Conclusion

(Silylamino)phosphines generally react smoothly with carbonyl compounds via nucleophilic attack by phosphorus with subsequent silyl migration to oxygen. This process is a convenient synthetic route to new *N*-silylphosphinimines or phosphine oxides which contain Me_3SiO-functionalized organic substituents.

Experimental Section

Materials and General Procedures. The (silylamino)phosphines were prepared according to the published procedures.[4,14] Acetone, acetaldehyde, benzaldehyde, cyclohexanone, and dichloromethane were obtained from commerical sources, distilled, and stored over molecular sieves prior to use. Acrolein was distilled and used immediately. Other reagents were used as obtained without further purification. All reactions were performed under an atmosphere of dry nitrogen with reagents being transferred by syringe. Proton NMR spectra were obtained on Varian EM390 or JEOL MH-100 spectrometers. Carbon-13 and ^{31}P NMR spectra were obtained on a JEOL FX-60 spectrometer operating in the FT mode. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Reactions of (Silylamino)phosphines with Aldehydes and Ketones. Typically, the phosphine (ca. 10–20 mmol) was dissolved in CH_2Cl_2 (ca. 10–15 mL) in a 25-mL flask equipped with a magnetic stirrer and an adapter with a gas-inlet side arm and a rubber septum. The carbonyl compound was then added via syringe to the stirred phosphine solution. Some reagents (see below) required addition at 0 °C to moderate the exothermic reaction. The progress of the reactions was monitored by ^1H NMR spectroscopy, and Table I lists the times by which disappearance of the starting phosphine was observed to be complete. Reaction times of <1 min indicate that the reaction is very rapid at 0 °C. Upon completion of the reaction, solvent was removed under reduced pressure, and the product was purified by fractional distillation (Table I).

In the above procedure, the reagents added at room temperature were acetone, cyclohexanone, and 2-cyclohexen-1-one. Those added at 0 °C were acetaldehyde, benzaldehyde, chloroacetone, dichloroacetone (as a CH_2Cl_2 solution), acrolein, and methyl vinyl ketone.

In the synthesis of the 10-membered ring **10**, the *Z* isomer was favored if methyl vinyl ketone was slowly swept into the reaction mixture at 0 °C under a stream of nitrogen.

In the syntheses of **5a** and **11**, hexafluoroacetone was introduced as a gas into an evacuated flask containing the phosphine, without solvent, which was being stirred at 0 °C. An exothermic reaction ensued in which only 1 equiv of hexafluoroacetone was consumed. Products were then purified by fractional distillation (Table I).

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Registry No. **1**, 63744-11-6; **2**, 68437-96-7; **3**, 68437-82-1; **4**, 68437-84-3; **5a**, 72805-01-7; **5b**, 72805-03-9; **5c**, 79200-64-9; **5d**, 79200-65-0; **5e**, 79200-66-1; **5f**, 79200-67-2; **5g**, 79200-68-3; **5h**, 79200-69-4; **6**, 79200-70-7; **7**(*Z*), 79200-71-8; **7**(*E*), 79200-72-9; **8**, 79200-73-0; **9**, 79200-74-1; **10**(*Z*), 79200-75-2; **10**(*E*), 79200-76-3; **11**, 72805-02-8; **13**, 79215-35-3; **14**, 79200-77-4; **15**, 79200-78-5; **16**, 79200-79-6; hexafluoroacetone, 684-16-2; acetone, 67-64-1; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; biacetyl, 431-03-8; chloroacetone, 78-95-5; dichloroacetone, 534-07-6; cyclohexanone, 108-94-1; methyl vinyl ketone, 78-94-4; acrolein, 107-02-8; 2-cyclohexen-1-one, 930-68-7.

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A Double Michaelis–Arbuzov Rearrangement Involving $(\eta^5\text{-}C_5H_5)CoI_2(CO)$ and $P(OCH_3)_3$. Formation of the Cobalt "Supersandwich" Complex

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The reaction of $(\eta^5\text{-}C_5H_5)CoI_2(CO)$ with $P(OR)_3$, R = CH_3 and C_2H_5, yields different products depending on the amount of phosphite and on conditions employed. By stoichiometric ligand substitution, $(\eta^5\text{-}C_5H_5)CoI_2[P(OCH_3)_3]$ is produced. However, with excess $P(OCH_3)_3$ a double Michaelis–Arbuzov reaction occurs to yield $(\eta^5\text{-}C_5H_5)Co[P(O)(OCH_3)_2]_2[P(OCH_3)_3]$ (**3**) with formation of CH_3I. Complex **3**, isolatable in both the anhydrous and monohydrated form, is converted to the cobalt supersandwich $(\eta^5\text{-}C_5H_5)_2Co_3[P(O)(OCH_3)_2]_6$ by pyrolysis or by the addition of anhydrous $CoCl_2$. The nature of **3** has been verified by a single-crystal X-ray diffraction study at −100 °C. It crystallizes as a monohydrate in space group C_{2h}^5—$P2_1/c$ with four formula units in a cell of dimensions a = 7.872 (1) Å, b = 15.105 (2) Å, c = 16.517 (2) Å, and β = 91.819 (1)°. Least-squares refinement of a data set containing 3238 reflections having $F_o^2 > 3\sigma(F_o^2)$ converged to conventional agreement indices (on F) of R = 0.031 and R_w = 0.034. The spectral, structural, and reactivity details of the complex, apparently unique in its formation via a double Michaelis–Arbuzov reaction, are discussed.

