Liquid Cobalt (I) Hydride Complexes as Precursors for Chemical Vapor Deposition

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Volatile cobalt (I) hydride complexes $HCo[R^1OP(OR^2)_2]_4$ were synthesized, where R^1 = Me, Et, *i*-Pr, *n*-Pr, *n*-Bu, *i*-Bu, Ph, and benzyl, and R^2 = Me and Et. The cobalt complexes were obtained as liquids as R^1 was lengthened from ethyl to longer chains. The thermal stability of the complex was lowered with bulky R^1, thus, $HCo[n\text{-}PrOP(OMe)_2]_4$ and $HCo[n\text{-}BuOP(OMe)_2]_4$ were distillable but $HCo[i\text{-}BuOP(OMe)_2]_4$ was not. Pure cobalt films of smooth and dense surface morphology were deposited on Si at temperatures as low as 270 °C using the cobalt hydrides as precursors under reduced pressure without employing H_2.

Introduction

Cobalt complexes such as $Co_2(CO)_8$, $Co(C_5H_7O_2)_2$, $Co(C_5H_7O_2)_3$, $Co(C_5H_5)_2$, and $Co(C_5H_5)(CO)_2$ which have been used as precursors to deposit Co films by chemical vapor deposition (CVD) exhibited serious drawbacks such as undesirable reaction pathways in the gas phase, low thermal stability, low vapor pressure, high deposition temperature, or low purity and rough surface morphology of the deposited films.[1−4] $Co(CO)_4(NO)$ has been reported as a more suitable precursor for its high vapor pressure, availability in liquid form, and improved thermal stability over $Co_2(CO)_8$, however, it requires stringent processing conditions to reduce the contamination in the deposited films.[5−7]

$HCo[P(OR)_3]_4$, where R = alkyl or aryl, exhibited unusually high thermal stability, low ligand lability, and high resistance toward bases such as OR^-, OH^-, or alkali metals, in contrast to the other cobalt complexes of the type $HCoL_4$, where L = PF_3 or CO.[8−13] Recognizing the high stability of these cobalt complexes, we have initiated a study on the CVD of Co using $HCo[P(OR)_3]_4$, where R = Me, Et, *i*-Pr, and *n*-Bu, as precursor.[14] The cobalt hydrides, which were volatile solids, produced dense and smooth Co films on Si substrates at temperatures as low as 300 °C under reduced pressure. In addition, no C or O contaminants were incorporated into the Co films deposited from these hydrides even though no H_2 was employed during the CVD processes. No gas-phase reaction was observed during the CVD processes. This study demonstrated attractive properties of the cobalt hydride complexes, $HCo[P(OR)_3]_4$, where R = Me, Et, *i*-Pr, and *n*-Bu, as CVD precursors to produce high-quality Co films. A challenge that followed was to design a liquid cobalt hydride complex, which would be more suitable for practical CVD processes, without compromising the volatility, stability, and deposition characteristics of these solid hydrides. Herein, we report novel liquid cobalt hydride complexes as CVD precursors to deposit Co films and discuss the effect of trialkyl phosphite ligands on the crystallization and stability of the cobalt hydride complexes. We also report the X-ray crystal structure for $HCo[P(OEt)_3]_4$, which has not been available to date.

Results and Discussion

Asymmetric trialkyl phosphite ligands were employed to synthesize liquid cobalt hydride complexes with the expectation that lowering the ligand symmetry would increase disorder in the complex and frustrate crystallization. The phosphites, $R^1OP(OR^2)_2$, where R^1 = Me, Et, *i*-Pr, *n*-Pr, *n*-Bu, *i*-Bu, Ph, and benzyl, and R^2 = Me and Et, were prepared by the reaction of phosphorus trichloride with the corresponding alcohols in diethyl ether.[15] $HCo[R^1OP(OR^2)_2]_4$ (**I**) was synthesized by the addition of $NaBH_4$ to a stirred solution of $CoCl_2$ and the corresponding phosphite ligand in 1,2-dimethoxyethane at −78 °C.[13,14] The product was isolated as a volatile liquid or solid. Table 1 summarizes the ^1H and ^{31}P NMR data showing the coordination of the hydride and

