Transfer to Organometallic Chemistry of Substituent Constants from Organic Chemistry. 1. Resolution of Longstanding Anomalies in the Chemistry of Organocobalt B_{12} Models and Organocobalamins

Luigi G. Marzilli,*† Fernando Bayo,† Michael F. Summers,† L. Brannon Thomas,† Ennio Zangrando,‡ Nevenka Bresciani-Pahor,‡ Marina Mari,‡ and Lucio Randaccio*‡

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322, and Dipartimento di Scienze Chimiche, Universita di Trieste, 34127 Trieste, Italy.
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Abstract: Previous difficulties in rationalizing the relative trans effect and trans influence of alkyl groups in organocobalt complexes, including organocobalt B_{12} species (i.e. organocobalamins), are resolved by using a modified dual-substituent-parameter (DSP) approach. In contrast to some previous studies, in which the entire alkyl axial ligand (R) was treated as the substituent, the new approach involves treating R groups with a methylene group bound to Co as a CH_2Y species, where Y is the substituent. This approach is tested in depth in cobaloxime compounds of the type $LCo(DH)_2CH_2Y$ (where DH = monoanion of dimethylglyoxime). It was found that when L = 4-cyanopyridine (4-CNpy) and Y = NO_2, CN, CF_3, I, CO_2Me, Br, COMe, Cl, H, $SiMe_3$, Ph, Me, and OMe, the 4-CNpy dissociation rate increased by a factor of more than 10^6 and that the log of the first-order rate constant could be linearly correlated with the equation $\log k = \rho_I\sigma_I + \rho_R\sigma_R^+$ in which σ_I and σ_R^+ are organic-inductive and resonance-substituent constants and ρ_I and ρ_R are the respective coefficients. With use of σ_I and $\sigma_R^+ = 0$ for Y = Me (i.e. R = CH_2Me), the linear correlation coefficient (lcc) was 0.9963 for 13 points and the goodness of fit (f) was excellent (0.093). A similar study with L = anisidine (without Y = NO_2) gave even better results (lcc = 0.9978 and f = 0.073). In contrast, the use of the substituent constant σ^* for the entire R group gave no clear relationship, especially for R = CH_2OMe. Thus, previous usage of σ^* for quantitative analysis of data for organocobalt systems is questioned. Likewise, the modified DSP approach works well for ^{13}C NMR shifts when the resonance parameter employed is σ_R^0. These findings can be explained by invoking n → σ conjugation involving nonbonded electron pairs on the alkyl group and the polarizable Co–C bond. Since R = CH_2OMe is a key alkyl group in our analysis and since no structural data are available to assess the structural trans influence of CH_2OMe, several structural studies of $PhNH_2Co(DH)_2R$ compounds were performed. Structural results for three compounds, (**1**) R = CH_2Me, (**2**) R = CH_2OMe, and (**3**) R = *i*-Pr, are reported. Crystallographic details follow: (**1**) $C_{16}H_{26}CoN_5O_4{\cdot}H_2O$, $P2_1/n$, a = 10.998 (1) Å, b = 8.417 (2) Å, c = 21.859 (2) Å, β = 96.81 (1)°, D_{calcd} = 1.42 g cm^{-3}, Z = 4, R = 0.042 for 3006 independent reflections. (**2**) $C_{16}H_{26}CoN_5O_5{\cdot}H_2O$, $P2_1/c$, a = 8.351 (3) Å, b = 27.038 (8) Å, c = 9.893 (2) Å, β = 107.37 (2)°, D_{calcd} = 1.39 g cm^{-3}, Z = 4, R = 0.046 for 2909 independent reflections. (**3**) $C_{17}H_{28}CoN_5O_4{\cdot}H_2O$, $P2_1/c$, a = 8.335 (1) Å, b = 27.046 (5) Å, c = 9.829 (1) Å, β = 106.71 (2)°, D_{calcd} = 1.39 g cm^{-3}, Z = 4, R = 0.043 for 3523 independent reflections. The structure of **2** reveals a trans influence for CH_2OMe between that of CH_2Me and *i*-Pr and no unusual steric effect of CH_2OMe to account for its large trans effect or trans influence. Therefore, we conclude that the high position of CH_2OMe in the trans effect/influence series is electronic and not steric in nature. Previous treatment of substituent effects of R groups demonstrates that the effects are additive and suggests that the DSP approach may eventually be extended to organocobalt systems with alkyl groups of the types CHY_1Y_2 and $CY_1Y_2Y_3$. Since previous analyses demonstrate that the effects of ligands on metal properties found in cobalt chemistry are parallel to those found with many other metal centers, it is possible that organic substituent constants may find broad applicability to organometallic compounds. Another extension of the approach, which seems feasible, is the use of organocobalt compounds to obtain values for σ_I, σ_R^+, and σ_R^0 for substituents unknown in organic chemistry. Finally, the dependence of the ^1H, ^{13}C, and ^{31}P NMR spectra of organocobalamins on R is similar to that of simple organocobalt species, and although the current data base is inadequate for a thorough analysis, the modified DSP approach appears applicable to organocobalamins.

The intimate relationship between structure and electron donor ability of alkyl groups in organocobalt species, combined with the clear relationship between structure and Co–C bond homolysis for alkyl B_{12} (cobalamin) systems, has led to many investigations of the influence of alkyl group substituents on the properties of the cobalt center.[1-9] Such investigations have significance in two areas. First, conformational changes in 5′-deoxyadenosyl cobalamin (coenzyme B_{12}) in the B_{12} holoenzymes are strongly implicated as essential features of the key step in initiation of the enzymic catalytic process, namely Co–C bond homolysis.[1,6-9] Second, the great importance of organometallic species in catalytic processes, both homogeneous and heterogeneous, calls for a detailed knowledge of the dependence of the properties of such compounds on the nature of the alkyl ligands.[10] In this respect, transferability of organic substituent constants directly to organometallic systems would have great utility. Indeed, there is extensive evidence that the effects of ligands on the properties of metal centers in diverse types of compounds are often similar. In particular, cobalt compound based ligand-substituent constants proposed by one of us about a decade ago[11] are clearly representative of the effects of ligands on properties of many metal complexes.[12] These properties include NMR chemical shifts and coupling constants and metal–ligand vibrational frequencies.

† Emory University.
‡ Universita di Trieste.

