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Kinetics and Mechanism of the Substitution Reactions of Some Nitrogen-Bridged Diiron Hexacarbonyl Complexes

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The kinetics and mechanism of the carbonyl substitution reactions of benzo[c]cinnolinebis(tricarbonyliron), μ-diphenyl-ureylene-bis(tricarbonyliron), and μ-bis(p-methoxyphenyl)ureylene-bis(tricarbonyliron) have been investigated. These complexes react with phosphines, phosphites, and triphenylarsine according to second-order rate laws, which are first order in each reagent. Second-order rate constants for the substitution reactions of a given substrate are sensitive to both the electronic and steric characteristics of the attacking nucleophile and insensitive to the nature of the solvent. Entropies of activation are negative. The data are consistent with an SN2 or I_a reaction mechanism. As a result of steric hindrance μ-2,3-(2,3-diazabicyclo[2.2.1]heptane)diyl-bis(tricarbonyliron) does not undergo carbonyl substitution reactions. The influence of the steric properties of the nitrogen-donor, bridging ligand is consistent with an activated complex whose structure is an octahedral wedge, in which the entering and leaving groups occupy an edge which is parallel to the edge defined by the two bridging nitrogen atoms.

Introduction

Earlier work[2] has shown that reactions in which Lewis bases displace carbon monoxide from di-μ-mercapto-bis-(tricarbonyliron) complexes obey a second-order rate law, which is first order in each reagent and independent of the carbon monoxide concentration. Second-order rate constants are sensitive to both electronic and steric characteristics of attacking nucleophiles. The structures of the nitrogen-donor[3,4] complexes investigated here are very similar to those of the sulfur-bridged[5] systems. These complexes can be viewed as two approximately octahedrally coordinated iron atoms sharing an octahedral face. The vertices of the shared face are occupied by the two bridging nitrogen atoms and an iron–iron bond.

For the mercapto-bridged complexes, the kinetic data imply an SN2 or I_a substitution mechanism and suggest that the activated complex is an octahedral wedge in which the entering and leaving groups occupy an edge which is parallel to the edge defined by the two bridging sulfur atoms. Because SN2 substitution mechanisms for octahedral transition metal complexes are unusual,[6,7] these results are particularly significant. The present investigation was undertaken in the expectation[8] that isostructural, nitrogen-donor-bridged complexes would undergo carbonyl substitution reactions by a similar mechanism and also provide a test of the stereochemical details of the proposed activated complex.

Kinetic data are reported for the displacement of carbon monoxide from benzo[c]cinnolinebis(tricarbonyliron) (I), μ-diphenylureylene-bis(tricarbonyliron) (II), and μ-bis(p-methoxyphenyl)ureylene-bis(tricarbonyliron) (III) with phosphines, phosphites, and triphenylarsine. Mono- and disubstituted derivatives of benzo[c]cinnolinebis(tricarbonyliron) have been characterized.[8] As for analogous nitrogen-[9] and sulfur-bridged[10,11] systems, substitution occurs prefer-

entially at the site trans to the iron–iron bond. The present paper reports the preparation and characterization of several monosubstituted derivatives of the ureylene–bis(tricarbonyliron) complexes, which have analogous structures. Only a disubstituted derivative of μ-diphenylureylene-bis(tricarbonyliron) has been reported earlier.[12] It is found that the closely related complex μ-2,3-(2,3-diazabicyclo[2.2.1]heptane)diyl-bis(tricarbonyliron) (IV) does not undergo carbonyl substitution reactions.

