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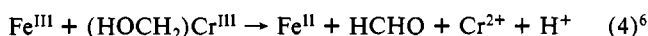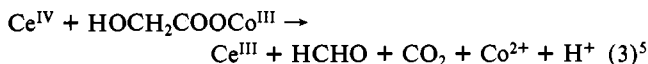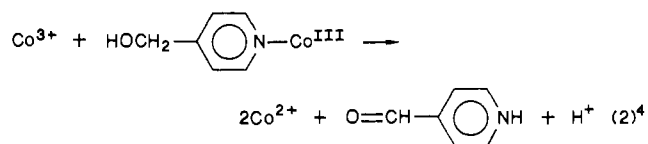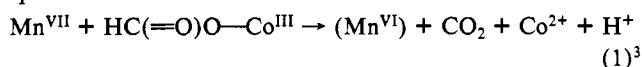# Electron Transfer. 88. Cobalt(III)-Bound Phosphite and Hypophosphite[1]

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Phosphite and hypophosphite coordinate to cobalt(III) in $(NH_3)_5Co^{III}$ through oxygen, rather than through phosphorus. The resulting complexes undergo electron-transfer reactions with $Ru(NH_3)_6^{2+}$ much more slowly than with Eu^{2+} or V^{2+}, indicating that the latter two reactants preferentially utilize ligand bridging. Reductions with Cr^{2+} are shown to be accompanied by transfer of the phosphorus-containing ligands, and reaction of the protonated phosphito (biphosphito) derivative (pK_A = 3.06 at 23 °C) proceeds through a combination of acid-independent and inverse-acid paths, both routes yielding the same phosphito-bound Cr(III) product. The hypophosphito, but not the biphosphito, complex reacts with Ce(IV), producing Co^{2+} in an induced electron-transfer process. The yield of Co^{2+} falls off progressively as $[Ce^{IV}]$ is increased, pointing to a sequence in which a Co(III)-bound P(II) radical is formed in initial attack by Ce(IV) but subsequently undergoes partition between competing reaction paths, i.e. internal electron transfer to Co(III) vs external oxidation by a second Ce(IV) center. The hypophosphito complex, but not the biphosphito complex, smoothly decomposes in basic media via an internal redox reaction, yielding Co(II) quantitatively, along with a 1:1 mixture of phosphite and hypophosphite. This transformation, which fails with mixtures of $(NH_3)_5Co(H_2O)^{3+}$ and $H_2PO_2^-$, appears to be catalyzed specifically by OH^-. Deuterium-labeling experiments disclose a solvent isotope effect, k_{H_2O}/k_{D_2O}, of 1.14–1.23 and a substrate isotope effect, k_{H_2P}/k_{D_2P}, of 2.1–2.3, in better accord with a hydride-transfer mechanism than with a homolytic process or removal of hydrogen as H^+. The proposed sequence entails a hydroxide-induced hydride shift from phosphorus to Co(III), yielding a protonated Co(I) species, which then reacts very rapidly with a second Co(III), yielding two Co(II) species and releasing hypophosphite. The suggested mechanism is similar to those proposed for a number of conversions proceeding through organometallic species and is also analogous to the Cannizzaro reaction of aldehydes in basic media.

In transformations proceeding by induced electron transfer, a ligand bound to a reducible metal ion reacts with an external 1e oxidant, forming a metal-bound radical intermediate. Internal electron transfer within this intermediate then consummates a net 2e oxidation of the ligand, yielding two reduced metal centers, one derived from the ligated metal ion, the other from the external oxidant.[2] Representative examples are shown schematically as eq 1–4.

$$Mn^{VII} + HC(=O)O-Co^{III} \rightarrow (Mn^{VI}) + CO_2 + Co^{2+} + H^+$$
(1)[3]

$$Ce^{IV} + HOCH_2COOCo^{III} \rightarrow$$
$$Ce^{III} + HCHO + CO_2 + Co^{2+} + H^+ \quad (3)^5$$

$$Fe^{III} + (HOCH_2)Cr^{III} \rightarrow Fe^{II} + HCHO + Cr^{2+} + H^+ \quad (4)^6$$

In each of these conversions the ligand undergoing oxidation is an organic species. The present study began as an attempt to extend this type of reaction to complexes derived from the inorganic ligands phosphite (HPO_3^{2-}) and hypophosphite ($H_2PO_2^-$), anions which generally (although not always[7]) undergo 2e oxidations. Induced electron transfer been found to occur in the oxidation, by Ce(IV), of the $(NH_3)_5Co^{III}$ complex of hypophosphite, but not with the analogous derivative of phosphite. Of principal interest, however, is an unexpected internal redox reaction involving the hypophosphito complex. This appears to proceed via hydride transfer and may be related to a number of transformations in which organometallic intermediates have been implicated.

Experimental Section

Physical Measurements. ^1H and ^{31}P NMR spectra were recorded on Varian EM-360 and FT-80 spectrometers: frequency 29.9448 MHz; spectral width 8 kHz; pulse width 5 μs; repetition time 6.015 s; 16 000 data points. Proton NMR spectra were referenced to $(CH_3)_3Si-(CH_2)_2SO_3^-$ (sodium salt, upfield singlet at $\delta = 0$ ppm) and ^{31}P NMR spectra to external H_3PO_4 (0 ppm). UV–visible spectra were taken on a Cary 15 spectrophotometer.

Analyses. Cobalt and perchlorate analyses were carried out as described.[8] Determinations of phosphite and hypophosphite (in solutions containing both) utilized the iodometric method of Jones and Swift.[9] Microanalyses were performed by Galbraith Laboratories.

