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Kinetics and Mechanism of Substitution Reactions of Cobalt(I) Derivatives. Evidence for π -Adduct Formation

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Received September 27, 1979

Kinetic studies of the reactions of acrylonitrile, methyl mercaptide, and cyanide ion with the phosphine-cobalt(I) complex of bis[(difluoroboryl)dimethylglyoximate]cobaltate(I), $[\text{Co}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$, have been carried out. The reaction occurs in a stepwise fashion, with dissociation of phosphine preceding entry of the other base. This corresponds to a dissociative mechanism with the limiting rate constant of 10.5 s^{-1} in methanol at 25°C . A limited amount of work was also done on similar reactions of $[\text{Co}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3]^-$ and $[\text{Co}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3]^-$. The results are discussed in terms of a mechanism in which a 16-electron, four-coordinate intermediate is involved.

Introduction

Cobalt is known in oxidation state I in vitamin $\text{B}_{12\text{s}}$ and in model complexes such as the cobalt(I) cobaloxime¹ $\text{Co}(\text{dmgH})_2\text{X}^-$ ($\text{X} = \text{py}, \text{PR}_3$, etc.). The chemistry of these complexes is rich in its variety, particularly so for the Co(I) state which is dominated by its nucleophilic character.¹ Among the reactions that the cobalt(I) complex can undergo, those involving olefinic and other ligands capable of π bonding are of special interest from the point of view of homogeneous catalysis. Schrauzer and co-workers² have, in fact, reported the formation of π complexes between Co(I) and olefinic ligands during the course of alkali-induced Co(III)-alkyl bond cleavage reactions in vitamin B_{12} and its related model compounds. In spite of the importance of such π complexes of Co(I) in catalytic phenomena, there is little information available on the mode of binding of olefinic ligands and the precise mechanism of their formation. Complexes of appreciable stability appear to form spontaneously from cobalt(I) and the olefin only for those olefins such as acrylonitrile having an electron-withdrawing substituent and do not form to a substantial extent with ethylene, for example.² We have found that the reaction is not simply one entailing acrylonitrile addition; rather a substitution process is involved such that the axial base in the parent complex is replaced by the olefin. The principal equilibrium in a typical example is that shown by reaction 1.



In light of this it was also of interest to consider the mechanism of more conventional ligand substitution reactions with groups other than these special olefinic compounds. We have thus studied reactions in which the phosphine is replaced by such ligands as cyanide and methyl mercaptide ions. It should be noted that the cobalt(I) ion has a d^8 electron configuration and that this 18-electron complex has coordination number of 5 in a square-pyramidal structure.³ This particular combination is likely to lead to interesting mechanistic work since the open geometry would tend to favor an associative mechanism, but this would be strongly disfavored by the electron pair in the d_{z^2} orbital on the central metal and by an intermediate having 20 electrons. In this work we report the results of equilibrium and kinetic studies of the systems mentioned above.

Experimental Section

Materials. The chlorocobaloximes with axial pyridine and tri-*n*-butylphosphine bases were prepared by standard methods.^{4,5} Gen-

erally, triply distilled acrylonitrile (Eastman) and vacuum-distilled tri-*n*-butylphosphine (Aldrich Chemical Co.) and alkyl halides were used. Propionitrile was prepared from ethyl sulfate and sodium cyanide⁶ and was subject to extensive purification; its identity and purity were confirmed by NMR. Other reagents were of reagent grade and were used without further purification. The literature methods for the preparations of boron difluoride adducts of various cobaloximes generally yielded products with unsatisfactory elemental analyses. Hence, suitable methods were standardized.

Chloro(tri-*n*-butylphosphine)bis[(difluoroboryl)dimethylglyoximate]cobalt(III), $\text{ClCo}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3$. Boron trifluoride etherate (3 mL) was added to a solution of $\text{ClCo}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3$ (3.2 g) in chloroform (50 mL) and stirred for a period of 3-4 h. The addition of anhydrous ethyl ether (25 mL) to the mixture gave rise to a golden yellow product which was filtered and dried with ethyl ether. The crude product was then dissolved in acetone (50 mL), and addition of an equal volume of chloroform followed by cooling with ice resulted in the crystallization of shiny crystals of the desired product with a yield of 2.4 g. The product thus obtained was recrystallized from an acetone-chloroform (1:1) mixture twice. The product was dried with ethyl ether and gave rise to a single spot on TLC when acetone-chloroform-methanol (1:4:1 mixture) was used for developing. Anal. Calcd for $\text{ClCo}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3$: C, 38.50; H, 5.64; N, 8.99; Co, 9.47. Found: C, 38.60; H, 6.40; N, 8.86; Co, 9.35.

