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Arbusov Rearrangement Involving $(\eta^5\text{-}C_5H_5)Co(dppe)I^+$ and $P(OCH_3)_3$. A ^1H and ^{31}P NMR Study of the Mechanism Leading to the Formation of an Organometallic Phosphonate Complex

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Abstract: The Arbusov reaction, in which an alkyl halide converts an alkyl phosphite to a phosphonate, can also occur with a transition-metal halide complex in place of the alkyl halide. Thus, the previously unreported complex $[(\eta^5\text{-}C_5H_5)Co(dppe)I]X$, (**1**), where X = I^- and BF_4^- and dppe = 1,2-bis(diphenylphosphino)ethane, undergoes the Arbusov reaction with $P(OCH_3)_3$ to produce $[(\eta^5\text{-}C_5H_5)Co(dppe)P(O)(OCH_3)_2]^+$, (**2**). The reaction is well suited for a mechanistic study of the Arbusov rearrangement involving an organometallic complex. According to the ^1H and ^{31}P NMR spectra, the reaction progresses by the equilibration of $P(OCH_3)_3$ and **1** to produce $\{(\eta^5\text{-}C_5H_5)Co(dppe)[P(OCH_3)_3]\}^{2+}$ (**3**). **3** is a significant intermediate complex that is unequivocally identified by its high-field ^1H and ^{31}P spectrum. The association of I^- probably with the methyl groups of the coordinated $P(OCH_3)_3$ molecule results in the actual Arbusov rearrangement to yield **2** and CH_3I ($k_{obsd} = 1.5 \times 10^{-2}$ L mol^{-1} s^{-1} at 16 °C). Comparison of this transition-metal-based Arbusov reaction with the classical reaction is given along with some possible conditions that optimize the likelihood of an Arbusov rearrangement occurring in a transition-metal halide complex.

The classical Arbusov reaction (also known as the Michaelis–Arbusov reaction) involves the attack of an alkyl halide on an alkyl phosphite to produce a phosphonate ester. The smooth conversion, summarized by reactions 1 and 2, has been shown to progress through a quasi-phosphonium ion, which is rarely isolated.[1]

$$R'X + (RO)_3P \rightarrow [R'P(OR)_3]^+X^- \qquad (1)$$

$$[R'P(OR)_3]^+X^- \rightarrow R'P(O)(OR)_2 + RX \qquad (2)$$

The Arbusov reaction has a broad application in organophosphorus chemistry. However, evidence showing that the Arbusov rearrangement also takes place with transition-metal complexes containing one or more metal–halogen bonds in place of R′X is rapidly accumulating.[2-8] The reaction may be far more widespread than is currently recognized. From a synthetic point of view, the Arbusov rearrangement is an effective method for synthesizing metal-to-phosphonate bonds. However, it can also be an unwanted and complicating reaction whenever certain metal–halide complexes and alkyl phosphites are combined.

The mechanism of the Arbusov reaction in which a transition-metal–halide complex functions in place of the alkyl halide (R′X) in reaction 1 has not been investigated. In the reaction of $CpCoI_2(CO)$ with excess $P(OCH_3)_3$, it appears that $CpCoI_2[P(OCH_3)_3]$ may initially form.[7,9] This compound subsequently converts through a series of Arbusov rearrangements to $CpCo[P(O)(OCH_3)_2]_2[P(OCH_3)_3]$ with the formation of $2CH_3I$. The multistep process apparently occurring in this reaction makes the system a poor candidate for an early study. It is more desirable to employ a coordinately saturated transition-metal center in which only one metal–halogen bond is present. Such a complex approximates the function of the alkyl halide (R′X) in reaction 1.

A series of previously unreported complexes of the type $[CpCoP_2I]^+$, where P_2 = ditertiary phosphine, has the desired similarity to an alkyl halide. The present paper describes the intermediate species and probable mechanism for the reaction of $[CpCo(dppe)I]^+$ with $P(OCH_3)_3$. The products, $\{CpCo(dppe)[P(O)(OCH_3)_2]\}^+$ and CH_3I, form from the Arbusov rearrangement. Comparison of this reaction with the classical Arbusov reaction suggests some guidelines on the conditions under which Arbusov chemistry might occur with transition-metal halide complexes.

