stable for indefinite periods in the solid state and in solutions of CH_2Cl_2, hexane, and THF.

The second band collected gave 1.5 mg of red-brown (η^5-C_5H_5)$Co[(CH_3)_2C_2B_3H_3]Fe(CO)_3$ (IV), R_f 0.76.

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Registry No. I, 58846-86-9; II($(CH_3)_4N$), 58815-25-1; III (isomer A), 58815-26-2; III (isomer B), 54387-54-1; IV, 58814-73-6; V, 58814-74-7; $(CH_3)_2C_2B_4H_6$, 20741-68-8; (η^5-C_5H_5)$Co(CO)_2$, 12078-25-0.

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Synthesis and Properties of Cobalt(I) Compounds. 3. Hydridoacetonitriletris(triaryl phosphite)cobalt Complexes

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The preparation and properties of the triaryl phosphite complexes $CoH[(ArO)_3P]_3(CH_3CN)$ are described. Surprisingly rapid selective hydrogenation of terminal olefins was observed with $CoH[(PhO)_3P]_3(CH_3CN)$. Qualitative data on ligand exchange are given.

Introduction

In contrast to the tertiary phosphine stabilized cobalt hydrides such as $CoH[Ph_3P]_3(N_2)$ the triaryl phosphite stabilized cobalt hydrides have been comparatively inert.[1] The triaryl phosphite Ni(0) complexes such as $[(PhO)_3P]_4Ni$ are also comparatively inert,[1a] but it was possible to increase greatly the reactivity of these complexes by increasing the bulk of the ligands.[2] The increased bulk led to greater reactivity because ligand dissociation made coordination sites available. In principle this same approach should lead to triaryl phosphite–cobalt hydride complexes of greatly enhanced activity. Unfortunately, the borohydride reduction which produced $CoH[P(OPh)_3]_4$ from cobalt(II) and the phosphite was not successful with more bulky phosphites.[1a]

A series of new triaryl phosphite cobalt hydrides, $CoH[(ArO)_3P]_3(CH_3CN)$, has now been prepared. These complexes are greatly more reactive than $CoH[(PhO)_3P]_4$ probably because dissociation of the nitrile ligand opens a coordination site. They are formally analogous to the complex $CoH(Ph_3P)_3(CH_3CN)$ prepared from $CoH(Ph_3P)_3(N_2)$ by Misono and co-workers[3] and characterized by elemental analyses and ir spectra.

Synthesis

The new hydridoorganonitrile complexes were prepared either by ligand exchange or by reaction of $Co(C_8H_{12})(C_8H_{13})$[4] with mixtures of acetonitrile and phosphorus ligands in a hydrogen atmosphere. A brief report of the use of this complex in cobalt hydride syntheses was made by Rossi and Sacco.[5] After some initial experiments in which a nonhydridic species was obtained when a nitrogen atmosphere was used[6] subsequent reactions were carried out in hydrogen atmospheres. This was true even when the goal was a complex of the type L_4CoH. Since the complex $Co(C_8H_{12})(C_8H_{13})$ reacts readily with hydrogen at room temperature to give cobalt metal and cyclooctane, care must be taken to add the hydrogen after the phosphorus and nitrile ligands have been added to the solutions. In some cases details of the procedures such as solvent composition appeared to be important. The hydridoacetonitriletris(triaryl phosphite)cobalt complexes were isolated and characterized. The analogous tertiary phosphine complexes were obtained by ligand exchange and were characterized only by their NMR spectra.

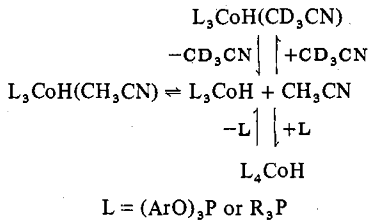
The ^1H and ^{31}P NMR measurements are summarized in Table I.

