

Substituent-Effect Analysis in Organocobaloximes: Studies of the Formation Constants and Cyano ^{13}C and ^{15}N NMR Chemical Shifts of Alkyl(cyano)cobaloximes

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Abstract: Formation constants have been measured for a series of 16 alkyl(cyano)cobaloximes of the type $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, where Y is an alkyl, aryl, heteroalkyl, or heteroatomic substituent. Cyano ligand ^{13}C and ^{15}N NMR chemical shifts are also reported for 17 $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)^{13}\text{C}^{15}\text{N}^-$ complexes and for 14 cyano-bridged complexes of the type $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)^{13}\text{C}^{15}\text{NCo}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$, which are formed when cyanide ion and cobaloxime are present at sufficiently high concentrations. These data, along with seven sets of literature data for various kinetic and equilibrium properties of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes, have been correlated using substituent-effect equations including only an inductive term, an inductive term plus a resonance term, or inductive, resonance, and steric terms. In every case, poor correlations using only an inductive term are markedly improved by inclusion of the steric term. In all but two cases, the correlations are significantly improved by inclusion of the steric term. In most cases, the resonance substituent effect is of comparable importance to the inductive substituent effect. The resonance effect can be interpreted in terms of hyperconjugation between the carbon-cobalt σ bond and the substituent. This concept is far more general than the concept of $n \rightarrow \sigma$ donation from Y lone pairs to the Co-C σ bond, previously invoked by others, as it encompasses substituents without lone pairs and those which are resonance withdrawing as well as those which are resonance donating. By placing the substituent in the β position, such hyperconjugation is accentuated and the multiparameter substituent effect approach permits a quantitative assessment of its importance. The steric influence of Y is found to be significant and capable of being transmitted indirectly via weakening of the inductive effect due to decreased C-Co overlap. The possibility that such decreased Co-C overlap increases the resonance effect of Y by promoting hyperconjugation is discussed.

Introduction

The use of structure-reactivity relationships in organocobalt chemistry has had a checkered past. While we have had substantial success understanding the influence of cobaloxime-chelated¹⁻⁵ cobalt centers and, to a lesser extent, corrin-chelated⁶ cobalt centers on the properties of covalently bound organic ligands, attempts to utilize the substantial literature on substituent effects in organic chemistry to understand the influence of the organic ligand on the properties of organocobalt complexes have been plagued by outlying data and nonlinear relationships.⁷⁻¹¹ This situation changed dramatically with the appearance of a report by Marzilli and co-workers¹² in which rate constants for ligand dissociation from an extensive series of organocobaloximes of the type $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}^1$ were successfully correlated using the classical dual substituent parameter equation¹⁴ (eq 1). In

$$Q_Y/Q_H = \rho_I\sigma_I + \rho_R\sigma_R \quad (1)$$

(1) Cobaloximes are bis(dimethylglyoximate)cobalt complexes. Alkyl-(ligand)cobaloximes are abbreviated herein as $\text{RCo}(\text{D}_2\text{H}_2)\text{L}$. Other abbreviations are as follows: py, pyridine; CNpy, 4-cyanopyridine; CH_3OAn , 4-methoxyaniline.

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this equation Q_Y and Q_H are rate, equilibrium, or spectroscopic properties (i.e., measures of relative energy) of the substituted and unsubstituted compounds, respectively, σ_I and σ_R are inductive and resonance substituent constants characteristic of the substituent, Y, and ρ_I and ρ_R represent the sensitivity of the property under investigation to inductive and resonance substituent effects. This treatment employed two significant departures from earlier attempts at substituent-effect analysis in organocobalt complexes: removal of the substituent from the α to the β position of the organic ligand (i.e., treatment of Y, rather than YCH_2 , as the substituent) and the inclusion of a resonance term in the substituent-effect equation. These two significant departures are obviously responsible for the success of the treatment and represent the most significant advance in the transfer of organic substituent-effect analysis to organometallic chemistry to date.

However, the specifics of the treatment used by Marzilli et al.¹² and, indeed, the very success of the method raise some problems as well as some interesting questions. In treatments relying on substituent-effect equations such as eq 1, the unsubstituted compound is generally taken to be the one for which $\text{Y} = \text{H}$, i.e., the effects of substituents, Y, are considered to be relative to the effects of H, with $\sigma_I = \sigma_R = 0$ for H. In general, the use of an equation such as eq 1, which correlates the substituent effects as the ratio of the susceptible property for the substituted compounds to that of the unsubstituted compound, risks bias in data sets due to the heavy reliance on the data for the unsubstituted compound. This problem was encountered by Marzilli et al.,¹² who found that data for $\text{Y} = \text{H}$ (i.e., $\text{CH}_3\text{Co}(\text{D}_2\text{H}_2)\text{L}$) did not agree well with data for the other $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$.¹⁵ This led these authors to choose $\text{CH}_3\text{CH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ (i.e., $\text{Y} = \text{CH}_3$) as the unsubstituted reference complex and to renormalize literature substituent param-

(13) These authors also successfully correlated ^{13}C chemical shift data sets including 10 or 11 $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ compounds. However, the variability of the chemical shifts in these data sets is extremely small (1.00-2.16 ppm chemical shift range in four data sets).¹² Successful correlations of data sets of such low variability are of less significance than the successful correlations of rate constants which vary over 6-7 orders of magnitude.¹²

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(15) Similar deviations of $\text{CH}_3\text{Co}(\text{D}_2\text{H}_2)\text{L}$ have been seen in earlier attempts at substituent-effect analysis in organocobaloximes.⁷

eters to $\sigma_I = \sigma_R = 0$ for CH_3 . While such renormalization of inductive substituent constants causes no harm, it has a bizarre effect on the resonance substituent constants. Correlation of hundreds of organic data sets^{14,16} via equations such as eq 1 has consistently shown the need for four sets of σ_R values due to the fact that certain reaction centers can be in direct conjugation with the substituent, Y. Thus σ_R^0 values are relevant when the reaction center cannot conjugate with the substituent, σ_R^{17} values when the reaction center is weakly resonance accepting, σ_R^+ values when the reaction center is strongly resonance accepting, and σ_R^- values when the reaction center is strongly resonance donating. Marzilli et al.¹² found that the renormalized σ_R^0 and σ_R^+ values gave the best correlation, with σ_R^+ being best for the ligand dissociation rate constants. However, certain relationships have been noted by Taft¹⁴ and by Charton,¹⁶ among the various resonance substituent constants for a given substituent. Thus, Taft notes that for resonance-donating (-R) substituents, $-\sigma_R^0 < -\sigma_R^+$, while for resonance-withdrawing (+R) substituents, $-\sigma_R^0 \equiv -\sigma_R^+$. These rules are violated for every substituent in the renormalized resonance substituent constants used by Marzilli et al.^{12,18} In addition, some substituents which are clearly resonance donating (CH_3 , C_6H_5 , and I) become resonance neutral in the renormalized scales. Perhaps the most bizarre effect of the renormalization of these resonance substituent constants is the result that $\sigma_R^0 \neq \sigma_R^+$ for Y = H, clearly an impossibility. Thus, the renormalization of the resonance substituent constants is not legitimate, and the best correlations, which were obtained with the renormalized constants, are fortuitous and, consequently, not significant. As will be shown in the current work, the problem of the heavy reliance on an unsubstituted reference compound inherent in eq 1 can be obviated by use of equations such as eq 2,¹⁶ in which each value of Q_Y is independently correlated and the intercept, C, becomes a fit parameter.

$$Q_Y = \rho_I \sigma_I + \rho_R \sigma_R + C \quad (2)$$

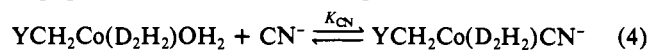
Another question raised by this method of treating organometallic substituent effects is the importance of steric effects in the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes. Marzilli et al.¹² logically argued that the steric effect of YCH_2 should not vary widely as Y is varied across a series of compounds. While the interposition of the methylene group between Y and the metal atom would surely seem to decrease the variability of the steric effect across such a series, some YCH_2 groups are more bulky than Y.¹⁹ Indeed, X-ray crystal structures of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes suggest that there are significant inner sphere geometry differences across a series of complexes with widely different Y steric bulk.²⁰ It is thus not at all clear if it is possible to ignore the steric effect in the treatment of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ data. This question is potentially answerable by application of a more complete substituent-effect equation,^{19,21} of the type shown in eq 3, where σ_S represents a steric substituent constant such as Taft's E_s ,²² Dubois's E_s' ,²³ or Charton's ν .²⁴

$$Q_Y = \rho_I \sigma_I + \rho_R \sigma_R + \rho_S \sigma_S + C \quad (3)$$

Finally, the success of the treatment of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ substituent effects via eq 1 compared to earlier work considering only inductive effects¹² raises the important question of the nature of the "resonance" effect in these complexes. As the σ_R constants

of equations such as eq 1-3 were developed by application to data from substituted benzenoid compounds, the relevance of such delocalization effects to organocobaloximes is not immediately obvious. Marzilli et al.¹² attributed the "resonance" effect in $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes to $n \rightarrow \sigma$ conjugation between Y lone pairs and the carbon-cobalt σ bond. However, several of the substituents, Y, successfully correlated by these authors have no lone pairs, and resonance-withdrawing substituents seem to correlate as well as resonance-donating substituents. Hence, $n \rightarrow \sigma$ conjugation seems inadequate to explain the "resonance" effect, and a more generally applicable picture of delocalization effects in $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes is clearly needed.

In order to explore some of these questions and to test the validity of substituent-effect equations of the type shown in eqs 2 and 3, we have chosen to study the formation constants for alkyl(cyano)cobaloximes (eq 4), as well as the ¹³C and ¹⁵N NMR chemical shifts of the enriched complexes, $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)^{13}\text{C}^{15}\text{N}^-$, for a series of 17 organocobaloximes. There are



several reasons for choosing this particular system. First, we are interested in determining if the multisubstituent parameter approach is applicable to equilibrium data (i.e., a comparison of relative ground-state energies) as well as to kinetic data (a comparison of transition-state and ground-state energies) and to spectroscopic data (a comparison of ground-state and excited-state energies). Second, cyanide is a small, linear ligand which binds very nearly collinearly with the trans axial ligand.²⁰ As such, its binding to cobaloximes should be subject to minimal direct steric effects due to the bulk of the trans organic ligand. However, the possibility exists that bulky alkyl ligands can influence the properties of the trans ligand indirectly, by a weakening of their electronic effect due to steric strain on the Co-C bond. This hypothesis of "nonsteric" transmission of steric effects is potentially testable in this system by application of eq 3. Finally, previous work with cyanocobalt complexes enriched with ¹³C and ¹⁵N in the cyano ligand^{25,26} have shown that changes in the inner coordination sphere of such complexes have opposite effects on the cyanide ¹³C and ¹⁵N NMR chemical shifts. In a recent study of (cyano)(ligand)cobaloximes,²⁶ 14 of 17 complexes displayed an excellent linear correlation between $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$, with a slope of -0.61. This effect has been attributed to the importance of cobalt-to-cyanide π -bonding in the interaction between cyanide ion and chelated cobalt centers. Since the multiparameter substituent-effect equations potentially permit a strict separation of inductive and "resonance" effects, the use of this approach with $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ complexes represents an ideal means to further characterize this interaction.