Chloro(tri-*n*-butylphosphine)[(difluoroboryl)dimethylglyoximate](dimethylglyoximate)cobalt(III), $\text{ClCo}(\text{dmgBF}_2)(\text{dmgH})\text{P}(\text{C}_4\text{H}_9)_3$. Boron trifluoride etherate (2.0 mL) was added to a suspension of $\text{ClCo}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3$ (3.5 g) in anhydrous ethyl ether (50 mL). The mixture was stirred on a magnetic stirrer after the addition of a further 10 mL of ethyl ether over ca. 30 min, during which period the reaction mixture became homogeneous. The mixture was filtered and stirred for another 30 min at room temperature (ca. 20°C). This resulted in the crystallization of reddish brown crystals of the desired product. The crude product was collected on a glass filter and washed with absolute alcohol and dried with ethyl ether. The product was then recrystallized twice from methanol and dried with ethyl ether. The compound obtained in a yield of 0.5 g gave rise to a single spot on TLC. Anal. Calcd for $\text{ClCo}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3$: C, 41.96; H, 6.82; N, 9.78; Co, 10.30. Found: C, 41.73; H, 7.05; N, 9.67; Co, 10.17.

Chloro(pyridine)bis[(difluoroboryl)dimethylglyoximate]cobalt(III), $\text{ClCo}(\text{dmgBF}_2)_2\text{C}_5\text{H}_5\text{N}$. Boron trifluoride etherate (3.0 mL) was added to a solution of $\text{ClCo}(\text{dmgH})_2\text{C}_5\text{H}_5\text{N}$ (4.0 g) in chloroform (50 mL). Although the reaction mixture was homogeneous, it was filtered and stirred for a period of 30-40 min. The reddish brown precipitate which formed was filtered, washed with ethanol and chloroform, and dried with ethyl ether. The crude product thus obtained was dissolved in methanol at ca. 40°C , to the filtered methanolic solution (20 mL) was added a mixture of acetone (10 mL) and chloroform (50 mL), and the mixture was cooled. This afforded shining cubic crystals of this reddish brown product in a yield of 1.5 g. Although the product gave rise to a single spot, it was recrystallized from methanol-acetone (4:1 mixture) and dried with ethyl ether. Anal. Calcd for $\text{ClCo}(\text{dmgBF}_2)_2\text{C}_5\text{H}_5\text{N}$: C, 31.22; H, 3.40; N, 14.00; Co, 11.80. Found: C, 31.61; H, 3.53; N, 14.13; Co, 11.62.

(1) (a) Schrauzer, G. N. *Acc. Chem. Res.* 1968, 1, 97. (b) Cobaloxime is the trivial name for bis(dimethylglyoximate)cobalt complexes.

(2) Schrauzer, G. N.; Weber, J. H.; Beckham, T. M. *J. Am. Chem. Soc.* 1970, 92, 7078.

(3) Schrauzer, G. N.; Windgassen, R. J.; Kohnle, W. J. *Chem. Ber.* 1965, 98, 3324.

(4) Schrauzer, G. N. *Inorg. Synth.* 1968, 9, 61.

(5) Costa, G.; Tazher, G.; Puxeddu, A. *Inorg. Chim. Acta* 1969, 3, 45.

(6) Jeffery, G. H.; Vogel, A. I. *J. Chem. Soc.* 1948, 674.

Preparation of the Solutions of Co(I) Complexes. Generally, methanolic solutions (50.0 mL) containing the necessary amounts of sodium hydroxide, axial bases, and other electrolytes (if any) were made up in a round-bottomed flask and deaerated through a rubber septum by means of nitrogen prepurified with solutions of Cr^{2+} , NaOH, water, and methanol. After about 20–30 min of deaeration, the required amounts of Co(III) compounds along with NaBH_4 (in a 1:(ca. 2–3) Co(III): NaBH_4 molar ratio) were added with minimum exposure to air, and deaeration continued for another 10–15 min, when the reduction to Co(I) was complete. Sometimes higher amounts of NaBH_4 were necessary (up to a 5:1 molar ratio per Co(III)), especially in the case of dimethylglyoxime adducts. Generally a stoichiometric reduction to a five-coordinate cobalt(I) was assumed.

Analyses and Separations. The concentrations of acrylonitrile were estimated by literature methods⁷ which essentially involve the conversion of the nitrile to an amide by reaction with hydrogen peroxide and steam distillation of the amide thus produced under alkaline conditions. The ammonia liberated by alkaline hydrolysis was titrated against hydrochloric acid after being complexed with boric acid. The mercaptide concentrations were estimated iodometrically, and cyanide concentrations were measured by iodometry according to standard procedures.⁸ Gel filtration on columns of Sephadex LH-20 (Pharmacia Fine Chemicals Co.) prove useful for isolation and separation of products. The gel (7 g) was allowed to swell overnight in absolute methanol and was used to prepare columns (0.8 × 30 cm) which were deaerated by passing 400 mL of deaerated methanol through them. Generally, 3–5 mL of a reaction mixture which had 0.003–0.005 M cobalt complex and 0.03–0.2 M acrylonitrile was placed on the column and eluted by air-free methanol. Two distinctly separated bands were observed. The first was identified as the product of interest (see Results) and the second as the parent cobalt(I) complex.