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Nevertheless, there have been relatively few studies directed at either truly understanding the ligand effects or relating these effects to well-defined concepts such as electronegativity or organic substituent constants. The utilization of the latter type of information would, at the very least, allow the transfer to organometallic compounds of the parameters developed by physical organic chemists.[13-18]

Selected examples of problems that have escaped resolution deserve mention. First, on the basis of electronegativity, one expects that the order of electron donation by CH_2X groups should follow the order I > Br > Cl > F.[19] The opposite order is found from the trans-labilizing effect of CH_2X, when information from several studies is combined.[1] There is no satisfactory explanation for this order.[19] Second, correlation of formation constants and ligand dissociation rates with σ^* (the polar substituent constant)[13] led to some rough trends, but several anomalies and curvature in plots of linear free energy relationships (LFER's) were noted.[16,17] These studies involved the extensively investigated B_{12} model systems, known trivially as cobaloximes (molecules of the type $LCo(DH)_2R$ where L = neutral ligand, DH = monoanion of dimethylglyoxime, and R = alkyl group). However, there is clear evidence that the relative effect of R variation on the property of organocobalt centers is minimally dependent on the nature of the equatorial ligand (chel) in model compounds of the type LCo(chel)R. Indeed, this conclusion also applies to organocobalamins.[2-4,20]

The investigation described here was prompted by a recent report by Espenson[5] that CH_2OMe and *i*-Pr, alkyl groups with very different σ^* values, have essentially the same trans *effect*. We have confirmed this similarity of trans effects, have established that these alkyl groups also have similar trans *influences*, and have developed a modified dual-subtituent-parameter approach that resolves the anomalies mentioned above and provides insight into the bonding in such compounds. We believe this new approach may have broad application in organometallic chemistry.

Experimental Section

Reagents. All reagents were from Aldrich except for neopentyl iodide (Fluka) and isobutyl iodide and anisidine (Kodak). Before use in the kinetic studies, trimethyl phosphite and tributylphosphine were distilled under vacuum and 1-methylimidazole was crystallized three times from its melt. All other materials were reagent grade and were used without further purification, including the CH_2Cl_2 used as the solvent in the rate determinations. Prepurified nitrogen was used to deoxygenate the solutions.

Instrumentation. ^{1}H NMR spectral measurements were made on the following instruments: a Varian 360L operating at 60 MHz; a Varian EM 390 operating at 90 MHz; and a Nicolet 360 NB FT NMR spectrometer operating at 360 MHz and equipped with a VT unit (four transients, quadrature detection, 16K data points, 6.1-μs (45°) pulse, 3.0-s delay, no resolution or signal enhancement). ^{13}C NMR data were collected on a Varian CFT-20 instrument operating at 20 MHz. Carbon-13 data for anisidine ($4\text{-}CH_3OPhNH_2$) are listed in supplementary material. All NMR spectra were collected at ambient temperature and referenced to TMS. Ligand-exchange rates for slow reactions ($k_{obsd} < 0.1\ s^{-1}$) were monitored on a Perkin-Elmer Lambda-3 spectrophotometer connected to the 3600 Data Station. Fast reactions were monitored on a Durrum-Gibson D-110 stopped-flow spectrophotometer. All instruments were equipped with thermostated compartments that maintained the reaction solution at 25.0 ± 0.04 °C.

Rate Measurements. The optimum wavelengths used to monitor the reaction rates were determined as described previously.[3] Suitable wavelengths were in the range of 410–590 nm for the complexes studied. Neither products nor reactants demonstrated photoinstability over the period required for the measurements. Absorbance data were collected continuously over at least 3 half-lives with final absorbance taken at ca. 8 half-lives.

Table I. Crystallographic Data with Esd's in Parentheses for Compounds **1–3**[a]

formula	$C_{16}H_{26}CoN_5O_4\cdot H_2O$ (**1**)	$C_{16}H_{26}CoN_5O_5\cdot H_2O$ (**2**)	$C_{17}H_{28}CoN_5O_4\cdot H_2O$ (**3**)
MW	429.4	445.4	443.4
a, Å	10.998 (1)	8.351 (3)	8.335 (1)
b, Å	8.417 (2)	27.038 (8)	27.046 (5)
c, Å	21.859 (2)	9.893 (2)	9.829 (1)
β, deg	96.81 (1)	107.37 (2)	106.71 (2)
D_{measd}, g cm^{-3}	1.43	1.38	1.38
D_{calcd}, g cm^{-3}	1.42	1.39	1.39
Z	4	4	4
systematic absences	$h0l$ ($h + l$ odd), $0k0$ (k odd)	$h0l$ (l odd), $0k0$ (k odd)	$h0l$ (l odd), $0k0$ (k odd)
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
μ, cm^{-1}	8.8	8.3	8.3
cryst dimens, cm^3	0.04 × 0.05 × 0.06	0.02 × 0.02 × 0.04	0.03 × 0.02 × 0.04
no. of reflcns measd	5284	5519	5484
no. of indep reflcns [I > 3σ(I)]	3006	2909	3523
no. of varied param	244	253	253
R	0.042	0.046	0.043
R_w	0.053	0.056	0.065

[a] For all compounds, maximum 2θ(Mo Kα) was 56°.

Data Analysis. The experimental absorbance vs time rate data were treated with the standard integrated expression for a first-order reaction by using linear least-squares analysis. For reactions following an S_N1 LIM mechanism and exhibiting mass law rate retardation, the pseudo-first-order rate constants (k_{obsd}) were plotted as $1/k_{obsd}$ vs. [L]/[L′] (L = leaving and L′ = entering ligands). A linear relationship is found by this analysis, where $1/k_1$, the y intercept, and k_{-1}/k_1k_2, the slope, were determined by a linear least-squares regression analysis. The rate constants are defined as

$$*\mathrm{CoL} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} *\mathrm{Co} + \mathrm{L}$$

$$*\mathrm{Co} + \mathrm{L'} \xrightarrow{k_2} *\mathrm{CoL'}$$

$$*\mathrm{Co} = \mathrm{Co(DH)_2R}$$

In most cases in this study, [L′] ≫ [L] and $1/k_{obsd} = 1/k_1$. For R = CH_2OMe and L = $4\text{-}CH_3OPhNH_2$, rate retardation was employed to bring k_{obsd} within the measurable region (≤5 × 10^1 s^{-1}).

Preparations. $4\text{-}CH_3OPhNH_2Co(DH)_2R$ (R = CH_2CH_2CN, CH_2Me, CH_2Ph), 4-CNpyCo(DH)$_2$CH$_2$NO$_2$. These compounds were prepared as described previously for $2NH_2pyCo(DH)_2X$.[21]

$4\text{-}CH_3OPhNH_2Co(DH)_2R$ (R = CH_2CN, CH_2CF_3, CH_2I, CH_2Br, Me, $CH_2Si(Me)_3$, CH_2CH_2Me, CH_2CHMe_2, CH_2CMe_3). These compounds were prepared as described previously[22] by using the appropriate alkylating agent ($ClCH_2CN$, ICH_2CH_3, CH_2I_2, CH_2Br_2, CH_3I, $ClCH_2Si(Me)_3$, $BrCH_2CH_2Me$, $BrCH_2CH(Me)_2$, $ICH_2C(Me)_3$).

$LCo(DH)_2CH_2OMe$ (L = $4\text{-}CH_3OPhNH_2$, py). Under continuous N_2 purging, a 4-fold excess of Na (0.83 g) was added to anhydrous MeOH (200 mL), and the mixture was stirred until all the Na had reacted. Then $LCo(DH)_2CH_2Br$ (4.25 g) was added, and the mixture was stirred for 10 min. The N_2 purging was terminated, the flask was stoppered, and the solution was left to stir at room temperature for 14 h. The solution volume was then reduced by rotoevaporation, and crystallization was induced by adding H_2O and leaving the mixture at 3 °C for 1–2 days. The product was collected by filtration.