Experimental Section

Reagent grade solvents were used without further purification. The phosphine ligands from commercial sources and $CpCo(CO)_2$ (Strem) were used as received. $CpCoI_2(CO)$ was prepared according to literature methods.[10,11]

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM-250 high-field FT spectrometer. ^1H NMR chemical shifts are reported relative to internal $(CH_3)_4Si$ ($\delta = 0.0$), while positive ^{31}P NMR shifts are referenced downfield to 85% H_3PO_4 (external). ^{31}P NMR spectral simulations were obtained by using the ITRCAL program on a Nicolet 1080 computer.

$[(\eta^5\text{-}C_5H_5)Co(dppe)I]I$ (1). dppe (1.074 g, 4.28 mmol) was dissolved in C_6H_6 and added to a 100-mL C_6H_6 solution of $CpCoI_2(CO)$ (1.739 g, 4.28 mmol). Gas evolution accompanied by a change in color from purple-black to brown occurred immediately upon mixing. After stirring the solution for several minutes, a microcrystalline brown precipitate formed. After several hours, the reaction solution was filtered. The resulting brown solid was washed with diethyl ether (2 × 50 mL) and hexanes (2 × 50 mL) and dried under vacuum to yield 3.05 g of **1** (91% based on $CpCoI_2(CO)$). The complex was recrystallized from chloroform/heptane (60/40 (v/v)) to produce dark brown crystals [mp 201 °C dec]. The complex is soluble in chloroform, methylene chloride, and acetone. Anal. Calcd for $C_{31}H_{29}CoP_2I_2$: 47.98, C; 3.74, H; 7.59, Co; 32.71, I. Found: 48.35, C; 3.82, H; 7.64 Co; 32.32, I. The BF_4^- salt of **1** was prepared by the addition of $AgBF_4$ to a $CHCl_3$ solution of **1**. After filtering the solution to remove the AgI, the dark brown solution was evaporated to dryness, and the residue purified as described for **1**.

$[(\eta^5\text{-}C_5H_5)Co(dppe)(P(O)(OCH_3)_2)]I$ (2). $P(OCH_3)_3$ (0.400 g, 3.23 mmol) was added to $[CpCo(dppe)I]I$ (2.504 g, 3.23 mmol) dissolved in 75 mL of chloroform. The brown solution immediately darkened and

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[9] Abbreviations: $\eta^5\text{-}C_5H_5$, Cp; 1,2-bis(diphenylphosphino)ethane, dppe.

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Table I. $^{31}P\{^1H\}$ and ^1H (0-7 ppm) NMR Chemical Shifts and Coupling Constant (Hz) Data in $CDCl_3$[a]

nucleus	ppm: $[CpCo(dppe)I]I$ (1)	$\{CpCo(dppe)[P(OCH_3)_3]\}^{2+}$ (3)	$\{CpCo(dppe)[P(O)(OCH_3)_2]\}I$ (2)
$^1H^{a,b}$			
η^5-C_5H_5	5.57	6.06	5.50
$(CH_2)_2$	3.27-3.35 (b m)[d]	3.07 (b)[d] 3.72-3.80 (m)[d]	2.69 (b)[d] 3.72-3.80 (m)[d]
$P(OCH_3)_3$		3.42 ($^3J_{HP} = 11.6$)	
$P(O)(OCH_3)_2$			2.82 ($^3J_{HP} = 11.1$)
$^{31}P\{^1H\}^c$			
dppe	80.91	75.65 (d)[d] ($^2J_{PP} = 90.3$)	83.2[e]
$P(OCH_3)_3$		125.34 (t)[d] ($^2J_{PP} \approx 88$)	
$P(O)(OCH_3)_2$			86.1 ($^2J_{PP} = 91.8$)[e]

[a] Phenyl region data are not given. [b] Referenced to internal Me_4Si. [c] Referenced downfield to external 85% H_3PO_4. [d] b = broad, d = doublet, t = triplet, m = multiplet. [e] From simulation of the AB_2 pattern. Coupling is between the phosphonate and the equivalent dppe phosphorus nuclei.

became momentarily turbid. After stirring the solution for several minutes, it turned clear orange-yellow. Removal of the solvent under reduced pressure at 35 °C produced a bright yellow solid, which was washed with diethyl ether (2 × 50 mL) and dried under reduced pressure [2.048 g (84% yield); mp. 160 °C dec]. The complex is soluble in methylene chloride, acetone, and methanol. The same product is obtained when the reaction is conducted in methanol. Anal. Calcd for $C_{33}H_{35}CoP_3O_3I$: 52.27, C; 4.62, H; 7.60, Co; 12.19, P; 16.75, I. Found: 52.55, C; 4.64, H; 7.53, Co; 12.15, P; 16.51, I.