Results and Interpretation

Characterization of Co(III) Complexes. The elemental analyses of the BF_2 derivatives were in satisfactory agreement with the formulations $\text{ClCo}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3$, $\text{ClCo}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3$, and $\text{ClCo}(\text{dmgBF}_2)_2\text{C}_2\text{H}_5\text{N}$. The infrared spectra of the BF_2 derivatives exhibited the characteristic $\gamma(\text{B-F})$ vibrations at 1180, 1000, and 825 cm^{-1} , consistent with T_d symmetry around the boron atom.⁹ The NMR spectra are consistent with the structures assigned; thus the parent complexes each show but one doublet from the dmg methyl protons: $\text{ClCo}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3$ (δ 2.33, $J_{\text{sp-CH}_3} = 1.25$ Hz) and $\text{ClCo}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3$ (δ 2.35, $J_{\text{sp-CH}_3} = 1.25$ Hz). The mono BF_2 derivative, on the other hand, renders the 12 dmg methyl protons magnetically inequivalent. Thus $\text{ClCo}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3$ shows a pair of doublets of equal intensity (δ 2.38, $J_{\text{sp-CH}_3} = 1.25$ Hz, 6 H; δ 2.46, $J_{\text{sp-CH}_3} = 1.25$ Hz, 6 H); the coupling constant is field independent, yet the chemical shifts are field dependent (60–100 MHz), as expected for the compound as formulated.

The electronic spectra of the Co(III) complexes as well as those of the Co(I) derivatives obtained from them show a dependence on the equatorial ligands as well as on the axial bases (Table I), indicating the possibilities of monitoring Co(I) reactions with various axial bases by spectroscopic means.

Preliminary Studies. The reaction of acrylonitrile with $\text{Co}^{\text{I}}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3$ is attended by large optical changes at 610 nm, and the kinetics of the reactions in methanol were measured by using a stopped-flow spectrophotometer under pseudo-first-order excess of acrylonitrile over $[\text{Co}(\text{I})]^-$. It was observed that even with 10^{-4} M concentrations of Co(I) and 10^{-3} M concentrations of acrylonitrile, the observed rate was very high, with $t_{1/2} \approx 1$ –2 ms. The variation of acrylonitrile concentrations between 10^{-2} and 10^{-4} M did not seem to alter the observed rate appreciably. Pseudo-first-order plots yielded observed rates for experiments in the acrylonitrile concen-

Table I. Electronic Spectra of Cobalt(I) Complexes and Their π Adducts with Acrylonitrile in Methanol 0.1 M in NaOH

complex	λ_{max} , nm (log ϵ)
$[\text{Co}^{\text{I}}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ ^a	610 (4.00), 500 (3.59), 405 (3.65)
$[\text{Co}^{\text{I}}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ ^b	610 (4.00), 500 (sh, 3.6), 401 (3.64)
$[\text{Co}^{\text{I}}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ ^c	613 (3.75), 508 (sh, 3.4), 405 (3.48)
$[\text{Co}^{\text{I}}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3]^-$ ^a	615 (3.96), 510 (sh, 3.57), 400 (3.66)
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ ^a	620 (3.94), 518 (sh, 3.43), 395 (3.64)
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{C}_2\text{H}_5\text{N}]^-$ ^{a,d}	645 (3.79), 526 (3.64), 434 (3.61)
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{C}_2\text{H}_5\text{N}]^-$ ^e	629 (3.64), 546 (3.48), 439 (3.45)
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{C}_2\text{H}_5\text{N}]^-$ ^c	615 (3.75), 520 (3.61), 440 (3.71)
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2(\text{CH}_2=\text{CHCN})]^-$ ^{a,f}	620 (3.74), 510 (3.49), 390 (3.63)
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2(\text{CH}_2=\text{CHCN})]^-$ ^{a,g}	546, 440
$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2(\text{CH}_2=\text{CHCN})]^- + \text{air}^g$	518 (3.43), 396 (3.40)

^a This work. ^b Chao, T.-H. M.S. Thesis, Iowa State University, 1977. Espenson, J. H.; Chao, T.-H. *Inorg. Chem.* 1977, 16, 2553. ^c Schrauzer, G. N. *Ann. N.Y. Acad. Sci.* 1969, 158, 526. ^d Additional peaks at 370 nm (ϵ 3.43) and 310 (sh, 3.57). ^e Reference 2. ^f Isolated by means of gel filtration in methanol on a column packed with LH-20; prepared from $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$. ^g Prepared^c from $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{C}_2\text{H}_5\text{N}]^-$.

tration range of 10^{-2} – 10^{-4} M of the order of 240 ± 20 s^{-1} , close to the upper limit of the flow techniques. The reaction of the corresponding $[\text{Co}^{\text{I}}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3]^-$ and $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ were, however, slower under comparable acrylonitrile concentrations, generally by a factor of 2–2.5 and 24–40, respectively. Thus, the delocalization of the net electron density in the equatorial ligands by way of derivatizing dmg with BF_2 provided a means of obtaining reliable rate constants for Co(I) reactions.

