvents. Alkali metal salts of the Co(−1) species were distinctive in composition, $M^+CoL_5^-$, and in their very high hydrocarbon solubilities. Reaction of η^3-$C_3H_5Co[P(O-i-C_3H_7)_3]_3$ with hydrogen produced $H_3Co[P(O-i-C_3H_7)_3]_3$, an active catalyst for olefin hydrogenation. A notable catalytic property of this trihydride was its selective hydrogenation of α,β-unsaturated ketones and amides to the saturated ketones and amides.

Cobalt has been a much studied metal center in modern coordination chemistry beginning with the classic investigations by Werner. The focus of these studies has somewhat shifted from cobalt complexes with hard ligands to soft ligands because the latter convey to cobalt a diverse chemistry that has substantial utility in such areas as catalysis. A family of these complexes of special note is derived from phosphine and phosphite complexes.[1-11] Here the more extensive classes are based on cobalt(I) with phosphite and phosphine ligands such as the diamagnetic CoL_5^+ and $HCoL_4$ complexes.[1-11] Within this family, we have sought distinctive chemical and catalytic properties by the employment of large, bulky phosphites and report herein a successful application with the triisopropyl phosphite ligand.

Results and Discussion

Cobalt(−I). Synthetically valuable alkali metal salts of cobalt(−I) complexes, $M^+Co[P(OR)_3]_4^-$ have been prepared with trimethyl and triethyl phosphite ligands[8b] by the reaction of the respective hydrides, $HCo[P(OR)_3]_4$, with alkali metal hydrides. This synthetic procedure failed completely[8b] when applied to $HCo[P(O-i-C_3H_7)_3]_4$. This observation was as-

cribed to a steric shielding of the Co-H bond by the isopropyl phosphite ligands, a hypothesis supported by inspection of carefully constructed moleular models of the five-coordinate hydride. Synthesis of cobalt(−I) triisopropyl phosphite complexes was achieved by the alkali metal amalgam reduction of cobalt(II) chloride in the presence of excess phosphite. These derivatives had two distinctive properties, a composition of the form $MCo[P(O-i-C_3H_7)_3]_5$ and a very high solubility in aliphatic hydrocarbons like pentane. Pentacoordinate d^{10} anionic complexes, although not impossible, are extremely unlikely in the light of established d^{10} structural chemistry. The impressive solubility of these $MCoL_5$ complexes in saturated hydrocarbons was in striking contrast to the intractability[9b] of the $M^+Co[P(OR)_3]_4^-$ (R = CH_3 and C_2H_5) complexes which did not dissolve in nonprotonic solvents and dissolved with reaction (formation of $HCoL_4$) in protonic solvents. Solubility features and conventional d^{10} structural characteristics may be subsumed in a $MCoL_5$ structure with a tetrahedral d^{10} CoL_4^- unit which partially satisfies the alkali metal cation coordination sphere with phosphite oxygen atoms and a noncobalt bound phosphite ligand which completes the alkali metal coordination sphere.[12] *One* possible representation is depicted in 1. Solution

1
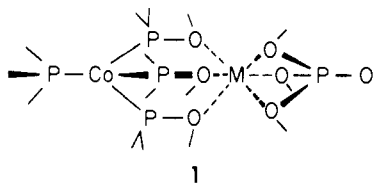
state characterization of a species like **1** is potentially feasible through ^{1}H NMR studies. In fact, these salts consistently exhibited two sets of isopropyl phosphite proton resonances[13] in approximately a 4:1 ratio, an observation that would be consistent with **1** if the phosphite complexed alkali metal atom were rapidly traversing (or dissociating from) the phosphite oxygen atom periphery of the tetrahedral cobalt complex. If the exchange process were dissociative in character, then MCoL$_5$ should exhibit a fast exchange between the unique phosphite ligand (bound only to M$^+$) and free phosphite. The spectrum of MCoL$_5$ + L at 25 °C showed three CH$_3$ doublets which basically represented a composite of the characteristic MCoL$_5$ and L spectra; thus a fast (NMR time scale) dissociative process may be excluded. It should also be noted that the two isopropyl CH proton resonances (multiplets) for MCoL$_5$ were well separated and that the multiplet of intensity 4 was in a region characteristic of CH protons associated with isopropyl phosphite ligands bound to cobalt. One inexplicable observation was the consistent 3.5 to 3.7:1 intensity relationship between the two isopropyl resonances (based on the sharp methyl doublets). Crystals of these complexes were obtained but none diffracted adequately for a full crystallographic analysis; poor diffraction capability was common to the crystals of the isopropyl phosphite cobalt complexes described in this paper.