Kinetics Studies. In order to determine the phosphite dependence of the conversion of **1** to **2**, we conducted three independent experiments in which the molar ratios of $[CpCo(dppe)I]I$ to $P(OCH_3)_3$ were 1:1, 1:2, and 1:3, respectively.

In a typical experiment, a standard solution of $[CpCo(dppe)I]I$ (0.6576 g, 0.848 mmol, 1.696×10^{-2} M) was prepared in 5 mL of solvent (a mixture of $CDCl_3$ and 1% Me_4Si). A 0.5-mL (8.48×10^{-5} mol) sample of this stock solution was transferred to an NMR tube by using a Hamilton microliter syringe. A reference spectrum was then recorded. The tube was removed, and the required amount of freshly distilled $P(OCH_3)_3$ was added with a microliter syringe. With the use of a 32K memory block, successive spectra were recorded typically at 60, 100, 150, 200, 300, 500, 800, and 1200 s after mixing. Several reactions were monitored for as long as 4260 s to ensure that no further changes occurred. These times are accurate to within ±3 s, which was the time required for the data acquisition. Kinetic runs were made with the sample and probe at 16 ± 1 °C, 10 ± 1 °C, and 0 ± 1 °C. The reaction shows considerable temperature dependence, but Arrhenius data were not calculated. The reaction order was the same at these three temperatures. After each experiment, the NMR tube and contents were weighed to give an additional measure of the amount of phosphite added.

A similar series of NMR experiments was conducted with constant [**1**] in the presence of variable amounts of $(C_4H_9)_4NI$ (1:1, 1:2, and 1:3 molar ratios). Twenty microliters of $P(OCH_3)_3$ was added in each case to initiate the reaction. Because 2 equiv of I^- are already present from **1** after the first step of the reaction, the effective [I^-] is increased in this series of experiments by about 50%, 100%, and 150%.

The relative concentrations of $\{CpCo(dppe)[P(O)(OCH_3)_2]\}^+$, $\{CpCo(dppe)[P(OCH_3)_3]\}^{2+}$, and $[CpCo(dppe)I]^+$ can be determined by integration of the ^1H NMR resonance lines due to Cp. The ^1H NMR intensities in successive spectra were standardized from the integrated intensity of the Me_4Si. The overall reaction was found to be independent of [I^-] but dependent on [$P(OCH_3)_3$]. A second-order plot of 1/[**1**] vs. time was constructed for the reaction in which [**1**] = [$P(OCH_3)_3$]. d[**1**]/dt is dependent on both [$P(OCH_3)_3$] and [**1**]. The slope of the line allows computation of the observed rate constant k_{obsd} at a given temperature. These plots are entirely reproducible. However, difficulties can be encountered in shimming the magnet in the time available. Shimming errors distort the integration of the lines. Practice and luck were needed to perform this operation effectively.

The kinetics of d[**1**]/dt can be obtained from the dppe signal of **1** in the $^{31}P\{^1H\}$ NMR spectrum. The simple line intensity was used, but the results are somewhat less accurate than the ^1H NMR data because of the lack of an internal standard in the solution and the longer T_1 of ^{31}P compared to that of ^1H. The $^{31}P\{^1H\}$ NMR spectrum used to identify the intermediate complex (**3**) was taken in $CDCl_3$ at 16 °C over a 200-ppm window. The spectrum was recorded 35 s after mixing 2 mL of the stock solution of **1** with 3 equiv of $P(OCH_3)_3$, following a single 90° pulse.

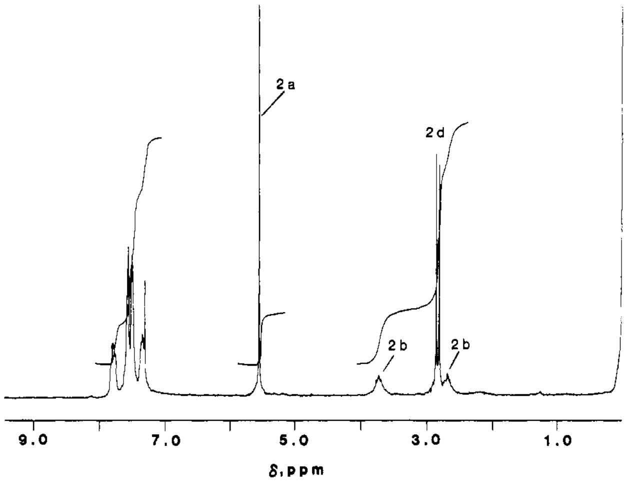
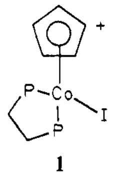


Figure 1. 250-MHz ^1H NMR spectrum of $CpCo(dppe)[P(O)(OCH_3)_2]I$ (**2**) in $CDCl_3$. Spectral assignments are keyed to Table I.