I

II, R = H
III, R = OCH₃

IV
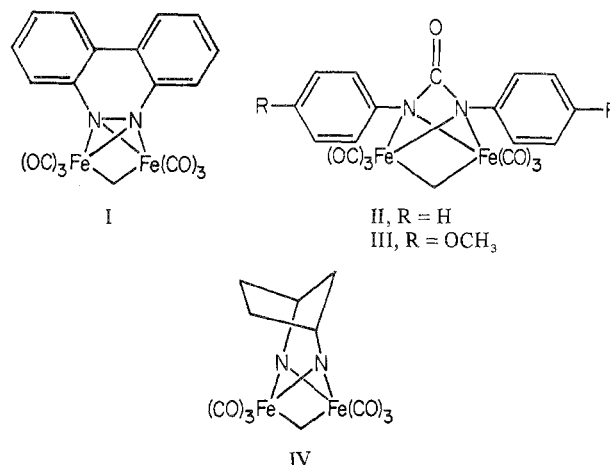
Experimental Section

Materials. Tricyclohexylphosphine was prepared by a literature method.[13] All other ligands were obtained commercially. Triphenylarsine was recrystallized from methanol. Tributylphosphine, trimethyl phosphite, and ethyldiphenylphosphine were distilled in a nitrogen atmosphere at reduced pressure. Triiron dodecacarbonyl was prepared by a literature method[14] and purified by Soxhlet extraction with pentane. Phenyl and p-methoxyphenyl azides were prepared from the corresponding amines by diazotization followed by treatment with sodium azide.[15] Solvents were refluxed over calcium hydride or phosphorus pentoxide (nitrobenzene and dichloromethane) before being distilled in a nitrogen atmosphere. Carbon

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monoxide was passed through a trap at $-78°$ before use. Other reagents were used as received.

Physical Measurements. Reaction rates were monitored by carbon monoxide evolution as previously described.[2] Infrared spectra were obtained for dichloromethane solutions and were calibrated vs. indene.[16] The reactivity of μ-2,3-(2,3-diazabicyclo[2.2.1]heptane)diyl-bis(tricarbonyliron) was investigated by monitoring its infrared spectrum.

Iron Carbonyl Complexes. The preparations of benzo[c]cinnolinebis(tricarbonyliron) and its derivatives have been described elsewhere.[8,17] Professor R. J. Doedens supplied a sample of μ-2,3-(2,3-diazabicyclo[2.2.1]heptane)diyl-bis(tricarbonyliron).

A modification of the reported procedure[12] was employed for the preparation of μ-bis(p-methoxyphenyl)ureylene-bis(tricarbonyliron). Triiron dodecacarbonyl (15 g, 30 mmol), p-methoxyphenyl azide (15 g, 100 mmol), 100 ml of benzene, and 200 ml of cyclohexane were refluxed in an inert atmosphere for 2 hr. The resulting solution was filtered, concentrated to one-half of the original volume, and chromatographed on a 4 × 70 cm silica gel column. Materials were eluted from this column with four successive solvent compositions. Hexane eluted a light green band which probably contained a small quantity of unreacted $Fe_3(CO)_{12}$. A 1:4 benzene:hexane mixture eluted a brown band, and a 1:1 benzene:hexane mixture eluted an orange band. Neither of these bands contained the desired product. Further elution with benzene produced two bands. The first of these was red and yielded a red oil whose infrared spectrum indicated the presence of the desired product. The second was very dark red and yielded a red-black oil, which was discarded.

Several unsuccessful attempts were made to separate the desired product from other components of the red oil by chromatography and fractional crystallization. This isolation was achieved by bubbling oxygen through a 500-ml dichloromethane solution of the oil until the color changed from red to orange (ca. 2 hr). This solution was then filtered through a bed of silica gel (ca. 30 cm³) supported on a sintered glass filter frit. The filtrate was concentrated. Dropwise addition of pentane to the concentrate gave dark red crystals. These were washed with pentane and vacuum dried to give 4.1 g (25% of theoretical) of μ-bis(p-methoxyphenyl)-ureylene-bis(tricarbonyliron): mp 140° dec; ir ν_{CO} 2085 (s), 2049 (vs), 2007 (vs), 1730 cm^{-1} (m). *Anal.* Calcd for $C_{21}H_{14}Fe_2N_2O_9$: C, 45.84; H, 2.47; Fe, 20.32. Found: C, 46.05; H, 2.64; Fe, 20.17.