Materials. Aquopentaamminecobalt(III) perchlorate,[8,10] lithium perchlorate,[11] and solutions of $Eu(ClO_4)_2$,[12] $V(ClO_4)_2$,[13] $Cr(ClO_4)_2$,[8] and $Ru(NH_3)_6Cl_2$[14] were prepared as described. Sodium perchlorate monohydrate and ethylenediaminetetraacetic acid sodium salt (Na_4EDTA) (Aldrich products) were recrystallized from water before use. Sodium hypophosphite, hypophosphorous acid-d_3 (D_3PO_2), phosphorous acid, dueterium oxide (99.8 atom % D), sodium deuterioxide, and perchloric acid (all Aldrich products) and cerium(IV) ammonium nitrate (Baker) were used as received.

Preparations of Cobalt(III) Complexes. Preparations of the $(NH_3)_5Co^{III}$ complexes of hypophosphorous and phosphorous acids were similar to those described by Sisley and Jordan,[15] but there were differences in detail. For the hypophosphito complex, a buffered solution (pH 1.8) prepared from 2.3 mL of 11 M $HClO_4$ and 14.3 g of $NaH_2P-O_2\cdot H_2O$ in 11 mL of water was added to a solution of 7.4 g of $(NH_3)_5-Co(H_2O)(ClO_4)_3$ in 22 mL of water at 70 °C. The mixture was maintained at 70 °C for 2 h and then allowed to cool to room temperature. Addition of 10 mL of concentrated $HClO_4$, followed by cooling to 0 °C, yielded 5.9 g of crystalline product. Separation of the desired derivative from the unreacted aquo perchlorate was accomplished by elution with water from a column of Bio Gel P-2 (20 × 4 cm; flow rate 2 mL/min). The first 15 mL of the burgundy red aqueous eluate was collected and the volume reduced to 3 mL by rotary evaporation at room temperature. Concentrated $HClO_4$ was added to incipient crystallization, and the mixture was then cooled to 0 °C, yielding 0.90 g (40%) of wine red platelets. Anal. Calcd for $Co(NH_3)_5O_2PH_2(ClO_4)_2$: P, 7.59; Co, 14.4; ClO_4, 48.8. Found: P, 7.48; Co, 14.3;[8] ClO_4, 50.1.[8] ^1H NMR (D_2O 0.5 M): δ 6.76 (d, J_{PH} = 548 Hz, 2 H, CoO_2PH_2), 2.85 (br s, 12 H, Co-

(1) Joint sponsorship of this work by the National Science Foundation (Grant No. 8619472) and by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health (Grant No. BRSG SO7 RR-07208-8) is gratefully acknowledged.
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Table I. pK_A Values for $(NH_3)_5Co^{III}$ Complexes and Their Parent Acids

acid	p$K_A{}^a$	n^b	ref
H_3O^+	≪0		1
$(NH_3)_5Co(OH_2)^{3+}$	6.21		23
H_3PO_4	1.72	3	
$(NH_3)_5Co(OPO_3H_2)^{2+}$	3.65	3	21
$H_2PO_4{}^-$	5.92	3	
$(NH_3)_5Co(OPO_3H)^+$	8.46	3	21
H_3PO_3	1.5	3	
$(NH_3)_5Co(OPHO_2H)^{2+}$	3.06		c
malonic	2.65	5	
$(NH_3)_5Co(O_2CCH_2COOH)^{2+}$	3.4		d
phthalic	2.66	7	
$(NH_3)_5Co(biphthalato)^{2+}$	3.03		e

^{a} Values have been selected (where available) to pertain to 25 °C and $\mu = 0.1$ M. pK_A's of unbound acids were taken from: Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1977; Vols. 3 and 4. ^{b} Number of atoms separating acidic hydrogens. ^{c} This work. ^{d} Svatos, G.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 4172. ^{e} Gould, E. S., unpublished experiments, Stanford University, 1962.

$(NH_3)_{eq})$, 1.7 (br s, 3 H, $Co(NH_3)_{ax})$. ^{31}P NMR (D_2O, 0.5 M): δ 18.9 (t, $J_{PH} = 549$ Hz). UV-vis (0.5 M $HClO_4$): λ_{max} 518.5 ($\epsilon = 60.6$ M^{-1} cm^{-1}), 355 nm ($\epsilon = 47.9$); lit.[15] 518 ($\epsilon = 61.7$), 354 nm ($\epsilon = 49.5$).

The P-deuteriated complex was obtained by an analogous ligation procedure, using D_3PO_2/NaD_2PO_2 in D_2O. Although the chromatographic separations were carried out with H_2O, ^1H NMR (internal standard formate buffer, pH 4) indicated the absence of the Co–PH$_2$ complex.[16] ^{31}P NMR showed the product to be a 84/16 mixture of the Co–O$_2$PD$_2$ and Co–O$_2$PHD complexes. ^{31}P NMR (D_2O, 0.5 M): δ 16.4 (quintent, $J_{PD} = 84$ Hz, CoO_2PD_2), 16.6 (dt, $J_{PH} = 547$ Hz, $J_{PD} = 84$ Hz, CoO$_2$PHD).[17,18]

The corresponding protonated phosphito (biphosphito) complex, $(NH_3)_5CoOPO_2H_2(ClO_4)_2$, was prepared similarly, by using a solution containing H_3PO_3 and NaH_2PO_3. Anal. Calcd for $Co(NH_3)_5O_3PH_2$-$(ClO_4)_2$: H, 4.33; P, 7.00; Co, 13.3; ClO_4, 45.0. Found: H, 4.30; P, 6.99; Co, 13.2; ClO_4, 47.0. ^1H NMR (D_2O, 0.5 M): δ 6.55 (d, $J_{PH} = 655$ Hz, 1 H, Co–O$_3$PH), 3.05 (br s, 12 H, $Co(NH_3)_{eq})$, 1.70 (br s, 3 H, Co-$(NH_3)_{ax})$. ^{31}P NMR (D_2O, 0.5 M): δ 13.6 (d, $J_{PH} = 663$ Hz). UV-vis (0.5 M $HClO_4$): λ_{max} 516.5 ($\epsilon = 62.2$), 353 nm ($\epsilon = 48.0$); lit.[15] 516 ($\epsilon = 62.9$), 353 nm ($\epsilon = 48.5$).