Introduction

The Michaelis–Arbuzov rearrangement, as illustrated in reaction 1, results in the production of a phosphonate

$$RX + P(OR')_3 \rightarrow P(O)R(OR')_2 + R'X \qquad (1)$$

species by alkyl transfer to phosphorus in a reaction between an alkyl halide and a trialkyl phosphite.[2–4] Analogous transformations which occur when certain organotransition-metal halides such as $CpFeX(CO)_2$,[5,6] CpNiX-

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Table I. Summary of NMR Data[a]

	^{1}H		^{31}P{^{1}H}		^{13}C{^{1}H}	
	δ [b]	J_{HP} [c]	δ [d]	J_{HP} [c]	δ [b]	J_{CP} [c]
$CpCoI_2[P(OMe)_3]$ (2)						
C_5H_5	5.30	0.8 (d)			87.17	
$P(OCH_3)_3$	3.87	10.7 (d)	132.5		56.53	8.2 (d)
$CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (3)						
C_5H_5	5.26				90.40	
$P(OCH_3)_3$	3.84	11.2 (d)	148.9	134 (t)	54.12	7.9 (d)
$P(O)(OCH_3)_2$	3.71	9.5, 2.0 (vt)	95.2	134 (d)	51.33	4.0 (d)

[a] Measured in $CDCl_3$. [b] Ppm downfield from $SiMe_4$. [c] Hz (multiplicity). [d] Ppm downfield from H_3PO_4.

$[P(OMe)_3]$[7] (X = halide), and $CpReBr_2(CO)_2$[8] are substituted for the alkyl halide lead to monophosphonate metal complexes. Several other variations which involve organometallic complexes have been reported.[9-11]

In the course of studies on the substitution chemistry of $CpCoI_2(CO)$ (1) we have found that while a simple exchange to yield $CpCoI_2[P(OMe)_3]$ (2) results from the reaction of 1 with 1 equiv of trimethyl phosphite, treatment with excess $P(OMe)_3$ produces a complex, $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (3), derived from an unprecedented double Michaelis–Arbuzov reaction. Because such transformations have not been previously reported, we have explored the systematics of this reaction as well as those of a series of novel related transformations. We find that complexes 1, 2, and 3 are transformed by various pathways into the trinuclear cobalt "supersandwich" $Cp_2Co_3[P(O)(OMe)_2]_6$ (4).[12] In contrast to previous syntheses these reactions proceed under mild conditions and involve air-stable reactants.

We report herein the results of our investigations into the substitution chemistry of complex 1, the formation of complex 3 via a double Michaelis–Arbuzov rearrangement, which includes a single-crystal X-ray diffraction study of 3 itself, and the facile preparation of the cobalt supersandwich complex.

Results and Discussion

Synthesis and Reactions. $(\eta^5\text{-}C_5H_5)CoI_2(CO)$ (1) reacts with $P(OMe)_3$ to yield a variety of products depending on reaction stoichiometry, temperature, and solvent. Figure 1 summarizes some of the transformations described below. As previously demonstrated by Heck[13] and King[14] the carbonyl group of complex 1 is highly labile. When 1 equiv of $P(OMe)_3$ is added to 1 in CH_2Cl_2 at ambient temperature, a gradual color change from violet to brown ensues with evolution of a gas (presumably CO). The brown-black monophosphite derivative is isolated as the sole metal-containing product of the reaction. Although complexes of the form $CpCoI_2L$, where L = N or P donor ligand, are well-known, complex 2 has not been previously reported. As indicated in Table I, which contains a summary of NMR data, the ^{31}P NMR spectrum of complex 2 consists of a broad absorption centered at δ 132.5 which is characteristic of a P(III) nucleus coordinated to a first-row element.[15] The ^{1}H NMR spectrum contains a C_5H_5 doublet at δ 5.30 and a methyl resonance centered at δ 3.87 of appropriate intensities (5:9). $^3J_{HP}$ for the Cp and methyl signals are 0.8 and 10.7 Hz, respectively. The ^{13}C NMR spectrum of complex 2 exhibits a cyclopentadienyl carbon resonance at δ 87.17 and a methyl carbon doublet centered at δ 56.53 ($^2J_{CP}$ = 8.2 Hz).

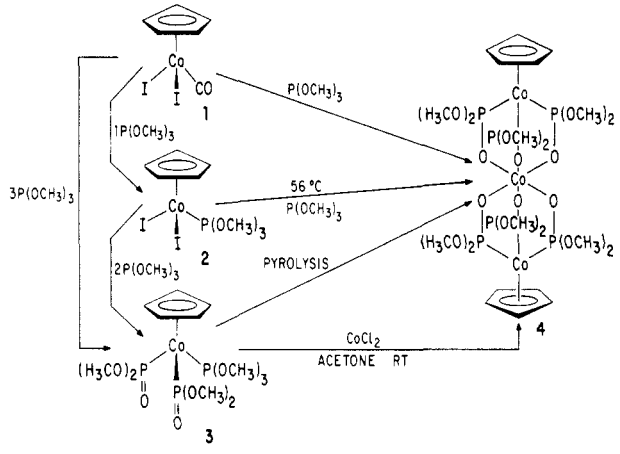

Figure 1. Reaction scheme of interconversions of complexes 1–4.

The addition of 3 or more equiv of $P(OMe)_3$ to complex 1 (CH_2Cl_2, 25 °C) causes a marked decolorization of the solution from deep violet to yellow which is complete within a matter of minutes. A bright yellow air-stable crystalline product is readily isolated. However, we observed different products depending upon solvent pretreatment and the extent of atmospheric exposure during workup. One product melts reproducibly at 108 °C while the other melts at 145 °C. On the basis of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, both complexes appeared to have the formula $(\eta^5\text{-}C_5H_5)Co[P(O)(OCH_3)_2]_2[P(OCH_3)_3]$. While the complex clearly contains Co(III), the various spectra do not unequivocably distinguish the two likely bonding modes: $MOP(OMe)_2$[16] and $M[P(O)(OMe)_2]$.[5,7-10,17,18] We subsequently found (vide infra) that the two complexes are the anhydrous and monohydrated forms of complex 3. The anhydrous form melts at 108 °C and is quite hygroscopic, although it is otherwise stable to atmospheric exposure. The monohydrate is neither air nor moisture sensitive and has the higher, 145 °C, melting point, undoubtedly because of lattice stablization afforded by the intermolecular hydrogen bonding of the water molecules.