Reaction of triiron dodecacarbonyl with phenyl azide, followed by a similar isolation procedure, gave an 18% yield of red-orange, crystalline μ-diphenylureylene-bis(tricarbonyliron): mp 130° dec (lit.[12] 130-134°); ir (ν_{CO}) 2087 (m), 2051 (vs), 2008 (vs), 1736 (m), 1710 cm^{-1} (w). *Anal.* Calcd for $C_{19}H_{10}Fe_2N_2O_7$: C, 46.56; H, 2.04; Fe, 22.81. Found: C, 46.82; H, 2.09; Fe, 22.69.

Monosubstituted derivatives of the ureylene complexes were prepared by reacting substrate with a slight excess of the desired ligand in benzene solution. When reaction was complete, solvent was removed, and the product was chromatographed with hexanebenzene on silica gel. In each case, red crystals were obtained from dichloromethane–hexane solution on cooling. Satisfactory carbon and hydrogen analyses were obtained for all derivatives. In all cases, infrared spectra were in agreement with expectations based on previously recorded spectra for monosubstituted derivatives in which substitution was at the apical carbonyl.[18] For $Fe_2(CO)_6(NC_6H_4OCH_3)_2P(C_6H_5)_3$: mp 200° dec; ir ($\nu_{CO}$) 2054 (s), 1990 (vs), 1931 (m), 1708 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_4OCH_3)_2P(OC_6H_5)_3$: mp 145-148°, ir ($\nu_{CO}$) 2062 (s), 2009 (vs), 1986 (s), 1955 (w), 1720 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_4OCH_3)_2P(C_2H_5)(C_6H_5)_2$: mp 130-132°; ir ($\nu_{CO}$) 2055 (s), 1990 (vs), 1930 (m), 1708 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_4OCH_3)_2P(n-C_4H_9)_3$: mp 130-135°; ir ($\nu_{CO}$) 2050 (s), 1987 (vs), 1944 (w), 1920 (m), 1695 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_4OCH_3)_2P(C_6H_{11})_3$: mp 150-155° dec, ir ($\nu_{CO}$) 2055 (s), 1984 (vs), 1919 (m), 1695 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_4OCH_3)_2P(OCH_3)_3$: mp 98-100° dec 160°; ir (ν_{CO}) 2059 (s), 2003 (vs), 1986 (s), 1945 (m), 1715 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_5)_2P(C_6H_5)_3$: mp 200° dec; ir ($\nu_{CO}$) 2056 (s), 1994 (vs), 1933 (m), 1718 (m), 1698 cm^{-1} (m). For $Fe_2(CO)_6(NC_6H_5)_2P(OC_6H_5)_3$: mp 112-114° dec 120°; ir (ν_{CO}) 2067 (s), 2010 (vs), 1990 (s), 1961 (w), 1727 (m), 1710 cm^{-1} (w).

Results and Discussion

The reactions of $Fe_2(CO)_6N_2C_{12}H_8$, $Fe_2(CO)_7(NC_6H_5)_2$,

and $Fe_2(CO)_7(p-NC_6H_4OCH_3)_2$ with large excesses of all reacting phosphines and phosphites exhibit good pseudo-first-order kinetics. Table I[19] lists the pseudo-first-order rate constants obtained in this study. In all cases in which the substitution reaction goes to completion, pseudo-first-order rate constants are proportional to the concentration of the incoming ligand, L, and independent of the carbon monoxide concentration. These results establish a second-order rate law, which is first order in each reactant (eq 1).

$$-d[\text{substrate}]/dt = k[\text{substrate}][L] \qquad (1)$$

The reaction of $Fe_2(CO)_6N_2C_{12}H_8$ with triphenylarsine (eq 2) does not go to completion. The approach to equilibri-

$$Fe_2(CO)_6N_2C_{12}H_8 + As(C_6H_5)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$Fe_2(CO)_5N_2C_{12}H_8As(C_6H_5)_3 + CO \qquad (2)$$
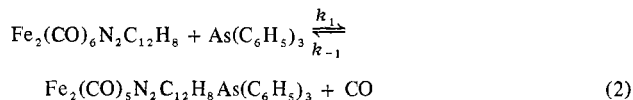
um exhibits pseudo-first-order kinetics in the presence of excess triphenylarsine. At a constant carbon monoxide pressure, plots of pseudo-first-order rate constants vs. triphenylarsine concentration are linear with positive intercepts. The magnitude of the intercept is directly proportional to the carbon monoxide pressure over the reaction solution (Table II). The observations establish a rate law of the form of eq 3. The rate constants in eq 3 can be identi-