Experimental Section

$\text{Na}^{13}\text{C}^{15}\text{N}$ (99 atom % ¹³C, 99 atom % ¹⁵N) was obtained from Cambridge Isotopes. Alkyl halides, buffer salts, KCl, and solvents were obtained in the highest purity commercially available and used without further purification. Doubly distilled water was used throughout. The $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ complexes were synthesized directly from dimethylglyoxime, cobaltous chloride, and the appropriate alkyl halides as previously described,²⁷ except for $\text{CH}_3\text{OCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ and $\text{O}_2\text{NC-H}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$. The latter were prepared as the pyridine complexes as described by Marzilli and co-workers^{12,28} and then converted to the aquo derivatives by treatment with Dowex 50W-X8 ion-exchange resin (H^+ form).²⁷ These complexes were characterized by their ¹³C NMR spectra, which are summarized in Table SI (available as supplementary material).

Electronic spectra and single-wavelength absorbance measurements were made on a Cary 219 recording spectrophotometer, the sample compartment of which was thermostated at 25.0 ± 0.1 °C. Apparent formation constants for the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ complexes were determined spectrophotometrically as previously described for the pyridine

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 (17) Charton's σ_R^{16} is essentially equivalent to Ehrenson et al.'s $\sigma_{\text{R(BA)}}^{14}$.
 (18) Charton's¹⁶ more detailed treatment shows that only six of the substituents used by Marzilli et al.¹² can possibly have $\sigma_R^0 \neq \sigma_R^+$. For the renormalized constants, 12 of 13 substituents have $\sigma_R^0 \neq \sigma_R^+$.
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Table I. Formation Constants and Cyano ^{13}C and ^{15}N Chemical Shifts for $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ Complexes and Cyano ^{13}C and ^{15}N Chemical Shifts for $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNCo}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$ Complexes^a

Y	$K_{\text{CN}} \times 10^{-8} (\text{M}^{-1})^b$	$\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-^c$			$\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNCo}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-^c$		
		$\delta_{^{13}\text{C}}^d$ (ppm)	$\delta_{^{15}\text{N}}^e$ (ppm)	$J_{^{13}\text{C}^{15}\text{N}}^f$ (Hz)	$\delta_{^{13}\text{C}}^d$ (ppm)	$\delta_{^{15}\text{N}}^e$ (ppm)	$J_{^{13}\text{C}^{15}\text{N}}^f$ (Hz)
CH_3O	0.183 ± 0.010	159.96	272.34	6.9	160.05	234.44	11.7
$(\text{CH}_3)_3\text{C}$	0.210 ± 0.005	160.18	268.56	7.1	158.76	233.07	11.6
$(\text{CH}_3)_2\text{CH}$	0.353 ± 0.011	159.93	270.83	7.1	159.43	232.04	10.4
$\text{CH}_3\text{CH}_2\text{CH}_2$	0.413 ± 0.032	160.15	271.03	7.4	159.74	231.98	10.5
CH_3CH_2	0.429 ± 0.019	160.14	271.01	7.4	159.74	231.99	10.4
CH_3	0.474 ± 0.023	159.15	270.98	7.5	158.88	228.84	11.1
$\text{C}_6\text{H}_5\text{CH}_2$	0.629 ± 0.014	159.16	271.32	7.4	g	g	g
$(\text{CH}_3)_3\text{Si}$	0.831 ± 0.021	158.31	269.44	7.4	g	g	g
H	1.06 ± 0.08	159.98	270.98	7.5	158.88	228.84	11.1
C_6H_5	2.10 ± 0.11	156.88	274.92	7.5	158.56	228.30	10.6
Cl	6.43 ± 0.09	154.21	274.51	8.0	155.93	223.01	12.3
Br	12.8 ± 0.5	152.88	274.83	7.7	154.69	220.69	11.2
I	13.6 ± 0.1	151.09	275.10	8.0	152.97	217.94	13.2
$\text{CH}_3\text{CH}_2\text{OOC}$	60.3 ± 0.6	149.95	275.84	8.2	152.55	215.72	12.5
O_2N	76.4 ± 1.2	144.21	279.83	8.5	149.23	208.96	11.3
NC	h	144.00	278.00	i	g	g	g
CF_3	115 ± 5	149.38	275.68	8.4	152.20	215.25	13.0

^a 25 °C. ^b Ionic strength 1.0 M (KCl). Average of at least four determinations calculated from $K_{\text{CN}}^{\text{app}}$ and eq 6. ^c In 5% D_2O . ^d Relative to TSP. ^e Measured relative to CH_3NO_2 but reported relative to $\text{NH}_3(\text{l})$, $\delta_{\text{CH}_3\text{NO}_2} = 380.23$ ppm relative to $\text{NH}_3(\text{l})$ (ref 30). ^f $J_{^{13}\text{C}^{15}\text{N}}$ is probably negative as is the case for CN^- (ref 41b) and HCN (ref 39). ^g Dimeric species not observed. ^h Not determined due to poor solubility. ⁱ Not resolved.

and dimethoxyethylamine complexes of (alkyl)cobaloximes.⁷ Complex formation was monitored at visible wavelengths between 434 and 464 nm and at UV wavelengths between 270 and 349 nm, depending on the complex. Cobaloxime concentration was 1.0×10^{-4} M at UV wavelengths, but varied from 2.75×10^{-4} to 1.0×10^{-3} M at visible wavelengths in 1.0-cm path length cells, and from 1.0×10^{-5} to 2.0×10^{-4} M in 10-cm path length cells in various determinations. Samples contained cobaloxime, KCN at various concentrations, chloroacetate, formate, acetate, or phosphate buffers (0.1 M) or HCl, as needed, to maintain pH (pH 1.05–5.96) and KCl (ionic strength 1.0 M). Samples were incubated at 25.0 ± 0.1 °C until equilibrium was achieved as determined by the cessation of absorbance changes. Sample pH was measured after absorbance measurements were complete using a Radiometer PHM 84 pH meter equipped with a Radiometer GK 23023 type C combination electrode. Formation constants were determined from the absorbance data as described previously.²⁹

NMR samples were prepared by stirring equimolar amounts (0.5–0.6 mmol) of $\text{Na}^{13}\text{C}^{15}\text{N}$ and $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ in 0.75–1.0 mL of 5% D_2O . Any undissolved solid was removed by centrifugation. Both ^{13}C and ^{15}N NMR observations were repeated after samples were diluted 1:1, and in some cases 1:4, with 5% D_2O . NMR spectra were recorded on a GE QE300 NMR spectrometer operating at 75.61 MHz (^{13}C) or at 30.47 MHz (^{15}N) at 25 °C. ^{13}C NMR spectra were observed with and without ^1H decoupling and were referenced to external TSP. ^{15}N NMR spectra were referenced to external neat CH_3NO_2 locked to D_2O in a concentric insert (Wilmad). ^{15}N chemical shifts are reported relative to $\text{NH}_3(\text{l})$ using $\delta_{\text{CH}_3\text{NO}_2} = 380.23$ ppm relative to $\text{NH}_3(\text{l})$.³⁰

Results

Formation Constants for the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ Complexes.

Apparent equilibrium constants for formation of the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ complexes were determined spectrophotometrically as was done previously for other $\text{RCo}(\text{D}_2\text{H}_2)\text{L}$ complexes.⁷ Because of the very high values of K_{CN} (eq 4), it was necessary to work at pH values (1.0–6.0) well below the $\text{p}K_a$ of the HCN^{31} in order to reduce the apparent equilibrium constant, $K_{\text{CN}}^{\text{app}}$ (eq 5), to the measurable range (8.0×10^2 to 3.0×10^4). The

$$K_{\text{CN}}^{\text{app}} = \frac{[\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-]}{([\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2][\text{HCN}] + [\text{CN}^-])} \quad (5)$$

anticipated dependence of $K_{\text{CN}}^{\text{app}}$ on pH was demonstrated for all complexes as shown in Figure 1 for selected examples. Slopes of these plots of $\log K_{\text{CN}}^{\text{app}}$ vs pH varied from 0.956 to 1.036. Values of K_{CN} (eq 4) were determined from each measurement via eq 6,

$$K_{\text{CN}} = K_{\text{CN}}^{\text{app}} / \alpha_{\text{CN}^-} \quad (6)$$

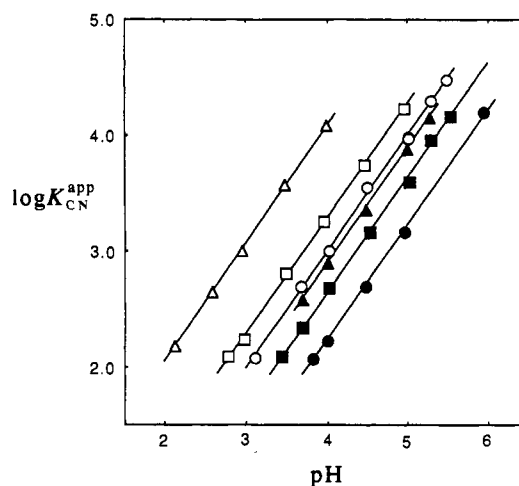


Figure 1. Plots of $\log K_{\text{CN}}^{\text{app}}$ (eq 5) vs pH, 25.0 \pm 0.1 °C, ionic strength 1.0 M (KCl): (●) $\text{CH}_3\text{OCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, $\lambda = 444$ nm, complex concentration 5.0×10^{-4} M (pH < 4.5) or 5.0×10^{-5} M (pH > 4.5); (■) $\text{CH}_3\text{CH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, complex concentration 2.75×10^{-4} M (pH < 5.1) or 3.0×10^{-4} M (pH > 5.1), each value is the average of determinations at 452 and 349 nm; (▲) $(\text{CH}_3)_3\text{SiCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, $\lambda = 458$ nm, complex concentration 7.5×10^{-4} M (pH < 4.75) or 6.0×10^{-5} M (pH > 4.75); (○) $\text{CH}_3\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, $\lambda = 441$ nm, complex concentration 5.0×10^{-4} M (pH < 5.1) or 5.0×10^{-5} M (pH > 5.1); (□) $\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, complex concentration 5.0×10^{-4} M (pH < 4.25, $\lambda = 464$ nm) or 1.0×10^{-4} M (pH > 4.25, $\lambda = 320$ nm); (Δ) $\text{BrCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, $\lambda = 436$ nm, complex concentration 7.5×10^{-4} M (pH < 3.75) or 7.5×10^{-5} M (pH > 3.75).

where α_{CN^-} is the fraction of cyanide present as cyanide ion, calculated from eq 7 using $\text{p}K_a = 9.04$ for HCN .³¹ Values of

$$\alpha_{\text{CN}^-} = K_a / (K_a + [\text{H}^+]) \quad (7)$$

K_{CN} thus determined were independent of measurement wavelength and complex concentration, which varied by as much as 12-fold for individual $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ complexes (Figure 1). A minimum of four values of K_{CN} were determined for each complex and averaged to provide the values listed in Table I. These values can be seen to be very large and vary by nearly 3 orders of magnitude over the range ca. 1×10^7 to 1×10^{10} M^{-1} . To our knowledge, these are the first reported values of equilibrium constants for formation of (cyano)cobaloximes.