4-CNpyCo(DH)$_2$CH$_2$COMe. This compound was prepared by the process described previously by Hill[23] using 4-CNpyCo(DH)$_2$Cl and $ClCH_2COMe$.

Crystal Data. Compounds of the type $PhNH_2Co(DH)_2R$, prepared as above for the anisidine analogues, were crystallized from acetone/H_2O.

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Table II. Atomic Positional Parameters of Non-Hydrogen Atoms with Esd's in Parentheses

atom	x	y	z	atom	x	y	z
			$PhNH_2Co(DH)_2CH_2CH_3$ (**1**)				
Co	0.30596 (4)	0.19715 (5)	0.10148 (2)	C4	0.1464 (4)	−0.1952 (5)	0.0078 (2)
O1	0.2668 (2)	0.3604 (3)	−0.0138 (1)	C5	0.4581 (4)	0.2918 (6)	0.2811 (2)
O2	0.2530 (3)	−0.1233 (3)	0.1271 (1)	C6	0.4046 (3)	0.2937 (5)	0.2151 (1)
O3	0.3524 (3)	0.0313 (4)	0.2157 (1)	C7	0.4048 (3)	0.4351 (4)	0.1759 (2)
O4	0.3600 (2)	0.5183 (3)	0.0752 (1)	C8	0.4482 (4)	0.5940 (5)	0.1976 (2)
O5	0.4838 (2)	0.2268 (3)	−0.0566 (1)	C9	0.1373 (3)	0.2585 (5)	0.1224 (2)
N1	0.2518 (2)	0.2234 (3)	0.0174 (1)	C10	0.0897 (4)	0.4172 (6)	0.1028 (3)
N2	0.2466 (3)	−0.0090 (3)	0.0840 (1)	C11	0.5894 (3)	0.1843 (4)	0.1162 (1)
N3	0.3574 (3)	0.1715 (4)	0.1856 (1)	C12	0.6362 (3)	0.1038 (5)	0.1686 (2)
N4	0.3629 (2)	0.4036 (3)	0.1192 (1)	C13	0.7383 (4)	0.1632 (6)	0.2048 (2)
N5	0.4825 (2)	0.1249 (3)	0.0789 (1e	C14	0.7918 (4)	0.3043 (6)	0.1893 (2)
C1	0.1523 (4)	0.1041 (6)	−0.0779 (2)	C15	0.7434 (3)	0.3843 (5)	0.1371 (2)
C2	0.2011 (3)	0.1010 (4)	−0.0115 (2)	C16	0.6414 (3)	0.3265 (4)	0.1008 (2)
C3	0.1980 (3)	−0.0369 (4)	0.0280 (2)				
			$PhNH_2Co(DH)_2CH_2COCH_3$ (**2**)				
Co	0.19871 (6)	0.12025 (2)	0.51911 (5)	C4	0.2344 (7)	0.0497 (2)	0.8988 (5)
O1	0.4763 (3)	0.0623 (1e	0.5068 (3)	C5	−0.0918 (7)	0.2339 (2)	0.2861 (6)
O2	0.0260 (3)	0.1205 (1)	0.7269 (3)	C6	0.0298 (5)	0.1938 (2)	0.3463 (5)
O3	−0.0696 (4)	0.1832 (1)	0.5362 (3)	C7	0.1516 (5)	0.1747 (2)	0.2791 (4)
O4	0.3586 (3)	0.1173 (1)	0.3006 (3)	C8	0.1658 (7)	0.1927 (2)	0.1407 (5)
O5	0.3943 (6)	0.2118 (2)	0.5701 (5)	C9	0.3502 (6)	0.1725 (2)	0.6357 (5)
O6	−0.1804 (3)	0.0376 (1)	0.6036 (3)	C10	0.5491 (9)	0.2051 (4)	0.534 (1)
N1	0.3685 (4)	0.0727 (1)	0.5800 (3)	C11	−0.0874 (5)	0.0794 (2)	0.2687 (4)
N2	0.1536 (4)	0.1010 (1)	0.6860 (3)	C12	−0.2395 (5)	0.1010 (2)	0.2627 (4)
N3	0.0367 (4)	0.1704 (1)	0.4615 (4)	C13	−0.3430 (6)	0.1181 (2)	0.1354 (5)
N4	0.2438 (4)	0.1402 (1)	0.3523 (3)	C14	−0.2966 (7)	0.1141 (3)	0.0155 (5)
N5	0.0253 (4)	0.0646 (1)	0.4021 (3)	C15	−0.1483 (7)	0.0930 (3)	0.0202 (5)
C1	0.5031 (6)	0.0113 (2)	0.7623 (5)	C16	−0.0403 (6)	0.0747 (2)	0.1471 (5)
C2	0.3777 (5)	0.0505 (2)	0.6983 (4)	O51[a]	0.5000	0.1600	0.7300
C3	0.2508 (5)	0.0676 (2)	0.7622 (4)	C101[a]	0.6320	0.1610	0.6600
			$PhNH_2Co(DH)_2CH(CH_3)_2$ (**3**)				
Co	0.21033 (4)	0.12395 (1)	0.52081 (4)	C4	0.2440 (5)	0.0508 (2)	0.8997 (4)
O1	0.4839 (2)	0.06504 (9)	0.5021 (2)	C5	−0.1077 (5)	0.2300 (2)	0.2771 (5)
O2	0.0354 (3)	0.1221 (1)	0.7309 (2)	C6	0.0233 (4)	0.1924 (1)	0.3402 (4)
O3	−0.0680 (3)	0.1835 (1)	0.5365 (3)	C7	0.1466 (4)	0.1747 (1)	0.2708 (3)
O4	0.3632 (3)	0.1203 (1)	0.2943 (2)	C8	0.1508 (5)	0.1903 (2)	0.1267 (4)
O5	−0.1747 (3)	0.0402 (1)	0.6084 (3)	C9	0.3695 (4)	0.1804 (1)	0.6181 (4)
N1	0.3803 (3)	0.07653 (9)	0.5800 (2)	C10	0.5452 (5)	0.1744 (2)	0.6129 (5)
N2	0.1657 (3)	0.1043 (1)	0.6893 (2)	C11	0.3593 (5)	0.1935 (2)	0.7642 (4)
N3	0.0397 (3)	0.1714 (1)	0.4612 (3)	C12	−0.0719 (3)	0.0770 (1)	0.2756 (3)
N4	0.2471 (3)	0.1426 (1)	0.3479 (3)	C13	−0.2250 (4)	0.0986 (1)	0.2675 (3)
N5	0.0422 (3)	0.0656 (1)	0.4122 (2)	C14	−0.3302 (4)	0.1123 (2)	0.1367 (4)
C1	0.5066 (4)	0.0118 (1)	0.7547 (4)	C15	−0.2834 (5)	0.1050 (2)	0.0159 (4)
C2	0.3880 (3)	0.0532 (1)	0.6970 (3)	C16	−0.1317 (5)	0.0840 (2)	0.0240 (4)
C3	0.2620 (4)	0.0701 (1)	0.7631 (3)	C17	−0.0241 (4)	0.0689 (2)	0.1541 (3)

[a] O51 and C101 were not refined.