A chemical property of these MCoL$_5$ complexes that was qualitatively distinct from the M$^+$CoL$_4^-$ (e.g., P(OCH$_3$)$_3$) salts was manifest in the allyl iodide reaction wherein the latter yielded the diamagnetic, well-characterized η^3-C$_3$H$_5$Co[P(OR)$_3$]$_3$ molecules[8] and the former the unusual paramagnetic MCo(C$_3$H$_5$)[P(O-i-C$_3$H$_7$)$_3$]$_3$I "salts". These latter salts like the parent MCoL$_5$ complexes possessed a very high solubility in aliphatic hydrocarbons. We note here, without a rigorous structural definition, the potential for a substantial solubilization of certain alkali metal salts in nonpolar solvents with the triisopropyl phosphite ligand.

Cobalt(0). A neutral monomolecular Co(0) derivative, Co[P(O-i-C$_3$H$_7$)$_3$]$_4$, was prepared by reduction of cobalt(II) chloride by 2 equiv of sodium amalgam in the presence of excess phosphite. The magnetic moment of this molecule was 2.0 μ_B, a value within the observed and expected range for a d^9 complex. No temperature dependence of the magnetic susceptibility, suggestive of an equilibrium with a binuclear species, Co$_2$L$_8$, was observed within the temperature range of +30 to −60 °C. A scale model of Co$_2$[P(O-i-C$_3$H$_7$)$_3$]$_8$ indicated that severe interligand repulsion would be present in such a dimeric molecule.

With the less bulky phosphite ligands, examples of both dimeric and monomeric cobalt derivatives have been isolated. The dimers Co$_2$[P(OR)$_3$]$_8$ with R = CH$_3$ and C$_2$H$_5$ were prepared from a radical dissociation of a (CH$_3$)$_3$GeCo[P(OR)$_3$]$_4$ intermediate and were found to be stable to homolytic dissociation up to 100 °C.[8b] A monomeric trimethyl phosphite derivative of Co(0) has also been prepared[14] by sodium amalgam reduction but this molecule exhibited no tendency to dimerize from 0 to 80 °C. Mass spectral analysis of the monomer showed the largest ion produced to be Co[P(OCH$_3$)$_3$]$_4^+$. Because of possible decomposition of the parent molecule under ionizing conditions, the mass spectral data did not eliminate the possible solid state composition Co[P(OCH$_3$)$_3$]$_5$ nor did analytical data conclusively distin-
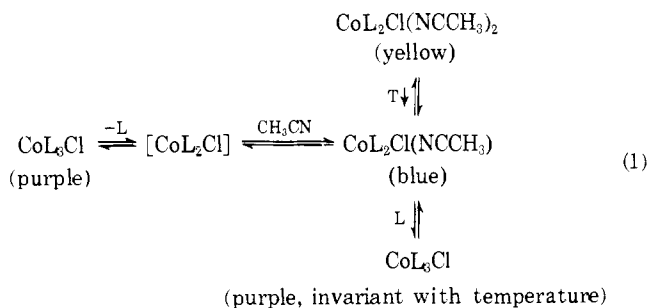
guish between the CoL$_4$ and CoL$_5$ formulations although the data more closely fitted those calculated for CoL$_5$. On the basis of comparative ESR data (toluene solutions or glasses at 77 to 300 K), the formulation Co[P(OR)$_3$]$_5$ might be more likely for the trimethyl phosphite derivative.[14]

A very complex ESR signal was observed for Co[P(O-i-C$_3$H$_7$)$_3$]$_4$ at 77 K. The splitting pattern was qualitatively very similar to that observed for Co[P(CH$_3$)$_3$]$_4$, for which two distinct g factors in a total 16-line pattern were apparent.[15] The ESR spectrum of Co[P(OCH$_3$)$_3$]$_x$, however, was distinctly different with a superhyperfine coupling pattern which was consistent with a square pyramidal array of five phosphite ligands although comparison[14] of observed with theoretical spectra for a distinction between C_{3v}, Co[P(OCH$_3$)$_3$]$_4$, and C_{4v} Co[P(OCH$_3$)$_3$]$_5$, was not structurally conclusive.