$$-d \ln [Fe_2(CO)_6N_2C_{12}H_8]/dt = k_1[As(C_6H_5)_3] +$$
$$k_{-1}P_{CO} \qquad (3)$$

fied with those in eq 2. This identification is supported by the observation that the equilibrium constant evaluated from the kinetic results (as $K = k_1/k_{-1}$) is consistent with the values obtained from the equilibrium positions of individual rate experiments.

For all of the substrates studied, second-order rate constants are strongly dependent on the properties of the attacking ligand. For example, at 10°, second-order rate constants for reactions of $Fe_2(CO)_6N_2C_{12}H_8$ with the ligands studied vary over more than four orders of magnitude. The nature of this dependence is very similar to that observed in the substitution reactions of analogous sulfur-bridged complexes.[2] For incoming groups whose steric requirements are not large, reactivity toward these substrates parallels both their proton basicity and their reactivity toward other, less hindered, metal carbonyl complexes whose substitution reactions obey second-order rate laws.[20-22] Thus, a strong dependence on the electronic (nucleophilic) properties of the incoming group is evident.

A strong dependence of the rate constant for substitution on the steric requirements of the incoming ligand is also evident. Thus, tricyclohexylphosphine is much less reactive than tri-n-butylphosphine; on the basis of the basicity correlation alone, it would be expected to be at least as reactive. This effect is readily ascribed to the fact that tricyclohexylphosphine has a much greater cone angle[23] than does tri-n-butylphosphine. Accordingly, its attack on the substrate is sterically hindered. Similarly, tri-o-tolylphosphine has a particularly large cone angle. Experimentally, it fails to

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Table II. Second-Order Rate Constants and Activation Parameters for Carbonyl-Substitution Reactions[a]

Ligand	$k \times 10^3$, M^{-1} sec^{-1}	T, °C	P_{CO}, Torr	$\Delta H^{\ddagger}$, kcal/mol	ΔS, eu
	Fe$_2$(CO)$_6$N$_2$C$_{12}$H$_8$				
P(C$_6$H$_5$)$_3$	2.5 (2)	10	725		
	2.6 (1)	10	390	10.2 ± 0.5	−34 ± 2
	6.8 (1)	25	710		
	12.4 (8)	35	690		
	2.9 (1)[b]	10			
	4.2 (1)[c]	10	740		
P(OC$_6$H$_5$)$_3$	1.20 (4)	10	725		
	3.8 (1)	25	710	12.2 ± 0.5	−28 ± 2
	7.8 (2)	35	690		
	14.4 (4)	45	660		
P(n-C$_4$H$_9$)$_3$	223 (12)	10	725		
PH(C$_6$H$_5$)$_2$	173 (2)	10	725		
P(C$_2$H$_5$)(C$_6$H$_5$)$_2$	156 (6)	10	725		
P(C$_6$H$_{11}$)$_3$	17.7 (7)	10	725		
As(C$_6$H$_5$)$_3$	(2.8 × 10^{-7})[d]	10			
	0.14 (1)	50	645		
	0.30 (3)	60	595	17.1 ± 1.0	−23 ± 4
	0.33 (4)	60	290		
	0.71 (6)	70	540		
	Fe$_2$(CO)$_5$N$_2$C$_{12}$H$_8$As(C$_6$H$_5$)$_3$				
CO	1.0 (1)[e]	50	645		
	1.4 (1)[e]	60	595		
	1.2 (1)[e]	60	290		
	3.1 (3)[e]	70	540		
	Fe$_2$(CO)$_7$(NC$_6$H$_4$OCH$_3$)$_2$				
P(C$_6$H$_5$)$_3$	0.61 (2)	10	725		
	1.56 (3)	20	720	15.0 ± 0.5	−20 ± 2
	3.8 (1)	30	700		
P(OC$_6$H$_5$)$_3$	0.24 (1)	40	680		
	0.63 (4)	50	645	16.4 ± 0.5	−23 ± 2
	1.21 (2)	60	595		
P(n-C$_4$H$_9$)$_3$	510 (10)	10	725		
P(OCH$_3$)$_3$	12.0 (1)	10	725		
P(C$_2$H$_5$)(C$_6$H$_5$)$_2$	26.1 (4)	10	725		
P(C$_6$H$_{11}$)$_3$	11 (1)	10	725		
P(o-C$_6$H$_4$CH$_3$)$_3$	No reaction (100°; 48 hr)				
	Fe$_2$(CO)$_7$(NC$_6$H$_5$)$_2$				
P(C$_6$H$_5$)$_3$	2.0 (1)	10	725		
	4.6 (4)	20	720	12.7 ± 0.5	−26 ± 2
	9.4 (6)	30	700		
P(OC$_6$H$_5$)$_3$	0.65 (8)	40	680		
	1.35 (8)	50	645	14.6 ± 0.5	−26 ± 2
	2.8 (2)	60	595		

