signal is attributed to forbidden transitions, *i.e.*, $(-3/2 \leftrightarrow 3/2)$, $(-3/2 \leftrightarrow 1/2)$, or $(-1/2 \leftrightarrow 3/2)$. However, the integrated intensity of the low-field signal is about the same as the resonance at normal field. This suggests a more probable assignment of the low-field signal to one of the $(-1/2 \leftrightarrow -3/2)$ transition. This would result if $D = 2.25$ cm^{-1} (assuming $E = 0$). It appears that zero-field splittings with magnitudes more than 3 times the highest previously reported[8] can be realized for transition metals in strongly trigonal environments. According to this assignment, the normal-field resonance is attributable to the remaining $(-1/2 \leftrightarrow -3/2)$ and $(1/2 \leftrightarrow 3/2)$ transitions when H_0 is parallel and perpendicular to the z axis, respectively.

The epr spectrum of tetrakis(diethylamino)vanadium-(IV)[9] has been reported. It is interesting to compare that with those spectra described above. No ^{14}N hyperfine splitting was resolved at all temperatures for all three transition metal derivatives. The spin density on the nitrogen atom in an aliphatic nitroxide radical is about 0.9; the hyperfine splitting is about 44 MHz. The observed line width could account for unresolved ^{14}N hyperfine splitting even if the electron density on each nitrogen atom is as high as 0.2. The actual electron density is probably much lower because of resonance structures such as Ti$^-$=$^+$NR$_2$. Intramolecular π coordination of this type has been invoked[3] to explain the monomeric structure of the low-coordination amido compounds, steric effect being the other.

Whereas highly anisotropic ^{51}V hyperfine splitting has been observed in V((C$_2$H$_5$)$_2$N)$_4$, the ^{47}Ti and ^{49}Ti splitting was not resolved in Ti((*i*-C$_3$H$_7$)$_2$N)$_3$, nor was ^{53}Cr hyperfine splitting discerned in Cr((*i*-C$_3$H$_7$)$_2$N)$_3$. The failure to detect these hyperfine features may be due to their low natural abundance (less than one-tenth of ^{51}V) and to their smaller hyperfine coupling constants (also less than one-tenth of ^{51}V values).

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The Hydrogenation of Pentacyanocobaltate(II) at High Pressures

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The uptake of molecular hydrogen by aqueous solutions of pentacyanocobaltate(II) has been interpreted by several investigators[1-5] in terms of the reversible

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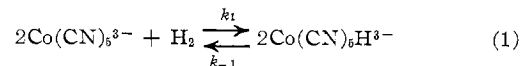(1) N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, **83**, 3366 (1961).

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formation of hydridopentacyanocobaltate(III) according to

$$2Co(CN)_5{}^{3-} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2Co(CN)_5H^{3-} \quad (1)$$

$$-d[Co(CN)_5{}^{3-}]/dt = 2k_1[Co(CN)_5{}^{3-}]^2[H_2] - 2k_{-1}[Co(CN)_5H^{3-}]^2 \quad (2)$$

Although supported by the results of several kinetic and equilibrium investigations, this interpretation has recently been questioned by Banks, *et al.*,[6] who proposed a considerably more complex scheme involving several additional species including cobalt(I) complexes arising from the disproportionation of pentacyanocobaltate(II). The interpretation advanced by these authors was based on several alleged departures from the behavior described by eq 1 and 2, including the observation of an induction period in the hydrogen uptake reaction, and a rather complicated pattern of cyanide dependence and salt effects. In view of the widespread interest in this system and of its importance in relation to various catalytic hydrogenation reactions,[7] an extension of the earlier investigations, with a view to achieving a clarification of these unresolved features, appeared to be warranted.

The study of the hydrogenation of pentacyanocobaltate(II) at atmospheric pressure is severely hampered by the slowness of the reaction, particularly in view of the competing decomposition[2,3,8] according to eq 3.

$$2Co(CN)_5{}^{3-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \quad (3)$$
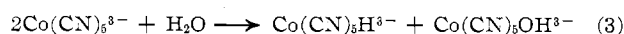
Because the reaction with hydrogen is markedly accelerated by added salts, most of the earlier quantitative studies were conducted at relatively high ionic strengths ($\geqslant 0.5$ *M*), *i.e.*, conditions under which the rate of the competing decomposition reaction, unfortunately, is also enhanced. In order to minimize the complications arising both from the competing decomposition reaction and from the uncertain effects of added salts, it seemed desirable to extend the quantitative study of reaction 1 to higher hydrogen pressures and at the same time to the lower ionic strengths that are thereby rendered practical. This paper describes the results of such a study.