For the three compounds characterized in this study with R = CH_2Me (**1**), CH_2OMe (**2**), and *i*-Pr (**3**), cell dimensions were determined from Weissenberg and precession photographs and refined on a CAD4 automated Nonius single-crystal diffractometer. The results are given in Table I. The intensity data were collected by the ω–2θ scan technique with use of graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å). Three standard reflections, measured every 50 min, showed no systematic variation throughout the data collections. The intensities for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors and anomalous dispersion but not for extinction. No absorption correction was applied because of the small size of the crystals employed and the low value of μ (Table I).

Solution and Refinement of the Structures. All the structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods. For all the compounds, the waters of crystallization were located on the Fourier maps. In **2** the alkyl group was found to be disordered, and on the basis of the respective electron peak density on the Fourier map, the OMe group was located at two different positions with occupancy factors of 0.8 and 0.2, respectively. The contribution of hydrogen atoms at calculated positions (except those attached to C10 in **2**), as well as non-hydrogen atoms of OMe in **2** in the lowest occupancy orientation, was held constant (B = 5.0 Å^2) and included in the final anisotropic refinement. Final R and R_w values are given in Table I. The final weighting schemes ($w = 1/(\sigma^2(F) + (pF)^2 + q)$, where p = 0.02 and q = 1.0) for all structures were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $\sin\theta/\lambda$. Atomic scattering factors are also given in ref 24. All the calculations were done with computer programs from Enraf-Nonius SDP programs.[25] Final positional parameters for non-hydrogen atoms are given in Table II. Anisotropic thermal parameters, calculated and observed structure factors, hydrogen atom fractional coordinates, and a full list of bond lengths and angles have been deposited as supplementary material.

Results

Evolution of This Study. It is instructive to outline the process that led to the accumulation of results and the treatment of the data. The CH_2OMe compound represents one of the most severe departures from any predictable behavior of cobaloximes based on σ^* values. For example, such deviations appear in both ligand-exchange rates for 4-CNpy and ^{13}C data for the γ-C of pyridine in the respective $LCo(DH)_2CH_2OMe$, results that give an indication of the trans effect (kinetics) and trans influence (ground state), respectively, of the alkyl group (vide infra). Preliminary graphical analysis of the data followed by standard computerized treatment made it clear that a dual-substituent-parameter (DSP) approach could resolve this anomaly for

(24) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(25) Frenz, B. A.; Okaya, Y. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1980.

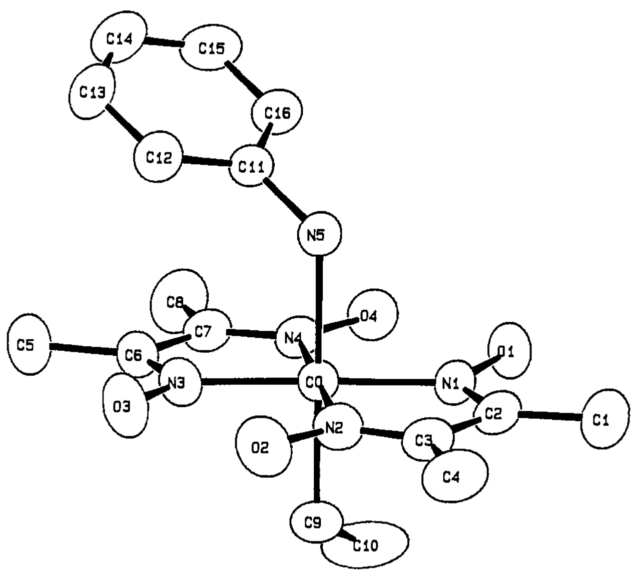

Figure 1. ORTEP drawing (thermal ellipsoid; 50% probability) for compound **1** with the non-hydrogen atoms numbering scheme.

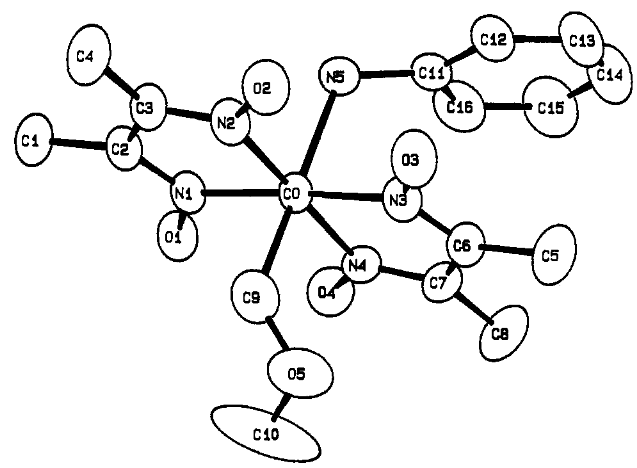

Figure 2. ORTEP drawing (thermal ellipsoid; 50% probability) for compound **2** with the non-hydrogen atoms numbering scheme.

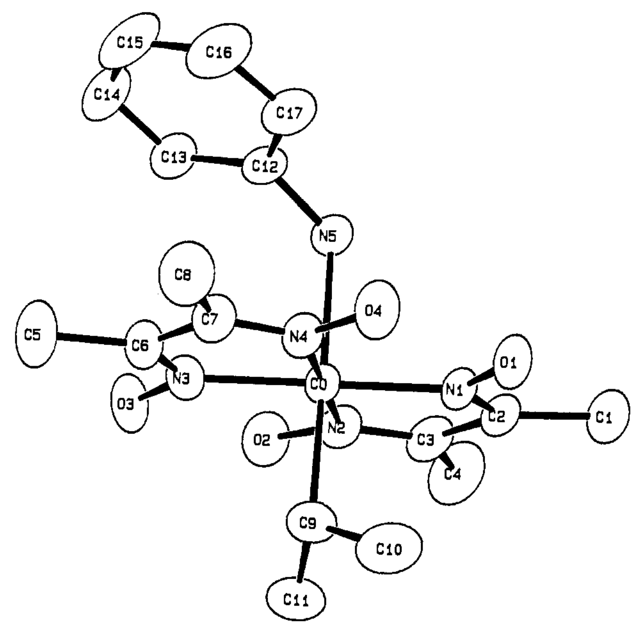

Figure 3. ORTEP drawing (thermal ellipsoid; 50% probability) for compound **3** with the non-hydrogen atoms numbering scheme.