[a] Second-order rate constants in toluene solution except as otherwise noted. Values in parentheses are estimated standard deviations in the least significant digits. [b] In tetrahydrofuran. [c] In nitrobenzene. [d] Extrapolated from rate constants at highter temperatures. [e] Second-order rate constants in units of 10^6 Torr^{-1} sec^{-1}.

react with either Fe$_2$(CO)$_6$N$_2$C$_{12}$H$_8$ or Fe$_2$(CO)$_7$(NC$_6$H$_4$-OCH$_3$)$_2$.

Although reaction rates are very sensitive to the nature of the incoming ligand for a given substrate, there is remarkably little difference in the rate constants or activation parameters for the reactions of a given incoming group with the benzo[c]cinnoline- and ureylene-bridged substrates (see Table II). Therefore, there would appear to be little dependence of the rate constant on the electronic properties of the organic moiety into which the bridging nitrogen atoms are incorporated. A similar observation was made for the substitution reactions of the analogous mercapto-bridged complexes.[2]

Second-order rate constants for the reaction of Fe$_2$(CO)$_6$-N$_2$C$_{12}$H$_8$ with triphenylphosphine are insensitive to the nature of the solvent (Table II); neither the coordinating ability nor the dielectric constant of the solvent appears to affect the rate constant. For all of the reacting substrates,
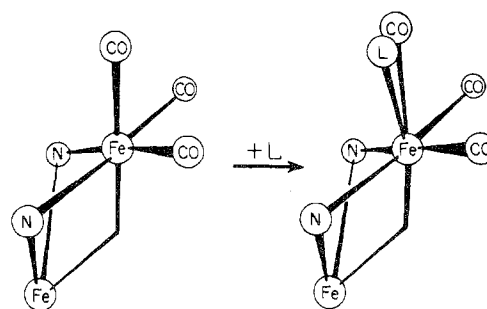
Figure 1. Proposed structure of the activated complex for substitution on nitrogen-bridged diiron hexacarbonyl complexes. For clarity, only the groups in the immediate vicinity of the iron atom undergoing substitution are shown.

entropies of activation are substantially less than zero, implying that considerable loss of freedom occurs upon formation of the activated complex.

All of these results are consistent with an S$_N$2 or I$_a$ mechanism involving an activated complex of expanded coordination number and minimal charge separation. Also, they are all closely parallel to the observations made on the analogous sulfur-bridged systems.[2] It would appear that the substitution reactions of these nitrogen- and sulfur-bridged complexes have closely related mechanisms. For the mercapto-bridged complexes, the dependence of the substitution rate constant on the nature of the mercapto substituent suggests that the activated complex has an octahedral wedge structure, in which the entering and leaving groups lie on an edge which is parallel to the edge defined by the two bridging sulfur atoms. The data reported here are clearly compatible with similar structures for the activated complexes in the substitution reactions of the benzo[c]cinnoline- and ureylene-bridged complexes (Figure 1).