Results

Synthesis, Reactions, and Spectra. The reaction of dppe with $CpCoI_2(CO)$ in benzene yields the monomeric salt $[CpCo(dppe)I]I$ (**1**). This complex exhibits a number of ligand substitution reactions owing to the lability of the coordinated iodide ion. Some of these reactions will be described elsewhere.[12] In the reaction of **1** as either the I^- or BF_4^- salt with $P(OCH_3)_3$, Co–I bond cleavage occurs according to the color change of the solution from dark brown to yellow. $CHCl_3$ and CH_3OH are equally good solvents for this reaction. Rather than the simple monophosphite-substituted complex, the major product is $CpCo(dppe)[P(O)(OCH_3)_2]X$ (**2**), which arises from an Arbusov rearrangement at the phosphorus site. The net reaction is given by reaction 3.



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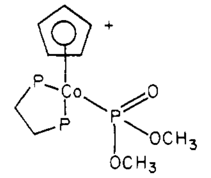

2

$$[CpCo(dppe)I]^+ + P(OCH_3)_3 \rightarrow \{CpCo(dppe)[P(O)(OCH_3)_2]\}^+ + CH_3I \quad (3)$$

The 250-MHz ^1H NMR spectra of **1** and **2** (as indicated in Table I) consist of the essential features of these complexes. The

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[12] Landon, S. J.; Brill, T. B., to be published.

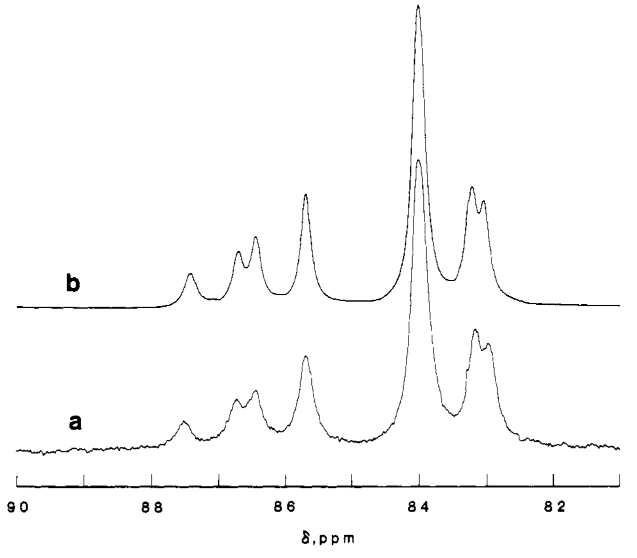

Figure 2. (a) 101.27-MHz ^{31}P NMR spectrum of **2** in $CDCl_3$ (16 scans). (b) Simulation of (a) using a AB_2 pattern.

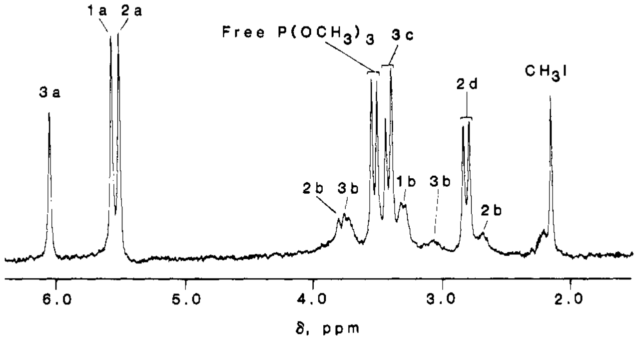

Figure 3. Assignments of ^1H NMR signals at 250 MHz (excluding the phenyl region) in the reacting solution of **1** and $P(OCH_3)_3$. Assignments are keyed to Table I.

methyl resonance of the phosphonate group appears as a ^{31}P split doublet ($^3J_{HP}$ = 11.1 Hz) centered at 2.82 ppm (Figure 1). Phosphonate resonances have been observed in this range for other cyclopentadienylcobalt(III) complexes.[7,13] The methylene resonances of dppe have very different chemical shifts at room temperature in **2**, whereas in **1** they are similar. The axial–equatorial positioning of the protons in **2** is apparently quite distinct. The CH_2 resonances are broad and poorly resolved in all cases due to complicated ^1H and ^{31}P coupling. The phenyl region is relatively uninformative and was not examined further. A good understanding of the ^1H NMR spectra of authentic **1** and **2** proved indispensable for describing the steps in reaction 3.