Crumblliss and Gaus^{32,33} have reported the synthesis and characterization of neutral, cyano-bridged dicobaloximes of the

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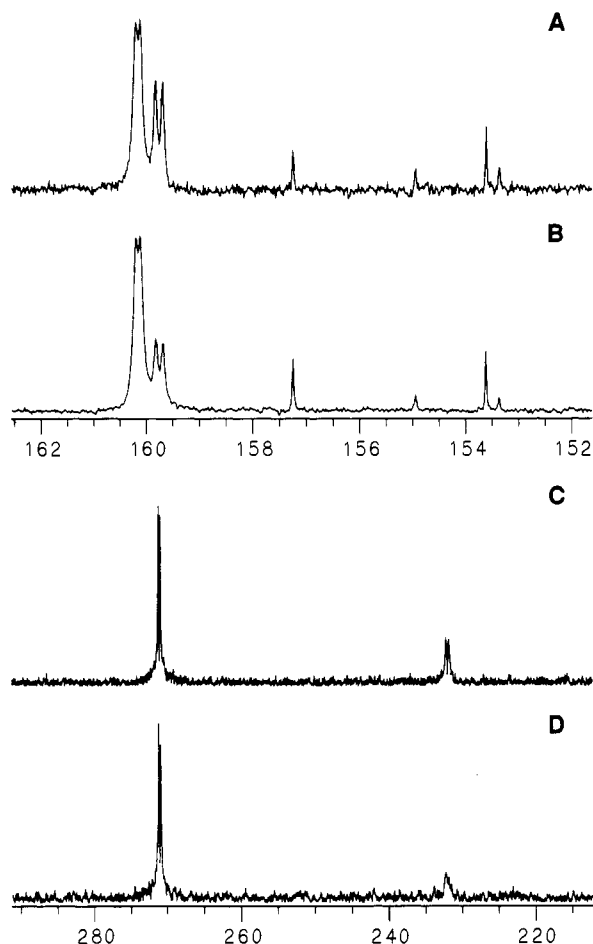


Figure 2. (A) Downfield portion of the ^1H -decoupled ^{13}C NMR spectrum of a sample (0.75 mL of 5% D_2O) saturated with equimolar amounts (0.045 mmol) of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ and $\text{Na}^{13}\text{C}^{15}\text{N}$. In addition to the cyano ^{13}C resonances at 160.15 ppm (monomeric cyano complex) and 159.74 ppm (dimeric, cyano-bridged complex) the equatorial quaternary carbon resonances of the uncomplexed aquo species (157.22 ppm), the monomeric cyano species (153.60 ppm), and the dimeric, cyano-bridged species (153.35 and 154.93 ppm) are visible. (B) Downfield portion of the ^1H -decoupled ^{13}C NMR spectrum of the sample described in part A after 2-fold dilution with 5% D_2O . (C) ^{15}N NMR spectrum of the sample described in part A. (D) ^{15}N NMR spectrum of the sample described in part A after 2-fold dilution with 5% D_2O .

type $\text{RCo}(\text{D}_2\text{H}_2)\text{NCCo}(\text{D}_2\text{H}_2)\text{L}$ and the in situ generation of cyano-bridged diorganocobaloximes of the type $\text{RCo}(\text{D}_2\text{H}_2)\text{NCCo}(\text{D}_2\text{H}_2)\text{R}'^-$.³⁴ As described below, we also find cyano-bridged dicobaloximes, $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNC}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$, in samples containing $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ complexes and CN^- at sufficient concentration (40–100 mM) for NMR observation. However, at the spectrophotometric concentrations utilized for determination of KCN (1.0×10^{-5} to 1.0×10^{-3} M), complicating equilibria due to formation of the cyano-bridged dimeric species do not interfere as indicated by the invariance of K_{CN} with total concentration (Figure 1).

Cyano ^{13}C and ^{15}N Chemical Shifts. Both the ^{13}C and ^{15}N NMR spectra of 5% D_2O solutions saturated with equimolar amounts of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ and $\text{Na}^{13}\text{C}^{15}\text{N}$ showed clear evidence of formation of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ and $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNC}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$ complexes except for $\text{Y} = \text{C}_6\text{H}_5\text{CH}_2$, $(\text{CH}_3)_3\text{Si}$, and NC , for which only the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ complex was observed. For all but these three complexes, two broad doublets in the ^{13}C NMR spectrum (Figure 2A) were attributable to the enriched cyano carbon due to their persistence in spectra obtained without ^1H decoupling. Similarly, the ^{15}N NMR spectra (Figure 2C) displayed two doublets, including a narrow resonance in the downfield region (268–276 ppm), very

close to the region where ^{15}N -enriched cyanocobaloximes and cyanocobalt corrins without trans organic ligands have been found to resonate (277–308 ppm),^{25,26} and a broader resonance 35–71 ppm upfield. These pairs of doublets could always be unambiguously assigned to the monomeric cyano species and the dimeric, bridged species on the basis of the following considerations. An upfield shift of the ^{15}N resonance is anticipated for the bridged, dimeric species on the basis of a similar upfield shift (47.8 ppm) of the ^{15}N resonance of HCN upon protonation at nitrogen.²⁵ Similarly, broadening of the ^{15}N resonance of the dimeric species is anticipated due to proximity of the ^{15}N nucleus to the ^{57}Co quadrupole ($I = 7/2$) in this species. Such broadening is always observed in the ^{13}C resonances of the α carbons of organocobalt species and has been attributed to quadrupolar relaxation.^{35–38} In addition, the more upfield of the ^{15}N resonances and one of the two ^{13}C resonances had a significantly larger ^{13}C – ^{15}N coupling constant (10.4–13.0 Hz) than the other resonance (6.9–8.5 Hz). Again, this enhanced coupling in the bridged, dimeric species is anticipated on the basis of the increase in the coupling constant of HCN upon protonation at nitrogen ($J_{^{13}\text{C}^{15}\text{N}} = 19$ Hz^{25,39} for HCN but 32 Hz for HCNH^+ ²⁵).⁴⁰ Assignments of the ^{13}C and ^{15}N NMR doublets to the monomeric cyano and bridged, dimeric species made in this manner were confirmed by the effect of dilution on the relative intensity of the signals. Thus, a 2-fold dilution of the original sample always produced a significant decrease in the relative intensity of the ^{13}C doublet with the larger coupling constant (Figure 2B) and of the more upfield ^{15}N signal (Figure 2D). Most importantly, dilutions of up to 4-fold had no effect on the observed chemical shifts despite the changes in intensity, indicating that exchange between the monomeric and dimeric species is stopped on the NMR time scale at both observation frequencies and that the spectra are not complicated by exchange broadening or chemical shift averaging. The cyano ^{13}C and ^{15}N chemical shifts for the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ and $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNC}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$ complexes thus assigned are listed in Table I, along with the observed ^{13}C – ^{15}N coupling constants.

In the ^1H -decoupled ^{13}C NMR spectra (Figure 2A,B) the natural abundance resonances of the other carbons in the complexes (except the α carbons of the organic ligand, which are broadened beyond detection by the Co quadrupole)^{36,42,43} could also be observed for the monomeric cyano species, the bridged, dimeric species, and the uncomplexed aquo species. These resonances could be assigned to the correct species on the basis of the effect of dilution on their relative intensities. These assignments for the monomeric cyano species and the bridged, dimeric species are listed in Tables SII and SIII (available as supplementary material).

The data in Table I show that the cyano ^{13}C chemical shifts vary by 16 ppm across the series of 17 $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$ complexes, while the ^{15}N chemical shifts vary by 75% as much. There is a distinct tendency for the ^{13}C resonances to shift upfield as the affinity of cyanide ion for the cobalt center increases, but the ^{15}N resonances shift downfield with increasing K_{CN} . While both the high sensitivity of the ^{15}N chemical shift and the opposite dependence of the ^{13}C and ^{15}N chemical shifts on the trans axial ligand are precisely what has been observed previously in cyanocobalt corrins²⁵ and cyano(ligand)cobaloximes,²⁶ the linear relationship between $\delta_{^{13}\text{C}}$ and $\delta_{^{15}\text{N}}$ previously found among 14

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Table II. Substituent-Effect Constants Used for Correlations via Eqs 2, 3, and 8

Y	σ_I^a	σ_R^a	$\sigma_R^{o,a}$	σ_R^{-a}	σ_R^{+a}	$E_s(Y)^b$	$E_s(YCH_2)^c$	$E_s'(Y)^d$	$E_s'(YCH_2)^e$	$\nu(Y)^f$	$\nu(YCH_2)^g$
CH ₃ O	0.30	-0.58	-0.44	-0.51	-0.66	-0.55	-0.19	<i>h</i>	<i>h</i>	0.36	0.11
(CH ₃) ₃ C	-0.01	-0.18	-0.18	-0.11	-0.13	-2.78	-1.74	-2.55	-1.63	1.24	0.82
(CH ₃) ₂ CH	0.01	-0.16	-0.16	-0.09	-0.16	-1.71	-0.93	-1.60	-0.93	0.76	0.46
CH ₃ CH ₂ CH ₂	-0.01	-0.16	-0.16	-0.09	-0.16	-1.60	-0.39	-1.43	-0.31	0.68	0.16
CH ₃ CH ₂	-0.01	-0.14	-0.14	-0.07	-0.14	-1.31	-0.36	-1.20	-0.31	0.56	0.16
CH ₃	-0.01	-0.16	-0.16	-0.09	-0.16	-1.24	-0.07	-1.12	-0.08	0.52	0.04
C ₆ H ₅ CH ₂	0.03	-0.13	-0.13	-0.06	-0.13	-1.63	-0.46	-1.51	-0.35	0.70	0.18
(CH ₃) ₃ Si	-0.11	0.12	0.12	0.19	0.12	-3.36	<i>h</i>	-2.91	<i>h</i>	1.40	<i>h</i>
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₆ H ₅	0.12	-0.11	-0.11	-0.04	-0.17	<i>h</i>	-0.39	-3.43	-0.39	0.57	0.18
Cl	0.47	-0.25	-0.25	-0.30	-0.21	-0.97	-0.24	-1.14	-0.18	0.55	0.08
Br	0.47	-0.25	-0.25	-0.28	-0.19	-1.16	-0.27	-1.34	-0.24	0.65	0.12
I	0.40	-0.16	-0.16	-0.18	-0.16	-1.40	-0.37	-1.62	-0.30	0.78	0.15
CH ₃ CH ₂ OOC	0.30	0.12	0.12	0.31	0.12	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>
O ₂ N	0.67	0.10	0.10	0.37	0.10	-1.01	-1.47	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>
NC	0.63	0.08	0.08	0.26	0.08	-0.51	-1.04	<i>h</i>	-0.89	<i>h</i>	0.37
CF ₃	0.40	0.11	0.11	0.18	0.15	-2.40	<i>h</i>	-1.90	<i>h</i>	0.91	<i>h</i>