The biphosphito complex exhibited an apparent pK_A (potentiometric titration of a 0.1 M solution in the absence of a supporting electrolyte, 23 °C) of 3.06 ± 0.06. On treatment with 1 M $NaCO_3$, its spectra shifted slightly, with λ_{max} at 518.5 ($\epsilon = 79.2$) and 353 nm ($\epsilon = 70$).

No significant problems in handling these perchlorate salts were encountered.

Kinetics of Electron Transfer. Rates were estimated from absorbance decreases as described.[8,12] Measurements were made at 516–518 nm. Reactions were first order each in Co(III) and reductant but were run by using at least an eightfold excess of the latter. Ionic strengths were generally 1.0 M ($LiClO_4$–$HClO_4$). Addition of 0.1 M CH_3CN to the $Ru(NH_3)_6{}^{3+}$ from which Ru(II) was generated allowed us to carry out reductions under N_2 (rather than argon), by using the perchlorates of the oxidants.[14b] Rate constants from successive half-life values within a run agreed to within 5%. Specific rates from replicate runs checked to within 8%.

The Cr(III) product from reduction of the hypophosphito complex with Cr^{2+} had λ_{max} values of 593.5 ($\epsilon = 15.1$) and 420.5 nm ($\epsilon = 17.6$), in agreement with the reported[19] spectrum for the hypophosphito complex

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(16) During the ligation procedure (requiring 2 h at 70 °C in a heavily buffered medium), nearly complete deuterium exchange for N-bound protons occurred. Virtually no "back-exchange" took place during the chromatographic separation (15 min at 23 °C with no buffer).

(17) Observed splitting patterns with relative intensities 1:2:3:2:1 and 1:1:1:1:1, in accord with couplings to the $s = {}^1/_2$ and $s = 1$ nuclei in these complexes.

(18) Note that ^1H and ^{31}P NMR spectra of the $(NH_3)_5Co^{III}$ complexes were similar to, but not identical with, those of the uncoordinated phosphorus ligands. Observed δ_H values (1 M solutions in D_2O): H_3PO_2, 6.56; NaH_2PO_2, 6.21; H_3PO_3, 6.86; NaH_2PO_3 6.79. Observe δ_P: NaH_2PO_2, 7.47; NaH_2PO_3, 9.87. J_{PH} (Hz): H_3PO_2, 572; NaH_2PO_2, 515; H_3PO_3, 606; NaH_2PO_3, 637. Phosphorus multiplets collapsed to the expected singlets upon proton decoupling.

(19) Espenson, J. H.; Binau, D. E. *Inorg. Chem.* **1966**, *5*, 1365. These workers report λ_{max} values of 596 ($\epsilon = 15.6$) and 420 nm ($\epsilon = 17.3$). Sisley and Jordan[15] recorded 592 ($\epsilon = 15.5$) and 416.5 nm ($\epsilon = 17.2$).

Table II. Specific Rates for Reductions of the Phosphito and Hypophosphito Derivatives of $(NH_3)_5Co^{III}$ with Eu^{2+}, V^{2+}, Cr^{2+}, and $Ru(NH_3)_6{}^{2+a}$

complex	[H$^+$]	$k_{Eu(II)}$	$k_{V(II)}$	$k_{Ru(II)}$	$k_{Cr(II)}$
biphosphito, $[Co(NH_3)_5O_3PH_2]^{2+}$	0.1	7.9	2.9	0.59^b	7.6
	0.5				5.4
	1.0	7.3	2.7		4.3
hypophosphito, $[Co(NH_3)_5O_2PH_2]^{2+}$	0.1	14.5	2.7	0.86^b	14.1
	1.0	13.6	2.7		13.0
hypophosphito, –PD$_2$ form					13.3

^{a} Specific rates (in M^{-1} s^{-1}) at 25 °C, $\mu = 1.0$ M ($HClO_4$–$LiClO_4$), $[Co^{III}]_0 = 0.0003–0.003$ M, and [reductant] $= 0.0024–0.03$ M. ^{b} Reductions with $Ru(NH_3)_6{}^{2+}$ were carried out in 0.50 M LiCl. [H$^+$] fell from 0.013 M at the beginning of the run to 0.003 M near the end (due to release of NH_3). No distortion of kinetic profiles was observed.