The $^{31}P\{^1H\}$ NMR spectra of dppe in **1** and **2** reveal the usual change in chemical shift resulting from bidentate complexation.[14] However, there is a coincidental similarity of the phosphonate and dppe chemical shifts in **2** that gives rise to a second-order $^{31}P\{^1H\}$ NMR spectrum (Figure 2). Simulation of this spectrum was successfully accomplished as an AB_2 pattern. The calculated coupling constant and chemical shift values are tabulated in Table I.

Reaction 3, in which **1** is converted to **2** by the Arbusov reaction, was examined as a function of time by using high-field ^1H (0–7 ppm) and ^{31}P (0–200 ppm) NMR spectroscopy. The resonances due to the reactants, intermediates, and products are sufficiently well separated to permit simultaneous analysis of each component. The ^1H NMR spectrum provides the greater detail. Figure 3 gives the assignments for each species, which are justified in the following discussion.

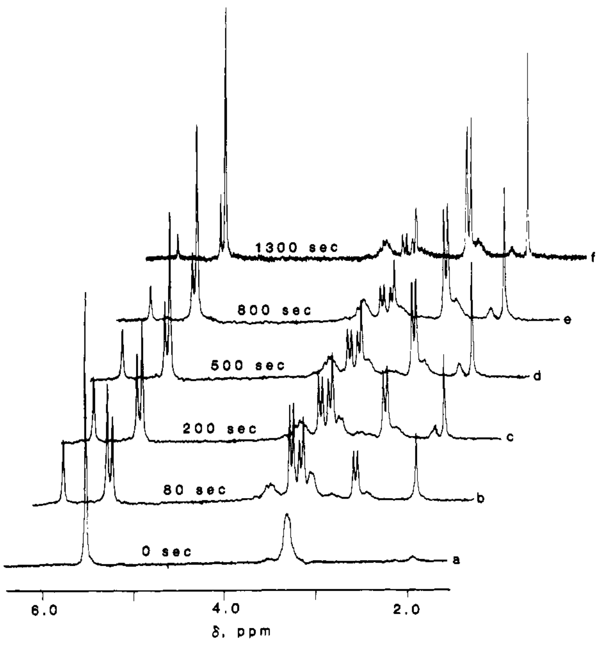

Figure 4. Variation with time of the ^1H NMR spectra for the reaction of equimolar amounts of **1** and $P(OCH_3)_3$ at 0 °C in $CDCl_3$.

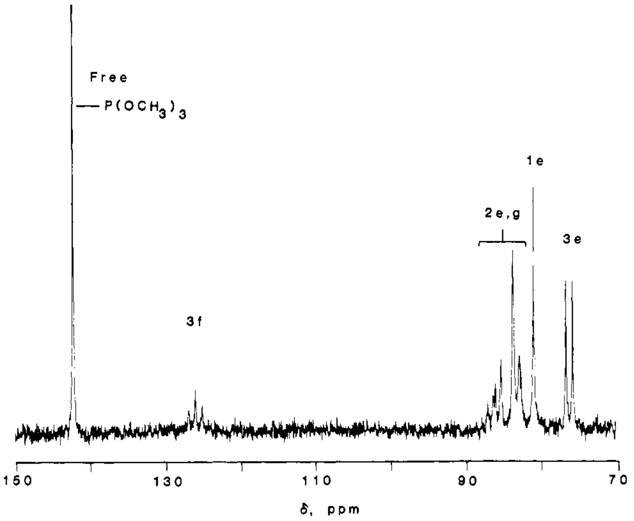

Figure 5. 101.27-MHz ^{31}P NMR spectrum using a single 90° pulse of reaction 3 taken 35 s after the addition of 3 equiv of $P(OCH_3)_3$ to **1**. Assignments are keyed to Table I. Temperature was 16 °C, and solvent was $CDCl_3$.