Equilibrium Studies. Analysis of the electronic spectrum of $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ in the range 310–660 nm at varying ratios of $[\text{P}(\text{C}_4\text{H}_9)_3]/[\text{CN}^-]$ indicated a measurable equilibrium was established, eq 2. The apparent molar ab-

$$[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^- + \text{CN}^- = [\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{CN}]^{2-} + \text{P}(\text{C}_4\text{H}_9)_3 \quad (2)$$

sorptivity of the mixture, ϵ_{obsd} (=absorbance/ $[\text{Co}]_{\text{T}}$), is related to the values for the two components, ϵ_{p} and ϵ_{CN} , by eq 3.

$$\epsilon_{\text{obsd}} = \frac{\epsilon_{\text{p}}[\text{P}(\text{C}_4\text{H}_9)_3] + \epsilon_{\text{CN}}K_{\text{CN}}[\text{CN}^-]}{[\text{P}(\text{C}_4\text{H}_9)_3] + K_{\text{CN}}[\text{CN}^-]} \quad (3)$$

Experiments were done at 25.0 °C in methanol containing 5% water (added to provide sufficient solubility of the sodium salt) and with $\mu = 0.2$ M ($\text{NaCN} + \text{NaOH} + \text{NaCl}$). The absorbance measurements were made at 610 nm with $[\text{P}(\text{C}_4\text{H}_9)_3] = 5.00 \times 10^{-4}$ M and $[\text{CN}^-] = (1-20) \times 10^{-3}$ M. A computer fit of the data to eq 3 gave $K_{\text{CN}} = 0.37 \pm 0.03$.

In the cases of CH_3S^- and $\text{CH}_2=\text{CHCN}$, the equilibrium constants are too large to permit their direct measurement. On the other hand, additions of even a large excess of propionitrile (3.5×10^{-2} M) and acetonitrile (2.0×10^{-2} M) did not alter the spectrum of $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$, indicating that these nitriles are very poor bases at best.

Kinetics Studies. The kinetics of the reactions of $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ with axial bases CN^- , $\text{CH}_2=\text{CHCN}$, and CH_3S^- were studied. In the case of CN^- , there is direct experimental evidence from equilibrium constant measurements for the displacement of $\text{P}(\text{C}_4\text{H}_9)_3$ by CN^- rather than the addition of CN^- to give a complex of increased coordination number. The kinetics of the reaction of CN^- with $[\text{Co}^{\text{I}}$

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(9) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* 1970, 9, 616 and references therein.

Table II. Dependence of k_{obsd} on the Concentrations of Various Entering Bases ($X = \text{CH}_2\text{CHCN}$, CN^- , and CH_3S^-) and of Tri-*n*-butylphosphine for Reactions with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ ^a

concn ratio, [X]/ [P(C ₄ H ₉) ₃]	$k_{\text{obsd}}, \text{s}^{-1}$		
	X = CH ₂ =CHCN	X = CN ^{-e}	X = CH ₃ S ⁻
1.0	3.92 ± 0.12		
1.3		0.34 ± 0.01	
2.0	5.98 ± 0.17		
2.5		0.43 ± 0.01	3.26 ± 0.05
4.0	6.95 ± 0.04		
5.0	7.83 ± 0.15	0.79 ± 0.03	
5.0		0.78 ± 0.02 ^f	
5.0		0.82 ± 0.05 ^g	
6.3		0.89 ± 0.01	
7.5			6.70 ± 0.10
10.0	8.90 ± 0.14	1.41 ± 0.08	6.70 ± 0.10
10.0	8.96 ± 0.03 ^b		
10.0	8.70 ± 0.16 ^c		
12.5		1.62 ± 0.04	6.84 ± 0.10
15.0			7.34 ± 0.10
20.0		2.21 ± 0.10	8.40 ± 0.10
30.0			8.75 ± 0.05
40.0	10.17 ± 0.10		9.05 ± 0.05
40.0	10.17 ± 0.03 ^d		
50.0		3.60 ± 0.10	

^a In methanol at 25.00 ± 0.02 °C and 0.10 M OH⁻ (except as noted); followed at 620 (CH₂=CHCN), 610 (CN⁻), or 330 nm (CH₃S⁻). ^b λ 550 nm. ^c [OH⁻] = 0.05 M, μ = 0.1 M (NaCl). ^d [OH⁻] = μ = 0.3 M. ^e μ = 0.20 M (NaCl). ^f [OH⁻] = 0.20 M. ^g [OH⁻] = 0.080 M.