Table I

	H		P	CH$_3$CN	
	δ^a	J^e	δ^b	δ^c	J^e
$[(o\text{-}CH_3C_6H_4O)_3P]_4CoH$	14.0	19 qn	136		
$[(C_6H_5O)_3P]_4CoH^d$	13.6^d	17 qn^d	140		
$[(C_6H_5O)_3P]_3CoHCH_3CN$	22.1	53 qr	144	0.1	4 qr
$[(o\text{-}CH_3C_6H_4O)_3P]_3CoHCH_3CN$	22.4	55 qr	139	0.4	4 qr
$[(o\text{-}(CH_3)_2CHC_6H_4O)_3P]_3CoH(CH_3CN)$	22.4	57 qr	136	0.4	4 qr
$[(o\text{-}C_6H_5C_6H_4O)_3P]_3CoH(CH_3CN)$	23.5	63 qr	136		
$[(C_2H_5)_3P]_4CoH$	19.9	34 qn			
$[(C_2H_5)_3P]_3CoH(N_2)^f$	21.2	50 qr			
$[(C_2H_5)_3P]_3CoH(CH_3CN)^f$	25.6	50 qr			
$[(C_2H_5)_2PC_6H_5]_4CoH$	19.9	35 qn			
$[(C_2H_5)_2PC_6H_5]_3CoH(N_2)^f$	21.0	50 qr			
$[(C_2H_5)_2PC_6H_5]_3CoH(CH_3CN)^f$	25.3	53 qr			
$[(C_6H_5)_3P]_3CoH(N_2)^d$	19^d	50 qr^d			
$[(C_6H_5)_3P]_3CoH(CH_3CN)^g$	24.4	52 qr			

[a] Ppm upfield from internal tetramethylsilane in C_6D_6. [b] Ppm downfield from external 85% H_3PO_4 (benzene solvent). [c] Ppm downfield from internal tetramethylsilane in C_6D_6. [d] Taken from J. P. Jesson, "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 4. [e] qn for quintet, qr for quartet; values in Hz. [f] Prepared in situ from the L_4CoH complex and N_2 or CH_3CN. [g] Prepared in in situ from $(Ph_3P)_3CoHN_2$.

Scheme I



$$\begin{array}{c} L_3CoH(CD_3CN) \\ {\scriptstyle -CD_3CN}\downarrow\uparrow{\scriptstyle +CD_3CN} \\ L_3CoH(CH_3CN) \rightleftharpoons L_3CoH + CH_3CN \\ {\scriptstyle -L}\uparrow\downarrow{\scriptstyle +L} \\ L_4CoH \\ L = (ArO)_3P \text{ or } R_3P \end{array}$$

Ligand Exchange

Ligand exchange in these complexes can be easily detected by ^{1}H NMR spectroscopy. For example, the replacement of a coordinated nitrile by a phosphorus ligand in converting a $CoHL_3(RCN)$ complex to a $CoHL_4$ complex causes the high-field signal from the hydride to change position (downfield) and also to change from a quartet to a quintet. Replacement of coordinated acetonitrile was also followed in some cases by observing the disappearance of the quartet of coordinated acetonitrile and the appearance of the single peak from free acetonitrile further downfield. The observations made in these ways are consistent with the view that the enhanced reactivity of $CoH[P(OPh)_3]_3CH_3CN$ compared to that of $CoH[P(OPh)_3]_4$ is due to the comparatively facile release of the nitrile ligand producing a coordinatively unsaturated species as illustrated in Scheme I.

As in the case of the analogous triaryl phosphite complexes of zerovalent nickel,[2] the bulk of the ligands influences the properties of the complexes. For example, in a solution of ca. 0.12 M $CoH[(PhO)_3P]_3(CH_3CN)$ and ca. 0.40 M triphenyl phosphite in deuterated benzene the initial hydride was essentially completely converted to the corresponding $CoHL_4$ species in 3 h at room temperature. With a corresponding solution of $CoH[(o\text{-}CH_3C_6H_4O)_3P]_3(CH_3CN)$ and tri-*o*-tolyl phosphite little or no conversion to the $CoHL_4$ species occurred in 17 h at room temperature. These observations are consistent with the later observation that the $CoHL_4$ complex with tri-*o*-tolyl phosphite ligands was essentially totally converted to the $CoHL_3(CH_3CN)$ complex after a few minutes at 80 °C in 1:1 by volume benzene–acetonitrile. It was also observed that tris(*o*-isopropylphenyl) phosphite did not displace acetonitrile from the corresponding $CoHL_3(CH_3CN)$ complex at room temperature.