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(1) Gross, M. E.; Kranz, K. S.; Brasen, D.; Luftman, H. *J. Vac. Sci. Technol. B* **1988**, *6* (5), 1548.
(2) Maruyama, T. *Jpn. J. Appl. Phys.* **1997**, *36*, L705.
(3) Dormans, G. J. M.; Meekes G. J. B. M.; Staring, E. G. J. *J. Cryst. Growth* **1991**, *114*, 364.
(4) Rhee, H. S.; Ahn, B. T. *J. Electrochem. Soc.* **1999**, *146*, 2720.
(5) Ivanova, A. R.; Nuesca, G.; Chen, X.; Goldberg, C.; Kaloyeros, A. E.; Arkles, B.; Sullivan, J. J. *J. Electrochem. Soc.* **1999**, *146*, 2139.
(6) Lane, P. A.; Oliver, P. E.; Wright, P. J.; Reeves, C. L.; Pitt, A. D.; Cockayne, B. *Chem. Vap. Deposition* **1998**, *4*, 183.
(7) Longergan, A. R.; Nuesca, G.; Goldberg, C.; Peterson, G.; Kaloyeros, A. E.; Arkles, B.; Sullivan, J. J. *J. Electrochem. Soc.* **2001**, *148*, C21−C27.
(8) Frenz, B. A.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 2403.
(9) Titus, D. D.; Orio, A. A.; Marsh, R. E.; Gray, H. B. *Chem. Commun.* **1971**, 322.
(10) Levision, J. J.; Robinson, S. D. *J. Chem. Soc. (A)* **1970**, 96.
(11) Kruse, W.; Atalla, R. H. *Chem. Commun.* **1968**, 921.
(12) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5271.
(13) Mutterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920.
(14) Choi H.; Park S.; Jang H. G. *J. Mater. Res.* **2002**, *17*, 267.
(15) Landauer, S. R.; Rydon, H. N. *J. Chem. Soc.* **1953**, 2224.

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Table 1. Selected ^{1}H and ^{31}P NMR Chemical Shifts (δ) for $HCo[R^1OP(OR^2)_2]_4$

R^1	R^2	H−Co	≡P−Co
CH_2CH_3	CH_3	−15.2	173.5
$CH(CH_3)_2$	CH_3	−15.2	171.3
$CH_2CH_2CH_3$	CH_3	−15.4	172.3
$CH_2CH(CH_3)_2$	CH_3	−15.4	173.5
$CH_2(CH_2)_2CH_3$	CH_3	−15.2	173.4
C_6H_5	CH_3	−15.4	173.5
CH_3	CH_2CH_3	−16.0	169.5
$CH_2CH(CH_3)_2$	CH_2CH_3	−15.4	169.9
$CH_2C_6H_5$	CH_2CH_3	−15.8	169.6

phosphite ligand to the cobalt, respectively. The ν_{Co-H} at 1965.5 cm^{-1} for $HCo[i\text{-}PrOP(OMe)_2]_4$ and $HCo[n\text{-}PrOP(OMe)_2]_4$ was consistent with that for $HCo[P(OR)_3]_4$, where R = Me, Et, *i*-Pr, and *n*-Bu.[16]