CH_2OMe and for other CH_2Y compounds if Y was treated as the substituent. The DSP approach is described in detail elsewhere.[14,15] Briefly, the difference in a measure of energy, Δ(meas), for a compound with one Y substituent and that for a standard Y substituent (usually H, but in this study Me), is correlated with an inductive parameter (σ_I) and a resonance parameter (σ_R) according to

$$\Delta(\text{meas}) = \rho_I\sigma_I + \rho_R\sigma_R$$

The values for σ_I and σ_R are zero for the standard Y group. Depending on the type of measurement, different σ_R values may be useful.[14,26] We have found that σ_R^+ and σ_R^0 give the best results for correlation of Δ log k_1 and ^{13}C shifts, respectively.

On the basis of these findings, we prepared and studied additional 4-CNpy and py compounds with CH_2Y where σ_I, σ_R^0, and σ_R^+ are known for Y.[14] Rather extensive information is available on the 4-CNpy dissociation rates from 4-CNpyCo(DH)$_2$R and on pyCo(DH)$_2$R ^{13}C spectra and structure.[1] However, interpretation of the trends from such studies is subject to uncertainties (vide infra), and we felt it was essential to obtain an X-ray structure of an LCo(DH)$_2$CH$_2$OMe compound. Unfortunately, many attempts at obtaining satisfactory crystals of pyCo(DH)$_2$CH$_2$OMe have failed.

For comparisons of any structurally characterized LCo(DH)$_2$CH$_2$OMe compound, there is a need for other structurally characterized compounds of the type LCo(DH)$_2$R with the same L. Crystals of PhNH$_2$Co(DH)$_2$R are readily obtained, and we succeeded in preparing PhNH$_2$Co(DH)$_2$CH$_2$OMe crystals. Furthermore, the range of trans effect of R ligands is quite large (a million fold), and the related ligand 4-CH$_3$OPhNH$_2$ gives compounds with dissociation rates at the upper end of measurable rates for good trans labilizing R groups. Thus, the ligand-exchange rates of a series of 4-CH$_3$OPhNH$_2$Co(DH)$_2$R compounds could be studied conveniently even for compounds with weak trans effect R groups.

In the remainder of this section, we will describe (a) the PhNH$_2$Co(DH)$_2$R structures studied here, (b) the ligand-exchange results, (c) the ^{13}C NMR results, (d) the DSP approach for ligand-exchange rates, and (e) the DSP approach for ^{13}C results.

Description of the Structures. The ORTEP drawings with the atom numbering scheme for **1–3** are given in Figures 1–3, respectively. Bond lengths and angles of the Co(DH)$_2$ unit are quite normal.[1] In all the structures, the cobalt atom has a distorted octahedral geometry, with the PhNH$_2$ and the alkyl groups occupying the axial positions. The four N atoms of the equatorial ligand are coplanar with deviations from their mean plane not larger than 0.04 Å. The O···O distances of the oxime bridge vary from 2.478 (3) Å in **1** to 2.495 (5) Å in PhNH$_2$Co(DH)$_2$(adamantyl).[27]

The crystals of all compounds are built up by discrete PhNH$_2$Co(DH)$_2$R molecules held together by van der Waals forces. In addition, two oxime O atoms of the complexes are involved in hydrogen bonding with the water of crystallization, and two different hydrogen bonding schemes are found. In **1**, the oxygen atoms of the oxime bridge involved in the hydrogen bond belong to different "DH" units, while in **2** and **3** they belong to the same "DH" moiety. The scheme for **1** was also found in crystals of other PhNH$_2$Co(DH)$_2$R complexes with R = Me and CH$_2$C(Me)(COOEt)$_2$, and for R = adamantyl, one crystallographically independent molecule exhibits a scheme similar to that of **1**, the other a scheme similar to that of **2** and **3**.[27] As will be discussed in a later paper,[27] the equatorial ligands of molecules with H-bonding schemes similar to **1** are best formulated as (DH)$_2$, whereas those with schemes similar to **2** and **3** can be formulated as (D^{2-}DH$_2$). Palenik et al.[28] have attributed this latter arrangement to a π-bonding interaction between the Ph group of

(26) Molock, F. F.; Boydkin, D. W. *J. Heterocycl. Chem.* **1982**, *19*, 695.

(27) Unpublished results.

(28) Palenik, G. J.; Sullivan, D. A.; Naik, D. V. *J. Am. Chem. Soc.* **1976**, *98*, 1177.

Table III. Rate and NMR Spectroscopic Data for $LCo(DH)_2R$[a]

R	log k_1, s^{-1} 4-CNpy	log k_1, s^{-1} 4-CH_3OPhNH_2	^{13}C[b] γ-C (py)	^{13}C[b] C-N- (4-CH_3OPhNH_2)	^{13}C[b] C-O- (4-CH_3OPhNH_2)	^{13}C[b] C-H- (4-CH_3OPhNH_2)[c]
CH_2OMe	1.38	2.18	137.24	132.14	156.29	120.21
CH_2Me	-0.018	0.892	137.34	131.76	156.44	120.48
CH_2Ph	-0.48	0.447	137.36	131.35	156.60	120.64
CH_2SiMe_3	-0.37	0.152	137.42	130.93	156.79	120.72
Me	-1.39	-0.328	137.48	131.48	156.62	120.58
CH_2Cl	-2.51	-1.47	137.91	131.01	157.00	120.94
CH_2COMe	-3.23	-2.49	137.95	130.07	157.17	121.20
CH_2Br	-2.59	-1.76	137.96	130.91	157.01	121.01
CH_2CO_2Me	-3.57	-2.62	137.97	130.14		121.19
CH_2I	-2.80	-2.03	137.98	130.79	157.06	121.01
CH_2CF_3	-3.57	-2.96	138.03	129.98	157.32	121.21
CH_2CN	-4.52	-3.77	138.25			
CH_2NO_2	-5.37		138.46			
CH_2CMe_3[d]	1.04	1.54	137.29	131.29	156.55	120.54
CH_2CHMe_2[d]	0.146	1.11	137.32	131.54	156.48	120.48
CH_2CH_2Me[d]	0.079	0.932	137.32	131.69	156.50	120.48
CH_2CH_2CN[d]	-1.59	-0.81	137.78	130.63	156.91	120.79

[a] Rates measured in CH_2Cl_2; $T = 25.0$ °C. NMR measurements were made in $CDCl_3$ at ambient T; internal reference TMS. See text for further details. [b] Shifts in ppm for aromatic C's. Values for γ-C (py) from ref 1 or this study. [c] Downfield signal for CH; assignment not made. [d] Values for σ_R^+ are not available for the Y of these groups.

axial ligands and the dioxime. However, we prefer to attribute this effect to differences in H bonding, since the orientation of the Ph group is largely independent of the $(DH)_2$ or $(D^{2-}DH_2)$ formulations.[27]

Dependence of Ligand-Exchange Rates on R. Observed first-order rate constants analyzed below are collected in the supplementary material, including both new measurements and previously determined values. A summary of these data can be found in Table III, and error limits and other details can be found in the supplementary tables. The exchange reactions are classical examples of S_N1 LIM behavior, and the dependence of reaction rates on both L and R for cobaloximes has been analyzed by us and others in several previous papers.[1]

^{13}C NMR Data. Selected ^{13}C chemical shifts for the $pyCo(DH)_2CH_2Y$ and $4\text{-}CH_3OPhNH_2Co(DH)_2CH_2Y$ compounds evaluated in this study are presented in Table III.