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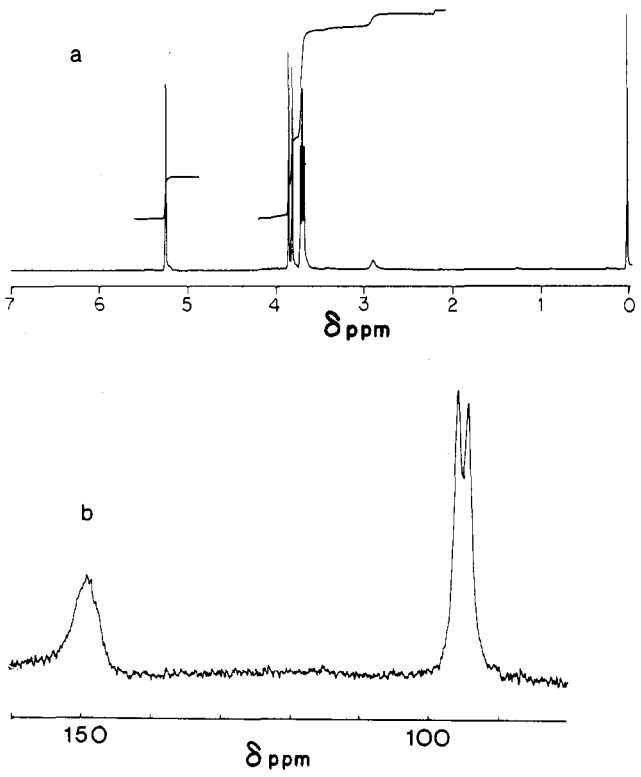

Figure 2. ^1H (a) and $^{31}P\{^1H\}$ (b) NMR spectra of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (**3**).

The use of rigorously anhydrous conditions yields the anhydrous form, but if no special precautions are exercised, the hydrated form often results.

The essential structural features of complex **3** are established by its NMR spectra, as listed in Table I. The ^{31}P NMR spectrum, as shown in Figure 2, consists of a broad, partially resolved triplet at δ 148.9 and a doublet centered at δ 95.29 ($^2J_{PP}$ = 134.4 Hz) arising from the phosphite and phosphonate phosphorus nuclei, respectively. The integrated intensities conform to the expected 1:2 ratio. Coupling with the ^{59}Co quadrupole moment may give rise to the broadened phosphite signal. The observed chemical shifts are in accord with those previously reported for $P(OMe)_3$ and $P(O)(OMe)_2$ ligands bound to transition metals.[17-19] Compare the shifts for complex **3** with those of $CpMo[P(O)(OMe)_2](CO)_2[P(OMe)_3]$,[17] δ 188.0 and 115.0, and $CpRu[P(O)(OMe)_2](CO)[P(OMe)_3]$,[18] δ 160 and 110 [$P(OMe)_3$ and $P(O)(OMe)_2$ signals, respectively, in each case]. Free trimethyl phosphite exhibits a resonance at δ 141[20] while nonmetallic phosphonates give rise to signals in the range δ 0–30.[21] Thus the change in chemical shift upon complexation is smaller for $P(OMe)_3$ than for the $-P(O)(OMe)_2$ group.

The ^1H NMR spectrum of complex **3**, as shown in Figure 2, contains a C_5H_5 resonance, a $P(OCH_3)_3$ doublet centered at δ 3.84, and a triplet at δ 3.71, in the expected 5:9:12 ratio of integrated intensities. The triplet resonance arises from the phosphate methyl protons. The observed splitting is invariant at 90, 220, and 250 MHz, and thus inequivalent $P(O)(OMe)_2$ groups, which could produce an apparent triplet, are precluded. Rather, the triplet signal is the AA′ portion of a $A_6XX'A'_6$ spectrum in which the phosphonate methyl protons are virtually coupled to both phosphonate phosphorus nuclei. The observed second-order spectrum results from a large coupling between the X and X′ (phosphonate phosphorus) nuclei. We have successfully simulated the observed pattern by using 2.0 and 9.5 Hz for $^5J_{HP}$ and $^3J_{HP}$, respectively. Variation of $^2J_{PP}$ between 100 and 150 Hz has negligible effect on the simulated pattern. The ^1H NMR parameters of complex **3** are entirely those reported for $CpCoX[P(O)(OMe)_2][P(OMe)_3]$, where X = I and CH_3.[10]

The cyclopentadienyl carbon nuclei give rise to a singlet at δ 90.40 while complex patterns centered at δ 54.12 and 51.33 are observed for the phosphite and phosphonate carbon atoms, respectively.

The formation of complex **3** is related to the classical Michaelis–Arbuzov transformation of a phosphite to a phosphonate by an alkyl halide reagent. The reaction occurs by initial addition of the alkyl halide to the phosphite to form a phosphonium salt which subsequently rearranges to yield a trialkyl phosphonate and the alternative alkyl halide.[2-4] In the reaction of complex **1**, $CpCoI_2(CO)$, with trimethyl phosphite the CpCoXI group, where X = I or $P(O)(OMe)_2$, may function analogously to the alkyl group of the alkyl halide as it coordinates a $P(OMe)_3$ molecule. In the presence of excess trimethyl phosphite, the reaction proceeds with successive liberation of two molecules of CH_3I via a double Michaelis–Arbuzov reaction as shown in equ 2. The required byproduct

$$CpCoI_2(CO) + 3P(OMe)_3 \rightarrow CpCo[P(O)(OMe)_2]_2[P(OMe)_3] + 2MeI + CO \quad (2)$$

methyl iodide is readily observed in the yellow reaction mixture by ^1H NMR spectroscopy. In the mechanism described above the final phosphite to coordinate should remain unchanged.