$HCo[EtOP(OMe)_2]_4$, $HCo[MeOP(OEt)_2]_4$, and $HCo[i\text{-}PrOP(OMe)_2]_4$ were isolated as solids, whereas $HCo[n\text{-}PrOP(OMe)_2]_4$, $HCo[n\text{-}BuOP(OMe)_2]_4$, $HCo[i\text{-}BuOP(OMe)_2]_4$, $HCo[i\text{-}BuOP(OEt)_2]_4$, $HCo[PhOP(OMe)_2]_4$, and $HCo[PhCH_2OP(OEt)_2]_4$ were liquids.[17] This indicated that liquids were formed as R^1 was lengthened. The effect of the R^1 length on the melting point of the solids was difficult to measure quantitatively due to the decomposition prior to melting. However, a solid-to-liquid transition was observed as R^1 was lengthened from ethyl to a longer chain whether R^2 was methyl or ethyl. Thus, $HCo[n\text{-}PrOP(OMe)_2]_4$ was obtained as a liquid while $HCo[i\text{-}PrOP(OMe)_2]_4$ was a solid, which suggested that the length of R^1 would be a more important factor than its steric bulkiness to form a liquid. The phase of $HCo[PhP(OEt)_2]_4$, which was reported to be solid,[9] could be explained by this as well considering the shorter length of phenyl than that of the ethoxy group. The thermal stability of the hydrides, on the other hand, was lowered with bulky R^1. $HCo[n\text{-}PrOP(OMe)_2]_4$ and $HCo[n\text{-}BuOP(OMe)_2]_4$ were stable enough to be distilled, but $HCo[i\text{-}BuOP(OMe)_2]_4$ was decomposed during the distillation process.[17] Further, *t*-$BuOP(OMe)_2$, which is sterically more hindered than *i*-$BuOP(OMe)_2$, failed to give the corresponding cobalt complex $HCo[P(t\text{-}BuOP(OMe)_2]_4$. The steric effect of the ligand on the stability was even more significant for $HCo[P(OR)_3]_4$. $P(n\text{-}BuO)_3$ produced $HCo[P(n\text{-}BuO)_3]_4$ which was stable up to 150 °C, but the more hindered $P(i\text{-}BuO)_3$ and $P(t\text{-}BuO)_3$ failed to give the corresponding cobalt complexes, $HCo[P(i\text{-}BuO)_3]_4$ and $HCo[P(t\text{-}BuO)_3]_4$, respectively.

Because of the unavailability of the crystal structure of $HCo[P(OR)_3]_4$, where R = alkyl or aryl, it has been regarded as a trigonal bipyramidal structure based on that of $HCo[PhP(OEt)_2]_4$.[9] Herein, we obtained crystals of $HCo[P(OEt)_3]_4$ from acetone solvent and carried out an X-ray analysis. Crystal parameters and structure refinement data are provided in Table 2. Unlike $HCo[PhP(OEt)_2]_4$, it revealed two discrete, nearly identical cobalt molecules in a cell. Figure 1 shows the inner coordination sphere of each cobalt molecule in the cell where four phosphorus atoms formed a distorted tetrahedral arrangement at each metal atom. The hydrogen atoms H(1) and H(2), in Co(1) and Co(2) molecules, respectively, were not seen in Figure 1. On the basis of the Co−P bond distances and P−Co(1)−P angles listed in Table 3, a reasonable position for each H atom would be the one trans to P(1) or P(5), displaced away from P(4) or displaced toward P(8), respectively, in each molecule. This indicated that the configuration about each cobalt atom was roughly trigonal bipyramidal with the cobalt atoms positioned 0.3309 Å [Co(1)] and 0.3233 Å [Co(2)] out of the equatorial plane defined by the phosphorus atoms [P(2), P(3), and P(4)] and [P(6), P(7), and P(8)], respectively. The position of the H atom, whether it was displaced toward or away from an equatorial phosphite ligand, seemed to be a major difference in the configuration of each molecule. The Co−P bond distances in the present work were 0.02 to 0.05 Å shorter than those in $HCo[PhP(OEt)_2]_4$,[9] and 0.02 to 0.06 Å longer than those in $HCo(PF_3)_4$,[8] consistent with the π-bonding capabilities of $P(OEt)_3$.

CVD experiments were carried out using **I** as precursors at substrate temperatures of 270−360 °C under pressures of 0.01−5 Torr. No reducing agent such as

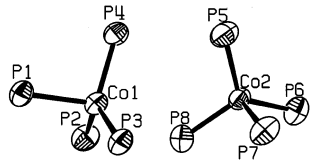

Figure 1. Inner coordination spheres of the two molecules of $HCo[P(OEt)_3]_4$.