^a Taken from ref 16. ^b Taft steric substituent constant (ref 22) for the substituent Y. Values from ref 19. ^c Taft steric substituent constant for the substituent YCH₂. Values from ref 19. The $E_s(YCH_2)$ constants have been normalized to $E_s(YCH_2) = 0$ for YCH₂ = CH₃. ^d The modified Taft steric substituent constant, according to Dubois (ref 23), for the substituent Y. The $E_s'(Y)$ constants have been normalized so that $E_s'(Y) = 0$ for Y = H. ^e The modified Taft steric substituent constant for the substituent YCH₂. Values from ref 23. ^f The steric substituent constant of Charton (ref 24) for the substituent Y. ^g The steric substituent constant of Charton (ref 24) for the substituent YCH₂. The $\nu(YCH_2)$ values have been normalized so that $\nu(YCH_2) = 0$ for YCH₂ = CH₃. ^h Constant not available.

Table III. Results of the Correlations of the Data in Table I via Eqs 2, 3, and 8

complex	Q_Y^a	eq ^b	R ^c	S ^d	ρ_I	ρ_R	ρ_S	C	f ^e	N ^f
YCH ₂ Co(D ₂ H ₂)CN ⁻										
	log K _{CN}	8			3.15			7.77	0.575	16
	δ_{13C}	8			-19.94			159.6	0.375	17
	δ_{15N}	8			11.17			270.9	0.324	17
	log K _{CN}	2	σ_R		3.17	2.92		8.10	0.253	16
	δ_{13C}	2	σ_R		-18.94	-13.98		157.9	0.107	17
	δ_{15N}	2	σ_R^-		10.60	3.58		271.1	0.247	17
	log K _{CN}	3	σ_R^-	$\nu(YCH_2)$	4.60	4.13	-0.28	8.03	0.096	12
	δ_{13C}	3	σ_R	$E_s(Y)$	-19.29	-13.19	0.25	158.5	0.107	15
	δ_{15N}	3	σ_R^-	$E_s(Y)$	10.18	3.79	0.46	271.7	0.155	15
YCH ₂ Co(D ₂ H ₂)CNC(D ₂ H ₂)CH ₂ Y ⁻										
	δ_{13C}	8			-13.15			159.5	0.444	14
	δ_{15N}	8			-29.49			231.9	0.498	14
	δ_{13C}	2	σ_R		-12.22	-9.68		158.1	0.182	14
	δ_{15N}	2	σ_R		-27.19	-24.10		228.2	0.134	14
	δ_{13C}	3	σ_R	$E_s(Y)$	-12.35	-8.67	0.62	159.1	0.149	12
	δ_{15N}	3	σ_R	$E_s(Y)$	-27.14	-22.84	0.28	228.8	0.133	12

^a Correlated property. ^b Equation used. ^c Resonance substituent constant giving the best correlation. ^d Steric substituent constant giving the best correlation. The superscript "Y" indicates that the substituent was taken to be Y, while the superscript "YCH₂" indicates that the substituent was taken to be YCH₂. ^e Reference 14. A correlation is considered to be acceptable if $0.1 < f < 0.2$, or excellent if $f < 0.1$ (ref 44). ^f Number of data points correlated.

NCCo(D₂H₂)L complexes²⁶ is not found among the YCH₂Co(D₂H₂)CN⁻ complexes. Within the latter complexes there is a distinct tendency for J_{13C15N} to increase with increasing strength of cyanide binding as might be expected from the ¹³C-¹⁵N coupling constants of free cyanide (6 Hz)^{25,41a} and HCN (19 Hz).^{25,39,40} For the cyano-bridged YCH₂Co(D₂H₂)CNC(D₂H₂)CH₂Y⁻ species, both the ¹³C resonances, which vary by 11 ppm across the series, and the ¹⁵N resonances, which vary by 26 ppm across the series, shift upfield with increasing K_{CN}, although the ¹³C-¹⁵N coupling constants show no trend. Assuming that the formation constants for the cyano-bridged dimeric species from the cyano and aquo species vary in roughly the same order as K_{CN}, the upfield trend of both resonances is anticipated from the upfield shift of both the ¹³C resonance (10.3 ppm) and the ¹⁵N resonance (47.8 ppm) upon protonation of HCN at nitrogen.²⁵

Substituent-Effect Analyses. In order to determine the suitability of eqs 2 and 3 and the necessity of inclusion of the resonance and steric terms, each of the five data sets in Table II was correlated via eq 8, which includes only an inductive term, as well as by eqs 2 and 3. We have chosen to use the inductive and

$$Q_Y = \rho_I \sigma_I + C \quad (8)$$

resonance substituent constants of Charton¹⁶ rather than those of Ehrenson et al.¹⁴ simply because Charton provides values for

a vast array of substituents so that none of the data in Table II must be omitted from correlations due to the lack of σ_I or σ_R constants. For steric substituent constants, we have used the large number of values tabulated by Unger and Hansch¹⁹ for the Taft E_s steric substituent parameter,²² the modified E_s' values of Dubois et al.,²³ and the independently derived values, ν , of Charton.²¹ Since it is not immediately obvious whether it is most efficacious to use the steric substituent constant for Y or for YCH₂, correlations have been attempted using both methods. The substituent constants used are listed in Table II, where it can be seen that steric substituent constants are not available for all Y and YCH₂ in any of the three series of substituent constants. For analysis via eq 2, correlations were attempted using each of the four resonance substituent constant scales, and for correlations via eq 3, every combination of the four resonance substituent constant scales and the six steric substituent constant scales was used. We have used the f statistic¹⁴ to judge the goodness of fit, and Topsom's criterion⁴⁴ that $0.1 < f < 0.2$ (i.e., $0.96 < r^2 < 0.99$) represents an acceptable fit, while $f < 0.1$ (i.e., $r^2 > 0.99$) is an excellent fit.

The results of the correlations of the data in Table I via eqs 2, 3, and 8 are shown in Table III. Results are only shown for

correlations using the resonance substituent parameter (eq 2) or combination of resonance and steric substituent parameters (eq 3) which gave the best fit (i.e., the lowest f value). For all five data sets, correlations using only the inductive term (eq 8) are poor, with $f > 0.3$ in all cases. Inclusion of the resonance term (eq 2) provided substantial improvement with the correlations of δ_{13C} and δ_{15N} for the cyano-bridged dimeric complexes and δ_{13C} for the monomeric cyano complexes becoming acceptable (and the latter bordering on excellent). However, the correlations of $\log K_{CN}$ and δ_{15N} for the monomeric species remain poor, with $f > 0.2$. Inclusion of the steric term (eq 3) significantly improves three of the five correlations, including a dramatic improvement of the $\log K_{CN}$ correlation to just inside the excellent region. However, two of the correlations, δ_{13C} for the monomeric species and δ_{15N} for the cyano-bridged species, are not improved. Inspection of the correlation parameters in Table III shows that the σ_R and σ_R^- resonance substituent constants consistently give the best fits. The $E_s^{(Y)}$ steric substituent constant gave the best correlations, except for $\log K_{CN}$, for which $\rho^{(YCH_2)}$ was the preferred parameter. However, the use of $E_s^{(Y)}$ for this correlation only slightly degraded the fit ($f = 0.116$, $N = 13$).

The "resonance effect" can be seen to be quite important in all five data sets, with the ratio of ρ_R/ρ_I being as high as 0.9 for $\log K_{CN}$, i.e., the inductive and resonance effects of Y are nearly equally important in the binding of cyanide to the $YCH_2Co(D_2H_2)OH_2$ complexes. For the monomeric cyano complexes, this ratio decreases monotonically in the order $\log K_{CN}$ (0.90), δ_{13C} (0.68), and δ_{15N} (0.37). For δ_{13C} , the relative sensitivity to the resonance effect of Y is essentially identical for the monomeric complexes and the cyano-bridged dimeric species ($\rho_R/\rho_I = 0.70$). However, the sensitivity of δ_{15N} to resonance effects is substantially enhanced in the cyano-bridged dimeric complexes ($\rho_R/\rho_I = 0.84$) compared to the monomeric complexes ($\rho_R/\rho_I = 0.37$). This suggests that the importance of the resonance effect on the properties of the trans ligand is directly related to proximity to the metal atom.

In contrast, the sensitivity of these data sets to the steric effect, ρ_S , seems relatively small, even for the data sets for which inclusion of the steric term substantially improves the correlation. Despite the lack of improvement in two of the five correlations upon inclusion of the steric term, the substantial improvement that the steric term provides to the other correlations suggests that steric effects in alkyl(cyano)cobaloximes are indeed significant, even if small.