Under some circumstances the competition between nitrile and phosphorus ligands for the coordinatively unsaturated intermediates (see Scheme I) could also be observed. For example, $CoH[(PhO)_3P]_3(CH_3CN)$ (ca. 0.10 M) and triphenyl phosphite (ca. 0.2 M) in benzene reacted to convert essentially all of the starting material to the $CoHL_4$ complex in ca. 2 h at room temperature. In a similar solution which also contained acetonitrile (ca. 1.6 M) no conversion of $CoHL_3(CH_3CN)$ to $CoHL_4$ was apparent under the same conditions.

The balance between the nitrile and phosphorus ligands was also readily observed by ^{1}H NMR with diethylphenylphosphine and triethylphosphine complexes. In two experiments, benzene–10% acetonitrile solutions containing ca. 10 wt % of the hydrides $CoH[(C_2H_5)_3P]_4$ and $CoH[(C_2H_5)_2PC_6H_5]_4$ were prepared. By the time the ^{1}H NMR spectra were recorded, the triethylphosphine complex had ca. two-thirds of the total hydride signal as a quartet (J = 50 Hz), 25.6 ppm upfield from TMS. The addition of 10 vol % triethylphosphine to the solution caused the 19.9-ppm quintet from the $CoHL_4$ complex to increase to more than half the total hydride signal. In the case of the solution initially containing $CoH[(C_2H_5)_2P(C_6H_5)]_4$ and acetonitrile the ^{1}H NMR spectrum showed no more than a trace of the initial $CoHL_4$ quintet. Almost all of the hydride signal was a quartet (J = 53 Hz), 25.3 ppm. Addition of 10 vol % diethylphenylphosphine to the solution caused the 19.9-ppm quintet of the $CoHL_4$ compound to increase to ca. one-third of the total hydride signal. The solutions for these experiments were prepared in an argon atmosphere to avoid the complication of nitrogen complex formation. Exposure of benzene solutions of either of these tertiary phosphine complexes of $CoHL_4$ to molecular nitrogen caused almost immediate formation of the corresponding $CoHL_3(N_2)$ complexes.

The appearance of the signal from coordinated acetonitrile as a quartet just downfield from tetramethylsilane in the ^{1}H NMR spectra of the $CoH[(ArO)_3P]_3(CH_3CN)$ complexes provided a convenient way to judge the rate of exchange between free and coordinated acetonitrile. Addition of a 20-fold excess of CD_3CN to benzene solutions of either $CoH[(PhO)_3P]_3(CH_3CN)$ or the analogous tri-*o*-tolyl phosphite complex caused the quartet to disappear and the single line of free CH_3CN to appear. At 35–40 °C probe temperature both the diminished quartet and the free CH_3CN could be observed in the first couple of minutes after addition of the CD_3CN. In about 5 min the exchange appeared to be complete. Addition of benzonitrile or triphenyl phosphite to solutions of $CoH[(PhO)_3P]_3CH_3CN$ also caused replacement of the quartet of bound acetonitrile by the downfield singlet of free acetonitrile. (The coupling of the methyl protons of coordinated acetonitrile to the phosphorus of coordinated phosphorus ligands has been observed in some platinum complexes.[7])

The exchange of bound and free acetonitrile is thus a facile process but is not rapid on the NMR time scale. This is in contrast to the behavior of a similar nitrile–triaryl phosphite complex of zerovalent nickel. In organonitrile solvents the coordinately unsaturated nickel complex tris(*o*-tolyl phosphite)nickel forms nitrile complexes, but in these complexes exchange between free and bound nitrile is rapid on the NMR time scale at room temperature.[8]

Catalytic Hydrogenation

The new triaryl phosphite–cobalt hydride complexes. $CoH[(ArO)_3P]_3(CH_3CN)$, are surprisingly active and selective hydrogenation catalysts. For example, at 30-psig hydrogen pressure, a benzene solution of $CoH[(PhO)_3P]_3(CH_3CN)$ gave rapid production of butane from 1-butene at 25 °C with little or no isomeric 2-butenes. Under similar conditions, the more