Analysis of the dependence of ^{13}C shifts on R is more complex than L dissociation rates. Not only does the question arise as to the influence of R, but also there may not be a clear relationship between the electronic effect of R and the measured shift. Additionally other factors, such as solvation, heavy-atom effects, etc., could influence these shifts.[1,29,30] However, several studies indicate that shifts for C atoms or P atoms remote from the Co center reflect the trans Co–N bond lengths, which are, in turn, clearly influenced by the electronic properties of R.[1] For C atoms close to the Co center, for other nuclei (e.g. P) directly bound to Co, and for ^1H, the shifts can be influenced by the anisotropy of Co or of the other ligands bound to the Co.[1,20,29,31] Thus, shifts of the γ-C of pyridine have proved useful in the past.[1] Since the 4-CH_3OPhNH_2 compounds were available, we have also recorded ^{13}C spectra for these compounds and found a good correlation with the pyridine series. It is especially important to note that a relatively large data set is required to analyze NMR shift correlations since anomalies are quite common. This requirement has hindered the study of metal compounds in comparison to organic compounds, where a larger number and greater diversity of related compounds are usually available.[26]

DSP Analysis of Exchange Rates. Early in the analysis, it became clear that typically the data for Y = H (R = Me) were in poor agreement with those from other R groups. Unlike organic compounds where the C–C bond lengths are quite insensitive to steric effects, organocobalt compounds have a very broad range of Co–C bond lengths.[1] However, there is relatively little difference between Co–C bond lengths in CH_2Y compounds as compared to the difference in Co–C bond length between CH_2Y compounds CH_3 or CHY_2 compounds. Therefore, since the analysis of necessity perfectly fits the 0,0 point, we felt a more reasonable zero was CH_2Me (i.e., σ_I, σ_R^+, and σ_R^0 for Y = Me were set equal to zero (Table IV)). This change improved the overall fit as judged by the f test and the correlation coefficient (Table V). For example, an f value of 0.2–0.1 is considered good, whereas a value below 0.1 is considered excellent.[15] For both series of ligand-exchange rates, the fits were excellent (Figure 4; supplementary material). This result is particularly gratifying in view of the much greater range of rates we have studied in comparison

Table IV. Organic Substituent Constants from the Literature Rescaled to $\sigma_{Me} = 0$

Y	σ_I	σ_R^0	σ_R^+
OMe	0.31	-0.34	-0.77
Me	0	0	0
Ph	0.14	0	-0.05
$SiMe_3$	-0.06	0.17	0.31
H	0.04	0.11	0.25
Cl	0.5	-0.12	-0.11
COMe	0.32	0.27	0.41
Br	0.48	-0.08	-0.05
CO_2Me	0.34	0.25	0.39
I	0.43	-0.05	0
CF_3	0.49	0.19	0.33
CN	0.6	0.24	0.38
NO_2	0.69	0.26	0.4

Table V. Summary of Statistical Results for the Dual-Substituent-Parameter Calculations Where Values Were Normalized to Me or to CH_2Me

observable	$\sigma_H = 0$ f[a]	$\sigma_H = 0$ lcc[b]	$\sigma_{Me} = 0$ f[a]	$\sigma_{Me} = 0$ lcc[b]	ρ_R/ρ_I[d]
log k_1(4-CH_3OPhNH_2)	0.104	0.9955	0.073	0.9978	0.667
log k_1(4-CNpy)	0.160	0.9891	0.093	0.9963	0.665
γ-C (py), $\delta(^{13}C)$	0.196	0.9843	0.165	0.9884	0.738
C—N(4-CH_3OPhNH_2), $\delta(^{13}C)$	0.284	0.9666	0.148	0.9910	1.46
C—O(4-CH_3OPhNH_2), $\delta(^{13}C)$	0.267	0.9710	0.187	0.9859	1.08
C═C(4-CH_3OPhNH_2), $\delta(^{13}C)$	*c*	*c*	0.187	0.9856	1.23

[a] f test values (f) less than 0.1 are considered "excellent", and values less than 0.2 are considered "good"; see ref 15. [b] lcc = linear correlation coefficient. [c] Not determined. [d] This ratio provides an indication of the relative importance of the resonance and inductive contributions.[15] The ρ_R and ρ_I values are given in captions for Figures 4–6.

(29) Parker, W. O., Jr.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1986**, *25*, 3489.
(30) Lopez, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chem.* **1986**, *25*, 2962.
(31) Brown, K. L.; Hakimi, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 496.

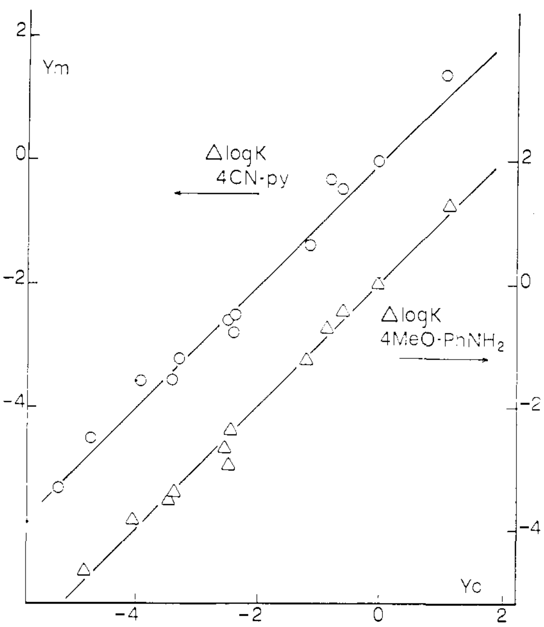

Figure 4. Plots of measured values of $\Delta \log k_1$ for $LCo(DH)_2CH_2Y$ vs values calculated with the following relationships. Top: L = 4-CNpy; $\Delta \log k_1 = -5.53(\sigma_I) - 3.68(\sigma_R^+)$. Bottom: L = $4\text{-}CH_3OPhNH_2$; $\Delta \log k_1 = -5.68(\sigma_I) - 3.79(\sigma_R^+)$.