Table III. Reactions of Cerium(IV) with $(NH_3)_5Co^{III}$ Complexes of Phosphorus Oxyacids^a

reactant	$[Co^{III}]$, M	$[Ce^{IV}]$, M	reacn time, h	$[Co^{II}]/[Co^{III}]^b$
$[(NH_3)_5Co(OPO_3H_2)]^{2+c}$	0.020	0.201	41–53	0.0
$[(NH_3)_5Co(OPHO_2H)]^{2+}$	0.020	0.201	45–57	0.003
$[(NH_3)_5Co(H_2O)]^{3+} + H_3PO_2$	0.020	0.201	41–53	0.0
$[(NH_3)_5Co(OPH_2O)]^{2+}$	0.00725	0.0588	36–48	0.40
	0.00718	0.101	36–48	0.34
	0.0143	0.201	22–28	0.29
	0.0143	0.407	36–48	0.18

^{a} Reactions were carried out with cerium(IV) ammonium nitrate in 1 M $HClO_4$ at 22 °C (see Experimental Section). ^{b} Ratio of Co(II) found to Co(III) taken. ^{c} Dihydrogen phosphato complex prepared by the method of Schmidt and Taube.[21]

of $(H_2O)_5Cr^{III}$, whereas that from the biphosphite oxidant, with λ_{max} at 592 ($\epsilon = 16.3$) and 419.5 nm ($\epsilon = 18.0$), corresponded to the Cr(III)–phosphite complex described by Sisley.[15] The product resulting from reduction of the biphosphito complex in 0.1 M $HClO_4$ was indistinguishable from that from reduction in 0.01 M $HClO_4$.

Reactions with Cerium(IV). Solutions containing measured concentrations of the cobalt(III) complexes and cerium(IV) ammonium nitrate in 0.5 M $HClO_4$ were allowed to stand at 22 °C for extended periods. Aliquots were removed and diluted with excess HCl, and concentrations of Co(II) were measured at 692 nm.[8] Samples were taken until the Co(II) content showed no increase with time (generally 20–50 h). Results are summarized in Table III.

Reaction of the Hypophosphito Complex with Bases. Treatment of solutions of the hypophosphito complex with excess Na_2CO_3 or NaOH resulted in fading of the Co(III) color and formation of precipitates that dissolved in HCl, yielding blue $CoCl_4{}^{2-}$. When such reactions were carried out in the presence of Na_4EDTA, precipitation did not occur, and the resulting solution exhibited, after removal of dissolved NH_3 by purging with N_2, a spectrum corresponding to the Co(II) complex[20] of $(EDTA)^{4-}$. Analyses of the reaction mixture for Co(II),[8] P(I),[9] and P(III)[9] are summarized in Table IV. This reaction did not release a detectable quantity of H_2. Substitution of the chloride salt of the hypophosphito complex for its perchlorate salt did not alter the course of the reaction. Analogous transformations did not occur with the corresponding phosphito complex or with an equimolar mixture of $(NH_3)_5Co(H_2O)^{3+}$ and $H_2PO_2{}^-$.

Attempts were made to study this reaction kinetically, both in mixtures of NaOH and Na_4EDTA and in Na_4EDTA alone. Rates were found to increase markedly with pH, but only in the latter medium were satisfactory exponential decay curves obtained. With OH$^-$ in excess, kinetic complications, including the rapid formation of a transient absorbing at 320 nm, were evident, although the net stoichiometry was unchanged. Further investigation of the reaction under the latter conditions is continuing.

When the reaction was carried out with the PD$_2$-labeled form of the hypophosphito complex, biphasic kinetic profiles resulted, reflecting in-

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(20) This spectrum, which was generated independently by treating $Co(OAc)_2$ with Na_4EDTA, showed λ_{max} at 462 nm ($\epsilon = 15.5$) and shoulders at 485 ($\epsilon = 14.3$) and 505 nm ($\epsilon = 13.2$). These features suffer significant alteration in the presence of dissolved NH_3, due presumably to partial incorporation of NH_3 in the coordination sphere of the substitution-labile Co(II) center.

Table IV. Products from the Reaction of the Hypophosphito Complex $[(NH_3)_5Co(OPH_2O)]^{2+}$ with Aqueous Base[a]

Co^III complex	mmol of complex	base	mmol of base	$[Co^{II}]/[Co^{III}]_0$	$[P^{III}]/[Co^{III}]_0$	$[P^I]/[Co^{III}]_0$
$(NH_3)_5Co(OPH_2O)^{2+}$	0.739	Na_2CO_3	30	0.966	0.502	0.483
	0.736	Na_4EDTA	3.0	0.962	0.472	0.492
	0.732	NaOH	0.70	0.943	0.488	0.448
	0.703	NaOH	0.25[b]	0.952	0.464	0.492
$(NH_3)_5Co(OPHO_2)^+$	0.10	Na_2CO_3	0.50	0.00		
$(NH_3)_5Co(H_2O)^{3+}$	0.10	$NaH_2PO_2 + Na_2CO_3$	0.10			
			0.50			
		$Na_2HPO_3 + Na_2CO_3$	0.10	0.00		
			0.50			

[a] Reactions were carried out at 23 °C under N_2[9] for at least 12 h prior to iodometric determination of P^I (hypophosphite) and P^{III} (phosphite). Reaction volume was 6.7 mL. [b] Reaction time 24 h.

dividual reactions of the PHD and PD_2 species. These were handled as combinations of two parallel pseudo-first order transformations involving the same change in molar absorbance according to eq 5, where A_t and

$$A_t - A_\infty = ae^{-k_a t} + be^{-k_b t} \qquad (5)$$

A_∞ are absorbances at time t and infinite time, k_a and k_b are the rate constants for the major and minor components, and a and b are the absorbance changes attributable to the two components. Nonlinear least-squares treatment of kinetic data, employing (5) and keeping the ratio a/b as 84/16 (in accordance with the isotopic analysis of the reactant by NMR), yielded values of the two specific rates. When all parameters in (5) were allowed to "float", refinement yielded a ratio a/b very close to that estimated by NMR. In either case, however, the estimated uncertainty in k_b exceeded its magnitude as obtained from the refinement (probably reflecting the slight degree of distortion and the identity of $\Delta\epsilon$ values associated with the two components). Thus, only values of k_a are considered trustworthy.