Table 2. Crystal Parameters and Structure Refinement for $HCo[P(OEt)_3]_4$

chemical formula	$C_{24}H_{61}CoO_{12}P_4$
formula weight	724.54
temperature	183(2) K
wavelength	0.71073 Å
crystal system, space group	triclinic, $P\bar{1}$
unit cell dimensions	a = 11.311(3) Å, α = 101.871(5)° b = 17.884(5) Å, β = 100.200(5)° c = 19.196(5) Å, γ = 95.204(5)°
volume	3707.3(17) Å^3
Z, calculated density	4, 1.298 mg/m^3
absorption coefficient	0.686 mm^{-1}
theta range for data collection	1.42 to 25.03 deg.
limiting indices	$-13 \le h \le 13$, $-21 \le k \le 21$, $-22 \le l \le 22$
reflections collected	27706
independent reflections	12988 [R(int) = 0.1291]
completeness to theta = 25.03°	99.1%
absorption correction	empirical
max. and min. transmission	0.9216 and 0.8200
data/restraints/parameters	12988/1756/821
goodness-of-fit on F^2	0.938
final R indices [$I>2\sigma(I)$]	R1 = 0.0894, wR2 = 0.2239
R indices (all data)	R1 = 0.2070, wR2 = 0.2808
largest diff. peak and hole	1.185 and −0.538 e Å^{-3}

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $HCo[P(OEt)_3]_4$

Co(1)−P(1)	2.111(3)	Co(2)−P(5)	2.105(3)
Co(1)−P(2)	2.096(3)	Co(2)−P(6)	2.075(3)
Co(1)−P(3)	2.094(3)	Co(2)−P(7)	2.086(3)
Co(1)−P(4)	2.086(3)	Co(2)−P(8)	2.106(3)
P(1)−Co(1)−P(2)	100.11(1)	P(5)−Co(2)−P(6)	100.11(12)
P(1)−Co(1)−P(3)	99.02(1)	P(5)−Co(2)−P(7)	98.41(13)
P(1)−Co(1)−P(4)	98.26(1)	P(5)−Co(2)−P(8)	98.18(12)
P(2)−Co(1)−P(3)	109.78(1)	P(6)−Co(2)−P(7)	114.56(13)
P(2)−Co(1)−P(4)	122.42(1)	P(6)−Co(2)−P(8)	121.76(13)
P(3)−Co(1)−P(4)	120.37(1)	P(7)−Co(2)−P(8)	116.61(12)

(16) The ν_{Co-H} values for $HCo[P(OR)_3]_4$, where R = Me, Et, *i*-Pr, and *n*-Bu, were in the range of 1940−1973 cm^{-1}.

(17) $HCo[n\text{-}PrOP(OMe)_2]_4$ and $HCo[n\text{-}BuOP(OMe)_2]_4$ were distilled at 170 °C/0.05 Torr and 190 °C/0.05 Torr, respectively. Other liquid complexes were decomposed during the distillation process. The solid complexes were sublimed at 77−90 °C/0.05 Torr.

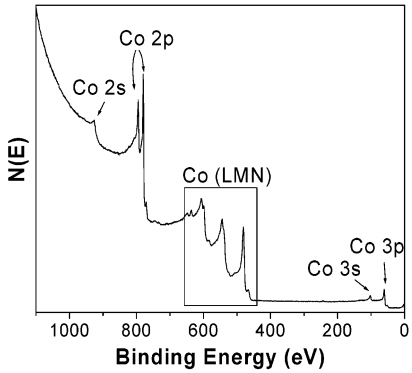

Figure 2. X-ray photoelectron spectrum of a Co film deposited from **I** on Si at 300 °C.

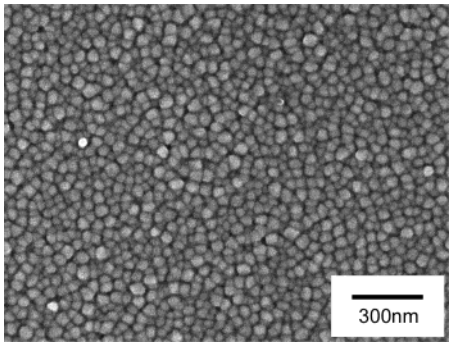

Figure 3. Scanning electron micrograph of a Co film deposited from HCo[*n*-PrOP(OMe)$_2$]$_4$ on Si at 300 °C.