Figure 4a shows the ^1H NMR spectrum of **1** in $CDCl_3$. Upon the addition of $P(OCH_3)_3$, reaction 3 begins. Insight into its progress in terms of the organometallic components is obtained by focusing on the C_5H_5 region (5–7 ppm in Figure 4b–d). Commensurate with the decrease in intensity of the C_5H_5 signal from **1** is the appearance of a new signal at 6.06 ppm. In addition, a doublet from coordinated $P(OCH_3)_3$ rises at 3.42 ppm. These new peaks are attributable to a complex in which phosphite has displaced I^- from **1** to yield $\{CpCo(dppe)[P(OCH_3)_3]\}^{2+}$ (**3**). Because of the double positive charge on **3**, the C_5H_5 protons should be and are highly deshielded with respect to those of **1** and **2**. Confirmation of the formulation of **3** is obtained from the $^{31}P\{^1H\}$ NMR spectrum taken 35 s after the addition of $P(OCH_3)_3$ (Figure 5). The expected doublet due to dppe and a lower field triplet due to $P(OCH_3)_3$ are observed. These resonances are not present in **1** or **2** and disappear entirely in the completed reaction.

Farther along in the reaction time (Figure 4c–e), **1** and **3** diminish in concentration and are replaced by a C_5H_5 resonance at 5.50 ppm resulting from the phosphonate-containing product (**2**). The methyl resonances of the phosphonate group and a single

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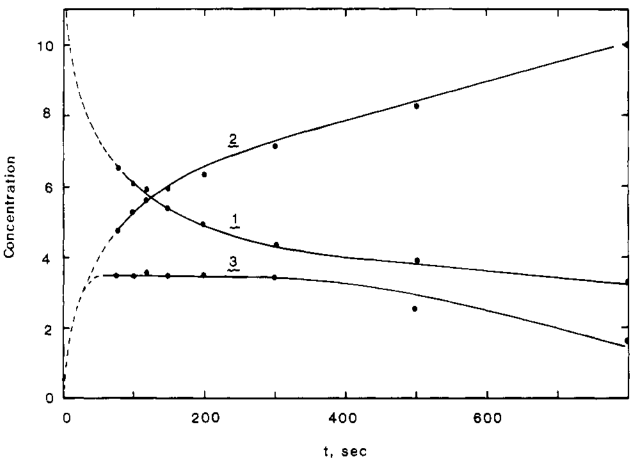


Figure 6. Variation in concentration with time of the metal-containing complexes in an equimolar solution of **1** and $P(OCH_3)_3$ at 0 °C.

line at 2.16 ppm from the other product of reaction 3 (CH_3I) grow in unison with this C_5H_5 signal.

In addition to the distinct indicators above, the methylene resonances of dppe can be detected for each complex in the reaction. These broad, poorly resolved signals are assigned in Figure 3. The axial–equatorial discrimination of the methylene protons in **2** and **3** is found to be large. On the basis of the intensity, it appears that a set of these signals from **2** and **3** overlaps in the 3.7–3.8-ppm region. The second methylene resonance of **3** lies at 3.07 ppm and, as expected, diminishes in intensity with time. The other methylene resonance from **2** is readily identified by comparison with the spectrum in Figure 1. No attempt was made to analyze the phenyl region (not shown).

On the basis of these spectra, the essential components in the reaction of **1** with $P(OCH_3)_3$ to produce **2** are those given by reactions 4 and 5.

$$\mathrm{CpCo(dppe)I^+ + P(OCH_3)_3 \rightarrow \{CpCo(dppe)[P(OCH_3)_3]\}^{2+} + I^-} \quad (4)$$

$$\mathrm{\{CpCo(dppe)[P(OCH_3)_3]\}^{2+} + I^- \rightarrow CpCo(dppe)[P(O)(OCH_3)_2]^+ + CH_3I} \quad (5)$$

Kinetics. The variations in [**1**], [**2**], and [**3**] with time are shown in Figure 6. The most notable feature is the fact that [**3**] remains roughly constant for a substantial part of the reaction. Systematic variations in [**1**] and [$P(OCH_3)_3$] revealed first-order dependence of the rate of reaction 4 on each reactant in $CDCl_3$. The overall second-order kinetics of reaction 4 is demonstrated by the linear dependence with time of 1/(the integrated intensity of ^1H from C_5H_5 of **1**) when **1** and $P(OCH_3)_3$ have equimolar concentrations (Figure 7). A line having the same slope was obtained when the ^{31}P signal of **1** was plotted in the same manner vs. time. Reactions 4 and 5 show no dependence on [I^-], which was varied by the addition of specific amounts of tetrabutylammonium iodide.

According to the results, the overall reaction is governed by rate law 1 (R1) where $k_{obsd} = (1.5 \pm 0.2) \times 10^{-2}$ L mol^{-1} sec^{-1}

$$d[\mathbf{1}]/dt = -k_{obsd}[\mathbf{1}][P(OCH_3)_3] \quad (R1)$$

at 16 °C. This rate law is valid for the reaction times (ca. 40–800 s) and concentration ranges used.