Cobalt(I). Reduction of cobalt(II) chloride with zinc powder in the presence of excess triisopropyl phosphite produced the deep purple Co[P(O-i-C$_3$H$_7$)$_3$]$_3$Cl molecule which was very soluble in nonpolar solvents like aliphatic hydrocarbons. Of the two possible polytopal forms, planar and tetrahedral, purely steric considerations would seem to favor the nonplanar form. Magnetic data clearly vindicated this view in that the observed magnetic moment of 2.9 μ_B was similar to that of tetrahedral CoL$_3$X derivatives[4,10,11] although a lesser orbital contribution to the moment was apparent. The electronic spectrum of Co[P(O-i-C$_3$H$_7$)$_3$]$_3$Cl also was found consistent with the assignment of a d^8 metal ion in tetrahedral geometry. In noncoordinating solvents, such as heptane or benzene, the spectrum of the complex was invariant. Two spin allowed d → d transitions were observed in the infrared and visible regions at 7750 cm^{-1} (ϵ 200) and 12 500 cm^{-1} (ϵ 210). The third, lowest energy transition was not observed in these spectra. It would seem quite evident that the CoL$_3$X (L = R$_3$P or (RO)$_3$P) compositional set should be dominated by paramagnetic nonplanar structural forms.

Co[P(O-i-C$_3$H$_7$)$_3$]$_3$Cl underwent no detectable reaction with isopropyl phosphite as evidenced by the absence of any change in the electronic spectrum of a CoL$_3$Cl + L mixture in noncoordinating solvents over a period of weeks. Under these reaction conditions, there was no tendency to form either a five-coordinate CoL$_5^+$Cl$^-$ complex, a reaction characterized for the P(OC$_2$H$_5$)$_3$ case,[4] or an ionic CoL$_4^+$X$^-$ form which was realized, vide infra, under special reaction conditions.

Dissolution of Co[P(O-i-C$_3$H$_7$)$_3$]$_3$Cl in solvents with moderate coordinating properties led to a complex set of color changes. In acetonitrile, this chloride complex dissolved to give a blue solution with a spectral shift, from the characteristic (hydrocarbon solution) CoL$_3$Cl spectrum, to a primary set of d → d transitions at 7300 cm^{-1} (160) and 11 800 cm^{-1} (150). This shift was generated by a phosphite dissociation process in CoL$_3$Cl; addition of triisopropyl phosphite to these blue acetonitrile solutions shifted the bands of the electronic spectrum back towards those characteristic of CoL$_3$Cl. Equilibria in the acetonitrile solutions of CoL$_3$Cl were complex as clearly illustrated in the temperature dependence of the electronic spectra. Within the narrow temperature range of +20 to −15 °C, the solution color shifted from blue to yellow and the magnetic susceptibility of the solution species, monitored by the Evan's NMR technique, fell substantially. Careful NMR assessment of solution phenomena below ca. −20 °C was precluded by solubility and viscosity problems. The yellow color we find characteristic of diamagnetic five-coordinate Co(I) species,[16] and therefore, we ascribe the equilibria shown in eq 1 to this CoL$_3$Cl–acetonitrile system. In this complex set of equilibria, the five-coordinate CoL$_2$Cl(NCCH$_3$)$_2$ complex would be diamagnetic and yellow and would predominate at low temperatures. Solvation, at least of the less sterically encumbered complexes, of tetrahedral cobalt(I) to give a five-coordinate complex is a facile, important solution process.[16]

CoL$_2$Cl(NCCH$_3$)$_2$
(yellow)

T↓↑

CoL$_6$Cl $\xrightarrow{-L}$ [CoL$_2$Cl] $\xrightarrow{CH_3CN}$ CoL$_2$Cl(NCCH$_3$)   (1)
(purple)   (blue)

L↑↓

CoL$_6$Cl

(purple, invariant with temperature)

Oxidation of Co[P(O-i-C$_3$H$_7$)$_3$]$_4$ with I$_2$ and NO led to formation of CoL$_3$I and CoL$_3$NO molecules and with Ag$^+$PF$_6^-$ to CoL$_4^+$PF$_6^-$. The latter tetrahedral complex dissociated in acetonitrile to give primarily the CoL$_3$NCCH$_3^+$ complex although at low temperatures the primary species was yellow and was probably CoL$_3$(NCCH$_3$)$_2^+$. Dissociation of CoL$_4^+$ in acetonitrile was suppressed by the addition of excess phosphite. Co[P(OR)$_3$]$_4$L$^+$ cations (L = CH$_3$CN and NH$_3$) which have been fully characterized in the trimethyl and triethyl phosphite systems[16] were not isolated with isopropyl phosphite ligands. The equilibria set out in eq 2 must be extant in coordinating solvents (S) but reaction 3 must lie far to the left for steric reasons.