Following Wells et al.,⁴⁵ correlations via the complete equation (eq 3) may be visualized using the two-dimensional transformation shown in eq 9, where $\bar{\rho}$ and $\bar{\sigma}$ are defined in eqs 10–13. These

$$Q_Y = \bar{\rho}\bar{\sigma} + C \quad (9)$$

$$\bar{\sigma} = (\sigma_I + \lambda_1\sigma_R + \lambda_2\sigma_S)/(1 + |\lambda_1| + |\lambda_2|) \quad (10)$$

$$\bar{\rho} = \rho_I(1 + |\lambda_1| + |\lambda_2|) \quad (11)$$

$$\lambda_1 = \rho_R/\rho_I \quad (12)$$

$$\lambda_2 = \rho_S/\rho_I \quad (13)$$

graphical representations of the correlations are shown in Figures 3 and 4. As readily seen in Figure 4A, most of the error in both of the δ_{13C} correlations is due to two data points, those for Y = Cl and Y = I. Similar deviations of data for Y = I were previously noted by Marzilli et al.¹²

The success of the complete equation (eq 3) in correlating the data for the alkyl(cyano)cobaloximes prompted us to attempt to correlate data sets from the literature for $YCH_2Co(D_2H_2)L$ complexes in the same manner. Results of correlations of the rate constants (k_{off}^L , eq 14) for dissociation of $CNpy^I$ and CH_3OAn^I



from the appropriate alkyl(ligand)cobaloximes previously corre-

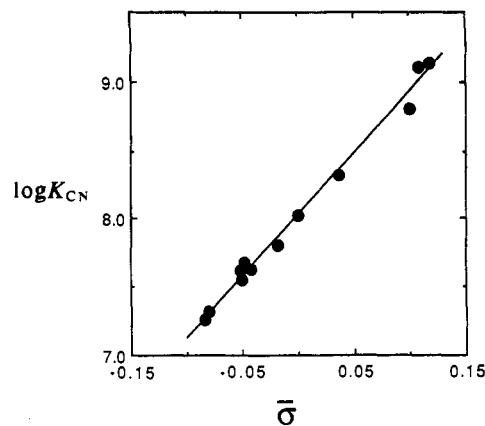


Figure 3. Plot of $\log K_{CN}$ (eq 4 and Table I) vs $\bar{\sigma}$, according to eq 9. The values of $\bar{\rho}$ (9.01) and $\bar{\sigma}$ were calculated from eqs 11–13 and the data in Tables II and III.

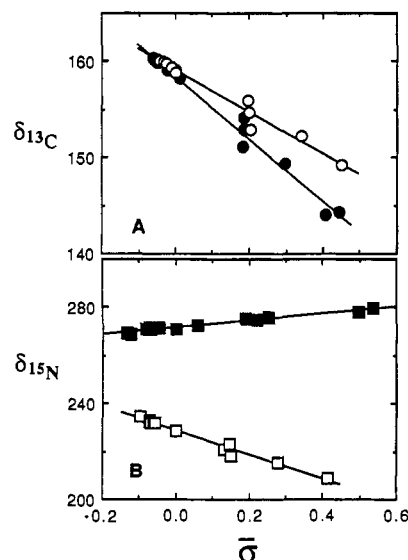


Figure 4. (A) Plots of δ_{13C} (Table I) for the monomeric $YCH_2Co(D_2H_2)^{13}C^{15}N^-$ complexes (●) and the dimeric $YCH_2Co(D_2H_2)CNCo(D_2H_2)CH_2Y^-$ complexes (○) vs $\bar{\sigma}$ according to eq 9. The values of $\bar{\rho}$ (−32.73 and −21.63 for the monomeric and dimeric complexes, respectively) and $\bar{\sigma}$ were calculated from eqs 11–13 and the data in Tables II and III. (B) Plots of δ_{15N} (Table I) for the monomeric $YCH_2Co(D_2H_2)^{13}C^{15}N^-$ complexes (■) and the dimeric $YCH_2Co(D_2H_2)CNCo(D_2H_2)CH_2Y^-$ complexes (□) vs $\bar{\sigma}$ according to eq 9. The values of $\bar{\rho}$ (14.44 and −50.26 for the monomeric and dimeric complexes, respectively) and $\bar{\sigma}$ were calculated from eqs 11–13 and the data in Tables II and III.

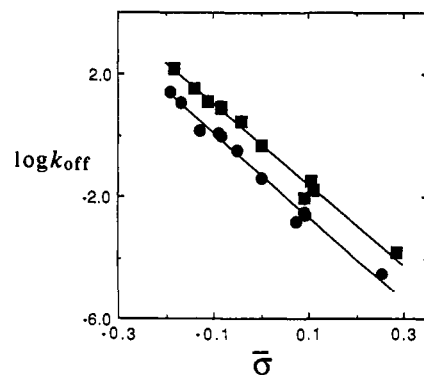


Figure 5. Plots of $\log k_{off}$ (eq 14) for ligand dissociation from $YCH_2Co(D_2H_2)CNpy$ (●) and $YCH_2Co(D_2H_2)CH_3OAn$ (■) complexes vs $\bar{\sigma}$ according to eq 9. The data are from ref 12. The values of $\bar{\rho}$ (−13.65 for L = py and −13.09 for L = CH_3OAn) and $\bar{\sigma}$ were calculated from eqs 11–13 and the data in Tables II and IV.

(45) Wells, P. R.; Ehrenson, S.; Taft, R. W., Jr. *Prog. Phys. Org. Chem.* 1968, 6, 147.

Table IV. Results of the Correlation of Literature Data for $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ Complexes via Eqs 2, 3, and 8

Q_Y^a	eq ^b	R ^c	S ^d	ρ_1	ρ_R	ρ_S	C	f ^e	N ^f
$\log k_{\text{off}}^{\text{CNpy}g}$	8			-6.64			-0.11	0.576	17
$\log k_{\text{off}}^{\text{CH}_3\text{OAn}h}$	8			-6.10			0.64	0.642	16
$\log k_{\text{off}}^{\text{CNpy}g}$	2	σ_R^+		-6.12	-5.58		-0.73	0.205	17
$\log k_{\text{off}}^{\text{CH}_3\text{OAn}h}$	2	σ_R^+		-6.08	-5.78		0.06	0.184	16
$\log k_{\text{off}}^{\text{CNpy}g}$	3	σ_R^+	$\nu(\text{YCH}_2)$	-5.70	-6.23	1.72	-1.30	0.113	11
$\log k_{\text{off}}^{\text{CH}_3\text{OAn}h}$	3	σ_R^+	$\nu(\text{YCH}_2)$	-5.84	-6.06	1.19	-0.26	0.119	11
$\text{p}K_{\text{OH}_2}^i$	8			-3.13			12.45	0.417	13
$\text{p}K_{\text{py}}^j$	8			-3.30			13.63	0.207	6
$\log K_f^{\text{py}k}$	8			0.818			3.16	0.686	10
$\log k_{\text{on}}^{\text{py}l}$	8			-5.99			2.67	0.399	9
$\log k_{\text{off}}^{\text{py}l}$	8			-6.90			-4.40	0.438	9
$\text{p}K_{\text{OH}_2}^i$	2	σ_R		-2.87	-3.51		12.34	0.173	13
$\text{p}K_{\text{py}}^j$	2	σ_R^-		-2.21	-1.87		13.60	0.058	6
$\log K_f^{\text{py}k}$	2	σ_R		0.80	0.98		3.19	0.438	10
$\log k_{\text{on}}^{\text{py}l}$	2	σ_R		-5.25	-4.95		2.25	0.106	9
$\log k_{\text{off}}^{\text{py}l}$	2	σ_R		-5.98	-6.13		-0.96	0.122	9
$\text{p}K_{\text{OH}_2}^i$	3	σ_R	$E_s(\text{YCH}_2)$	-2.36	-1.69	0.57	12.72	0.096	8
$\text{p}K_{\text{py}}^j$	3	σ_R	$E_s(\text{YCH}_2)$	-1.59	-2.23	0.62	13.58	0.021	5
$\log K_f^{\text{py}k}$	3	σ_R	$E_s(\text{YCH}_2)$	0.88	1.51	0.16	3.32	0.288	9
$\log k_{\text{on}}^{\text{py}l}$	3	σ_R	$E_s(\text{YCH}_2)$	-5.64	-5.61	-0.52	2.05	0.093	8
$\log k_{\text{off}}^{\text{py}l}$	3	σ_R	$E_s(\text{YCH}_2)$	-6.47	-7.09	-0.62	-1.21	0.099	8

^a Correlated property. ^b Equation used. ^c Resonance substituent constant giving the best correlation. ^d Steric substituent constant giving the best correlation. The superscript "Y" indicates that the substituent was taken to be Y, while the superscript "YCH₂" indicates that the substituent was taken to be YCH₂. ^e Reference 14. A correlation is considered to be acceptable if $0.1 < f < 0.2$, or excellent if $f < 0.1$ (ref 44). ^f Number of data points correlated. ^g k_{off} (eq 14) for L = CNpy. Data from ref 12. ^h k_{off} (eq 14) for L = CH₃OAn. Data from ref 12. ⁱ Equation 15. Data from ref 7. ^j Equation 16. Data from ref 7. ^k Equations 17 and 18. Data from ref 7. ^l Equation 17. Data from ref 7.

lated by Marzilli et al.¹² are shown in Table IV. Extremely poor correlations are obtained using eq 8, including only the inductive term ($f > 0.5$). Inclusion of the resonance term (eq 2), using properly defined resonance substituent constants, improves the fits substantially, essentially into the acceptable range. The use of the complete equation (eq 3), including the steric term, improves both correlations significantly ($f = 0.113$ and 0.119). Plots of these correlations according to eqs 9–13 are shown in Figure 5. For these data sets, σ_R^+ gave the best fits and the sensitivities to resonance and inductive effects are essentially equal. For the complete equation, the $\nu(\text{YCH}_2)$ steric parameters gave the best correlations, although correlations very nearly as good ($f = 0.118$ and 0.123) were obtained using $E_s(\text{YCH}_2)$. The sensitivity of both data sets to the steric effect, ρ_S , has the expected sign, i.e., increasing steric bulk increases the rate of ligand dissociation. In addition, the sensitivity of these data sets to steric effects is substantially larger than that of the (cyano)cobaloxime data sets (Table III). This difference is even more pronounced when one takes into account the fact that the spectroscopic properties of the cyanocobaloximes were best correlated with a steric parameter for the substituent Y, but the ligand dissociation rate constants (eq 14) correlate best with steric substituent constants for YCH₂. As most of the YCH₂ steric substituent constants are of smaller magnitude than the Y steric substituent constants for a given Y, the difference in sensitivity to steric effects is larger than a direct comparison of the ρ_S values would suggest. Hence ρ_S values are only directly comparable between data sets correlated with either Y or YCH₂ steric substituent constants.