Table II. Elemental Analyses

	% C	% H	% N	% P	% Co
Found for $[(C_6H_5O)_3P]_3CoH(CH_3CN)$	65.15	4.78	1.33	9.30	5.68
Calcd for $C_{56}H_{49}O_9NP_3Co$	65.18	4.79	1.36	9.01	5.71
Found for $[(o\text{-}CH_3C_6H_4O)_3P]_3CoH(CH_3CN)$	66.96	5.84	1.31	8.22	5.12
Calcd for $C_{65}H_{67}O_9NP_3Co$	67.41	5.83	1.21	8.02	5.09
Found for $[(o\text{-}(CH_3)_2CHC_6H_4O)_3P]_3CoH(CH_3CN)C_6H_6$	71.75	7.25	1.01	6.56	3.92
Calcd for $C_{83}H_{103}O_9NP_3CoC_6H_6$	71.80	7.38	0.94	6.24	3.96
Found for $[(o\text{-}C_6H_5C_6H_4O)_3P]_3CoH(CH_3CN)$	77.02	5.32	0.95	5.37	3.04
Calcd for $C_{110}H_{85}O_9NP_3Co$	76.96	4.99	0.82	5.41	3.43
Found for $[(o\text{-}CH_3C_6H_4O)_3P]_4CoH(C_6H_6)$	69.22	5.88		8.55	4.02
Calcd for $C_{84}H_{85}O_{12}P_4CoC_6H_6$	69.85	5.93		8.00	3.81
Found for $[(C_2H_5)_3P]_4CoH$	54.28	11.66		23.37	11.06
Calcd for $C_{24}H_{61}P_4Co$	54.12	11.55		23.27	11.07
Found for $[(C_2H_5)_2PC_6H_5]_4CoH$	65.96	8.40		16.92	8.35
Calcd for $C_{40}H_{61}P_4Co$	66.29	8.49		17.10	8.13

coordinately saturated complex, $CoH[(PhO)_3P]_4$, was essentially inert and even at 90 °C gave very slow hydrogenation.

The triphenylphosphine complexes such as $CoH[Ph_3P]_3(N_2)$ are well known as active hydrogenation and isomerization catalysts for olefins under mild conditions.[9] With $CoH(Ph_3P)_3(N_2)$ as the catalyst precursor both reactions were rapid under the conditions above and both butane and isomeric 2-butenes were produced rapidly at room temperature. When $CoH[(C_2H_5)_3P]_4$ or $CoH[(C_2H_5)_2PC_6H_5]_4$ was the catalyst precursor, a similar result was obtained. Both isomerization to the 2-butenes and hydrogenation to butane occurred rapidly at room temperature.

Reaction with HCl and HBr

Tetrahydrofuran solutions of $CoH[(PhO)_3P]_3(CH_3CN)$ reacted with hydrogen chloride or hydrogen bromide in less than 5 min at room temperature with approximately stoichiometric production of hydrogen. The cobalt(I) halide complexes were then isolated from the solutions.[10] This is similar to the behavior of $CoH(Ph_3P)_3(N_2)$ which is reported[11] to react with hydrogen chloride to give $[Ph_3P]_3CoCl$ with the liberation of hydrogen and nitrogen.

The compound $CoH[P(OPh)_3]_4$ was essentially inert to HCl under the conditions used to convert $CoH[(PhO)_3P]_3(CH_3CN)$ to $[(PhO)_3P]_3CoCl$. This suggests that a key step in this reaction is interaction of HCl with the coordinatively unsaturated metal center formed by dissociation of acetonitrile rather than by attack of HCl on the hydrogen bound to cobalt.

Experimental Section

The general procedure used for the hydride syntheses was the same in all cases. Solutions of $Co(C_8H_{12})(C_8H_{13})$ and the ligands were prepared in glass pressure bottles using gloveboxes filled with oxygen-free nitrogen or argon. The bottles had closures with stainless steel fittings which allowed them to be attached to a stainless steel manifold so that the bottles could be evacuated or filled with hydrogen. Immediately after the solutions were prepared in the bottles, the pressure was reduced until the solutions boiled (room temperature). Hydrogen was then admitted to a pressure of ca. 50 psig. At the end of the reaction period, the materials were isolated as described below. In some cases the syntheses seemed to be quite sensitive to the details of solvent composition and procedure. The elemental analyses are given in Table II.

The high-field ^1H NMR spectra were obtained with a Varian 220-MHz instrument. The ^{31}P NMR spectra were obtained with a 36.43-MHz Bruker instrument in Fourier transform mode. Varian A60 and HA100 spectrometers were used for the other ^1H NMR measurements. The NMR data are summarized in Table I. Infrared spectra were recorded with a Perkin-Elmer 467 spectrometer.