Experimental Section

Solutions of the desired composition were prepared by dissolving analytical reagent grade cobalt(II) chloride, potassium cyanide, potassium hydroxide, and potassium chloride (used to adjust the ionic strength) in distilled water with rigorous exclusion of oxygen. The kinetic and equilibrium experiments were conducted in a glass-lined Parr Series 4500 stirred autoclave pressurized to the desired constant partial pressure of hydrogen and thermostated to ±0.2°. Samples of the solution were withdrawn periodically for spectrophotometric analysis in a Cary 14 recording spectrophotometer. The reaction was followed by monitoring the 970-nm (ϵ 290 M^{-1} cm^{-1}) band of Co(CN)$_5{}^{3-}$. Hydrogen concentrations were computed from the measured partial pressures using literature solubility data.[9]

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Results and Discussion

Over a considerably greater range of solution compositions (extending to ionic strengths as low as 0.04 M) and hydrogen partial pressures (up to 10 atm in the kinetic experiments and 27 atm in the equilibrium experiments) than previously examined, the pattern of our results was generally in accord with those reported by DeVries,[2] Simandi and Nagy,[5] and Burnett, Connolly, and Kemball[3] and failed to reveal any significant departures or complications of the type described by Banks, *et al.*[6]

Using the known spectra of $Co(CN)_5{}^{3-}$ (λ_{max} 970, ϵ 290; λ_{max} 280, ϵ 4.9 $\times$ 10³) and of $Co(CN)_5H^{3-}$ (λ_{max} 305, ϵ 610), the spectral changes accompanying the reaction of $Co(CN)_5{}^{3-}$ with H_2 could be accurately fitted to eq 1. Departures, if any, from the stoichiometry represented by this equation were too small to be spectrally detectable.

The results of equilibrium measurements on solutions of $Co(CN)_5{}^{3-}$ saturated with H_2 at partial pressures ranging from 6.8 to 27 atm are summarized in Table I. The time required for attainment of equilibrium in these experiments ranged from about 2 to 8 hr, respectively, following which no further spectral changes were observed. The constancy of the values of the equilibrium quotient, K_e, computed according to eq 4, supports the stoichiometry described by eq 1. Allowing

$$K_e = [Co(CN)_5H^{3-}]^2[Co(CN)_5{}^{3-}]^{-2}[H_2]^{-1} \qquad (4)$$

for differences in ionic strength, the agreement between our value of K_e, $(1.0 \pm 0.1) \times 10^5\ M^{-1}$ (at $\mu = 0.1\ M$), and earlier determinations, $(1-2) \times 10^5\ M^{-1}$ (at $\mu = 0.5\ M$),[3] is satisfactory.

TABLE I
EQUILIBRIUM DATA AT 25°[a]

H₂ partial pressure, atm	$10^3[H_2]$	$10^4[Co(CN)_5{}^{3-}]$	$10^3[Co(CN)_5H^{3-}]$	K_e, M^{-1}
6.8	5.3	2.41	5.76	1.08×10^5
13.6	10.5	1.79	5.82	1.01×10^5
20.4	15.7	1.65	5.83	0.80×10^5
27.2	21.0	1.21	5.88	1.10×10^5

[a] Initial solution composition: $6.0 \times 10^{-3}\ M\ Co(CN)_5{}^{3-}$; $6.0 \times 10^{-3}\ M\ CN^-$; $5.0 \times 10^{-4}\ M\ OH^-$; ionic strength adjusted to 0.1 M with KCl.

Kinetic measurements were made over an extensive range of H_2 partial pressures (1–10 atm) as well as of other pertinent variables (3×10^{-3} to $6 \times 10^{-3}\ M$ initial $Co(CN)_5{}^{3-}$, 6×10^{-4} to $6 \times 10^{-2}\ M\ CN^-$, 1×10^{-4} to $6 \times 10^{-2}\ M\ OH^-$, 0–35°). At the high H_2 concentrations prevailing in most of our experiments, the conversion to $Co(CN)_5H^{3-}$ according to eq 1 proceeded sufficiently far toward completion that the contribution of the back-reaction to the rate law (*i.e.*, the last term in eq 2) could be neglected. The limiting simple third-order rate law under these conditions assumes the integrated form of eq 5. Typical linear plots of $[Co(CN)_5{}^{3-}]^{-1}$ *vs.* t, in accord with eq 5 are