Results and Discussion

Characterization of the Complexes. The hypophosphito and phosphito derivatives of $(NH_3)_5Co^{III}$ have been prepared in solution by Sisley and Jordan,[15] who did not, however, report properties of the crystalline complexes. The close similarity between the electronic spectra of our products and the analogous phosphato complex described by Schmidt and Taube[21] indicates that in all three cases Co^{III} is O-bound, rather than P-bound, and our NMR spectra, which show that both P-bound hydrogens in $H_2P(O)OH$ and the single P-bound hydrogen in $HP(O)(OH)_2$ are retained in ligation, are in accord with this assignment. As expected, coordination to Co(III) leaves only one accessible acidic center in phosphite and none in hypophosphite (although it is possible that additional protonation equilibria may be observable in unusually acidic[21] or very strongly basic media).

It has been emphasized[21,22] that replacement of H^+ by $(NH_3)_5Co^{III}$ in a species having two or more ionizable protons lowers its acidity, reflecting the much higher density of positive charge on H^+. This effect is most striking when H_3O^+ is compared to $(NH_3)_5Co(OH_2)^{3+}$ ($pK_A = 6.2$),[23] for the substituents under consideration are bound to the same oxygen atom. It is much less marked for other couples (Table I), in which several atoms separate the centers. As anticipated, the analogous increases in pK_A (1.5–2.5 units) are similar for phosphoric and phosphorous acids (each with three atoms between acidic substituents) and fall between that for H_3O^+ (one intervening atom) and that for malonic acid (five atoms).[24]

Reactions with Metal-Center Reductants. Specific rates for reduction of the biphosphito and hypophosphito complexes are summarized in Table II. Values of $k_{Ru(II)}$, pertaining to the (necessarily outer-sphere) reductions by $Ru(NH_3)_6^{2+}$, are about 10 times those for carboxylato derivatives of $(NH_3)_5Co^{III}$,[14a] indicating a stronger electron pull by the phosphorus-containing

ligands, which is reflected as well in the lower pK_A's of the parent acids.[25,26] Reductions by Eu^{2+}, V^{2+}, and Cr^{2+} may be taken to proceed predominantly by bridged paths, for rates lie well above those for $Ru(NH_3)_6^{2+}$, whereas if an outer-sphere route were utilized by all, Ru(II) would maintain a kinetic advantage throughout.[14a,27] This conclusion, for Cr^{2+}, is in accord with that of Sisley,[15] and is confirmed here, based upon ligand transfer accompanying redox.

Specific rates for the Cr(II)–biphosphito reaction conform to (6).

In earlier work,[8] it was suggested that the $[H^+]^{-1}$ term describes

$$k_{obsd} = 4.1 + 0.38[H^+]^{-1} \ (M^{-1} \ s^{-1}) \qquad 25 \ °C, \ \mu = 1.0 \ M \qquad (6)$$

a component proceeding through a chelated activated complex, which, as a consequence of the substitution-inert character of Cr(III), should yield a chelated product.[28] Such a chelate, I, if

I   II
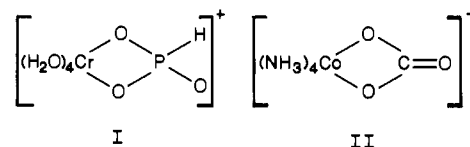
formed from reduction of the phosphito complex, would be structurally similar to the chelated (carbonato)cobalt(III) species II. The four-membered ring in II is known[29] to suffer rapid destruction, with Co(III)–O bond breakage, upon treatment with aqueous acid, and it is doubtful that complex I would survive the reaction conditions used. We find that the Cr(III) product from the phosphito reaction in 0.1 M H^+ (where 52% of the reaction proceeds by the acid-independent path) is indistinguishable from that arising from the reaction in 0.01 M H^+ (where 90% proceeds by the inverse-acid route). In neither case is there evidence for chelation.

Reactions with Cerium(IV). Induced Electron Transfer. When induced electron transfer occurs during the reaction of a cobalt(III) complex with an external oxidant, a ligand undergoes oxidation, and a portion of the oxidative function is borne by Co(III), yielding Co(II). The results summarized in Table III, describing experiments in which the external oxidant is Ce(IV), point to such induced transfer with bound hypophosphite, but not with phosphite.

(21) Schmidt, W.; Taube, H. *Inorg. Chem.* **1963**, *2*, 698. These authors report λ_{max} values for the $(H_2PO_4)^-$ complex as 517.5 ($\epsilon = 63.7$) and 356 nm ($\epsilon = 48.3$).
(22) Liang, A.; Gould, E. S. *Inorg. Chem.* **1973**, *12*, 12.
(23) Splinter, R. C.; Harris, S. J.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 901.
(24) If the appropriate statistical factor 2/1 is applied to the phthalate couple in Table I, the substitution of $(NH_3)_5Co^{III}$ for H^+ seven atoms away is seen to be virtually without effect. The same statistical factor pertains to the other couples, except for H_3O^+ and H_3PO_4, which require the factor 3/2.