$(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ was monitored at 610 nm. The kinetic data were also consistent with the equilibrium as in eq 2, and in general an equilibrium process with different degrees of reversibility can be considered also for CH₂=CHCN and CH₃S⁻. The kinetics of the reaction of CH₂=CHCN was monitored at 620 nm whereas the reaction with CH₃S⁻ was followed at 330 nm. A decrease in the absorbance in the case of CH₂=CHCN and an increase in the absorbance in the case of CH₃S⁻ were observed at the wavelengths chosen. In the cases of both CN⁻ and mercaptide, a single kinetic step was seen, and the observed absorbance changes (0.1–0.4 units) agreed with those expected. In the case of CH₂=CHCN, however, the reaction with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ in the presence of free phosphine exhibited two distinctly separated kinetic steps, one with $t_{1/2}$ of 50 ms and the other with $t_{1/2} \approx 7$ –10 s. The optical changes corresponding to the first step, however, were of the order of 0.4–0.5 units and were generally reproducible to a high degree. The optical changes in the second stage were not very reproducible but were independent (within a factor of 2) of many concentration variables such as [CH₂=CHCN], [P(C₄H₉)₃], and [OH⁻], which need further comment at a later stage. The faster kinetic step exhibited many meaningful dependences on the concentrations of CH₂=CHCN and phosphine, and, therefore, detailed kinetic measurements were made only for the kinetic process corresponding to the first step. Pseudo-first-order plots of the first kinetic step in spite of secondary reactions were generally linear to 4 half-lives and reproducible within 3–4% as in the case of the other two axial bases. The concentration ranges investigated were [Co(I)] = (1–2) × 10⁻⁴ M, [P(C₄H₉)₃] = (1–50) × 10⁻⁴ M, [acrylonitrile] = (1–5) × 10⁻³ M, [CH₃S⁻] = (1.25–8) × 10⁻³ M, [CN⁻] = (1.25–10) × 10⁻³ M, and [OH⁻] = 0.05–0.2 M. The data are summarized in Table II.

Ionic strength in the case of CN⁻ was maintained at 0.2 M (NaCl); perchlorate salts had to be avoided, owing to the oxidation of $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ in that medium. Further, in the reaction of CN⁻, owing to the limited solubility of both NaCl and NaCN in methanol, an aqueous methanolic

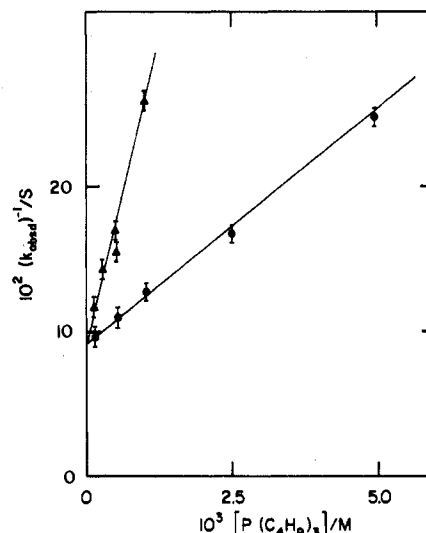
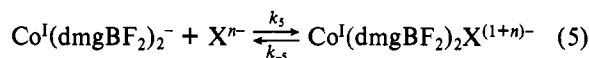
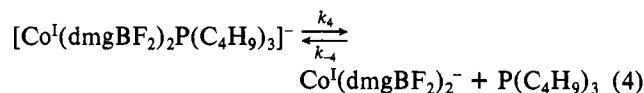


Figure 1. Dependence of k_{obsd} on the concentration of P(C₄H₉)₃ in the reaction of CH₂=CHCN with $\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3^-$ at 25 °C and [OH⁻] = 0.1 M in methanol. Acrylonitrile concentrations are 1.00 × 10⁻³ M (triangles) and 5.00 × 10⁻³ M (circles). See eq 7.

medium had to be used. However, the ratio of water to methanol did not alter the observed rate at [OH⁻] = 0.2 M when the water:CH₃OH ratio was varied from 1:99 to 1:3.76. Analysis of the dependence of k_{obsd} on [OH⁻] (0.20 and 0.08 M) indicated that the observed rate for the CN⁻ reaction was independent of [OH⁻] within one standard deviation. In the case of acrylonitrile with [OH⁻] = 0.05–0.30 M, the observed rates were within two standard deviations in spite of variations in ionic strength. Therefore, the bulk of the rate data in the reactions of all three axial bases were collected at [OH⁻] = 0.1 M.

Both CH₃SH and HCN are weak acids, but in the [OH⁻] range used for kinetics (at least in water) CH₃S⁻ and CN⁻ were the predominant and reactive species. The dependence of k_{obsd} on the concentration of acrylonitrile at a fixed phosphine concentration was less than first order. The variations of k_{obsd} on the [P(C₄H₉)₃] at a fixed [CH₂=CHCN] indicated an inverse-order dependence at two acrylonitrile concentrations with a common intercept (Figure 1). The observed dependences of k_{obsd} on the concentration of phosphine and axial bases can be explained by the reaction scheme of eq 4 and 5,



where $n = 0$ or 1 and $X = \text{CH}_2\text{CHCN}$, CN^- , or CH_3S^- . Assuming the steady-state approximation applies to the concentration of the intermediate, four-coordinate $\text{Co}^{\text{I}}(\text{dmgBF}_2)_2^-$, it is possible to derive a general rate law as in eq 6. Denoting