The melting or decomposition behavior was observed in evacuated capillaries using an uncalibrated Mel Temp apparatus.

Nitrogen- or argon-filled gloveboxes were used throughout the work to avoid contact of any of the materials or solutions with air.

Triphenyl phosphite and tri-*o*-tolyl phosphite were commercial samples used as received. Tris(*o*-isopropylphenyl) phosphite and tris(*o*-phenylphenyl) phosphite were prepared by reaction of the corresponding phenols with phosphorus trichloride in ether–triethylamine.[12] Nominally anhydrous acetonitrile was stored over molecular sieve. Tetrahydrofuran was distilled from lithium aluminum hydride and stored over sodium in a nitrogen atmosphere.

Hydridoacetonitriletris(triphenyl phosphite)cobalt. A solution of 1.34 g of triphenyl phosphite in 8 ml of acetonitrile was combined with a solution of 0.40 g of $Co(C_8H_{12})(C_8H_{13})$ in 2 ml of tetrahydrofuran in a pressure bottle. The bottle was evacuated and filled with 50 psig of hydrogen. Within 4 min at room temperature most of the initial red color had disappeared and yellow solid had formed. The bottle was left under 50-psig hydrogen pressure at 0 °C for 15 min before venting the hydrogen. The solid was collected, washed with acetonitrile, and dried; yield 1.1 g of yellow powder; mp ca. 145 °C dec. The elemental analyses and NMR data are given in Tables I and II. This material could be recrystallized satisfactorily from benzene solution by adding acetonitrile.

In a later experiment, two ca. 370-ml glass pressure bottles were charged with solutions of 20.0 ml of triphenyl phosphite in 140 ml of nominally anhydrous acetonitrile. Solutions of 7.3 g of $Co(C_8H_{12})(C_8H_{13})$ in 35 ml of purified tetrahydrofuran were then added. The pressure was immediately reduced until the mixtures boiled (room temperature), and then hydrogen was added to 50 psig. The mixtures were shaken vigorously for 10 min at room temperature and then cooled to ca. 0 °C for about 0.5 h. The hydrogen was vented and the solid was collected, washed with acetonitrile, and dried. The filtrate was concentrated under reduced pressure, diluted with acetonitrile, and cooled to −35 °C. The resulting solid was collected, washed with acetonitrile, and dried. Recrystallization of the first solid (obtained at 0 °C) from tetrahydrofuran solution by adding acetonitrile gave 27 g of $CoH[(PhO)_3P]_3(CH_3CN)$. Recrystallization of the second solid (obtained at −35 °C from the first filtrate) from a hot acetone solution gave 12.0 g of yellow solid, $[(PhO)_3P]_3CoC_6H_4OP(OPh)_2$.[6] The ^{31}P NMR spectra and ir spectra of the two materials are quite different and allow clear distinction between them.

Hydridoacetonitriletris(tri-*o*-tolyl phosphite)cobalt. A solution of 7.5 g of tri-*o*-tolylphosphite in 40 ml of acetonitrile was prepared and 2.0 g of $Co(C_8H_{12})(C_8H_{13})$ was dissolved in this solution. After stirring under 50 psig of hydrogen for 4.5 h, at room temperature, the pressure was released and the solution was cooled to −35 °C. The yellow solid was collected, washed with acetonitrile, and dried (7.8 g). A 1.0-g sample was recrystallized from benzene–acetonitrile to give 0.87 g of yellow solid, mp 140–145 °C dec. The elemental analyses and NMR data are given in Tables I and II. In a later experiment, a solution of 22.5 g of tri-*o*-tolyl phosphite in 120 ml of acetonitrile and 30 ml of tetrahydrofuran was prepared in an ca. 370-ml glass pressure bottle and 6.0 g of $Co(C_8H_{12})(C_8H_{13})$ was added. The pressure was reduced until the solution boiled at room temperature and then hydrogen was admitted to 50 psig. After 4 h of stirring at room temperature, the pressure was released and the mixture was filtered. The filtrate was concentrated under reduced pressure to a volume of ca. 50 ml and then diluted with 30 ml of benzene and 100 ml of acetonitrile. The mixture was left overnight at −35 °C. The solid was collected, washed with acetonitrile, and dried, yielding 21 g of fine yellow powder. The compound could be recrystallized by dissolving it in benzene and adding acetonitrile slowly.