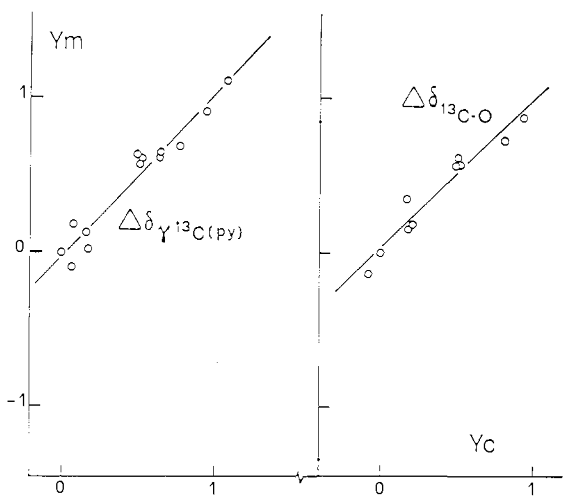

Figure 5. Left: Plot of $\Delta\delta$ for the γ-C in the series $pyCo(DH)_2CH_2Y$ vs values calculated with the relationship $\Delta\delta = 1.24(\sigma_I) + 0.91(\sigma_R^0)$. Right: Plot of $\Delta\delta$ for $^{13}C\text{–}O$ in the series $4\text{-}CH_3OPhNH_2Co(DH)_2CH_2Y$ vs values calculated with the relationship $\Delta\delta = 1.35(\sigma_I) + 1.46(\sigma_R^0)$.

to those typically found for more purely organic systems.

DSP Analysis of ^{13}C Shifts. With σ values of zero for Y = H, only the ^{13}C shift data in the pyridine series in Table V give a good fit. However, when the σ values are normalized to Y = Me, all four series of shifts in Table V give good fits (Figures 5 and 6). It should be noted that slight additional improvements can be made if the values for Y = I are excluded from the analysis.

Discussion

General Approaches Used Previously. Accurate theoretical treatments of ligand effects on reactivity, structure, and spectral properties of transition-metal compounds are hampered by the large basis sets needed for metal centers. Thus, prediction of properties and interpretation of trends have depended on empirical data combined with qualitative theory. Cobaloximes appear to be representative of most metal centers.[12] Unfortunately, very often systematic studies of a series of compounds have been limited to relatively few examples in each series, and it is quite uncommon to have the extensive series of compounds and measurements available in organic systems.[12,15] Thus, attempts have been made to utilize the organic substituent parameters in several ways. First,

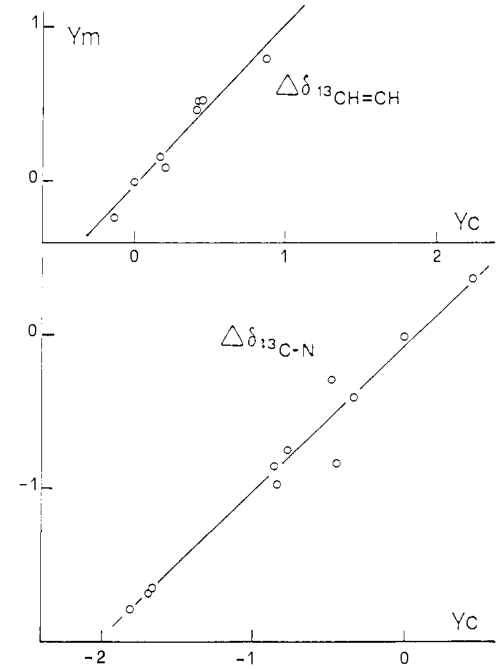

Figure 6. Same series for Figure 5 right. Top: $^{13}C{=}C$; $\Delta\delta = 1.14(\sigma_I) + 1.40(\sigma_R^0)$. Bottom: $^{13}C\text{—}N$; $\Delta\delta = -2.37(\sigma_I) - 3.46(\sigma_R^0)$.

the metal center could be viewed as a substituent on the organic moiety C_nH_nZ, such as LMC_nH_xZ.[18,32] By measuring some property of the function Z (^{19}F NMR, pK_a, reaction rate, etc.), the substituent effect of LM can be established with reference to YC_nH_xZ. Systematic variation of L can provide information about the properties of L. Second, $LM\text{–}C_6H_4\text{–}Y$ and $LM\text{–}CH_2\text{–}C_6H_4\text{–}Y$ compounds can be studied as a function of Y.[15] Within such series, the properties of Y are transmitted to LM in a manner easily correlated with organic systems. The binding of Y is to the aromatic ring and not to the metal. Third, LMR compounds can be studied, and the substituent effect of R from organic chemistry can be used directly.[16,17]

The previous most extensive investigation of organocobalt compounds employed this third approach.[16,17] Correlations with σ^* gave some good LFER's (mainly involving exchange rates) and some curved relationships (mainly involving equilibria) for cobaloximes. We call this method the "σ^* approach". The analysis of the nonlinear relationships found with the σ^* approach is complex, and the reader is referred to the original accounts.[16,17] Briefly, it was concluded that the curvature was indicative of the presence of five-coordinate species $Co(DH)_2R$, which were particularly stable when R was a good donor; i.e. σ^* has a negative value (*i*-Pr, CH_2Me).

However, in the analysis of both exchange rates and equilibria with the σ^* approach, certain R groups were often, although not always, excluded. These include Me, CH_2Cl, CH_2I, and $CH_2CH_2C(O)OMe$. No satisfactory reason was found for excluding these compounds. It was felt that steric effects could be important but, earlier, Brown and his co-workers noted that the trans effect order $CH_2Cl > CH_2Br$ was also opposite to predictions based on steric effects.[19]

Approach Developed in This Study. Since the CH_2OMe group plays such an important role in our analysis, we felt it necessary to structurally characterize a derivative. A complete discussion of the structural features of **1–3** is best presented in the context of our other studies of these $PhNH_2$ analogues.[27] The feature of primary interest here is the length of the $Co\text{–}N(PhNH_2)$ bond. This bond length increases from 2.019 (2) Å in $PhNH_2Co(DH)_2Cl$[33] to 2.129 (1) Å for $PhNH_2Co(DH)_2Me$ to 2.215 (4)

(32) Hosomi, A.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 3682 and references therein.

(33) Botoshanskii, M. M.; Simonov, Yu. A.; Malinovskii, T. I.; Simonov, M. A. *Dokl. Chem.* (*Engl. Transl.*) **1975**, *225*, 625.

Table VI. Structural Parameters of the $PhNH_2Co(DH)_2R$ Fragment

R	Co–N, Å	Co–C, Å	N–Co–C, deg	Co–C–C, deg	Co–N–Ph, deg	d, Å	α, deg
Me[a]	2.129 (1)	1.992 (2)	178.19 (7)		118.2 (1)	+0.035	+3.5
CH_2Me	2.147 (2)	2.030 (3)	178.3 (1)	117.8 (3)	118.1 (2)	+0.014	+2.8
CH_2OMe	2.169 (3)	2.013 (4)	176.4 (2)	119.4 (3)[c]	116.6 (2)	+0.026	+2.7
i-Pr	2.177 (2)	2.068 (3)	178.3 (1)	114.2 (2)[b]	117.5 (2)	−0.017	−5.6

[a] Reference 27. [b] Mean values. [c] Co–C–O.