The formation of complex **3** via the Michaelis–Arbuzov rearrangement is not unlike reactions which occur when $CpNiX[P(OMe)_3]$(X = halide,[7] $CpFeCl(CO)_2$,[5] or $CpReBr_2(CO)_2$[8] react with trimethyl phosphite to produce organometallic monophosphonate complexes and alkyl halides. Note that in the case of $CpReBr_2(CO)_2$ only one Br atom is replaced by a phosphonate group. Apparently the steric requirements of the complex dictate the extent of phosphonate-for-halide replacement.

The formation of ethyl analogues of complexes **2** and **3** result from the treatment of complex **1** with triethyl phosphite. Complete transformation of complex **1** to $CpCo[P(O)(OEt)_2]_2[P(OEt)_3]$ proceeds at a rate slower than that of the trimethyl phosphite reaction, possibly because of the lower volatility of ethyl vs. methyl iodide. The physical and spectral properties of the ethyl derivatives are entirely in accord with those of the methyl congeners, complexes **2** and **3**.

Complexes **1**, **2**, and **3** are readily converted to the trinuclear cobalt "supersandwich" complex $Cp_2Co_3[P(O)(OMe)_2]_6$ (**4**). Complex **4** was initially prepared by Harder, Dubler, and Werner,[12] whose synthesis involved heating cobaltacene with $P(OCH_3)_3$ or $HP(O)(OCH_3)_2$ in a sealed tube at 140–150 °C for several days. Complexes **1**, **2**, and **3** are transformed into **4** under much less vigorous conditions. Heating $CpCoI_2(CO)$ (**1**) with excess $P(OMe)_3$ in CH_2Cl_2 produces a small amount of complex **4**, probably by the sequence **1** → **2** → **3** → **4** as depicted in Figure 1. When $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (**3**) is refluxed in acetone with 3 equiv of $P(OMe)_3$, the trinuclear complex is produced in 50% yield. Complex **4** is also formed (70% yield) from the reaction of complex **3** with 0.5 molar equiv of $CoCl_2$. Note that Michaelis–Arbuzov rearrangements are required for these reactions to proceed but are not

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Table II. Selected Distances (Å) and Angles (Deg) in $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]\cdot H_2O$

			Distances		
Co-P(1)	2.196 (1)	P(1)-O(3)	1.618 (2)	O(6)-C(4)	1.439 (3)
Co-P(2)	2.202 (1)	P(2)-O(4)	1.492 (3)	O(7)-C(5)	1.441 (3)
Co-P(3)	2.151 (1)	P(2)-O(5)	1.598 (2)	O(8)-C(6)	1.456 (3)
Co-C(10)	2.093 (2)	P(2)-O(6)	1.613 (2)	O(9)-C(7)	1.438 (3)
Co-C(11)	2.094 (2)	P(3)-O(7)	1.572 (2)	C(10)-C(11)	1.414 (3)
Co-C(12)	2.077 (2)	P(3)-O(8)	1.583 (2)	C(10)-C(14)	1.417 (3)
Co-C(13)	2.103 (2)	P(3)-O(9)	1.596 (2)	C(11)-C(12)	1.410 (3)
Co-C(14)	2.112 (2)	O(2)-C(1)	1.437 (3)	C(12)-C(13)	1.427 (3)
P(1)-O(1)	1.487 (2)	O(3)-C(2)	1.428 (3)	C(13)-C(14)	1.410 (3)
P(1)-O(2)	1.614 (2)	O(5)-C(3)	1.422 (3)	O-H(1)	0.75 (3)
				O-H(2)	0.80 (4)
O(1)····H(2)	2.03 (4)	O(4)····H(1)	2.03 (3)		
			Angles		
P(1)-Co-P(2)	91.87 (2)	O(7)-P(3)-O(8)	101.20 (9)	P(2)-O(5)-C(3)	123.7 (2)
P(1)-Co-P(3)	93.50 (2)	O(7)-P(3)-O(9)	99.15 (9)	P(2)-O(6)-C(4)	118.1 (2)
P(2)-Co-P(3)	95.67 (2)	O(8)-P(3)-O(9)	106.52 (9)	P(3)-O(7)-C(5)	126.5 (2)
Co-P(1)-O(1)	120.77 (7)	P(1)-O(2)-C(1)	118.16 (1)	P(3)-O(8)-C(6)	121.4 (2)
Co-P(1)-O(2)	104.45 (6)	P(1)-O(3)-C(2)	120.9 (2)	P(3)-O(9)-C(7)	123.0 (2)
Co-P(1)-O(3)	110.31 (7)	O(1)-P(1)-O(2)	110.94 (9)	C(11)-C(10)-C(14)	108.1 (2)
Co-P(2)-O(4)	116.77 (7)	O(1)-P(1)-O(3)	109.23 (9)	C(10)-C(11)-C(12)	108.3 (2)
Co-P(2)-O(5)	113.51 (7)	O(2)-P(1)-O(3)	98.86 (9)	C(11)-C(12)-C(13)	107.6 (2)
Co-P(2)-O(6)	103.50 (6)	O(4)-P(2)-O(5)	108.70 (9)	C(12)-C(13)-C(14)	108.1 (2)
Co-P(3)-O(7)	122.47 (7)	O(4)-P(2)-O(6)	110.89 (9)	C(13)-C(14)-C(10)	107.9 (2)
Co-P(3)-O(8)	107.35 (7)	O(5)-P(2)-O(6)	102.48 (10)	H(1)-O-H(2)	109 (3)
Co-P(3)-O(9)	118.09 (6)				
P(1)-O(1)···H(2)	144 (1)	P(2)-O(4)···H(1)	136 (1)		
O(1)···H(2)-O	169 (4)	O(4)···H(1)-O	171 (3)		