$$CoL_4^+ \rightleftharpoons CoL_3S^+ \xrightarrow{T\downarrow} CoL_3S_2^+ \quad (2)$$

$$CoL_4^+ + L \rightleftharpoons CoL_5^+ \quad (3)$$
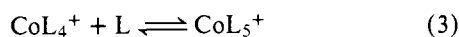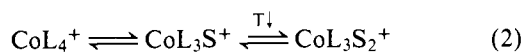
Preparation and Chemistry of H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$. The η^3-allyl derivatives of cobalt(I) with phosphite ligands, η^3-C$_3$H$_5$CoL$_3$, have been of particular interest because of their ability to catalyze the hydrogenation of arenes under mild homogeneous conditions. The preparation of the triisopropyl phosphite derivative of this series from CoL$_3$Cl and C$_3$H$_5$Li and its relative efficiency as a catalyst for arene hydrogenation have been discussed previously.[17] A characteristic of the catalytic reaction which limited the allyl cobalt species' utility as an arene hydrogenation catalyst was the competitive reaction of η^3-C$_3$H$_5$CoL$_3$ with hydrogen to eliminate propene, thereby destroying the catalyst.[17] The trihydride was produced in quantitative yield from reaction 4.

$$\eta^3\text{-}C_3H_5Co[P(O\text{-}i\text{-}C_3H_7)_3]_3 + 2H_2$$
$$\rightarrow C_3H_6 + H_3Co[P(O\text{-}i\text{-}C_3H_7)_3]_3 \quad (4)$$
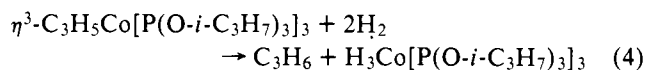
In the solid state this product was stable in an inert atmosphere and was stable indefinitely at temperatures below 0 °C whereas in solution, H$_3$CoL$_3$ very slowly liberated H$_2$ unless kept under an atmosphere of hydrogen. Proton NMR studies in toluene indicated that the complex decomposed rapidly at ~70 °C. Liberation of hydrogen (1 molar equiv) also occurred when triisopropyl phosphite was added to H$_3$CoL$_3$. The only isolated product of the above decompositions was the stable monohydride HCoL$_4$, even in the *absence* of excess phosphite. No evidence for the highly reactive HCoL$_3$ intermediate was observed in these studies. Attempts to prepare the trihydride by the reaction of Co[P(O-i-C$_3$H$_7$)$_3$]$_3$Cl with KH in a hydrogen atmosphere produced only trace amounts of the desired complex (NMR analysis). Once again a rapid and uncharacterized disproportionation of HCoL$_3$ prevailed to yield HCoL$_4$ as the major product.

Only one hydride resonance, a quartet at 12.7 ppm, was observed in the ^{1}H NMR spectrum of H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$ in the temperature range +60 to −60 °C. A facial stereochemistry is consistent with the NMR data, but the alternatives of a highly fluxional meridianal and of a mixture of fluxional facial and meridianal isomers are also consistent with

the data. We have been unable to isolate the corresponding H$_3$CoL$_3$ derivatives with L = trimethyl or triethyl phosphite; a stability of H$_3$CoL$_3$ complexes which appears to be promoted by sterically demanding ligands is also illustrated by the stability characteristics of H$_3$Co[P(C$_6$H$_5$)$_3$]$_3$.[18]

A variety of other donor ligands reacted with H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$ to reversibly or irreversibly replace two hydrogen atoms. Molecular nitrogen reacted slowly with H$_3$CoL$_3$ as shown in eq 5. The dinitrogen adduct was not sufficiently stable

$$N_2 + H_3Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$$
$$\rightleftharpoons H(N_2)Co[P(O\text{-}i\text{-}C_3H_7)_3]_3 + H_2 \quad (5)$$
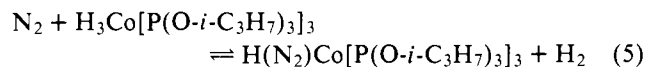
to be isolated in pure form by conventional techniques; accordingly, reaction 5 was followed by solution infrared studies. After an hour of nitrogen purge through a hexane solution of H$_3$CoL$_3$, a band, ν_{N-N}, was observed at 2030 cm^{-1} in the infrared spectrum and this absorption increased in intensity with further purging. A strong sharp band at this frequency was present after 3 h and the characteristic H$_3$CoL$_3$ hydride absorptions were very weak. H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$ was readily re-formed by a brief hydrogen purge.