(25) The relationship between outer-sphere redox rates and ligand basicities was enunciated by Linck,[26] and its limitations were pointed out by Fan.[14a] Note that $k_{Ru(II)}$ values for the biophosphito- and hypophosphito-substituted oxidants are about five times those for complexes derived from those halogenated carboxylic acids (e.g., CCl_3COOH) having pK_A's comparable to those of H_3PO_3 and H_3PO_2. It may be argued that the strengths of carboxylic acids are boosted by stabilization of their anions via π-electron delocalization, a feature not present with the phosphorus-containing acids. This factor does not extend to reductions of the corresponding Co(III) complexes, for which σ-attractive effects are assumed to predominate.
(26) Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945.
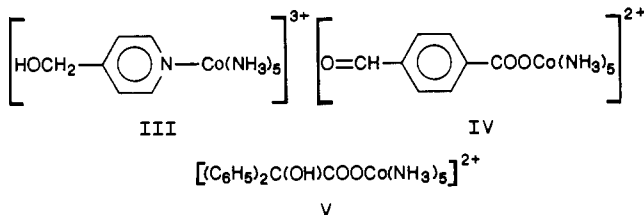(27) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.
(28) Such a description is inapplicable to reductions of a number of oxidants featuring pyridine-derived ligands. See, for example: Thamburaj, P. K.; Loar, M.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1946.
(29) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1953**, *75*, 4099. For a study of analogous five-ring derivatives of P(III), which are much more robust, see: Usher, D. A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1964**, *86*, 4732.

Reactions (carried out at 22 °C in 0.5 M HClO$_4$) are found to be sluggish, and only the hypophosphito complex (in contrast to mixtures of $(NH_3)_5Co(H_2O)^{3+}$ and free hypophosphorous acid) yields appreciable quantities of Co(II). Not all of the Co(III) taken is reduced, even after long standing, and the fraction so converted is observed to drop as the ratio Ce(IV)/P(I) in the reaction mixture is increased.

From the limited data, it is clear that the action of hypophosphite is more closely related to that of bound 4-pyridinemethanol (III)[4] and *p*-formylbenzoate (IV)[30] than to coordinated

$$\left[HOCH_2\text{—}\bigcirc\text{—}N\text{—}Co(NH_3)_5\right]^{3+} \qquad \left[O\text{=}CH\text{—}\bigcirc\text{—}COOCo(NH_3)_5\right]^{2+}$$

$$\text{III} \qquad\qquad\qquad \text{IV}$$

$$[(C_6H_5)_2C(OH)COOCo(NH_3)_5]^{2+}$$

$$\text{V}$$

oxalate[31] and benzilate (V)[5] in this mediating role. In all cases the reaction is initiated by external 1e oxidation of the ligand, but the two categories differ in the extent of the delay preceding internal electron transfer from the resulting radical-cation intermediate to bound Co(III). With coordinated oxalate and benzilate, this waiting period is so short that virtually all Co(III) taken is converted to Co(II), and it may be that the two acts of electron transfer (as well as the attendant C–C bond breakage peculiar to these reactions) are synchronous. With the other ligands, as with hypophosphite, competition between followup processes occurs, and a fraction of the intermediate reacts with the external oxidant, competing a net 2e conversion but leaving cobalt in its tripositive state bound to the oxidation product. As expected, the latter transformation, which should be first order in external oxidant, becomes relatively more important as [Ce^{IV}] is increased.[32] The behavior of the hypophosphito complex in this transformation is of interest, for it indicates that its 1e oxidation product, which is derived in a formal sense from P(II), is stable enough to undergo partition between reaction paths, a conclusion in accord with evidence derived from a recent study[7] of the reaction of hypophosphite with Cr(V).

Only a trace of Co(II) was obtained from the biphosphito derivative under similar conditions. We suspect here that attack on the weakly reducing –OPHO$_2$H ligand is so slow that it competes unfavorably with aquation of the complex.[33] Attempted reaction with a still more powerful oxidant, perhaps Cr(IV),[34] might prove instructive.

Reaction of the Hypophosphito Complex with Base. Undoubtedly the most novel facet of the present study is the observed decomposition of the hypophosphito complex, by an internal redox process, in basic solutions. In this reaction, all coordinated phosphorus is released, a portion is converted to phosphite, and

Table V. Kinetic Data for the Reaction of the Hypophosphite Complex $[(NH_3)_5Co(OPH_2O)]^{2+}$ with Aqueous EDTA[a]

complex	solvent	[EDTA^{4-}], M	[HEDTA^{3-}], M	pH (pD)	10^4k,[b] s^{-1}
–PH$_2$	H$_2$O	0.14	0	10.99	5.3 ± 0.4
	H$_2$O	0.28	0	11.13	9.7 ± 0.2
	H$_2$O	0.14	0.14	8.69	0.03 ± 0.01[c]
	D$_2$O	0.28	0	11.13	7.9 ± 0.2
–PD$_2$	H$_2$O	0.28	0	11.01	4.2 ± 0.1[d]
	D$_2$O	0.28	0	11.13	3.7 ± 0.1[d]

[a] Reactions at 40 °C, μ = 3.0 M. [Co^{III}]$_{init}$ = 0.047 M throughout. Runs were carried out in duplicate. [b] Pseudo-first-order specific rates = $-d(\ln[\text{Co}^{III}])/dt$. [c] Obtained from Guggenheim plot. (See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; p 25). [d] From analysis of biphasic profiles (see text).