Data sets for the $\text{p}K_a$ for proton dissociation from the axial water ligand of alkyl(aquo)cobaloximes, $\text{p}K_{\text{OH}_2}$ (eq 15); the $\text{p}K_a$ for equatorial proton ionization from alkyl(pyridine)cobaloximes, $\text{p}K_{\text{py}}$ (eq 16); the rate constants for formation of the pyridine complexes, $k_{\text{on}}^{\text{py}}$, and pyridine dissociation from these complexes, $k_{\text{off}}^{\text{py}}$ (eq 17); and the equilibrium constants for formation of the pyridine complexes, K_f^{py} (eq 18),⁷ have also been correlated via eqs 2, 3, and 8. These results are also given in Table IV. Again, the use

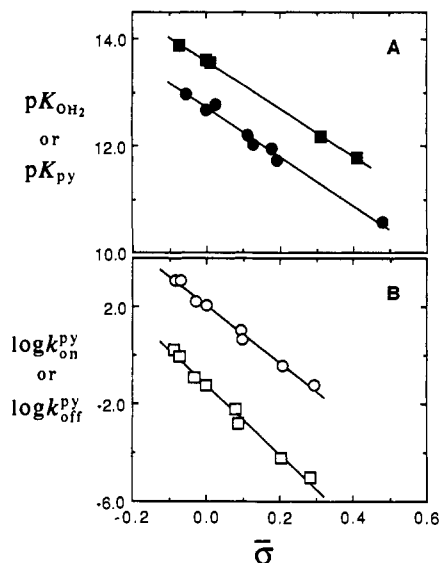
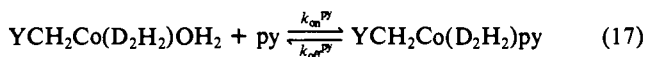


Figure 6. (A) Plots of $\text{p}K_{\text{OH}_2}$ (●) (eq 15) and $\text{p}K_{\text{py}}$ (■) (eq 16) for the ionization of the axial water ligand of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$ complexes and the ionization of the equatorial ligand of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{py}$ complexes, respectively, vs $\bar{\sigma}$ according to eq 9. The data are from ref 7. The values of $\bar{\sigma}$ (-4.61 for $\text{p}K_{\text{OH}_2}$ and -4.44 for $\text{p}K_{\text{py}}$) and $\bar{\sigma}$ were calculated from eqs 11–13 and the data in Tables II and IV. (B) Plots of $\log k_{\text{on}}^{\text{py}}$ (○) and $\log k_{\text{off}}^{\text{py}}$ (□) (eq 17) for the formation of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{py}$ and the dissociation of pyridine from these complexes, respectively, vs $\bar{\sigma}$ according to eq 9. The data are from ref 7. The values of $\bar{\sigma}$ (-11.77 for $\log k_{\text{on}}^{\text{py}}$ and -14.20 for $\log k_{\text{off}}^{\text{py}}$) and $\bar{\sigma}$ were calculated from eqs 11–13 and the data in Tables II and IV.

of eq 8, including only the inductive term, gives poor fits with $f \geq 0.4$ for all of the data sets except $\text{p}K_{\text{py}}$. The latter data set is, however, quite small ($N = 6$), and conclusions regarding the correlations of this data set must be made cautiously. Inclusion of the resonance term (eq 2) improves all of the correlations dramatically, with three of the five data sets giving acceptable correlations and the small data set, $\text{p}K_{\text{py}}$, giving an excellent fit. The correlation of $\log K_f^{\text{py}}$, however, remains poor. Use of the complete equation (eq 3) improves all of the correlations significantly, and all of the correlations fall into the excellent range except for the $\log K_f^{\text{py}}$ correlation, which remains poor. The failure to obtain an acceptable correlation for $\log K_f^{\text{py}}$ is not surprising

as this data set has the least variability of any of the 12 data sets correlated here, the values of $\log K_f^{py}$ varying by only 0.934 across the series of 10 compounds. Ehrenson et al.¹⁴ have commented previously on the effect of such small variability on fit statistics and have dismissed the significance of such data sets with respect to the overall suitability of multiparameter substituent-effect equations. The correlations of these data sets (except for the unsuccessful correlation of $\log K_f^{py}$) via eq 3 are shown graphically via eqs 9–13 in Figure 6.

All of these data sets were best correlated by the resonance substitution parameter σ_R . The fit parameters (Table IV) again show the importance of resonance effects, with values of ρ_R/ρ_I for fits using the complete equation varying from 0.72 to 1.40. Steric effects are again seen to be significant, and all of these data sets are best correlated using the $E_s^{(YCH_2)}$ parameter. Increasing steric bulk can be seen to decrease the pK_a both for axial water ligand dissociation and for equatorial ligand dissociation (i.e., $\rho_S > 0$). As anticipated, ρ_S is negative (i.e., steric bulk enhances reactivity) for both $\log k_{off}^{py}$ and $\log k_{on}^{py}$, in accord with the dissociative nature of both ligand substitutions.⁷ Although the value of $|\rho_S|$ for $\log k_{off}^{py}$ is significantly smaller than those for $\log k_{off}^{CNpy}$ and $\log k_{off}^{CH_3OAn}$ (Table IV),⁴⁶ this is a consequence of the different scaling of the E_s values (which best correlate the former) and the ν values (which best correlate the latter). As $|E_s|$ values are approximately 2-fold larger than ν values for the same substituent, the sensitivity of the rate constants for pyridine dissociation is comparable to that for CNpy and CH_3OAn dissociation.

Discussion

Applicability of Multiparameter Substituent-Effect Equations to $YCH_2Co(D_2H_2)L$ Complexes. One of the problems encountered by Marzilli et al.¹² in the use of the classical dual substituent parameter equation (eq 1), in which the ratio of the property under consideration for the substituted compound to that of the unsubstituted compound is correlated, was the heavy reliance on the data for the unsubstituted compound implicit in this approach. Any deviations in behavior of the unsubstituted compound ($Y = H$, i.e., $CH_3Co(D_2H_2)L$) affect every ratio value in the correlation. Unfortunately, such deviations for $CH_3Co(D_2H_2)L$ complexes are common.^{12,15} The use of equations of the form of eqs 2 and 3 obviates this problem by correlating the properties of interest for each compound independently and providing an additional parameter to allow for a nonzero intercept. Thus, the unsubstituted compound (all $\sigma = 0$) is given no special weight and is treated like any other compound in the series. Although Ehrenson et al.¹⁴ argue against the use of the nonzero intercept, the inclusion of such a term is quite common in substituent-effect analysis.^{19,21} Its efficacy in the current case is adequately demonstrated by the success of the correlations including this term (Tables III and IV).

The original solution offered by Marzilli et al.¹² for the problem of the unsubstituted reference compound in the use of eq 1 was to choose a more satisfactory reference compound than $CH_3Co(D_2H_2)L$ (i.e., one that produces better fit statistics). However, this clearly fails to obviate the general problem of the heavy reliance of eq 1 on the data for a single compound. In addition, it is distinctly ad hoc and suggests the possibility that each data set could be searched for the "unsubstituted" reference compound which gives the best fit. In addition, as pointed out above, the required renormalization of the resonance substituent parameters is not supportable and leads to violations of known relationships among the several types of resonance substituent constants, causes resonance-donating (–R) substituents to become resonance neutral (i.e., $\sigma_R = 0$), and leads to the impossible conclusion that the resonance neutral substituent, H, is resonance withdrawing (+R) and has different values for its resonance substituent constants depending on the resonance demands of the reaction center (i.e., $\sigma_R^- \neq \sigma_R^+$). As shown in the current results, this renormalization

of the resonance substituent constants and the damage it inflicts on the rationality of resonance substituent effects are not necessary for the successful application of the multiparameter substituent-effect approach to $YCH_2Co(D_2H_2)L$ complexes.

The assumption that the steric effect of YCH_2 on the properties of the $YCH_2Co(D_2H_2)L$ complexes should not vary widely as Y is varied through a series of complexes¹² is testable using the available data and eqs 2 and 3. While interposition of a methylene group between the substituent, Y, and the metal atom seems likely, in most cases, to decrease the steric influence of Y, the assumption that variations in the bulk of Y will not have steric consequences for the $YCH_2Co(D_2H_2)L$ complexes is not supported by available X-ray crystal structure data. For instance, comparison of the structures of $(CH_3)_3CCH_2Co(D_2H_2)L$ ^{20,47} (i.e., $Y = (CH_3)_3C$) and $CH_3Co(D_2H_2)L$ ^{20,48} (i.e., $Y = H$) for $L = H_2O, py, P(CH_3)_3$, and $P(C_6H_5)_3$ shows that α , the angle of bending of the two dimethylglyoximate units, varies by 3–12° between the two complexes (depending on L), while d , the displacement of the metal atom from the plane of the equatorial nitrogens, varies by 0.04–0.07 Å. If these variations are not due to crystal packing forces, they must be due to steric effects as these two organic ligands have nearly identical inductive and resonance effects.¹⁶ While it has been previously impossible to relate such geometric distortions quantitatively to steric effects on the kinetic, thermodynamic, and spectroscopic properties of $YCH_2Co(D_2H_2)L$ complexes, the comparison of correlations of data sets of all three types by eqs 2 and 3 confirms the importance of steric effects in these complexes (Tables III and IV). Ten of the 12 data sets correlated are significantly better fitted by the complete equation (eq 3) than by eq 2. In addition, dramatic improvement of the fit (f decreased by 1.6- to 2.6-fold) is obtained for five of the data sets by inclusion of the steric term. For three of the data sets, acceptable fits could only be obtained by use of the complete equation. Thus, steric effects are important in the $YCH_2Co(D_2H_2)L$ complexes and can be quantitatively accounted for by use of eq 3. The results show, for example, that 60% (1.41 log units) of the difference in $\log k_{off}^{CNpy}$ (eq 14) between $(CH_3)_3CCH_2Co(D_2H_2)CNpy$ and $CH_3Co(D_2H_2)CNpy$ (2.43 log units, observed; 2.28 log units, calculated) is attributable to steric effects. In contrast, only 32% (0.23 log units) of the difference in $\log K_{CN}$ (eq 4) between $(CH_3)_3CCH_2Co(D_2H_2)CN^-$ and $CH_3Co(D_2H_2)CN^-$ (0.703 log units, observed; 0.730 log units, calculated) is due to steric effects.

While some data sets show relatively little dependence of f on the choice of steric substituent constant scales, there does seem to be a pattern in which spectroscopic data is best fit by steric constants for the substituent Y, while kinetic and equilibrium data are best fit by steric constants for the alkyl group, YCH_2 . It is not at all clear why this might be so, but further data will be needed to confirm this trend before any interpretation is justified.

The resonance substituent parameter which best fits data for a given $YCH_2Co(D_2H_2)L$ property is potentially informative regarding the nature of the resonance interactions into which the reaction center is capable of entering. Thus, σ_R^0 values are applicable to situations in which the reaction center is unable to conjugate directly with the substituent, σ_R^- values when the reaction center is weakly or strongly resonance accepting, and σ_R^+ values when the reaction center is strongly resonance donating. While all of the data sets addressed here involve cobaloxime-chelated cobalt centers, it is reasonable to expect that a (cy-

(46) As the signs of the E_s and ν parameters are opposite (i.e., all $E_s < 0$, all $\nu > 0$) the signs of ρ_S for correlations of ligand dissociation rate constants are expected to be opposite for correlations using E_s and ν (i.e., $\rho_S > 0$ for ν but $\rho_S < 0$ for E_s indicates that steric bulk enhances reactivity).