According to reaction 5, the ratio of the concentrations of **2** and CH_3I must remain constant. This will be true if no additional reactions produce a change in the concentration of either species. The experimental data show that [**2**]/[CH_3I] remains constant to the time limit of data collection (ca. 15 min).

It is noteworthy that even after prolonged heating, no reaction is observed between $P(OCH_3)_3$ and $(C_4H_9)_4NI$ in $CHCl_3$. The Co(III) center is apparently a required component for the conversion of phosphite to phosphonate in this reaction.

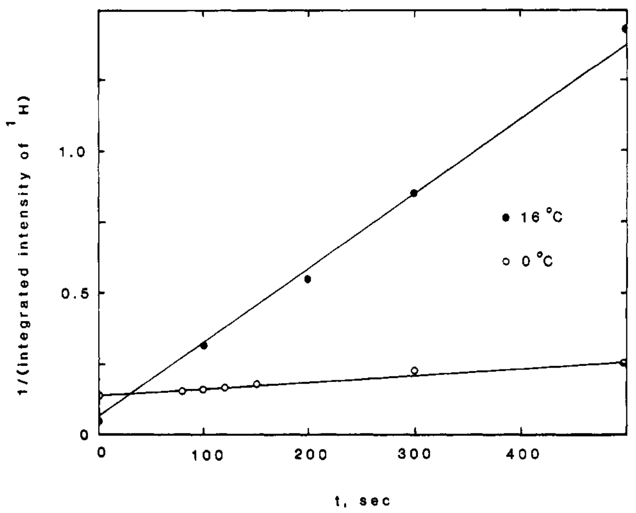


Figure 7. Second-order plot of the loss of **1** in an equimolar solution of **1** and $P(OCH_3)_3$.

Discussion

Mechanistic Considerations. The reaction sequence, (6 and 7) is consistent with rate law 1 and the other experimental findings noted above. The equilibrium in (6) through a large part of the reaction[15] is suggested by the fact that [**3**] remains essentially constant, while [**1**] is depleted and [**2**] increases. In the later stages of the reaction, [**3**] diminishes as expected. The overall rate law for reactions 6 and 7 is

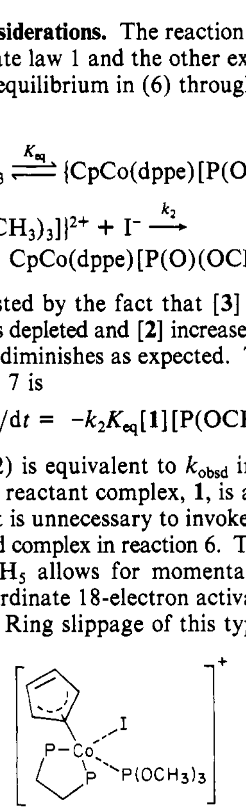
$$\mathrm{CpCo(dppe)I^+ + P(OCH_3)_3 \xrightleftharpoons{K_{eq}} \{CpCo(dppe)[P(OCH_3)_3]\}^{2+} + I^-} \quad (6)$$

$$\mathrm{\{CpCo(dppe)[P(OCH_3)_3]\}^{2+} + I^- \xrightarrow{k_2} CpCo(dppe)[P(O)(OCH_3)_2]^+ + CH_3I} \quad (7)$$

$$d[\mathbf{1}]/dt = -k_2K_{eq}[\mathbf{1}][P(OCH_3)_3] \quad (R2)$$

where k_2K_{eq} in (R2) is equivalent to k_{obsd} in (R1).

Even though the reactant complex, **1**, is a six-coordinate 18-electron complex, it is unnecessary to invoke a seven-coordinate 20-electron activated complex in reaction 6. The special tridentate character of η^5-C_5H_5 allows for momentary ring slippage to η^3-C_5H_5. A six-coordinate 18-electron activated intermediate is represented by **4**. Ring slippage of this type was proposed by Basolo et al. to account for the second-order kinetics found in the substitution reactions of 18-electron $CpM(CO)_2$ complexes, M = Co, Rh, Ir.[16,17] Casey and Jones have detected this type of ring slippage spectroscopically.[18] The equilibrium reaction 6 should be retarded when the steric constraints of the coordination sphere of the metal are increased. Indeed, when dppe is replaced by 1,3-bis(diphenylphosphino)propane (dppp) neither reaction 6 nor 7 occurs at 15 °C. The increased PCoP angle on going from dppe to dppp[19] apparently reduces the space available to the



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[15] We thank a referee for pointing out this fact.