Co(III) is reduced very nearly quantitatively to Co(II). No H$_2$ is evolved, and ClO$_4^-$, the counterion in the reacting complex, plays no part. Neither the phosphito complex nor mixtures of $(NH_3)_5Co(H_2O)^{3+}$ and H$_2$PO$_2^-$ undergo this reaction.
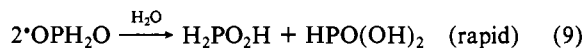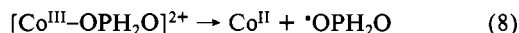
The ratios of products from several such decompositions are recorded in Table IV. Irrespective of the base used, phosphite and hypophosphite are formed in equimolar quantities, each corresponding to just half the cobalt(III) taken, 94–97% of which is recovered as Co(II). The transformation may then be represented

$$2[(NH_3)_5Co(OPH_2O)]^{2+} + H_2O \xrightarrow{\text{B:}}$$
$$2Co^{II} + HPO_3^- + H_2PO_2^- + 3NH_4^+ + 7NH_3 \quad (7)$$
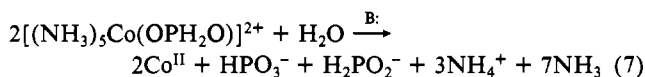
Kinetic data pertaining to this conversion, carried out in the presence of EDTA^{4-}, are summarized in Table V. Catalysis by EDTA^{4-} appears to reflect only the concentration of OH$^-$ in equilibrium with this –4 ion, for when its conjugate acid, HEDTA^{3-}, is added in equivalent amount, lowering the pH by 2.4 units, the observed rate drops by a factor of $10^{2.2}$.

Experiments with deuterium-labeled species indicate the operation of two deuterium kinetic isotope effects. A solvent isotope effect, k_{H_2O}/k_{D_2O} = 1.14–1.23, is observed on transferring the reaction from water to D$_2$O, and a much more marked "substrate isotope effect" (which we infer to be a primary isotope effect), k_{H_2P}/k_{D_2P} = 2.1–2.3, is evident when the PD$_2$-labeled form of the complex is substituted for the PH$_2$ form. The latter effect substantially exceeds those reported for hydride-transfer reactions involving breakage of Si–H (k_H/k_D = 1.15)[35a] and B–H (1.52)[35b] bonds, is only slightly greater than that for hydride transfer from C–H (1.84),[36,37] but falls far below those associated with measurably slow proton transfers near room temperature (4.7–8.0).[37b,38] In particular, the observed deuterium isotope effect lies close to that reported for the Cannizzaro reaction of benzaldehyde (1.8).[39]

Of several mechanistic sequences conceivable for this reaction, perhaps the simplest is that triggered by homolysis of the Co^{III}–O bond in the hypophosphito complex, eq 8, in analogy to the path

$$[\text{Co}^{III}\text{–OPH}_2\text{O}]^{2+} \rightarrow \text{Co}^{II} + {}^{\bullet}\text{OPH}_2\text{O} \quad (8)$$

$$2{}^{\bullet}\text{OPH}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{PO}_2\text{H} + \text{HPO(OH)}_2 \quad (\text{rapid}) \quad (9)$$

proposed for a number of transformations catalyzed by the cobalt(III)–corrin coenzyme, vitamin B$_{12}$.[40] Disproportionation of

(30) Robson, R.; Taube, H. *J. Am. Chem. Soc.* **1967**, *89*, 6487.

(31) Saffir, P.; Taube, H. *J. Am. Chem. Soc.* **1960**, *82*, 13.

(32) If only redox processes were significant here, it should be possible to calculate the ratio of specific rates for internal and external oxidations (but not individual values of each) by considering the yields of Co(II) (Table III) as a function of [Ce(IV)]. When this is attempted, it is found that the process producing Co(II) becomes *more* important at higher [Ce(IV)], i.e. that the yields of Co(II) do not drop off in proportion to the external oxidant added. This discrepancy almost certainly arises because aquation of the complex taken (which does not produce Co^{II}) competes with initial attack by Ce(IV), and this competition is most effective at highest dilution. However, the yield of Co(II) at the highest [Ce(IV)] taken corresponds to a lower limit of 0.088 M (22 °C, 1 M HClO$_4$) for the ratio k_{int}/k_{ext}.

(33) Aquation of the biphosphito and hypophosphito complexes is found to be slow but measurable. Estimated specific rates (0.5 M HClO$_4$) are 1.3 × 10^{-5} s^{-1} (25 °C) and 2.0 × 10^{-4} s^{-1} (70 °C) for the hypophosphito complex and 9.5 × 10^{-5} s^{-1} (70 °C) for the biphosphito, well above the reported[21] rate constant for the corresponding phosphato complex (2.6 × 10^{-7} s^{-1} at 25 °C, pH 1.3–2.0). Whether these differences reflect dissimilar reaction media or substantially lower substitution lability of the phosphato derivative remains to be determined.

(34) See, for example: (a) Garner, C. S.; House, D. A. *Inorg. Chem.* **1966**, *5*, 840. (b) Srinivasan, V. S. *Inorg. Chem.* **1982**, *21*, 4328.

(35) (a) Kaplan, L.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1955**, *77*, 1297. (b) Hawthorne, M. F.; Lewis, E. S. *J. Am. Chem. Soc.* **1958**, *80*, 4296.

(36) Bartlett, P. D.; McCollum, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 1441.

(37) (a) Hydride-transfer reactions exhibiting much greater deuterium isotope effects have been reported but are uncommon. See, for examples: Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 746. (b) For a review of deuterium and tritium kinetic isotope effects see: Saunders, W. H., Jr. *Tech. Chem. (N.Y.)* **1974**, *6*, 222.

(38) Saunders, W. H., Jr.; Edison, D. H. *J. Am. Chem. Soc.* **1960**, *82*, 138.

(39) Wiberg, K. B. *J. Am. Chem. Soc.* **1954**, *76*, 5371.