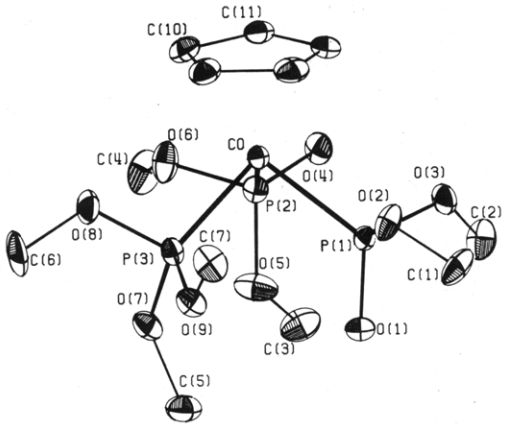

Figure 3. A perspective view of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]\cdot H_2O$ (**3**). The vibrational ellipsoids are drawn at the 50% level here and in subsequent figures. The water molecule and the hydrogen atoms have been omitted for clarity. Atom labels are included.

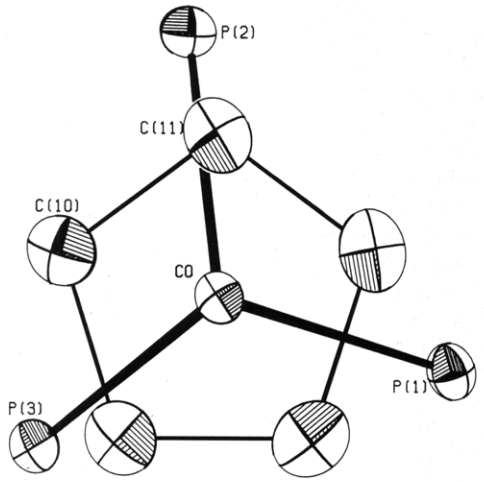

Figure 4. A perspective view normal to the cyclopentadienyl plane.

necessary in the following transformation. A solid sample of $CpCo[P(O)(OMe_2]_2[P(OMe)_3]$ (**3**) is smoothly converted to $Cp_2Co_3[P(O)(OMe)_2]_6$ (**4**) by simply heating the mononuclear complex above its melting point. The anhydrous form of complex **3** melts at 108 °C and then recrystallizes as the yellow "supersandwich" complex. A gas, presumably a mixture of trimethyl phosphite and a cyclopentadiene-derived product, possibly dicyclopentadiene, is evolved as the complex solidifies. Although the volatile products were not completely characterized, the pyrolysis reaction appears to be a shown in reaction 3. The hydrated form of

$$3CpCo[P(O)(OMe)_2]_2[P(OMe)_3] \rightarrow Cp_2Co_3[P(O)(OMe)_2]_6 + 3P(OMe)_3 + 0.5C_{10}H_{10} \quad (3)$$

3 melts at 145 °C and remains a liquid up to approximately 170 °C. At this temperature gas evolution is observed and the material solidifies as yellow crystals. The yield of complex **4** from these thermolysis reactions is approximately 70–80%. The reaction of the hydrated form of complex **3** to **4** appears to be a thermal dehydration followed by the transformation shown in reaction 3.

Description of the Structure of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]\cdot H_2O$ (3). The crystal structure of **3** consists of the packing of four molecules linked by hydrogen-bound water molecules. The molecules are well separated, having no significant close intermolecular contacts other than those associated with the bridging water molecule. Bond distances and angles are compiled in Table II. Figure 3 contains a representation of the unsolvated molecule and includes the atom labels which are used in this discussion. The piano stool conformation of the molecule is emphasized in the depiction of the inner coordination sphere shown in Figure 4. The intermolecular hydrogen bonding involving the water of hydration is illustrated in Figure 5.

The observed molecular structure confirms the spectroscopic characterization of complex **3** described above. The molecule contains a Co(III) center surrounded by an unremarkable η^5-cyclopentadienyl ring, a trimethyl phosphite ligand, and two phosphorus-bound dimethyl phosphonate groups. As shown in Figures 3 and 4 the

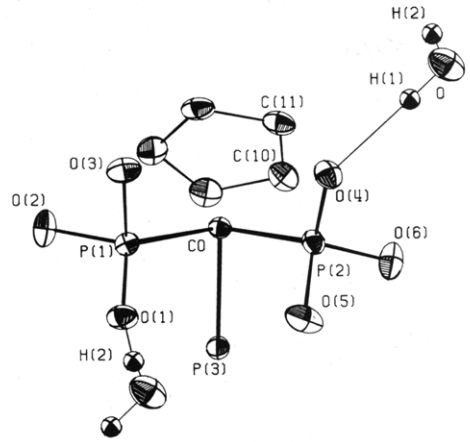

Figure 5. A perspective view of the molecule showing the molecule of hydration. A number of atoms have been omitted for clarity. Two water molecules have been included to illustrate the intermolecular hydrogen bonding.

coordination geometry is pseudooctahedral with the η^5-C_5H_5 ligand occupying three facial sites. The P–Co–P angles approximate the octahedral value as they range from 91.9 to 95.7 (2)°. The water molecule of complex **3** bridges the unique phosphonate oxygen atoms of adjacent molecules. At 2.773 and 2.828 (3) Å, the O–O separations of the hydrogen-bonding fragments are normal as are the near linear (ca. 170°) but unsymmetrical O–H···O arrays.[22] These latter values are based upon refined hydrogen atom positions. Although these atoms were readily located and refined smoothly, the derived O–H bond distances, 0.75 (3) and 0.80 (4) Å, are substantially shorter than expected. In the absence of neutron diffraction data, these values must be regarded with caution.