$$k_{\text{obsd}} = \frac{k_{-5} + \frac{k_4 k_5 [\text{X}^{n-}]}{k_{-4} [\text{phosphine}]}}{1 + \frac{k_5 [\text{X}^{n-}]}{k_{-4} [\text{phosphine}]}} \quad (6)$$

k_5/k_{-4} as Q and $[\text{X}^{n-}]/[\text{phosphine}]$ as R , eq 6 can be written as eq 7. In the cases of both CH₂=CHCN and CH₃S⁻ there

$$k_{\text{obsd}} = \frac{k_{-5} + k_4 QR}{1 + QR} \quad (7)$$

was no evidence for any appreciable contribution from the k_{-5}

Table III. Summary of Kinetic Parameters for the Reactions of CH_2CHCN , CN^- , and CH_3S^- with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ at $25.0 \pm 0.02^\circ\text{C}$ in Methanol 0.10 M in OH^- ^a

ligand	k_4, s^{-1}	k_5/k_{-4}	k_{-5}, s^{-1}
CH_2CHCN	10.5 ± 1.8	0.59 ± 0.05	
CH_3S^-	10.3 ± 1.8	0.19 ± 0.015	
CN^- ^a	9.1 ± 5.0	0.011 ± 0.005	0.28 ± 0.02

^a A value of 0.37 for the equilibrium constant, obtained from spectrophotometric determinations, was used as a fixed quantity in the fit of the kinetic data to eq 7.

term, and the equation in those cases could be simplified to eq 8. A nonlinear least-squares fit of the rate data given in

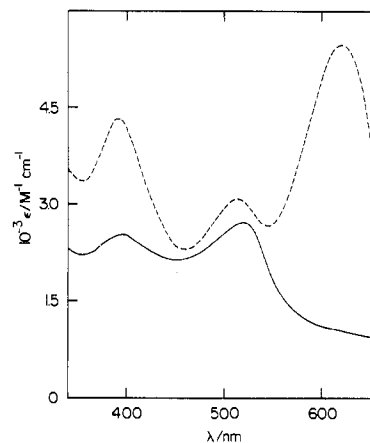
$$k_{\text{obsd}} = k_4QR/(1 + QR) \quad (8)$$

Table II to eq 7 or 8 gave the values of k_4 and k_5/k_{-4} for CH_2CHCN , CH_3S^- , and CN^- and k_{-5} as well for CN^- at $25 \pm 0.02^\circ\text{C}$. The values of the various rate parameters obtained are listed in Table III. One requirement of the mechanism given in eq 4 and 5 is that k_4 be independent of the entering group. Within a rather substantial experimental error, this is the case.

Analysis of Products from the Reaction of Acrylonitrile with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$. An attempt to isolate and characterize the products of the reaction of acrylonitrile with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ was made in view of the several intriguing features of the reaction. The addition of acrylonitrile to $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ at various ratios of Co(I) to olefinic ligand did not generate a red or purple species, contrary to earlier reports,² unless minute traces of oxygen were also present. Rather, we observed a greenish blue product with strict exclusion of air, a product having an electronic spectrum similar to that of the parent, five-coordinate complex $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$. The anaerobic product is, indeed, believed to be the claimed π complex, but with an electronic spectrum different from the one published.² The experiments underlying these statements are as follows.

The products were separated by gel filtration on a column of Sephadex LH-20 under strictly air-free conditions, yielding a greenish blue product containing some 50–70% of the total cobalt, the remainder being the parent cobalt(I)-phosphine complex which separates cleanly. The product proved remarkably sensitive to even traces of oxygen, yielding a red solution. In this form, the product had a spectrum distinctly different from that obtained before oxygenation (see Table I and Figure 2), with maxima at λ 518 and 396 nm, contrasted to 620, 512, and 396 nm for the original bluish green product. In comparison, the literature² reports a product with λ 546 and 440 nm that has a spectrum quite similar to ours when exposed to oxygen throughout the UV-visible region.

Several attempts to characterize the greenish blue product by means of NMR were made. The utility of NMR in distinguishing π complexes of $\text{CH}_2=\text{CHCN}$ in the chemistry of Pt(II) compounds is well established.¹⁰ A similar approach in the case of the $\text{Co}^{\text{I}}-(\text{CH}_2=\text{CHCN})$ adduct was, however, difficult because of the need to choose suitable NMR solvents which would be unreactive with Co(I). Solvents such as CDCl_3 , CD_2Cl_2 , and CS_2 were found to react with the greenish blue product. With CH_3OH and CD_3OD as solvents, however, no conclusive evidence could be obtained, owing to the appearance of OH signal at δ 4.8, a position where the signals due to π -bonded olefin are expected to occur. Where NMR spectra of the reaction mixture without any chromatographic separation were attempted, even with very concentrated solutions, only weak and broad signals could be observed, possibly due to some paramagnetic species. Thus no firm structural

**Figure 2.** UV-visible spectra in methanol containing 0.1 M OH^- of the acrylonitrile π adduct of $\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3^-$ (dashed line) and of the oxidized form obtained by exposure to traces of air (solid line).

evidence has yet been obtained; however, the kinetic and all other indirect evidence point out that the primary product of the reaction of $\text{CH}_2=\text{CHCN}$ with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ is indeed a π adduct as assigned by Schrauzer et al.,² although its formation is accompanied by loss of phosphine as shown in eq 1, 4, and 5.