A variety of olefins also underwent a reversible reaction, eq

$$H_3CoL_3 + \text{olefin} \rightleftharpoons H_2 + HCoL_3(\text{olefin}) \quad (6)$$
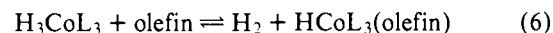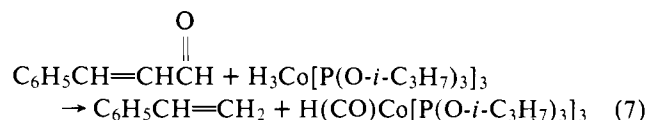
6, with H$_3$CoL$_3$, and this interaction played a central role in the catalytic properties of this hydride complex. Carbon monoxide reacted irreversibly with H$_3$CoL$_3$ to form HCo[P(O-i-C$_3$H$_7$)$_3$]$_3$CO. The relatively high stability of the carbon monoxide derivative placed constraints on the utility of H$_3$CoL$_3$ as a homogeneous catalyst for certain unsaturated carbonyl derivatives.

Catalytic Behavior of H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$: Selective Hydrogenation of α,β-Unsaturated Carbonyl Derivatives. The trihydride, H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$, was an active catalyst for the hydrogenation of both terminal and internal olefins at 20 °C and 1 atm hydrogen pressure. Olefin isomerization was competitive with the hydrogenation process as shown from a study of hexenes (Table I). Interestingly, this hydride was also a homogeneous catalyst for hydrogenation of arenes—but only for activated arenes such as allylbenzene; it was inactive for benzene and alkylbenzenes (e.g., propylbenzene) hydrogenation. In the hydrogenation of allylbenzene, propylbenzene and propylcyclohexane were the reduced products; the propylbenzene was not an intermediate to propylcyclohexane.

Few soluble complexes have been reported to selectively catalyze the hydrogenation of α,β-unsaturated ketones.[19-24] H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$ selectively catalyzed the conversion of unsaturated ketones and amides to the saturated ketones and amides (Table I). Hydrogenation rates were low at 20 °C but were substantially raised at 70 °C without loss of selectivity. The trihydride reacted with α,β-unsaturated nitriles to give the saturated nitriles.

Unsaturated aldehydes were not reduced to significant extents by H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$ and hydrogen at 20 °C. The stoichiometric reaction of the hydride with cinnamaldehyde was found to involve a very slow decarbonylation of the organic substrate as shown in eq 7. Styrene was identified by GC-MS

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{C_6H_5CH{=}CHCH}} + H_3Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$$
$$\rightarrow C_6H_5CH{=}CH_2 + H(CO)Co[P(O\text{-}i\text{-}C_3H_7)_3]_3 \quad (7)$$

analysis, and the cobalt derivative was identical with the monohydride-carbonyl derivative prepared by a different method (see Experimental Section). The decarbonylation of saturated aldehydes by H$_3$Co[P(C$_6$H$_5$)$_3$]$_3$ has been reported previously.[25] The above reaction (7) was presumably responsible for the lack of significant olefin hydrogenation in unsaturated

Table I. Catalytic Hydrogenations with H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$ at 20 °C and 1 atm of H$_2$ (~100:1 Substrate to Catalyst Ratio)

Unsaturated molecule	Reaction Time (days)	Products	% conversion
1-Hexene	1	Hexane	13
		2-Hexene (cis–trans)	16, 60
		3-Hexene (trans)	10
2-Hexene	3	Hexane	28
		1-Hexene	1
		3-Hexene (trans)	11
3-Hexene (trans)	1.7	Hexane	5
		1-Hexene	1
		2-Hexene (cis–trans)	9, 39
Allylbenzene	2	Propylbenzene	18
		Propylcyclohexane	7
		2-Propenylbenzene (cis–trans)	4, 70
2-Cyclohexenone	1	Cyclohexanone, cyclohexanol	6, 0 (70, <1; 70 °C)
Benzalacetone[a]	1	Benzylacetone	50 (70 °C)
Benzalacetophenone[a]	1	Benzylacetophenone	45 (70 °C)
Acrylamide[a]	3	Propionamide	~30%
Cinnamaldehyde[a]	3	3-Phenylpropionaldehyde	1
Cinnamonitrile[a]	3	3-Phenylpropionitrile	1
Methyl vinyl ketone	1	Polymer	>95
		Methyl ethyl ketone	~2

[a] Diethyl ether solvent.

aldehydes since the carbonyl derivative showed only slight activity as a hydrogenation catalyst under the mild conditions used here.