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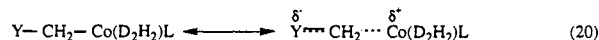
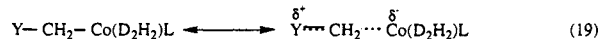
no)cobaloxime center may well have different delocalization capabilities than, for example, a (pyridine)cobaloxime center. Indeed, the fact that two of the three data sets for $YCH_2Co(D_2H_2)CN^-$ complexes correlate best with σ_R^- (Table III) while $YCH_2Co(D_2H_2)OH_2$ and $YCH_2Co(D_2H_2)py$ data sets correlate best with σ_R (Table IV) suggests that this may indeed be so. However, it seems surprising that the rate constants for ligand dissociation from the $YCH_2Co(D_2H_2)py$ complexes correlate best with σ_R while those for $YCH_2Co(D_2H_2)CNpy$ complexes correlate best with σ_R^+ (Table IV). If this observation is significant, it suggests that the delocalization capabilities of the cobalt center are quite sensitive to the properties of the axial ligand. In fact, studies of the substituent effect of cobaloxime-chelated cobalt centers on the properties of covalently bound organic ligands have shown that this is correct. While all such studies have shown these centers to be extremely inductively electron donating,²⁻⁵ studies of the base-catalyzed hydrolysis of $CH_3OCC_6H_5Co(D_2H_2)L$ complexes^{2b} and the basicity of $(CH_3)_2NC_6H_5Co(D_2H_2)L$ complexes⁵ have shown the resonance effects of the $Co(D_2H_2)L$ centers to be strongly dependent on the nature of the axial ligand, with some such centers being resonance donating and some being resonance withdrawing.

The Nature of the "Resonance" Effect. The results of the correlations of $YCH_2Co(D_2H_2)L$ properties with eqs 2 and 3 (Tables III and IV) clearly show the importance of the resonance effect in these substituent-effect analyses. Values of ρ_R frequently approach, or even exceed, those of ρ_I . While it must be pointed out that the inductive effect of Y is diminished by interposition of the methylene group, the resonance effect remains quite significant. In fact, it is clear that inclusion of the resonance effect is crucial to the success of the substituent-effect analyses of these complexes.

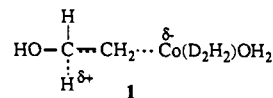
Marzilli et al.¹² originally characterized the resonance interactions in such complexes as being due to $n \rightarrow \sigma$ conjugation between lone pairs on Y and the Co-C σ bond. This description is clearly inadequate to account for delocalization in $YCH_2Co(D_2H_2)L$ complexes on two counts, both because most of the substituents involved in these correlations have no lone pairs and because complexes with resonance-withdrawing substituents correlate as well as those with resonance-donating substituents. Thus, a more general picture of delocalization in these complexes requires accommodation of substituents without lone pairs as well as provision for resonance acceptance in addition to resonance donation. We attribute the necessity of the resonance term to the occurrence of significant hyperconjugation in these complexes. The success of the multiparameter substituent-effect approach when the substituent is in the β position appears to demonstrate the importance of, and lead to a quantitation of, hyperconjugation in organocobaloximes.

There is substantial evidence for the importance of hyperconjugation in organometallic systems in which $\sigma \rightarrow \pi$ conjugation (or exalted hyperconjugation)⁴⁹ has been shown to be responsible for the organometallic " β -effect". Thus, the feeble acidity of (1-carboxyalkyl)cobaloximes² and (carboxymethyl)cobalt corins,^{6,50} the anomalously low carbonyl stretching vibration of (formylmethyl)cobaloximes,⁵¹ the upfield shift of the ¹H NMR resonance of the aldehyde hydrogen of (formylmethyl)cobalamin,⁵² and the anomalous ¹⁹F NMR shifts of (*p*-fluorobenzyl)cobaloximes^{4a,53} have all been attributed to exalted hyperconjugation.^{3b} In our view, the most important aspect of the success of the multiparameter substituent-effect approach, including the resonance term, in correlating the properties of $YCH_2Co(D_2H_2)L$ complexes is the demonstration that hyperconjugation is significant

in organocobaloximes which do not have a low-lying π system involving the β atom. Unlike the known cases of exalted hyperconjugation, in which the β atom always accepts electron density from the Co-C σ bond, the hyperconjugation displayed here demonstrates delocalized interactions between the substituent, Y, and the Co-C σ bond, in which Y can be either hyperconjugatively donating (eq 19) or accepting (eq 20). Recently, evidence

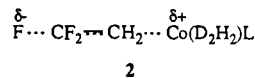


has been obtained for the importance of such hyperconjugation in organocobaloximes by observation of a substantial inverse secondary deuterium isotope effect on the axial water ligand ionization (K_{OH_2} , eq 15) of ([1,2-²H₄]-2-hydroxyethyl)(aquo)cobaloxime ($K_{OH_2}(H)/K_{OH_2}(D) = 0.64 \pm 0.10$).⁵⁴ This effect must be attributed to the β secondary deuterium isotope effect as the α deuterons must surely lead to a decrease in acidity of the axial water ligand.^{55,56} Such β secondary deuterium isotope effects are well-known to be due to hyperconjugation.^{55,57} The relevant resonance hybrid is shown in 1, in which stabilization of negative charge on the cobalt atom suppresses the ionization of the axial water ligand. Due to the loss of zero-point energy in the hy-



perconjugated species, hyperconjugation is less significant for the deuterated species, thus increasing the acidity of the axial water ligand.

There is additional, structural evidence for the importance of hyperconjugation in the $YCH_2Co(D_2H_2)L$ complexes. Bresciani-Pahor et al.²⁰ have pointed out that the X-ray crystal structures of $CF_3CH_2Co(D_2H_2)L$ complexes⁵⁸ display a number of distortions in the organic ligand including an unexpected shortening of the C-C bond, a widening of the Co-C-C bond angle to as much as 125°, and inequivalent C-F bond lengths. These structural features are consistent with the existence of the hyperconjugated resonance hybrid, 2. Similarly, for the resonance-withdrawing



substituent, CN, in $NCCH_2Co(D_2H_2)P(C_6H_5)_3$ ⁵⁹ and for the resonance-donating substituent, Br, in $BrCH_2Co(D_2H_2)P(C_6H_5)_3$,⁵⁹ the C-CN and C-Br bond distances (1.41 and 1.84 Å, respectively) are significantly shorter than expected,²⁰ consistent

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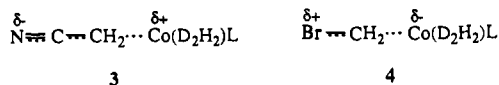
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with the resonance hybrids **3** and **4**. Taken together with the



demonstrated need to include resonance interactions in substituent-effect analyses of organocobaloximes when the substituent is in the β position, these results strongly suggest that delocalization by hyperconjugation, as in eqs 19 and 20, is responsible for the resonance effect in $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes.

Substituent Effects in $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ Complexes. Inspection of the results of the correlations of $\log k_{\text{off}}^{\text{L}}$ (eqs 14 and 17) shows that $\rho_{\text{I}} < 0$ and $\rho_{\text{R}} < 0$ for all three data sets. Hence, as anticipated, both inductive withdrawal (+I) and resonance withdrawal (+R), as in eq 20, stabilize positive charge on the metal, making it more electrophilic. This is expected to stabilize the ground state of a $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complex more than the transition state for ligand dissociation ($\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\cdots\text{L}$), slowing the rate of ligand dissociation. Conversely, both inductive and resonance donation (eq 19) destabilize the ground state, but destabilize the transition state for ligand dissociation less, increasing the rate of ligand dissociation. Similarly, the steric effect on all three $k_{\text{off}}^{\text{L}}$ data sets is in the anticipated direction, once the difference in sign of the E_{s} and ν substituent constants has been taken into account.⁴⁶ Thus, increased steric bulk increases the rate of ligand dissociation for all ligands studied. Importantly, the inductive, resonance, and steric effects on $k_{\text{on}}^{\text{py}}$ (eq 17) are of the same sign and of similar magnitude to those for the $k_{\text{off}}^{\text{L}}$ data sets, in accord with the dissociative nature of the former ligand substitution.⁷

The successful correlation of $\log K_{\text{CN}}$ (eq 4, Table III) shows that the multiparameter substituent-effect approach is applicable to equilibrium data as well as kinetic and spectroscopic data. For this correlation, both inductive and resonance withdrawal increase the magnitude of K_{CN} . Since CN^- is a much better donor than H_2O , this is the expected electronic effect of both +I and +R substituents which increase the electrophilicity of the cobalt atom. The steric effect on K_{CN} is small, but is clearly significant since inclusion of the steric term decreases f from 0.253 to 0.096 (Table III). The changes in cobaloxime geometry associated with sterically bulky organic ligands²⁰ seem highly unlikely to be capable of influencing the binding of a small, linear ligand such as cyanide ion. Thus, the improvement of the correlation of $\log K_{\text{CN}}$ by inclusion of the steric term would seem to provide evidence for the indirect transmission of steric effects in organocobaloximes, i.e., organic ligand steric bulk decreases Co-C overlap and decreases the inductive effect of Y.

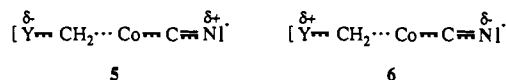
Two other equilibrium data sets are also well correlated (Table IV) by eq 3, including $\text{p}K_{\text{OH}_2}$ (eq 15) and $\text{p}K_{\text{py}}$ (eq 16). However, as noted above, the small size of the latter data set precludes the use of its successful correlation as evidence for the utility of eq 3. The values of $\text{p}K_{\text{OH}_2}$ are lowered (i.e., the axial water ligand becomes a better acid) by +I and +R substituent effects. This can be productively viewed as being due to stabilization of the conjugate base ($\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}^-$) relative to the acid, upon withdrawal of electron density from the cobalt atom. Surprisingly, the steric effect on $\text{p}K_{\text{OH}_2}$ is opposite to what might be expected, i.e., increasing steric bulk lowers the $\text{p}K_{\text{a}}$ of the coordinated water. Regardless of whether the steric effect is transmitted directly or indirectly in this case, the interaction between the axial water ligand and the metal atom would be expected to be decreased, thus lowering the acidity of the coordinated water. This raises the interesting possibility that the indirect steric effect of the organic ligand, while lowering the inductive effect of Y, actually increases the resonance effect by promoting the hyperconjugation depicted in eqs 19 and 20. While this is an interesting possibility, this effect is inexplicably absent in the $\log K_{\text{CN}}$ correlation. All of the effects described above for $\text{p}K_{\text{OH}_2}$ are also observed in the correlation of $\text{p}K_{\text{py}}$, but the comparable sensitivity of $\text{p}K_{\text{py}}$ to inductive, resonance, and steric effects is somewhat surprising, given the remoteness of the site of ionization from the metal atom.