The reactivity of μ-2,3-(2,3-diazabicyclo[2.2.1]heptane)-diyl-bis(tricarbonyliron) provides a clear test of this interpretation. The molecular structure of this complex has been determined by X-ray diffraction.[4] The aliphatic rings which include the bridging nitrogen atoms extend over the iron octahedral faces defined by the bridging nitrogen atoms and the carbon monoxide ligands trans to the metal–metal bond. Formation of a seven-coordinate activated complex in which the entering and leaving groups occupy an edge of an octahedral wedge parallel to the edge occupied by the two bridging nitrogen atoms is therefore excluded.

This complex is observed to be substitution inert. This result cannot be ascribed to the electronic properties of the bridging ligand, because substitution rates for closely related complexes are insensitive to the electronic properties of bridging ligands (*vide supra*). Therefore, the observed substitution inertness must be a consequence of steric destabilization of the activated complex; the aliphatic rings prevent formation of a seven-coordinate activated complex of the requisite structure.

Registry No. I, 27081-59-0; II, 20935-93-7; III, 51472-19-6; Fe$_2$(CO)$_6$(NC$_6$H$_4$OCH$_3$)$_2$P(C$_6$H$_5$)$_3$, 51472-20-9; Fe$_2$(CO)$_6$(NC$_6$-H$_4$OCH$_3$)$_2$P(OC$_6$H$_5$)$_3$, 51472-21-0; Fe$_2$(CO)$_6$(NC$_6$H$_4$OCH$_3$)$_2$P(C$_2$-H$_5$)(C$_6$H$_5$)$_2$, 51472-22-1; Fe$_2$(CO)$_6$(NC$_6$H$_4$OCH$_3$)$_2$P(n-C$_4$H$_9$)$_3$, 51472-23-2; Fe$_2$(CO)$_6$(NC$_6$H$_4$OCH$_3$)$_2$P(C$_6$H$_{11}$)$_3$, 51472-24-3; Fe$_2$-(CO)$_6$(NC$_6$H$_4$OCH$_3$)$_2$P(OCH$_3$)$_3$, 51472-25-4; Fe$_2$(CO)$_6$(NC$_6$H$_5$)$_2$-P(C$_6$H$_5$)$_3$, 51472-26-5; Fe$_2$(CO)$_6$(NC$_6$H$_5$)$_2$P(OC$_6$H$_5$)$_3$, 51472-27-6;

$P(C_6H_5)_3$, 603-35-0; $P(OC_6H_5)_3$, 101-02-0; $P(n\text{-}C_4H_9)_3$, 998-40-3; $PH(C_6H_5)_2$, 829-85-6; $P(C_2H_5)(C_6H_5)_2$, 607-01-2; $P(C_6H_{11})_3$, 2622-14-2; $As(C_6H_5)_3$, 603-32-7; $P(OCH_3)_3$, 121-45-9.

Supplementary Material Available. Table I, a listing of reagent concentrations, experimental conditions, and observed rate constants, will appear following these pages in the microfilm edition of this

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Synthesis and Properties of Cobalt(I) Compounds. I. Triethyl Phosphite Complexes

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The preparation and properties of $[CoL_5]Cl$, $[CoClL_3]$, $[CoL_5][B(C_6H_5)_4]$, $[CoL_5][CoCl_3]$, and $[CoL_2B(C_6H_5)_4]$ are described (L = triethyl phosphite). The reaction of cobalt(II) chloride and triethyl phosphite in the presence of triethylamine gave $[CoL_5]Cl$. It appears that two products previously formulated as $[CoClL_4]$ and $[CoClL_3]$ are respectively $[CoL_5]Cl$ and a salt $[CoL_5]_{n-2}[CoCl_n]^{2-n}$. In the complex $[CoL_2B(C_6H_5)_4]$, one of the phenyl groups σ bonded to boron appears to be π bonded to cobalt.