Only a few complexes which incorporate a phosphonate ligand have been structurally characterized.[23-29] The best comparisons can be drawn between the structural parameters of complex **3** and those of $CpCr[P(O)(OMe)_2](CO)_2[P(OMe)_3]$ (**5**), the only other structurally characterized complex which contains both phosphonate and phosphite ligands.[23] In both complexes the M–P(phosphite) separations (2.267 (3) and 2.151 (1) Å, Cr and Co) are shorter than the respective M–P(phosphonate) distances, 2.360 (3) and 2.199 (1) Å. These differences must be electronic in origin because the steric demand of $P(O)(OMe)_2$ and $P(OMe)_3$ ligands appear comparable. The phosphonate phosphorus atom should be a much poorer σ donor than its phosphite counterpart on the basis of the former atom's higher oxidation state. This σ term apparently dictates the M–P bond length but contributions from π withdrawal must also be present. Preliminary NQR experiments reveal that complex **3** closely resembles the cobalt(I) species $CpCo(CO)_2(HgCl_2)$ and indicate that the phosphonate ligand may be similar to carbon monoxide in its donor–acceptor properties.[30] Thus, in complex **5** competition between the CO and $P(O)(OMe)_2$ ligands accentuates the M–P bond length difference with respect to that of complex **3**, in which analogous π competition is absent. The longer metal-bonding radius and the presence of an additional ligand in the Cr complex undoubtedly also contribute to the observed differences between complexes **3** and **5**.

The observed orientation of the P=O vectors in complex **3** probably results from hydrogen-bonding considerations rather than from bonding requirements within the complex itself. The P=O bond distances, at 1.487 and 1.492 (2) Å, are only marginally longer than that reported for the Cr complex **5**, 1.478 (6) Å, despite the absence of hydrogen bonding in the latter complex. There is, in fact, only a minor deviation in this separation in coordinated phosphonate groups, regardless of secondary oxygen interaction. These distances range from 1.44 (7) to 1.53 (2) Å, for $HgCl[P(O)(OEt)_2]$[28] and $Os_5C(H)[OP(OMe)OP(OMe)_2](CO)_{13}$,[25] respectively. The mercury complex shows a strong O—Hg interaction while an osmium atom is clearly oxygen bound in the carbide cluster. Of the reported phosphonate complex structures only the Cr complex **5** exhibits no secondary oxygen interactions although its P=O separation is bracketed by values of the oxygen-coordinated complexes.

Table III. Summary of X-ray Diffraction Data

complex	$(\eta^5\text{-}C_5H_5)Co[P(O)(OCH_3)_2]_2[P(OCH_3)_3]\cdot H_2O$
formula	$C_{12}H_{28}CoO_{10}P_3$
fw	484.21
a, Å	7.872 (1)
b, Å	15.105 (2)
c, Å	16.517 (2)
β, deg	91.819 (1)
V, Å^3	1963.0 (8)
Z	4
ρ_{calcd}, g cm^{-3}	1.638
space group	C_{2h}^5—$P2_1/c$ (no. 14)
cryst dimens, mm	0.20 × 0.26 × 0.26
temp, °C	-100
radiatn	Mo Kα (0.710 69 Å) from graphite monochromator
μ, cm^{-1}	12.01
transmissn factors	0.928–0.993; av 0.967
2θ limits, deg	4.0–55.0
total no. of observns	4496
unique data, $F_o^2 > 3\sigma(F_o^2)$	3238
final no. of variables	243
R	0.031
R_w	0.034
error in observn of unit wt	1.54 electrons

Experimental Section

All solvents were of reagent grade, or better, and were used as received. Alkyl phosphites were obtained from ROC-RIC and were used without further purification. The complex $CpCo(CO)_2$ was obtained from Pressure Chemical and used as received.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM-250 spectrometer. $CDCl_3$ was the solvent for all NMR spectra. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (δ 0.0) while ^{31}P shifts are referenced downfield to 85% H_3PO_4 (external). ^1H NMR spectra were simulated by using an ITRCL program.

Mass spectra were obtained by using a Du Pont 21-492B mass spectrometer. Microanalyses were performed by MicroAnalysis, Wilmington, DE. All melting points were obtained by using a

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Table IV. Positional and Thermal Parameters for the Atoms of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]\cdot H_2O$