Hydridoacetonitriletris(tris(*o*-isopropylphenyl) phosphite)cobalt. A solution of 1.5 g of $Co(C_8H_{12})(C_8H_{13})$ and 7.1 g of tris(*o*-isopropylphenyl) phosphite in 40 ml of benzene was diluted with 5 ml of acetonitrile and stirred overnight at room temperature under 50 psig of hydrogen. A 10-ml portion of the reaction mixture was diluted with 10 ml of acetonitrile and the resulting solution was concentrated to ca. 2 ml under vacuum. Two liquid phases were present at this point. Alternate cooling and warming with intermittent scratching induced the formation of a yellow solid. A second 10-ml portion of the reaction mixture was treated in the same way. The solids were combined, washed with acetonitrile, and dried. The remainder of the original reaction mixture was treated similarly and this time crystals formed spontaneously as the volume was reduced. A small-scale experiment showed that recrystallization from benzene–acetonitrile was feasible so the combined product, ca. 6 g of yellow solid, was dissolved in 15 ml of benzene. Addition of 60 ml of acetonitrile to the filtered solution caused a yellow solid to form. This was collected, washed with acetonitrile, and vacuum dried; yield 4.0 g; mp ca. 130 °C dec. This solid was apparently a crystalline benzene solvate since ^{1}H NMR spectra in cyclohexane and tetrahydrofuran solutions showed the presence of approximately 1 mol of benzene. The elemental analyses and NMR data are given in Tables I and II.

Well-formed crystalline material was obtained by crystallization from ether–acetonitrile; mp ca. 130 °C dec. The ^{1}H NMR spectrum indicated that the solid was no longer a benzene solvate, but the ir spectrum (Nujol) showed both free (2255 cm^{-1}) and coordinated acetonitrile (2270 cm^{-1}) even after vacuum drying, and the elemental analysis (C, 69.73; H, 7.62; N, 2.15) also suggested that the crystals had acetonitrile in the lattice instead of benzene.

Hydridoacetonitriletris(tris(*o*-phenylphenyl) phosphite)cobalt. A solution of 11.5 g of tris(*o*-phenylphenyl) phosphite and 2.0 g of $Co(C_8H_{12})(C_8H_{13})$ in 40 ml of tetrahydrofuran was diluted with 100 ml of acetonitrile. This solution was stirred for ca. 24 h at room temperature under 50 psig of hydrogen. The filtered reaction mixture was vacuum concentrated to ca. 30 ml. The remaining liquid was decanted from the precipitated gum and set aside. The residual gum was triturated with 600 ml of acetonitrile taken in small portions. The combined acetonitrile extract was filtered and vacuum concentrated to ca. 75 ml. This solution was cooled to −35 °C and the yellow solid was collected, washed with cold acetonitrile, and dried cold under vacuum; yield 5.4 g; mp ca. 100 °C dec.

Hydridotetrakis(tri-*o*-tolyl phosphite)cobalt. A solution of 2.0 g of $Co(C_8H_{12})(C_8H_{13})$ and 10.3 g of tri-*o*-tolyl phosphite in 30 ml of benzene was stirred at room temperature under 50 psig of hydrogen overnight. The reaction mixture was diluted with 150 ml of pentane and the yellow solid was collected, washed with pentane, and dried (yield 8.4 g). The solid was dissolved in 200 ml of benzene. The solution was filtered and then concentrated under vacuum to ca. 30 ml. Pale yellow solid formed when 150 ml of pentane was added. This was collected, washed with pentane, and dried (yield 6.3 g); mp ca. 100 °C dec. The elemental analyses and NMR data are given in Tables I and II. The presence of benzene in the crystals was confirmed by the ^{1}H NMR spectrum of a tetrahydrofuran solution.