Experimental Section

All procedures were carried out either in an argon atmosphere in a Vacuum Atmosphere drybox equipped with a Model HE 493 Dri Train, or in a conventional vacuum system.

Reagents and Solvents. Triisopropyl phosphite, purchased from Strem Chemicals, was degassed and used without further purification. Anhydrous cobaltous chloride and potassium hydride were purchased from Alfa Chemicals. Reagent grade tetrahydrofuran was purified by a previously reported method.[17] Reagent grade acetonitrile, heptane, and benzene were refluxed over calcium hydride for 48 h and distilled and degassed before use.

Physical Measurements. Proton NMR were recorded at ambient tempertures, unless otherwise noted, on a Varian Associates A60-A or Bruker HFX 90 spectrometer. Chemical shifts are referenced to Me$_4$Si and the solvent was C$_6$D$_6$. Infrared spectra were recorded in hydrocarbon solutions on a Perkin-Elmer 337 grating infrared spectrophotometer. A Cary 14 recording spectrophotometer was used to record the electronic spectra. Air sensitive solutions were placed in a cell equipped with a Kontes high-vacuum stopcock. The magnetic moments were measured in benzene solutions using the NMR method outlined by Evans.[26]

Hydrogenation products were analyzed on a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector or on a Finnegan 3300 GC-MS interfaced with a System Industries System 150. Carbonyl derivatives were separated on an OV-101 (3%, 12 ft) column. Columns of squalane (3%, 12 ft) and ethyl N,N-dimethyloxamate (20%, 7 ft) joined in series were used to separate hexane and the hexene isomers.

Co[P(O-i-C$_3$H$_7$)$_3$]$_3$Cl. Anhydrous CoCl$_2$ (2.5 g, 0.019 mol) was slurried in 200 ml of tetrahydrofuran with 24 g (0.115 mol) of triisopropyl phosphite. The deep blue solution was stirred for ~1 h to ensure that all solid CoCl$_2$ had dissolved. Excess zinc dust (1.0 g, 0.013 mol) was added, and the reaction was stirred for 24 h. The solvent was removed in vacuo and the residue was extracted with 30 ml of pentane. The product was recrystallized from pentane at room temperature to give deeply colored purple crystals. μ_{eff} = 2.9 μ_B (benzene). Anal. Calcd: C, 45.10; H, 8.77; Co, 8.20. Found: C, 45.22; H, 8.92; Co, 7.76.

Co[P(O-i-C$_3$H$_7$)$_3$]$_4$. Anhydrous cobalt(II) chloride (2.5 g, 0.0192 mol) and 25 ml of triisopropyl phosphite (24 g, 0.115 mol) were slurried in tetrahydrofuran. After the salt had dissolved, 88 g of sodium amalgam (1% Na, 0.038 mol of Na) was added. The reduction

reaction was stirred vigorously for 48 h. After filering the mercury, the filtrate was evaporated to dryness and extracted with 75 ml of pentane. The pentane was removed in vacuo, and the remaining solid was dissolved in 20 ml of tetrahydrofuran and cooled to −40 °C to form orange-red crystals. Anal. Calcd: C, 48.48; H, 9.43; Co, 6.42. Found: C, 48.49; H, 9.47; Co, 6.34. μ_{eff} in benzene = 2.0 μ_B.

(NO)Co[P(O-i-C$_3$H$_7$)$_3$]$_3$. Co[P(O-i-C$_3$H$_7$)$_3$]$_4$ (1.0 g, 1.12 mmol) was dissolved in tetrahydrofuran and the solution was frozen and degassed on a standard vacuum line. Nitric oxide (1 mmol) was added and the solution was warmed to room temperature and stirred for 3 h. The color changed from orange to dark brown. Solvent was evaporated and the remaining brown residue was recrystallized from diethyl ether at −40 °C to form dark brown crystals. Anal. Calcd: C, 45.44; H, 8.84; Co, 8.27. Found: C, 44.99; H, 9.13; Co, 7.97. IR: ν_{NO} 1695 cm^{-1} (strong). ^{1}H NMR: δ −1.41 (doublet, 6), δ −4.91 (broad, 1).