$$[Co(CN)_5{}^{3-}]^{-1} - [Co(CN)_5{}^{3-}]^{-1}{}_{initial} = 2k_1[H_2]t = k_{obsd}t \quad (5)$$

depicted in Figure 1. Values of k_1, determined from the slopes ($=2k_1[H_2]$) of such plots are summarized in Table II and are seen to be substantially independent of the initial $Co(CN)_5{}^{3-}$ concentration and of the concentrations of CN^- and OH^- over the considerable ranges examined. No induction periods, such as those reported by Banks, *et al.*,[6] nor other deviations from the simple third-order rate law (eq 5) were detected in any of the experiments. The virtual temperature independence of k_1 ($\Delta H_1{}^{\ddagger} = -0.7 \pm 0.5$ kcal/mol; $\Delta S_1{}^{\ddagger} = -55 \pm 5$ eu at $\mu = 0.1\ M$) and the marked increase of k_1 with ionic strength are in substantial agreement with earlier observations.[2,3]
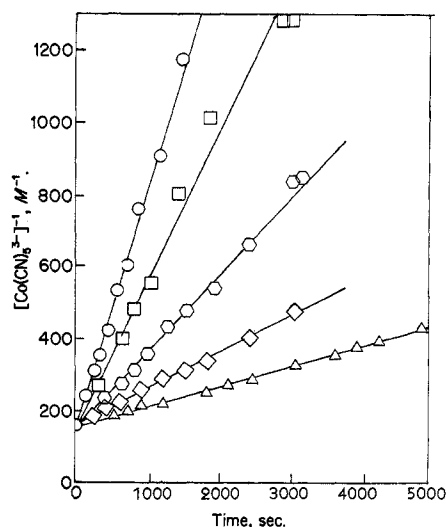

Figure 1.—Representative pseudo-second-order rate plots according to eq 5. H_2 partial pressures (atm): $\triangle$, 0.97; $\diamond$, 1.7; $\bigcirc$, 3.4; $\square$, 6.8; $\mathbf{O}$, 10.2. (Other conditions are given in Table II.)

We conclude that, even over a considerably greater range of hydrogen pressures and solution compositions than previously examined, the stoichiometry and kinetics of the reaction of pentacyanocobaltate(II) with hydrogen are accurately represented by eq 1 and 2. In contrast to the corresponding reactions with hydrogen peroxide, organic halides, etc., which have been shown to proceed through stepwise free-radical mechanisms,[10,11] the homolytic splitting of hydrogen by pentacyanocobaltate(II) thus appears to be a "concerted" process involving a transition state of the composition $Co_2(CN)_{10}H_2{}^{6-}$. An unresolved mechanistic question of some interest is whether the reaction is actually a "termolecular" process (as represented by eq 1) or a sequence of bimolecular steps comprising the preequilibrium formation of $Co_2(CN)_{10}{}^{6-}$ according to eq 6, followed by a rate-determining reaction between $Co_2(CN)_{10}{}^{6-}$ and H_2. Since equilibrium 6 is rapidly estab-

$$2Co(CN)_5{}^{3-} \rightleftharpoons Co_2(CN)_{10}{}^{6-} \qquad (6)$$
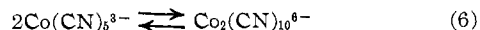
lished[12] in relation to the overall reaction with H_2, the two alternatives are kinetically indistinguishable.