Atom	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
CO	0.28602(4)	0.27488(2)	0.06806(2)	1.17(1)	1.26(1)	1.06(1)	-0.06(1)	0.03(1)	-0.02(1)
P(1)	0.06417(9)	0.31511(5)	0.14915(4)	1.42(2)	1.50(2)	1.05(2)	-0.10(2)	0.14(2)	-0.02(2)
P(2)	0.34397(9)	0.15612(5)	0.14112(4)	1.38(2)	1.49(3)	1.38(2)	0.16(2)	-0.11(2)	0.08(2)
P(3)	0.11228(9)	0.21012(5)	-0.01581(4)	1.48(2)	1.41(3)	1.29(2)	0.11(2)	-0.15(2)	-0.17(2)
O(1)	-0.0635(2)	0.2362(1)	0.1628(1)	1.62(7)	2.09(8)	2.11(8)	-0.57(7)	0.37(6)	-0.18(7)
O(2)	0.0223(2)	0.4103(1)	0.1130(1)	2.46(8)	1.75(8)	1.59(7)	0.73(7)	0.61(6)	0.46(7)
O(3)	0.1652(2)	0.3465(1)	0.2357(1)	2.40(8)	2.28(8)	1.12(7)	-0.61(7)	-0.01(6)	-0.20(7)
O(4)	0.4417(2)	0.1699(1)	0.2169(1)	1.84(8)	2.38(9)	1.37(7)	0.08(7)	-0.26(6)	0.06(7)
O(5)	0.1807(3)	0.0971(1)	0.1584(1)	2.19(8)	2.84(9)	2.68(9)	-0.89(8)	-0.68(7)	1.49(7)
O(6)	0.4465(3)	0.0942(1)	0.0806(1)	3.16(9)	1.99(8)	1.67(7)	1.06(8)	0.11(7)	0.04(7)
O(7)	0.0366(2)	0.1150(1)	0.0008(1)	1.90(8)	1.35(7)	2.31(8)	-0.09(7)	-0.21(7)	-0.14(7)
O(8)	0.2108(2)	0.1927(1)	-0.0984(1)	2.15(8)	2.92(9)	1.27(7)	0.14(8)	0.05(6)	-0.63(7)
O(9)	-0.0589(2)	0.2606(1)	-0.0419(1)	1.64(7)	1.68(8)	1.91(7)	0.11(7)	-0.38(6)	0.20(7)
O	0.7759(3)	0.1368(2)	0.2678(1)	1.85(8)	3.57(10)	3.00(9)	-0.30(8)	-0.22(8)	1.23(8)
C(1)	-0.1103(4)	0.4334(2)	0.1364(2)	2.3(1)	2.1(1)	2.8(1)	0.81(10)	1.09(10)	0.4(1)
C(2)	0.1413(4)	0.2953(2)	0.3071(2)	3.3(1)	2.6(1)	1.2(1)	0.33(11)	0.03(10)	0.3(1)
C(3)	0.1546(4)	0.0532(2)	0.2331(2)	2.4(1)	2.4(1)	3.1(1)	-0.21(11)	0.42(11)	0.9(1)
C(4)	0.5120(4)	0.0108(2)	0.1108(2)	3.8(1)	1.9(1)	2.8(1)	1.15(12)	0.79(12)	0.3(1)
C(5)	-0.1228(4)	0.0967(2)	0.0376(2)	2.2(1)	1.8(1)	3.3(1)	-0.54(10)	0.02(11)	0.0(1)
C(6)	0.1260(4)	0.1342(2)	-0.1676(2)	3.6(1)	3.6(1)	1.6(1)	0.39(13)	-0.43(11)	-1.2(1)
C(7)	-0.0616(4)	0.3302(2)	-0.0715(2)	2.7(1)	2.0(1)	2.0(1)	0.31(11)	-0.46(10)	0.3(1)
C(10)	0.3052(4)	0.2837(2)	0.0000(2)	1.6(1)	2.3(1)	1.9(1)	-0.12(10)	0.08(8)	0.1(1)
C(11)	0.3465(3)	0.3009(2)	0.0825(2)	1.3(1)	2.4(1)	2.0(1)	-0.45(9)	0.08(9)	0.1(1)
C(12)	0.4509(4)	0.3746(2)	0.1071(2)	1.9(1)	2.4(1)	2.0(1)	-1.07(10)	0.36(9)	-0.5(1)
C(13)	0.3542(4)	0.4052(2)	0.0381(2)	1.9(1)	1.5(1)	3.0(1)	-0.27(10)	0.69(10)	0.4(1)
C(14)	0.3874(4)	0.3488(2)	-0.0275(2)	2.0(1)	2.5(1)	1.7(1)	-0.51(11)	0.22(9)	0.5(1)
H(1)	0.603(4)	0.140(2)	0.260(2)	3.4(8)					
H(2)	0.833(5)	0.171(3)	0.245(2)	5.2(10)					

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:

EXP[-1/4(B(1,1) X H X H X A* X A* + ... + 2 X B(2,3) X K X L X B* X C*)].

Melt-Temp heating block and are not corrected. The molecular weight determination was made with an Hitachi Perkin-Elmer 115 vapor pressure osmometer, using CH_2Cl_2 solutions referenced to a calibration curve prepared with standard solutions of benzil.

$CpCoI_2(CO)$ was prepared according to standard literature methods.[13,14]

1:1 Reaction, $CpCoI_2(CO) + P(OMe_3)$. $CpCoI_2[P(OMe)_3]$ (2). Trimethyl phosphite (0.3 mL, 2.48 mmol) was added dropwise, as CH_2Cl_2 solution, to a 50-mL solution of 1, $CpCoI_2(CO)$ (1.0 g, 2.48 mmol), in the same solvent. Gas evolution occurred immediately, with a concomitant color change from dark purple to dark brown. After the solution was left standing for 60 min, 30 mL of heptane was added and the methylene chloride removed under reduced pressure at 25 °C to yield 0.90 g (73%) of brown, air-stable crystals of $CpCoI_2[P(OMe)_3]$ (2). The complex decomposes above 140 °C without melting and is soluble in polar organic solvents but insoluble in hydrocarbons or diethyl ether. Anal. Calcd for $C_8H_{16}CoO_3I_2P$: C, 19.07; H, 3.18; P, 6.15. Found: C, 18.92; H, 3.04; P, 6.10. Mass spectrum: 375.2, $[CpCoI[P(OMe)_3]]^+$; 251.0, $[CpCoI]^+$.

1:3 Reaction, $CpCoI_2(CO) + P(OMe)_3$. $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (3). A solution of $P(OMe)_3$ (0.61 mL, 5.04 mmol) in 20 mL of methylene chloride was added dropwise to a solution of 0.67 g (1.68 mmol) of complex 1 in the same solvent (150 mL). After approximately 20 min, a color change from purple to bright yellow, with accompanying gas evolution, was complete. Filtration, after the mixture was stirred for several hours, removed a small amount of brown residue. An orange oil resulted from evaporation of the solvent at 25 °C and reduced pressure. Extraction of this oil with 50 mL of acetone dissolved 3 and left a small amount of $Cp_2Co_3[P(O)(OMe)_2]_6$ (4), as an insoluble product. Addition of 100 mL of xylene to the acetone solution, followed by slow evaporation at 25 °C, produced 0.33 g (43%) of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]\cdot H_2O$ (3) as yellow needles, which were washed with hexane (2 × 50 mL) and dried in the air; mp 145 °C. Anal. Calcd for $C_{12}H_{28}CoO_{10}P_3$: C, 29.77; H, 5.83. Found: C, 29.78; H, 6.16. Mol. weight: calcd, 473.24; found, 453. The complex is soluble in acetone, CH_2Cl_2, and other polar organic solvents but insoluble in aliphatic hydrocarbons.