Co[P(O-i-C$_3$H$_7$)$_3$]$_4$PF$_6$. Co[P(O-i-C$_3$H$_7$)$_3$]$_4$ (1.05 g, 1.2 mmol) was dissolved in ~60 ml of diethyl ether. To this was added silver hexafluorophosphate (0.20 g, 1.2 mmol) dissolved in 1 ml of acetonitrile. After stirring for 2 h, the solvent was evaporated and the remaining solid was extracted with acetonitrile to give a deep green solution. Silver metal and unreacted CoL$_4$ were insoluble in CH$_3$CN and thus were separated from the product. The acetonitrile was removed leaving a green-blue solid which was recrystallized from a tetrahydrofuran-ether solution at −40 °C. Anal. Calcd: C, 41.70; H, 8.11; Co, 5.69. Found: C, 40.98; H 8.03; Co, 5.48.

NaCo[P(O-i-C$_3$H$_7$)$_3$]$_5$. Triisopropyl phosphite (14.87 g, 0.07 mol) was added to 1.56 g (0.012 mol) of anhydrous CoCl$_2$ slurried in 100 ml of tetrahydrofuran. After stirring for 1 h, 110 g of freshly prepared sodium amalgam 1%, 0.048 mol of Na) was added. The reaction was stirred vigorously for 36 h. Th excess amalgam was filtered and the filtrate was evacuated to dryness. The remaining salt was extracted with pentane (100 ml) and was recrystallized several times from the same solvent at −40 °C to give white crystals. Anal. Calcd: C, 48.13; H, 9.36; Co, 5.25; Na, 2.05. Found: C, 47.52; H, 9.40; Co, 5.12; Na, 2.01. ^{1}H NMR: δ −1.09 (doublet, 6) (J_{H-H} = 6.0 Hz), −1.45 (doublet, 22) (J_{H-H} = 6.0 Hz), −4.50 (septet, 1), −5.04 (broad, ~3.5).

Na(C$_3$H$_5$)Co[P(O-i-C$_3$H$_7$)$_3$]$_3$I. Four grams of Na[Co[P(O-i-C$_3$H$_7$)$_3$]$_5$ (3.6 mmol) was dissolved in ~75 ml of tetrahydrofuran. To this was added 0.4 ml of allyl iodide (0.0044 mol). The solution was slurried at room temperature for 4 days, then evaporated to dryness and extracted with pentane. The extract was dried, dissolved in 10 ml of diethyl ether, and cooled to −40 °C. Bright purple crystals formed. Anal. Calcd: C, 41.19; H, 7.78; Co, 6.75. Found: C, 41.00; H, 8.07; Co, 6.67. The presence of sodium was confirmed qualitatively by neutron activation analysis. μ_{eff} (benzene solution) = 2.8 μ_B.

H$_3$Co[P(O-i-C$_3$H$_7$)$_3$]$_3$. Two hundred milligrams of η^3-C$_3$H$_5$Co[P(OC$_3$H$_7$)$_3$]$_3$ (0.28 mmol) was dissolved in 3 ml of diethyl ether in

a 50-ml vessel equipped with a Kontes high vacuum stopcock. The solution was frozen at -196 °C and evacuated. One atmosphere of hydrogen was added to the cooled tube, the stopcock was closed, and the tube allowed to warm to room temperature. The solution was stirred for 12 h. Excess hydrogen and the solvent were removed in vacuo leaving the pale yellow-brown complex. Efforts to recrystallize the product resulted in some decomposition of the complex to $HCo[P(O-i-C_3H_7)_3]_4$. Anal. Calcd: C, 47.23; H, 9.62; Co, 8.60. Found: C, 47.11; H, 9.64; Co, 8.47. NMR: δ -4.98 ppm (doublet of septets, 9) ($J_{H-H} = 5.9$ Hz) ($J_{P-H} = 3.0$ Hz), -1.44 ppm (doublet, 54) ($J_{H-H} = 6$ Hz), $+12.97$ ppm (quartet) ($J_{H-P} = 29$ Hz). IR: ν_{Co-H} 1950 cm^{-1} (weak broad), 1830 cm^{-1} (sharp); $D_3Co[P(O-i-C_3H_7)_3]_3$, ν_{Co-D} 1330 cm^{-1}, others obscured.