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TABLE II
KINETIC DATA

Temp, °C	H₂ partial pressure, atm	$10^3[H_2]$	$10^3[Co(CN)_5{}^{3-}]$	$10^3[CN^-]$	$10^3[OH^-]$	Ionic strength, M	10^2k_{obsd}, M^{-1} sec^{-1}	k, M^{-2} sec^{-1}
25	3.37	2.59	3.0	3.0	0.5	0.10	21.6	41
25	0.97	0.76	6.0	6.0	0.5	0.10	5.5	36
25	1.67	1.29	6.0	6.0	0.5	0.10	10.1	39
25	3.37	2.59	6.0	6.0	0.5	0.10	21.3	41
25	6.8	5.18	6.0	6.0	0.5	0.10	41.1	39
25	10.2	7.76	6.0	6.0	0.5	0.10	63.8	41
25	3.37	2.59	6.0	6.0	0.1	0.10	21.3	41
25	3.37	2.59	6.0	6.0	10	0.10	21.2	41
25	3.37	2.59	6.0	6.0	40	0.10	21.0	40
25	3.37	2.59	6.0	6.0	58	0.10	21.5	41
25	3.37	2.59	6.0	0.6	0.5	0.10	21.6	41
25	3.37	2.59	6.0	1.5	0.5	0.10	21.6	41
25	3.37	2.59	6.0	3.0	0.5	0.10	21.7	41
25	3.37	2.59	6.0	10	0.5	0.10	21.0	40
25	3.37	2.59	6.0	40	0.5	0.10	21.3	41
25	3.37	2.59	6.0	64	0.5	0.10	21.5	41
25	3.37	2.59	6.0	6.0	0.5	0.043	6.1	12
25	3.37	2.59	6.0	6.0	0.5	0.068	12.2	23
25	3.37	2.59	6.0	6.0	0.5	0.143	33.1	63
25	3.37	2.59	6.0	6.0	0.5	0.243	68.0	131
0	3.41	3.26	6.0	6.0	0.5	0.10	29.5	45
15	3.39	2.85	6.0	6.0	0.5	0.10	24.2	42
35	3.33	2.50	6.0	6.0	0.5	0.10	19.0	38

This situation parallels that prevailing in the well-known reaction $H_2 + I_2$ (or 2I) → 2HI, where the path long designated as "bimolecular" has recently been demonstrated to be, in fact, termolecular.[13] The distinction between these two alternatives and between the corresponding alternatives (*i.e.*, whether or not $Co_2(CN)_{10}{}^{6-}$ is an intermediate) in the present reaction is presumably linked to the most favorable configurations (notably the degrees of residual I---I or Co---Co bonding) of the transition states of these reactions. Thus $Co_2(CN)_{10}{}^{6-}$ is likely to lie along the most favorable path for the formation of a transition state resembling I (*i.e.*, stabilized by residual Co–Co bonding) but not of a transition state resembling II. The latter situation apparently prevails in the case of the H_2–I_2 reaction and may well apply also in the present case where it would appear to be favored at least on steric grounds.
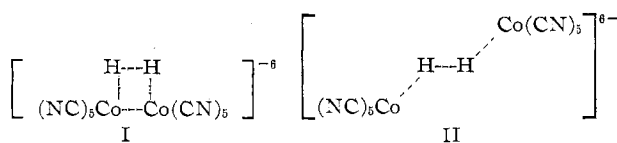
Acknowledgment.—Support of this work, through grants from the National Institutes of Health and the National Science Foundation, is gratefully acknowledged. M. P. also thanks the U. S. Government Fulbright–Hays Program for a travel grant and the University of Zagreb for a leave of absence.

(12) The rapid "reversible" transformation of the green $Co(CN)_5{}^{3-}$ to the intensely violet dimer $Co_2(CN)_{10}{}^{6-}$ (the salts of which are well known) is readily detected visually as the concentrations of aqueous $Co(CN)_5{}^{3-}$ solutions are increased, particularly at low temperatures (~0°). Attempts to study this reaction quantitatively were unsuccessful because of the instability of the solutions with respect to decomposition by reaction 3 under the conditions where reaction 6 is shifted measurably toward the right. Under the conditions of our hydrogenation experiments equilibrium 6 lay far to the left and the concentration of $Co_2(CN)_{10}{}^{6-}$ in solution was negligible.

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Contact Shift Studies and Spin Delocalization in Cobalt(I)–Tris(2,2′-bipyridine) Complexes

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There has been considerable interest lately in the use of nmr contact shifts to investigate the nature of the metal–ligand bond in substituted and unsubstituted tris (2,2′-bipyridine) complexes of first-row transition metals. The proton nmr contact shift data for Co(II),[2] Ni(II),[2,3] Cr(II),[4] and Fe(III)[4,5] have been reported. We report here the data for the Co(I) complexes.

Observed proton nmr contact shifts may arise from either a Fermi contact interaction or a dipolar interaction.

The Fermi contact interaction arises from a coupling of the delocalized electron spin and the nuclear spin. The relationship between the contact shift, $\Delta\nu$, and the hyperfine coupling constant A, in gauss, is then given by the modified Bloembergen equation[6]

$$\frac{\Delta\nu}{\nu_0} = -\frac{A g_{av}{}^2 \beta_e{}^2 S(S+1)}{g_N \beta_N 3kT} \quad (1)$$

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