H_2 was used for the film deposition experiments. Pure Co films were deposited from **I** on Si substrates at temperatures as low as 270 °C. Impurities such as C, O, or P were not detected from the deposited films by XPS as shown in Figure 2. The reaction exhaust was analyzed and determined to be the free phosphite ligand liberated from the precursor intact, which lends support to the high purity of the deposited Co film. That these complexes decompose to give cobalt and phosphite ligands without further decomposition offers an outstanding advantage as CVD precursors. For instance, the thermal decomposition of $Co(CO)_4(NO)$ was reported to be complicated by the Co catalyzed reactions of CO and NO to produce C, NO_2, N_2O, and O_2.[18] In fact, it was crucial to use high substrate temperature and H_2 flow, i.e., 390 °C and 750 sccm to reduce the C and O contamination in the Co films when $Co(CO)_4(NO)$ was used as a precursor.[5,7] Further, **I** exhibited neither gas-phase reactions nor Co deposition on the reactor wall in the temperature range used here, but such behaviors have been reported for $Co_2(CO)_8$ and $Co(CO)_3(NO)$ at temperatures even below 300 °C.[6] We attribute this to the high thermal stability of **I**. The SEM and AFM images in Figures 3 and 4 showed smooth and dense surface morphology of the Co film deposited from HCo[*n*-PrOP(OMe)$_2$]$_4$ at 300 °C. The rms surface roughness of the film was 3.70 nm.

Summary

In this report, we presented volatile, thermally stable, liquid or solid cobalt hydride complexes employing the asymmetric trialkyl phosphite ligands, $R^1OP(OR^2)_2$, and deposition of Co films using them as CVD precursors. It was observed that the phosphite ligands with long R^1 frustrated crystallization, whereas those with bulky R^1 lowered the stability of the cobalt hydrides. The hydride complexes deposited pure Co films of dense and smooth surface morphology at substrate temperatures as low as 270 °C without H_2. The liquid HCo[*n*-PrOP(OMe)$_2$]$_4$ and HCo[*n*-BuOP(OMe)$_2$]$_4$ were especially attractive as CVD precursors because of their distillability.

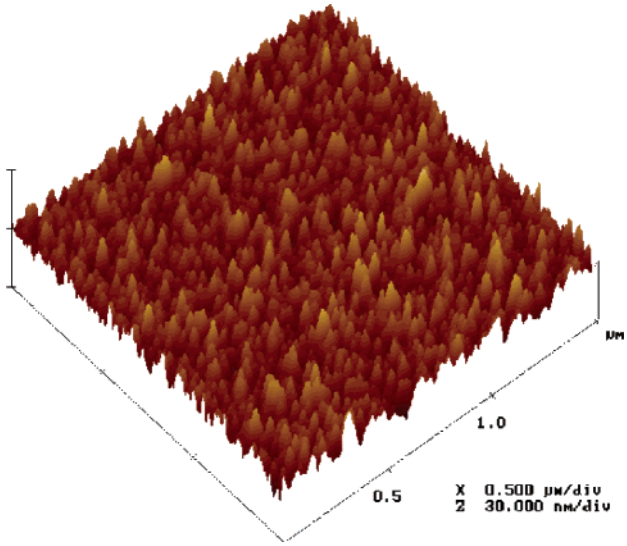

Figure 4. Atomic force micrograph of a Co film deposited from HCo[*n*-PrOP(OMe)$_2$]$_4$ on Si at 300 °C.

Experimental Section

Precursor Preparation. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium benzophenone, sodium, or calcium hydride immediately before use. All reagents were obtained from Aldrich and used as received. ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$, C_6D_6, or acetone-d_6 on a Varian Gemini 400 MHz spectrometer, with chemical shifts calculated from the solvent signals. Microanalyses were performed for HCo[*i*-PrOP(OMe)$_2$]$_4$ and HCo[*n*-PrOP(OMe)$_2$]$_4$ at the University of Illinois Microanalytical Laboratory. Infrared spectra were obtained on a Nicolet Nexus 670 spectrometer. Trialkyl phosphites and the corresponding cobalt complexes were prepared by modifying the method described in the literature.[13−15]

EtOP(OMe)$_2$ (1). Ethanol (15.85 g, 0.344 mol) and dimethylaniline (43.52 mL, 0.344 mol) were added to phosphorus trichloride (30 mL, 0.344 mol) in 1.5 l diethyl ether at −78 °C. The reaction mixture was warmed to room temperature followed by the addition of methanol (22.04 g, 0.688 mol) and dimethylaniline (87.04 mL, 0.688 mol) at −78 °C. After the reaction mixture was warmed to room temperature, the solids were filtered off. After removal of the ether, the product was distilled (60% yield) under vacuum (0.05 Torr, 25 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (2H, CH_2), 3.49 (6H, CH_3), and 1.25 (3H, CH_3). ^{31}P NMR (161.903 MHz, $CDCl_3$, 85% H_3PO_4): δ −141.68.