(40) See for example: (a) Halpern, J. in *B$_{12}$*; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, p 501; (b) Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238.

the odd electron (P^{II}) intermediate (a transient that may intervene also in other hypophosphite oxidations)[7] would be expected to yield a mixture of hypophosphite and phosphite. This route is open to several objections. It is doubtful whether it would lead to the observed quantitative yields of P(I) and P(III), for the disproportionation would almost certainly compete with dimerization to the P–P species, $H_4P_2O_4$,[41] which is reported to be stable under our reaction conditions and decomposes, at low pH, to PH_3 and H_3PO_4 as well as H_3PO_3. Moreover, a sequence in which (8) is rate-determining is not in accord with the pronounced deuterium isotope effect. Most seriously, it assigns no role to the OH$^-$ needed for initiation.

Instead, we favor a heterolytically induced process, represented by sequence given in eq 10 and 11, featuring hydride transfer to

$$H:Co^I + [Co^{III}-OPH_2O]^{2+} \rightarrow 2Co^{II} + H_3PO_2 \quad (11)$$
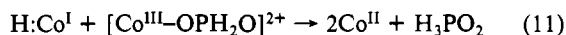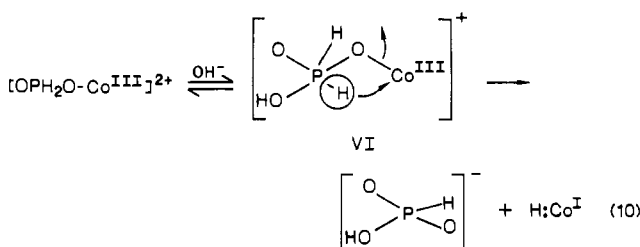
Co(III). This brings to mind paths forwarded for a variety of conversions proceeding through organometallic species, among them the oxidation of ethanol by Pt(II),[42] the decomposition of metal alkyls,[43] chain-termination in Ziegler–Natta polymerization,[44] decarbonylation of acyl halides to olefins,[45] and fragmentation of metallocycles.[46] The suggested sequence may also be regarded as an intramolecular inorganic analog of the Cannizzaro reaction (which has been shown to proceed via a base-induced hydride shift).[47] It is proposed that the primary attack occurs at phosphorus, forming a five-coordinate intermediate, VI, within which the hydride shift to Co(III) yields a product that may be considered either as a hydride complex of Co(III) or a protonated form of Co(I).[48] This species would be expected, on the basis of known Co(III)–Co(I) reactions,[49] to reduce unreacted

Co(III) very rapidly, leading to the observed overall stoichiometry.

The magnitude of the observed "primary" isotope effect is consistent with the proposed picture (although it does not demand it). The solvent isotope effect is, however, unexpected ($k_{H_2O}/k_{D_2O} > 1$, for in the suggested initiating sequence ionic charge is dispersed in proceeding from the reactants to the activated complex. This feature, according to Swain's model for simple reactions,[37b,50] should be reflected in a rate greater in D_2O than in H_2O. Note, however, that attack by OH$^-$ is depicted at the negative periphery of the metal complex, rather than at its positive center, and therefore may entail a significant, although localized, increase in solvation, hence a faster reaction in the nondeuteriated solvent.

Finally, it may be asked whether other complexes, aside from those having metal–carbon bonds, will react in a like manner. For operation of the proposed sequence, or one akin to it, the metal center must have two accessible oxidation states differing by two units, with (at least) the higher state relatively substitution inert. Eligible couples are Rh(III,I), Pt(IV,II), and Cr(V,III), although reactions of the latter may be complicated by intervention of Cr(IV).[7,51] Among ligands that may function as hydride donors, hydrazine, hydroxylamine, and isopropoxide (–OCHMe$_2$) lack sites that can accommodate an incoming hydroxide and would therefore be expected to reduce bound metal centers by an alternate route, possibly proton removal, followed by internal electron transfer. There is evidence that formate is an effective hydride donor in Pt(II)[42] and corrin-bound Co(III)[52] (vitamin B$_{12}$) systems,[53] but the formato complex of (NH$_3$)$_5$Co^{III} has been found to survive unchanged on treatment with 0.1 M NaOH for 4 h at room temperature.[54] Imposition of more severe conditions and extension of studies to the corresponding derivatives of glyoxylic, mucochloric, and 2-formylbenzoic acids (each of which features an aldehyde function further removed from the ligating carboxylate group) may be informative.[55]

Acknowledgment. We are grateful to Professor J. H. Espenson for valuable discussions and to Arla White for technical assistance.

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(47) (a) Hauser, C. R.; Hamrick, P. J., Jr.; Stewart, A. T. *J. Org. Chem.* **1956**, *21*, 260. (b) For evidence that the Cannizzaro reaction, under extreme conditions, may have a homolytic component, see: Swain, C. G.; Powell, A. L.; Lynch, T. J.; Alpha, S. R.; Dunlap, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 3584; and Chung, S.-K. *J. Chem. Soc., Chem. Commun.* **1982**, 480.

(48) See, for example: Pillai, G. C.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4740.

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(54) D. E. L., Jr., unpublished experiments, 1987.

(55) A reviewer reminds us that our treatment of the biphasic kinetics of the internal redox reaction of the PD$_2$-labeled complex implies that deuterium exchange is much slower than the redox conversion. This is in accord with the observed similarity of kinetic isotope effects in both H$_2$O and D$_2$O and with the absence of change in the ^{1}H and ^{31}P NMR spectra of this complex in D$_2$O after 5 h at room temperature. A second reviewer asks why the biphosphito complex does not appear to undergo the suggested hydride shift. Here, we suspect that attachment of a second oxygen atom withdraws electron density from the adjoining P–H bond, thus diminishing its hydride-like character.