The spectroscopic data in Table I are also well correlated by eq 3. For the monomeric $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)^{13}\text{C}^{15}\text{N}^-$ species, the

^{13}C resonance is shifted upfield by +I and +R substituents (i.e., $\rho_{\text{I}} < 0$, $\rho_{\text{R}} < 0$). As inductive and resonance withdrawal make the cobalt atom more electrophilic, these results are consistent both with the effect of protonation on $\delta_{^{13}\text{C}}$ of CN^- (an upfield shift of 52.4 ppm)²⁵ and with the observation that, in $\text{CNC}(\text{D}_2\text{H}_2)\text{L}$ complexes, increasing donation by L shifts the cyanide ^{13}C resonance downfield.²⁶ The steric effect on $\delta_{^{13}\text{C}}$, however, is to shift the resonance upfield with increasing steric bulk of Y. Thus, bulky Y groups seem to make the cobalt more electrophilic, which again implies that steric bulk may weaken the inductive effect but strengthen the resonance effect. For the ^{15}N resonance of the monomeric cyano species, +I and +R substituents shift the resonance downfield, i.e., in the opposite direction of the shift of the ^{13}C resonance, but the resonance effect is much smaller than the inductive effect. This opposite shifting of the ^{13}C and ^{15}N resonances of cyanocobalt complexes has been attributed to cobalt-to-cyanide π donation in cyanocobalt corrins²⁵ and in $\text{NCCo}(\text{D}_2\text{H}_2)\text{L}$ complexes.²⁶ In the latter complexes, stabilization of the π -bonded species by increasing electron donation from L shifts the ^{15}N resonance upfield. Hence, inductive and resonance withdrawal would be expected to shift the ^{15}N resonance downfield, as observed. Here, the steric effect is to shift the ^{15}N resonance upfield with increasing steric bulk of Y, i.e., steric bulk stabilizes the π -bonding interaction by weakening the Co-C inductive interaction. Even if the resonance effect is strengthened by steric interactions, the decrease in the inductive interaction would be expected to predominate since ρ_{I} is significantly larger than ρ_{R} .

In the dimeric $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNC}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$ complexes, the ^{13}C resonance of the bridging cyanide follows the same trends seen above for the ^{13}C resonance of the monomeric cyano species, but the effects are diminished due to donation from the cyanide nitrogen to the cobalt atom of the second cobaloxime moiety. Similarly, the ^{15}N resonances of the dimeric species have the opposite dependence on inductive and resonance effects relative to the monomeric species, i.e., withdrawal shifts the ^{15}N resonance upfield, as expected from the effect of N-protonation on $\delta_{^{15}\text{N}}$ of HCN (47.8-ppm upfield shift).²⁵ Here, the proximity of the cyanide nitrogen to the second cobalt center also leads to a substantial increase in sensitivity to both inductive and resonance effects compared to the monomeric cyano species.

Finally, these spectroscopic correlations also allow us to address the question of the possibility of cross conjugation in these complexes as in **5** (for +R substituents) and **6** (for -R substituents), in which the axial cyanide ligand is in direct conjugation with the substituent, Y. By analogy to the ^{15}N chemical shifts of the



terminal nitrogens of diazo compounds ($\text{RCH}=\text{N}^+=\text{N}^-$, as models of the hybridization of the hyperconjugated contributor to **6**), which resonate downfield (364–447 ppm)⁶⁰ from the terminal nitrogens of diazonium salts ($\text{RN}^+\equiv\text{N}$, $\delta = 316\text{--}364$ ppm,⁶⁰ as models of the unhyperconjugated contributor to **6**), resonance donation would be expected to shift the ^{15}N resonance of the cyanide ligand downfield if such cross-conjugated species were important. Instead, resonance withdrawal shifts the ^{15}N resonance downfield (i.e., $\rho_{\text{R}} > 0$). In addition, as pointed out above, the dependence of the relative sensitivity of correlated properties to resonance and inductive effects, $\rho_{\text{R}}/\rho_{\text{I}}$, decreases as distance from the cobalt atom increases (i.e., $\rho_{\text{R}}/\rho_{\text{I}} = 0.90, 0.68, 0.37$, for $\log K_{\text{CN}}$, $\delta_{^{13}\text{C}}$ (monomer) and $\delta_{^{15}\text{N}}$ (monomer), respectively). This implies that the resonance effect on the trans ligand is, in fact, a polar effect due to the stabilization of charge on the metal as in eqs 19 and 20, rather than the consequence of cross conjugation.

In sum, the complete multiparameter substituent-effect equation (eq 3) has been shown to be highly effective in correlating kinetic, equilibrium, and spectroscopic properties of $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{L}$ complexes. There is much promise for the utility of this approach

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both in its contributions to the understanding of the chemistry of organocobaloximes and other organocobalt complexes and in its ability to predict the properties of such complexes. Attempts to extend these concepts to organocobalt corrins are currently in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the National Science

Foundation (EPSCoR program, Grant No. RII-89-02064), the State of Mississippi, and Mississippi State University. We are grateful to Dr. Svein Saebo for helpful discussions.

Supplementary Material Available: Tables SI, SII, and SIII listing the ^{13}C spectral data for the $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{OH}_2$, $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CN}^-$, and $\text{YCH}_2\text{Co}(\text{D}_2\text{H}_2)\text{CNC}(\text{D}_2\text{H}_2)\text{CH}_2\text{Y}^-$ complexes (3 pages). Ordering information is given on any current masthead page.

Tautomerizations, Protonations, and Electrophilic Additions of η^2 -Coordinated Pyrroles

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Abstract: A series of complexes is synthesized of the form $[\text{Os}(\text{NH}_3)_5(2,3-\eta^2\text{-pyrrole})]^{2+}$, with pyrrole and various alkylated pyrroles. In contrast to the free ligands, these complexes can be protonated chemo- and stereoselectively at the β carbon, away from the metal, to produce pyrrolium species whose acidities range in $\text{p}K_a$ from 4.2 to 7.5. In the presence of a weak base, two of these 3*H*-pyrrolium species can be converted to the corresponding 2*H*-pyrrolium tautomer, $[\text{Os}(\text{NH}_3)_5(3,4-\eta^2\text{-2*H*-pyrrolium})]^{3+}$. In the case of L = 2,5-dimethylpyrrole, the 2*H*-pyrrolium species can be deprotonated at nitrogen ($\text{p}K_a = 7.9$), rendering a neutral 2*H*-pyrrole ligand. When L = 1-methylpyrrole, the 2*H*-pyrrolium species can be deprotonated at the α carbon, generating an unstable azomethine ylide complex bound through C3 and C4. Rapid rearrangement of this species yields the neutral 1*H*-pyrrole complex, $[\text{Os}(\text{NH}_3)_5(2,3-\eta^2\text{-1-methylpyrrole})]^{2+}$ ($\text{p}K_{\text{ep}} = 7.8$ (overall process)). Through consideration of $\text{p}K_a$ and electrochemical data, the pyrrole/pyrrolene isomerization energy (ΔG°) is found to decrease by about 16 kcal on osmium(II), to the point where these tautomers become virtually isoergic. In contrast, the pyrrole/pyrrolene equilibrium is largely unaffected by coordination to Os(III), in comparison to the free ligand.

Pyrroles are widely distributed in nature, serving as a subunit or precursor to chlorophylls, bile pigments, porphyrins, and corrins, as well as assorted antibiotics. They also represent an important class of synthons for alkaloids and other N-heterocyclic systems, potentially providing up to four activated carbons. However, the pronounced nature of pyrrole to undergo electrophilic attack at the α position often preempts reactivity at the biologically more significant β positions, and its tendency to rearomatize or polymerize in the presence of electrophiles limits the scope of useful addition reactions. Recently, three examples of η^2 -coordinated pyrrole complexes have been reported in which an $[\text{Os}(\text{NH}_3)_5]^{2+}$ moiety engages C2 and C3.¹ Such coordination renders the uncoordinated portion of the pyrrolic ligand an enamine, an action that is expected to enhance the nucleophilic nature of the β carbon, C4, and to inhibit activity at the α positions.

As we embarked on an investigation into the ligand activation and the stereocontrol offered by the osmium in these pyrrolic systems, it became apparent that many neutral and cationic tautomers of pyrrole are made possible by metal coordination (Figure 1) and that a firm understanding was needed of their relative stabilities and properties. This paper summarizes those findings.

Experimental Section

Routine ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer and are reported in parts per million shift from tetramethylsilane. Nonroutine spectra (e.g., low temperature, COSY, HETCOR, NOESY, or DEPT) were recorded on a General Electric GN-300 or Omega-500 spectrometer. Electrochemical experiments were performed under nitrogen by using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic

voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell² from +1.5 to -1.5 V with a glassy carbon or platinum disk working electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in acetonitrile (~ 0.5 M tetrabutylammonium hexafluorophosphate (TBAH)) with ferrocene ($E_{1/2} = 0.55$ V), decamethylferrocene ($E_{1/2} = 0.04$ V), or cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) in situ as a calibration standard. The peak-to-peak separation ($E_{\text{pa}} - E_{\text{pc}}$) was between 70 and 100 mV for all reversible couples reported unless otherwise noted. This work was carried out under nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox, separate boxes being used for aqueous and nonaqueous reactions.

Solvents. All distillations were performed under nitrogen, and all solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated by repeated freeze-pump-thaw cycles. Methylene chloride was refluxed for at least 8 h over P_2O_5 and distilled. Diethyl ether was refluxed for at least 8 h over Na/benzophenone and distilled. Methanol was refluxed over $\text{Mg}(\text{OMe})_2$, prepared in situ from Mg^0 activated by I_2 , and distilled.³ 1,2-Dimethoxyethane was refluxed over Na and distilled. Acetonitrile was refluxed over CaH_2 and distilled. *N,N*-Dimethylacetamide (DMA) was refluxed over CaH_2 for 24 h and distilled. Acetone was used as received (Burdick and Johnston), except that it was deoxygenated prior to use.

Reagents. $[\text{Os}(\text{NH}_3)_5(\text{OTf})](\text{OTf})_2$ ($\text{OTf}^- = \text{CF}_3\text{SO}_3^-$) was synthesized as described by Lay et al.⁴ Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME (1,2-dimethoxyethane) under nitrogen, stirring for several hours, and washing with

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