The simple phosphite complexes of cobalt(I), CoX(phosphite)$_n$, which have been reported are, with one exception, complexes of trimethyl phosphite or of sterically constrained polycyclic phosphites with nitrate, perchlorate, or tetraphenylborate counterions.[1] The exception is work by Vol'pin and Kolomnikov[2] who report the preparation of CoCl(triethyl phosphite)$_4$ and CoCl(triethyl phosphite)$_3$. Because of the potential for interesting catalytic properties in these complexes, we have investigated their report. Our study suggests that they did indeed obtain cobalt(I) complexes with phosphite ligands but that the products are derivatives of the $[CoL_5]^+$ ion (L = triethyl phosphite).

Although the experiments in ref 2 are reported in insufficient detail to be repeated with confidence, we have carried out procedures like those described and have obtained products with similar properties. We isolated a yellow compound with moderate water stability and a peak at *ca.* 390 nm in the visible spectrum as reported for the $[CoClL_4]$ formulation.[2] We also isolated a green, water-sensitive compound with a peak at *ca.* 390 nm as reported[2] for $[CoClL_3]$. The work described below shows that our yellow compound is $[CoL_5]Cl$ and that our green compound is $[CoL_5][CoCl_3]$. It is likely that the yellow compound in the earlier work was also $[CoL_5]Cl$ and that the green compound was $[CoL_5][CoCl_3]$ or $[CoL_5]_2[CoCl_4]$. We have prepared $[CoClL_3]$ and its properties, including its ease of conversion to $[CoL_5]Cl$, indicate that it is unlikely that $[CoClL_4]$ was a product of the reaction described by Vol'pin and Kolomnikov.

The Reaction of CoCl₂ with Triethyl Phosphite

Vol'pin and Kolomnikov treated $CoCl_2 \cdot 6H_2O$ in ethanol with triethyl phosphite and triethylamine to prepare their yellow and green compounds. We have used dry $CoCl_2$ in place of the hydrate so that the amount of water in the

mixtures could be controlled more easily. We have found that the rate of the reaction is quite sensitive to the presence of water. Under nominally anhydrous conditions the reaction is at best very slow. The reaction mixture remains dark blue-purple and clear for at least 24 hr at room temperature. Addition of small amounts of water, up to *ca.* 3% by volume, produced increasingly rapidly a transition to a cloudy green liquid followed by transition to a pale yellow liquid containing a large amount of dark flocculent precipitate. The green compound was obtained by interrupting the sequence when the liquid had become dark green and isolating the product. The yellow compound was obtained easily by waiting until the green color had faded to pale yellow. Figure 1 shows the 550–750-nm region of the spectrum at *ca.* 0.1 *M* for the green compound isolated from the green reaction mixture, for a green compound obtained by adding cobalt(II) chloride to the yellow compound, and for mixtures of tetraethylammonium chloride and cobalt(II) chloride. It is clear that both green compounds contain the same chromophore as is obtained by adding ionic chloride to cobalt(II) chloride in a 1:1 ratio. It can also be seen that there is a clear qualitative difference between the spectrum for 3:1 chloride:cobalt(II) and 4:1 chloride:cobalt(II). (The spectra of these systems are known to be dependent on the nature and concentration of the anions.[3]) Meakin and Jesson[4] have shown by computer simulation of the low-temperature (*ca.* −130°) ^{31}P nmr spectrum that our yellow compound contains the trigonal bipyramidal $[CoL_5]^+$ cation. The *ca.* 390-nm peak observed in the spectrum of our yellow compound and in that described by Vol'pin is very similar to that reported for $\{Co[P(OCH_3)_3]_5\}ClO_4$.[1d] Preparation of a salt, $\{Co[P(OCH_3)_3]_5\}_2[Co(NO_3)_4]$, from $\{Co[P(OCH_3)_3]_5\}$-NO_3 and cobalt(II) nitrate has also been described.[1d]

It is thus clear that, in the synthesis procedure, $[CoL_5]Cl$ is the primary species produced and that interruption of the procedure before complete consumption of the cobalt(II) chloride can permit the isolation of the green salts containing $[CoL_5]^+$ and a chlorocobaltate anion. In principle either

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