Secondary Reactions. The reaction of acrylonitrile with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ shows a second and much slower kinetic step. This step is seen not only with mixing of the given reagents but also with prior purification of the cobalt(I) complex by chromatography on Sephadex LH-20. In contrast, both CH_3S^- and CN^- react with the cobalt(I) complex in a single kinetic step. The rate constant for this secondary process with acrylonitrile shows no dependence on $[\text{CH}_2=\text{CHCN}]$. The corresponding reaction of acrylonitrile and $[\text{Co}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3]^-$ also occurs in two stages, the second being accompanied by a large increase in absorbance and regeneration of the spectrum of the cobalt(I) reactant ($k = 1.1 \times 10^{-3} \text{ s}^{-1}$). It thus appears that acrylonitrile is being removed in a slow reaction which re-forms the parent phosphine complex. In light of reports¹¹ that tertiary phosphines add readily to activated olefins and serve as catalysts for polymerization, it seems likely that similar processes are occurring here. Indeed, tributylphosphines and acrylonitrile in the absence of cobalt(I) do react over a period of 2–3 h under these conditions. NMR determinations at various concentrations of reactants showed a variety of organic products ranging from propionitrile and its derivatives to polyacrylonitrile. Indeed, at 10^{-2} M Co(I) and 7 M acrylonitrile, a polymeric solid with NMR and IR spectra corresponding to the latter was obtained. Since nucleophiles such as sodium cyanide, sodium bisulfide, and tertiary phosphines in methanol catalyze the polymerization of acrylonitrile,¹² it is not surprising that such a powerful nucleophile as this cobalt(I) complex would do so well.

Reactions with Benzyl Chloride and *n*-Butyl Bromide. To explore the effect of the π -bonding interaction on the nucleophilicity of the cobalt(I) complexes, we undertook a brief investigation of their reactions with organic halides. In agreement with Schrauzer,² we find that the acrylonitrile adduct of $\text{Co}^{\text{I}}(\text{dmgH})_2^-$ is essentially unreactive toward these organic halides. In contrast, for the dmgBF_2 derivatives, both the parent complex and its π adduct react at comparable rates. For $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2(\text{CH}_2=\text{CHCN})]^-$, $k = 2.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

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(12) Sandler, S. R.; Karo, W. "Polymer Synthesis"; Academic Press: New York, 1974; p 326 and references therein.

for PhCH_2Cl and $3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for $n\text{-BuBr}$. Clearly a different explanation for these seemingly conflicting findings is needed. The products were found to be different; benzyl chloride reacted with the cobalt(I) complex to yield the expected benzyl derivative, whereas the π $\text{CH}_2=\text{CHCN}$ adduct also gave appreciable quantities of the inorganic cobalt(III) complex, chlorocobaloxime. Thus a halide ion abstraction mechanism seems to intervene in this case.

Discussion

The earlier assignments of a five-coordinate structure to Co(I) cobaloxime complexes seem well supported by the large changes in the spectra of Co(I) cobaloxime complexes in solutions containing different bases. Further, coordination of five ligands to a d^8 ion would give rise to an 18-electron configuration giving stability to a geometry which is generally visualized as only a transition state in the chemistry of octahedral and square-planar complexes. The observed kinetic rate law for at least the reactions of CH_2CHCN and CH_3S^- rules out a simple bimolecular mechanism involving a geometry of higher (6) coordination number. On the other hand, the rate law is consistent with an intermediate of reduced coordination number.

We note that the values of k_5/k_{-4} for CH_3S^- and CH_2CHCN are rather close, 0.59 and 0.19, supporting the mechanism of eq 4-8. Also, as remarked earlier, the constancy of k_4 between the three systems provides supporting evidence as well.

The observation that $[\text{Co}^{\text{I}}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ and $[\text{Co}^{\text{I}}(\text{dmgH})(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ react with $\text{CH}_2=\text{CHCN}$ faster than $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$ by factors of 25-40 and 10-20, respectively, is consistent with a dissociative process. (These rates reflect variations in k_4 .) With greater delocalization of the electron density in the equatorial ligands, the dissociation rate of the $[\text{Co}^{\text{I}}-\text{P}(\text{C}_4\text{H}_9)_3]^-$ bond decreases. In

view of the 18-electron configuration, it is not surprising that a 16-electron transition state seems more favorable.