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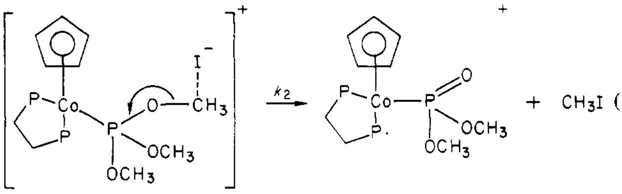
incoming $P(OCH_3)_3$ and thereby stops reaction 6.

Being coordinately saturated, $\{CpCo(dppe)P(OCH_3)_3\}^{2+}$ is able to accumulate in an amount readily detectable by ^1H and ^{31}P NMR spectroscopy (vide supra). We have isolated $\{CpCo(dppe)(PO_3C_5H_{11})\}^{2+}$, which is formally analogous to **3**.[12] The protons of C_5H_5 in this and other doubly positive organometallics[20] are strongly deshielded to the same extent as observed for $\{CpCo(dppe)P(OCH_3)_3\}^{2+}$.

Because the product of reaction 6 carries a net 2+ charge, ion pairing probably should occur between this species and the only anion present in the reaction I^-. In truth, the intermediate cation identified above as $\{CpCo(dppe)P(OCH_3)_3\}^{2+}$ may be the ion pair having a time-averaged positioning of one or more iodide ions about the complex.

The final step of the reaction is the nucleophilic attack of I^- on $P(OCH_3)_3$[4] to produce the phosphonate complex and CH_3I. The reactant ion pair involved can be arranged favorably by electrostatics. The iodide ions should seek the most positive points in the outer sphere of the complex cation, and the methyl groups are a reasonable site for a considerable amount of association by I^-. This being the case, the conditions for the Arbusov rearrangement are properly set. Reaction 8 depicts the required electron rearrangement. The driving force for this step is the energy released in the formation of the P=O bond. However, as a result of the bond-breaking and bond-forming processes, it is reasonable to expect that this step will be comparatively slow. Indeed, the products of the reaction form over a 10-min period at 16 °C.



(8)

Comparison With the Classical Arbusov Reaction. The results of the present study, in which a transition-metal-based complex replaces R′ in reaction 1, are similar to those found with the classical Arbusov reaction. The normally accepted mechanism of the Arbusov reaction is given by reactions 1 and 2.[1] There is evidence of equilibration of the quasi-phosphonium ion intermediate with a five -coordinate intermediate formed from oxidative addition of the R′X reactant to the phosphite.[1,21,22] However, the actual Arbusov rearrangement is thought to occur with the phosphonium ion rather than this five-coordinate species.[21,22] Whether reaction 1 or 2 is rate determining depends on the nature of R and R′.[1]

Likewise, the initial step of the present transition-metal-based Arbusov reaction (reaction 6) involves the equilibration of the substrate halide and $P(OCH_3)_3$. The loss of I^- from the coordination sphere produces an intermediate (**3**, the product of reaction 6) that is formally equivalent to the quasi-phosphonium ion of reaction 1. This intermediate species is seldom detected but has been identified in the present study. The effectiveness of the Co(III) center in trapping the quasi-phosphonium species is undoubtedly responsible for the stability of **3**.

The final step of the reaction involves the nucleophilic attack of I^- on phosphite to produce the phosphonate complex and has the earmarks of a straightforward Arbusov reaction. However, the positive metal center appears to increase the rate of the reaction compared to the classical Arbusov reactions involving an alkyl iodide and trialkyl phosphite where hours of refluxing or sealed-tube heating may be required to accomplish the rearrangement. In the case described here, the reaction occurs at 16 °C in a matter of a few minutes.

Possible Conditions Leading to the Arbusov Rearrangement. The above description of the mechanism of the Arbusov reaction does not preclude other pathways from yielding Arbusov products.[23,24] However, the present study and other data currently available suggest that several features optimize the likelihood of an Arbusov rearrangement with metal–halide complexes. These include the existence or creation of conditions in which a phosphite can readily replace the halide in the metal coordination sphere to produce a cationic species, and the existence of essentially naked halide ions in solution to associate with the phosphite-containing cationic complex. Optimally, the halide ions must be able to locate in the vicinity of the alkyl groups of the coordinated phosphite molecule. These conditions can lead to Arbusov products.

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