$H(CO)Co[P(O-i-C_3H_7)_3]_3$. Two hundred milligrams of $H_3Co[P(O-i-C_3H_7)_3]_3$ (0.29 mmol) was dissolved in 5 ml of diethyl ether in a 50-ml vessel equipped with a Kontes high vacumm stopcock. The solution was frozen at -196 °C and evacuated, and 1 equiv (0.29 mmol) of carbon monoxide was added. The stopcock was closed and the solution was allowed to warm to room temperature with rapid stirring. After 3 h, the evolved hydrogen and the solvent were removed in vacuo leaving a pale yellow product. Anal. Calcd: C, 47.19; H, 8.99; Co, 8.28. Found: C, 46.92; H, 9.02; Co, 8.13. NMR: δ -1.40 (doublet, 54) ($J_{H-H} = 6.3$ Hz), -4.91 (doublet of septets, 9) ($J_{H-H} = 5.9$ Hz), ($J_{P-H} = 2.7$ Hz), $+14$ ppm (quartet, 1) ($J_{P-H} = 45.5$ Hz). IR: ν_{CO} 1930 cm^{-1}.

$H(N_2)Co[P(O-i-C_3H_7)_3]_3$. Prepurified nitrogen (99.998%) was passed through columns of $CaCl_2$ and "BTS Catalyst" (BASF Corp.) and then bubbled through a hexane solution of $H_3Co[P(O-i-C_3H_7)_3]_3$ (25 ml, 2.8×10^{-2} M) for 3 h. The solution changed in color from yellow brown to nearly colorless. Attempts to isolate the complex were unsuccessful. IR: (hexane solution) ν_{N-N} 2130 cm^{-1} (sharp); ν_{Co-H} 1950 cm^{-1}. Bubbling hydrogen through the solution re-formed $H_3Co[P(O-i-C_3H_7)_3]_3$ within 30 min.

Catalytic Reactions—Procedure. Experimental conditions for the catalytic hydrogenation reactions are summarized in Table I. The reaction scale was typically 10^{-2} mol of the unsaturated molecule with 10^{-4} mol of cobalt catalyst. Reactions were run at 20 or 70 °C and an *average* hydrogen pressure of 1 atm. A reaction vessel ($\sim$300 ml volume) fitted with a Teflon stopcock was charged with a catalyst and the unsaturated organic compound (if this compound was not easily vacuum transferred) and with a Teflon stirring bar; the operation was effected in the Dri Lab in a nitrogen or argon atmosphere. The stopcock was closed. Then the reaction vessel was removed and connected to a vacuum train. The reaction vessel was thoroughly evacuated (at -78 °C if the organic molecule had an appreciable vapor pressure at

20 °C). Volatile organic unsaturated compounds were vacuum transferred to the vessel. Then hydrogen was admitted to the reaction vessel (final pressure was $\sim$1.2–1.3 atm). The stopcock was closed and the reaction mixture was stirred throughout the reaction period. About 1 ml of diethyl ether was added (vacuum transfer) to all reaction systems that used organic compounds that were solids.

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Metal Clusters in Catalysis. 6.[1] Synthesis and Chemistry of Ni4[CNC(CH3)3]7 and Related Clusters

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Abstract: Reaction of alkyl isocyanides with bis(cyclooctadiene)nickel in $\sim$1.75 to 1 molar ratio gave in high yield a nickel cluster, $Ni_4(CNR)_x$, in which the four nickel atoms describe the vertices of a highly compressed tetrahedron. The $Ni_4[CNC-(CH_3)_3]_7$ molecule was stereochemically nonrigid and underwent a two-step intramolecular rearrangement at high rates in the 10–100 °C range that may have been accompanied at 80–120 °C by a fast dissociative process ($Ni_4L_7 \rightleftharpoons Ni_4L_6 + L$). Ligand dissociation from solid Ni_4L_7 was demonstrated at 60 °C. These nickel clusters are catalysts for a variety of catalytic reactions which include the trimerization of acetylenes to benzenes, butadiene to 1,5-cyclooctadiene, polymerization of allene, and the selective hydrogenation of acetylenes to cis olefins. Possible intermediates in the catalytic acetylene reactions that have been identified include $Ni_4L_{7-x}(acetylene)_x$.

We pursue the thesis[2] that metal cluster molecules or ions can in some instances serve as plausible models of surface modes of chemisorption and heterogeneous catalysis. In known

clusters[3] and in devised new clusters, we have sought the elements of catalytic processes that require the intervention of two or more metal atoms in a catalytic transformation. In this ar-