MeOP(OEt)$_2$, *i*-PrOP(OMe)$_2$, *n*-PrOP(OMe)$_2$, *t*-BuOP(OMe)$_2$, *i*-BuOP(OMe)$_2$, *n*-BuOP(OMe)$_2$, PhOP(OMe)$_2$, *t*-BuOP(OEt)$_2$, *i*-BuOP(OEt)$_2$, and $PhCH_2OP(OEt)_2$, were prepared by the same method as described for EtOP(OMe)$_2$ using the corresponding alcohols.

HCo[EtOP(OMe)$_2$]$_4$ (2). To a 1,2-dimethoxyethane (150 mL) solution of $CoCl_2$ (5 g, 0.038 mol) and **1** (26.242 g, 0.19 mol) maintained at −78 °C, $NaBH_4$ (2.875 g, 0.076 mol) was added. After the reaction mixture was warmed to room

(18) Baev, A. K.; Gubar, Y. L.; Gasanov, K. S. *Russ. J. Phys. Chem.* **1982**, *56*, 1490.

temperature, the solvent was removed under vacuum and the residue was extracted with pentane. The pentane extracts were concentrated and eluted with pentane through a neutral alumina column. The eluate was collected and the solvent and free phosphite were removed under vacuum. The product was a light yellow solid (yield 66%; subl., 77 °C/0.05 Torr). ^{1}H NMR (400 MHz, C_6D_6): δ 4.06 (8H, CH_2), 3.57 (24H, CH_3), 1.15 (12H, CH_3), and −15.2 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 173.5.

HCo[MeOP(OEt)$_2$]$_4$ (3). Complex **3** was prepared by the same method as described above using $MeOP(OEt)_2$. The product was a light yellow solid (subl., 80 °C/0.05 Torr). ^{1}H NMR (400 MHz, C_6D_6): δ 4.10 (16H, CH_2), 3.62 (12H, OCH_3), 1.26 (24H, CH_3), and −15.2 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 171.3.

HCo[*i*-PrOP(OMe)$_2$]$_4$ (4). Complex **4** was prepared by the same method as described above using *i*-$PrOP(OMe)_2$. The product was a light yellow solid (subl., 90 °C/0.05 Torr). ^{1}H NMR (400 MHz, C_6D_6): δ 4.86 (4H, CH), 3.62 (24H, OCH_3), 1.26 (24H, CH_3), and −15.4 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 172.3. IR (NaCl): Co−H, 1965.5 cm^{-1}. Anal. Calcd for $C_{20}H_{53}O_{12}P_4Co$: C, 35.94; H, 7.99; P, 18.53; Co, 8.82. Found: C, 35.64; H, 8.07; P, 15.62; Co 7.66.

HCo[*n*-PrOP(OMe)$_2$]$_4$ (5). Complex **5** was prepared by the same method as described above using *n*-$PrOP(OMe)_2$. The product was light yellow liquid with volatility. ^{1}H NMR (400 MHz, acetone-d_6): δ 3.70 (8H, OCH_2), 3.48 (24H, OCH_3), 1.56 (8H, CH_2), 0.92 (12H, CH_3), and −15.4 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 173.5. IR (NaCl): Co−H, 1965.5 cm^{-1}. Anal. Calcd for $C_{20}H_{53}O_{12}P_4Co$: C, 35.94; H, 7.84; P, 18.53; Co, 8.82. Found: C, 36.10; H, 7.87; P, 17.99; Co, 8.75.