Hydridotetrakis(triethylphosphine)cobalt. A solution of 10 g of $Co(C_8H_{12})(C_8H_{13})$ in 80 ml of argon-sparged benzene was combined with a solution of 16 g of triethylphosphine in 10 ml of benzene in a pressure bottle. After addition of 10 ml of acetonitrile the bottle was swept with argon and closed. It was then evacuated and charged with 50 psig of hydrogen. The color of the liquid changed from deep purple to brown-green immediately after the addition of hydrogen. After about 35 min at room temperature the solution was green. The pressure was released and the solvent was removed under vacuum. The residue was then dissolved in 250 ml of room-temperature pentane. (An argon-filled glovebox was used for this and all subsequent manipulations.) The filtered pentane solution was vacuum concentrated to about 50 ml and cooled to −35 °C. The golden yellow crystals were collected, washed with cold pentane, and dried in a stream of argon; yield 9.2 g. The crystals were recrystallized from cold pentane to give 8.5 g of golden yellow crystals; mp ca. 60 °C dec (?). The elemental analyses and NMR data are given in Tables I and II.

Hydridotetrakis(diethylphenylphosphine)cobalt. A solution of 6.5 g of $Co(C_8H_{12})(C_8H_{13})$ in 50 ml of benzene was combined with a solution of 16 g of $(C_2H_5)_2P(C_6H_5)$ in 20 ml of benzene in a pressure bottle. Both solutions were argon sparged before mixing. The bottle was flushed with argon, closed, and evacuated. Hydrogen was admitted to 50 psig. The initial deep purple color changed to dark red immediately when the hydrogen was added. The mixture was stirred at room temperature for 3 h and then the volatiles were removed under vacuum. The residue was then mostly dissolved in 600 ml of pentane at room temperature *using an argon-filled glovebox* for the subsequent manipulations. The solution was filtered to remove a trace of black sludge and then vacuum concentrated to ca. 100 ml. The solution was cooled to −35 °C. The dark maroon crystals were collected cold, washed with cold pentane, and dried at 0.1 mmHg at room temperature; mp 85 °C dec (?). The elemental analyses and NMR data are given in Tables I and II.

Reaction of $Co(C_8H_{12})(C_8H_{13})$ with Hydrogen. Solid crystalline $Co(C_8H_{12})(C_8H_{13})$ was placed in a pressure bottle. The bottle was evacuated and hydrogen was admitted to 15 psig. Within seconds the bottle warmed and the crystals sintered. The hydrogen pressure was increased to 50 psig for a few minutes. The pressure was released and the residue was treated with deuteriobenzene–TMS. The mixture was filtered. The ^{1}H NMR spectrum of the filtrate showed only one peak, a singlet at τ 8.51 (cyclooctane). The black residue was ferromagnetic and was probably metallic cobalt.

Hydrogenation of 1-Butene. A glass pressure bottle was charged with 0.10 mmol of cobalt complex and 10 ml of benzene. The bottle was evacuated and then charged with ca. 30 mmol of 1-butene and 30 psig of hydrogen. The solutions were stirred magnetically and samples of the gas phase were withdrawn at intervals by syringe for gas chromatographic analysis on a $^1/_8$ in. × 8 ft column with silicone nitrile XE 60 packing. Temperatures above room temperature were supplied by an oil bath when desired.

Registry No. $[(C_6H_5O)_3P]_3CoH(CH_3CN)$, 58527-60-9; $[(o\text{-}CH_3C_6H_4O)_3P]_3CoH(CH_3CN)$, 58527-61-0; $[(o\text{-}(CH_3)_2CHC_6H_4O)_3P]_3CoH(CH_3CN)$, 58527-62-1; $[(o\text{-}C_6H_5C_6H_4O)_3P]_3CoH(CH_3CN)$, 58602-21-4; $[(o\text{-}CH_3C_6H_4O)_3P]_4CoH$, 58602-22-5; $[(C_2H_5)_3P]_4CoH$, 58602-23-6; $[(C_2H_5)_2PC_6H_5]_4CoH$, 58602-24-7; $[(C_2H_5)_3P]_3CoH(N_2)$, 22044-05-9; $[(C_2H_5)_3P]_3CoH(CH_3CN)$, 58602-25-8; $[(C_2H_5)_2PC_6H_5]_3CoH(N_2)$, 25481-14-5; $[(C_2H_5)_2PC_6H_5]_3CoH(CH_3CN)$, 58602-26-9; $[(C_6H_5)_3P]_3CoH(CH_3CN)$, 22992-02-5; $Co(C_8H_{12})(C_8H_{13})$, 34829-55-5; triphenyl phosphite, 101-02-0; triethylphosphine, 554-70-1.

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