The melting point varied between 108 and 145 °C, depending upon the degree of hydration of this compound. The anhydrous form of 3 can be prepared by taking precautions to work with dry solvents and in a dry atmosphere. The melting point of anhydrous 3 is 108 °C. Intermediate melting points are believed to result from intermediate stages of hydration.

$Cp_2Co_3[P(O)(OMe)_2]_6$ (4). Method A. A mixture of complex 1 (0.50 g, 1.24 mmol) and trimethyl phosphite (0.15 mL, 1.24 mmol) in 30 mL of acetone was stirred for 1 h at ambient temperature. An additional 0.30 mL of $P(OMe)_3$ (3.72 mmol total) was then added. The resulting solution was degassed by N_2 purge

and subsequently refluxed for 2 h. The yellow brown solid which formed on cooling was shown to be a mixture of the desired product and cobalt oxide. Extraction with CH_2Cl_2 yielded a yellow solution from which 0.23 g (58%) of $Cp_2Co_3[P(O)(OMe)_2]_6$ (4) was isolated on concentration. The complex was identified by comparison of its spectral features, including mass spectrum, with those previously reported.[12]

Method B. A solid sample (0.040 g, 0.086 mmol) of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]$ (3) in a 5-mm o.d. tube was slowly heated in an oil bath. The complex melted at 138 °C and vigorous bubbling immediately ensued. Crystallization occurred at 145 °C but the sample was heated to 170 °C to ensure complete reaction. After the yellow solid cooled to room temperature and was washed with acetone to remove unreacted starting material, 0.022 g (0.026 mmol, 79%) of complex 4 was collected.

Method C. A mixture of anhydrous $CoCl_2$ (0.012 g, 0.09 mmol) and 3 (0.083 g, 0.18 mmol) was dissolved in 10 mL of acetone at ambient temperature. Yellow crystals of the product resulted within 30 min. After the solution was left standing overnight, 0.030 g (0.09 mmol, 35% based on Co) of yellow crystals of complex 4 was collected.

X-ray Data Collection and Structure Solution and Refinement. Crystals of $CpCo[P(O)(OMe)_2]_2[P(OMe)_3]\cdot H_2O$ (3) suitable for diffraction studies were obtained by slowly evaporating a 1:1 benzene–xylene solution. The crystal chosen was encapsulated in a glass capillary under an atmosphere of N_2. Preliminary photographic investigations indicated the crystal system, space group, and approximate cell dimensions. These and other crystallographic data are summarized in Table III. The crystal was then placed on a Syntex P3 diffractometer and shown to be suitable for diffraction on the basis of ω scans which showed the peak width at half-height to be ca. 0.16° at −100 °C. The cell parameters were then refined on the basis of 48 computer-centered reflections chosen from diverse regions of reciprocal space.

Intensity data were collected by using the ω-scan technique (variable scan range, 4.0–10.0° min^{-1}; total background time equals scan time). The intensities of four standard reflections were measured every 200 reflections. No significant deviations in the intensities of these standards were observed. The intensities of several reflections were measured at 10° increments about the diffractor vector. Empirical corrections for absorption thereby derived were subsequently applied. The data were processed by using counting statistics and a p value of 0.02 to derive standard deviations.[31]

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of programs supplied by the Enraf-Nonius Corp.[32] The cobalt and phosphorus atoms were located by direct methods (Multan series). The positions of the remaining nonhydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinements. In the least-squares refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are respectively the observed and calculated structure amplitudes and where $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from the compilations of Cromer and Waber.[33a] Anomalous dispersion terms used were those of Cromer.[33b] After convergence of the nonhydrogen portion of the molecule in which the atoms were allowed to vibrate anisotropically, the hydrogen atoms were located in a difference Fourier synthesis. The hydrogen atoms of the water molecule were included as isotropic bodies in subsequent refinements in order to elaborate the hydrogen bonding in which they are involved. The remainder of the hydrogen atoms were placed in idealized positions by using a C–H distance of 0.95 Å and included as fixed contributions ($B_H = 4.0$). Least-squares refinement then converged to values of $R = 0.031$ and $R_w = 0.034$ where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o]^{1/2}$. A number of peaks on the order of 0.3 e $Å^{-3}$ remain in a final difference Fourier synthesis.

The final positional and thermal parameters of the refined atoms appear in Table IV. Tables of hydrogen atom positions and structure amplitudes (observed and calculated) are available.[34,35]

Acknowledgment. T.H.T. wishes to thank Mr. L. Lardear for skilled technical assistance. T.B.B. thanks Dr. R. Crecely for help with the NMR spectra.

Registry No. 1, 12012-77-0; 2, 79018-67-0; $3\cdot H_2O$, 79255-76-8; 4, 59113-93-8.

Supplementary Material Available: A table of idealized hydrogen atom positions and a listing of the observed and calculated structure amplitudes (25 pages). Ordering information is given on any current masthead page.

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(33) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

(34) See paragraph at end of paper regarding supplementary material.

(35) After acceptance of this paper we became aware of a report of 3 [Werner, H., Juthani, B. (*J. Organomet. Chem.* **1981**, *209*, 211)] prepared by a somewhat different route.