HCo[*i*-BuOP(OMe)$_2$]$_4$ (6). Complex **6** was prepared by the same method as described above using *i*-$BuOP(OMe)_2$. The product was a light yellow volatile liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 4.02 (8H, OCH_2), 3.61 (24H, OCH_3), 1.60 (4H, CH), 0.90 (24H, CH_3), and −15.2 (1H, Co−H). ^{31}P NMR (161.903 MHz, $CDCl_3$, H_3PO_4): δ 173.4.

HCo[*n*-BuOP(OMe)$_2$]$_4$ (7). Complex **7** was prepared by the same method as described above using *n*-$BuOP(OMe)_2$. The product was a light yellow volatile liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 4.01 (8H, OCH_2), 3.61 (24H, CH_3), 1.60 (8H, CH_2), 1.39 (8H, CH_2), 0.87 (12H, CH_3), and −15.4 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 173.5.

HCo[PhOP(OMe)$_2$]$_4$ (8). Complex **8** was prepared by the same method as described above using $PhOP(OMe)_2$. The product was a light yellow volatile liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.28 (8H, C_6H_5), 7.12 (12H, C_6H_5), 3.62 (24H, CH_3), and −16.0 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 169.5.

HCo[*i*-BuOP(OEt)$_2$]$_4$ (9). Complex **9** was prepared by the same method as described above using *i*-$BuOP(OEt)_2$. The product was a light yellow volatile liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 4.12 (16H, CH_2), 3.82 (8H, CH_2), 1.94 (4H, CH), 1.24 (24H, CH_2CH_3), 1.05 (24H, $CHCH_3$), and −15.4. (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 169.9.

HCo[PhCH$_2$OP(OEt)$_2$]$_4$ (10). Complex **10** was prepared by the same method as described above using $PhCH_2OP(OEt)_2$. The product was a light yellow volatile liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.42 (8H, C_6H_5), 7.20 (12H, C_6H_5), 5.35 (8H, CH_2), 4.15 (16H, CH_2), 1.17 (24H, CH_3), and −15.8 (1H, Co−H). ^{31}P NMR (161.903 MHz, C_6D_6, H_3PO_4): δ 169.6.

Structure Determination of HCo[P(OEt)$_3$]$_4$ (11). Ivory crystals of **11** were crystallized from acetone at −20 °C, and a crystal of size 0.1 × 0.3 × 0.4 mm^3 was selected for the X-ray analysis. The crystallographic data were obtained on a Bruker SMART/CCD 3-circle diffractometer equipped with graphite-monochromated molybdenum radiation (λ(Kα) = 0.71073 Å) at −90° under N_2. Preliminary measurements on several crystals suggested the ambiguous triclinic space and very limited resolution. The average I/σ for the data crystal at a resolution of 0.95 Å was less than 1. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 [19]. All non-hydrogen atoms in the heavily restrained model were anisotropically refined. Hydrogen atoms were included as idealized contributors. Metal hydride positions did not surface in late difference Fourier maps. The proposed model includes a discrete rotational disorder for the ethoxy moieties bonded to P(8). Crystal parameters and structure refinement for **11** are given in Table 2.

Film Deposition and Characterization. CVD experiments were carried out using the cobalt compounds in a cold-wall glass reactor with a bubbler-type precursor vessel.[14] No reducing agent such as H_2 was used for the film deposition experiments. The precursor was injected upward into the reactor with argon as a carrier gas with flow rates of 50−600 sccm. The precursor vessel was maintained at 55−115 °C during the deposition process. Film depositions were conducted on Si substrates using a resistive heater at temperatures of 270−360 °C. The CVD chamber was evacuated to a background pressure of 10^{-6} Torr and maintained at 0.01−5 Torr during the deposition processes. The films prepared by CVD were analyzed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). XPS spectra were obtained by using a Physical Electronics PHI 5400 X-ray photoelectron spectrometer with a monochromatized Mg K X-ray source (1253.6 eV). All the films were cleaned extensively by Ar-sputtering at 8 keV before data collection. SEM and AFM images were taken from a Hitachi S-4700 scanning electron microscope and a Digital Instruments Multimode NanoScope IIIa, respectively.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for $HCo[P(OEt)_3]_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Sheldrick, G. M. SHELX-97-2, Program for crystal structure solution and refinement. Institute für Anorg. Chemie, University of Göttingen: Germany, 1998.