Another notable finding is that while $\text{CH}_3\text{CH}_2\text{CN}$ does not form complexes with $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$, the olefinic analogue $\text{CH}_2=\text{CHCN}$ forms relatively stable complexes and competes very favorably for the four-coordinate intermediate as seen for k_5/k_{-4} (Table III). Were the $\text{C}\equiv\text{N}$ group the ligating site in $\text{CH}_2=\text{CHCN}$, it would be difficult to account for (a) the much greater stability of the acrylonitrile adduct as compared to that with CN^- ($K > \text{ca. } 10^3$ vs. $K = 0.37$) and (b) the much more effective competition of $\text{CH}_2=\text{CHCN}$ than of CN^- for the four-coordinate intermediate, 0.59 vs. 0.011 for k_5/k_{-4} .

On the basis of our kinetic data and other evidence, it is reasonable to conclude that the five-coordinate $\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3$ reacts with CH_2CHCN , CN^- , and CH_3S^- by a dissociative mechanism to give products with different degrees of π bonding. The reactions of Co^{I} acrylonitrile adducts with H^+ should be of considerable interest from the point of view of the mechanisms of homogeneous hydrogenation processes.

Acknowledgment. This work was supported by the U.S. Department of Energy, Contract No. W-7405-Eng-82, Office of Basic Energy Sciences, Division of Chemical Sciences, budget code AK-01-03-02-1.

Registry No. $\text{ClCo}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3$, 73117-41-6; $\text{ClCo}(\text{dmgBF}_2)(\text{dmgH})\text{P}(\text{C}_4\text{H}_9)_3$, 73117-42-7; $\text{ClCo}(\text{dmgBF}_2)_2\text{C}_5\text{H}_5\text{N}$, 73117-43-8; $[\text{Co}^{\text{I}}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3]^-$, 63902-69-2; $[\text{Co}^{\text{I}}(\text{dmgH})(\text{dmgBF}_2)\text{P}(\text{C}_4\text{H}_9)_3]^-$, 73117-26-7; $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{P}(\text{C}_4\text{H}_9)_3]^-$, 73117-27-8; $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2\text{C}_5\text{H}_5\text{N}]^-$, 31319-33-2; $[\text{Co}^{\text{I}}(\text{dmgBF}_2)_2(\text{CH}_2=\text{CHCN})]^-$, 73117-28-9; CH_2CHCN , 107-13-1; CH_3S^- , 17032-46-1; CN^- , 57-12-5; $\text{ClCo}(\text{dmgH})_2\text{P}(\text{C}_4\text{H}_9)_3$, 24501-27-7; PhCH_2Cl , 100-44-7; $n\text{-BuBr}$, 109-65-9; $\text{ClCo}(\text{dmgH})_2\text{C}_5\text{H}_5\text{N}$, 23295-32-1.

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Electrochemistry of Aqueous Molybdenum(VI), -(V), and -(III) Catechol Complexes. Dimerization of Molybdenum(V) in Weakly Acidic Solution

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Received October 9, 1979

Electrochemical reduction of the *cis*-dioxo molybdenum(VI)-catechol complex, $\text{MoO}_2(\text{cat})_2^{2-}$, in pH 3.5-7 aqueous buffers occurs by sequential one- and two-electron transfers to yield transiently stable Mo(V) and Mo(III) species, $\text{MoO}(\text{H}_2\text{O})(\text{cat})_2^-$ and $\text{Mo}(\text{H}_2\text{O})_2(\text{cat})_2^-$. Uptake of two protons accompanies each electron-transfer step and converts an oxo group to a coordinated water molecule. Pyridine substitution occurs at these aquo sites. Formation constants of the species $\text{MoO}(\text{py})(\text{cat})_2^-$, $\text{Mo}(\text{H}_2\text{O})(\text{py})(\text{cat})_2^-$, and $\text{Mo}(\text{py})_2(\text{cat})_2^-$ are determined from voltammetric half-wave potential measurements. The reduced molybdenum monomers are not stable indefinitely at pH < 7. Dimerization to the di- μ -oxo species, $\text{Mo}_2\text{O}_4(\text{cat})_2(\text{H}_2\text{O})_2^{2-}$, occurs after reduction to the Mo(V) state. The mechanism of the reaction has been investigated by cyclic voltammetry. The mechanism involves dissociation of one molecule of pyridine and one molecule of catechol from $\text{MoO}(\text{py})(\text{cat})_2^-$ to produce a 1:1 molybdenum(V)-catechol monomer, which undergoes dimerization by acid-dependent and acid-independent pathways.

Recent electrochemical studies of molybdenum compounds¹⁻⁸ have sought to establish relationships between

structural and electron-transfer properties which may prove helpful in understanding the redox behavior of molybdoenzymes. Most of this work has dealt with oxo- or sulfido-bridged molybdenum(V) dimers, which are prevalent structural forms of this oxidation state. However, recent X-ray absorption studies indicate that the active sites of nitrogenase,⁹ sulfite oxidase,¹⁰ and xanthine oxidase¹¹ may be mononuclear

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