Å in $PhNH_2Co(DH)_2$(adamantyl).[27] This distance in $PhNH_2Co(DH)_2CH_2OMe$ is 2.169 (3) Å, a value establishing the trans influence of CH_2OMe as being essentially the same as *i*-Pr in $PhNH_2Co(DH)_2$-*i*-Pr (Co–N = 2.177 (2) Å) and somewhat greater than CH_2Me in $PhNH_2Co(DH)_2CH_2Me$ (Co–N = 2.147 (2) Å). Other structural features of these compounds are given in Table VI along with those for R = Me. It is clear that CH_2OMe has no unusual structural effects that could account for the long Co–N($PhNH_2$) bond length. In particular, if the long bond were the result of the bulk of CH_2OMe, we would have expected d (the displacement of Co out of the four N equatorial plane) to be negative (displacement toward CH_2OMe) and the dihedral angle, α, between the planes of dimethylglyoxime moieties to be negative (bending toward $PhNH_2$). Furthermore, the α and d values for CH_2Me and CH_2OMe are similar, suggesting a similar bulk for these ligands. On the basis of published structural information on cobaloximes, the class of organometallic compounds most extensively studied by X-ray diffraction methods,[1] there is good evidence for assuming that steric effects will not vary so greatly across the CH_2Y series as to preclude a meaningful analysis. Justification of this assumption will derive from the excellent correlation of our data to be described below.

Comparison of Approaches to the Use of Organic Substituent Constants. The first approach given above is less relevant to this study in that the metal center is viewed as a substituent. However, Traylor's studies in this area[32] lead to valuable insights into the binding in our compounds (see below).

The second approach is limited to aromatic R groups. Substituents on aromatic rings lead to comparatively small variations in properties of metal centers. For our purposes, a large range of properties is desirable and the biologically relevant organocobalt compounds are limited to CH_2Y type R groups.

The third approach is not restricted to CH_2Y and at present is superior to our approach in the range of R ligands that may be studied. However, below we illustrate that our approach can be extended beyond CH_2Y ligands. Given our current limitations, we now compare in detail our DSP approach with the σ^* approach, the most extensive application of the third approach.

Ehrenson, Brownlee, and Taft[34] have concluded that an analysis of substituent effects should rely on data from representative compounds with four classes of substituents (a: NR_2, OMe. b: CF_3, CO_2R, COMe, CN, NO_2. c: H, Me. d: Cl, Br, I). Although Brown and co-workers were treating the entire R group as a substituent,[16,17] we attribute their previous success with the σ^* approach in obtaining linear correlations to the use of compounds from only two of the four classes of substituents. We have used compounds from all four classes.

It should be noted that ligand dissociation rates we have measured in noncoordinating solvents correlate linearly with those reported in aqueous solution.[16,17] This correlation extends to R groups we cannot analyze by our methods, either because they do not fall into the class of CH_2Y or because σ_I, σ_R^+, and σ_R^0 are not available for Y. However, we believe that since σ^* is inadequate for R groups of the class CH_2Y we have studied, the use of σ^* is inappropriate for all R groups. Again, dissociation rates for *i*-Pr and CH_2OMe compounds are almost identical. The σ^* values are −0.19 and +0.52, respectively.[13] This range of σ^* values exceeds many of the ranges used previously where nonlinearity was observed.[16,17]

If the σ^* approach were appropriate, the dissociation rates for $LCo(DH)_2CH_2OMe$ should be about 10^3 times slower than those we observed. Brown's principal conclusion that five-coordinate $Co(DH)_2R$ species exist in aqueous solution was based on several types of experimental observations.[16,17] However, the quantitative calculations of equilibrium constants for the reaction, $H_2OCo(DH)_2R \rightleftarrows Co(DH)_2R + H_2O$, need to be reevaluated since the calculations are based on σ^* values.

It should be noted that σ^* and σ_I are related.[13] The success of our approach depends both on the introduction of the resonance term and on the transmission of the substituent effect via an intervening organic moiety. This second feature is shared with the second approach mentioned above.

Potential Extensions. It would be valuable to extend our analysis to CHY_1Y_2 and $CY_1Y_2Y_3$ derivatives. Recently, we proposed a scale of substituent parameters (EP) based on ^{13}C NMR shifts.[35] This scale had the relationship

$$EP = \Delta Y_1 + \Delta Y_2 + \Delta Y_3$$

Here, ΔY_i is a substituent constant for substituent Y_i. Since steric effects were not considered, the constant for the $CY_1Y_2Y_3$ group was considered to be an electronic parameter (EP).

In that study,[35] it was clear that the effects of Y_i on ^{13}C NMR shifts were *additive*. In the present study, we have shown that ^{13}C shifts can be correlated with organic substituent constants.[36] Therefore, we believe that eventually the two approaches can be combined and that organic substituent constants for Y_1 and Y_2, for example, can be used to explain the effects of R groups of the type CHY_1Y_2. A potential problem is that steric effects are likely to be more important when data from much bulkier R groups are analyzed. However, a preliminary analysis is promising. Unfortunately, the basis of the analysis must begin with R = Me since the substituents are replacing more than one H. Thus, the following equation holds:

$$\Delta(\text{meas}) = \rho_I({}^1\sigma_I + {}^2\sigma_I + {}^3\sigma_I) + \rho_R({}^1\sigma_R{}^0 + {}^2\sigma_R{}^0 + {}^3\sigma_R{}^0)$$

In this case, we use $\sigma_I = \sigma_R{}^0 = 0$ for Y = H. For R = CHBrCN, the γ-^{13}C shift is 138.64[1] or 1.16 ppm downfield from R = Me (i.e., Δ(meas) = 1.16 ppm). Therefore, for 1 = H, 2 = Br, and 3 = CN

$$\text{calcd} = 1.24(0 + 0.44 + 0.56) + 0.91(0 + -0.19 + 0.13) = 1.24 - 0.06 = 1.18 \text{ ppm}$$

Thus, the calculated and measured values are in excellent agreement.

Two additional general applications of the new transfer approach are contemplated. First, we feel it should be possible to analyze ^1H, ^{31}P, and ^{13}C NMR shifts in cobalamins with the DSP approach applied to CH_2Y compounds. Preliminary analyses of results for CH_2Y cobalamins with the DSP approach appear promising, but insufficient data are currently available. Since the adenosyl moiety can be categorized as a CH_2Y group, it may

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(36) The current data base in Table III allows for an interesting comparison between the DSP approach, based on organic substituent constants, and the single-parameter approach, based on EP parameters derived from ^{13}C shifts in cobaloximes.[35] Correlations of the data with EP lead to linear relationships with the following lcc: log k_1(4-CNpy), 0.9794; log k_1(4-CH_3OPhNH_2), 0.9787; ^{13}C—N(4-CH_3OPhNH_2), 0.8664; ^{13}C—O(4-CH_3OPhNH_2), 0.9514; ^{13}C=C(4-CH_3OPhNH_2), 0.9536; and ^{13}C(py), 0.9977. Thus, the EP approach works best when the ρ_R/ρ_I value (Table V) is close to 0.738, the value found for the ^{13}C(py) shifts on which the EP values are based. As the resonance contribution becomes more important, the correlation becomes increasingly poor. However, it is possible that the additive properties found for the ^{13}C in the pyridine series will also apply to the 4-CH_3OPhNH_2 series, but separate ρ_I and ρ_R values will be needed for each type of carbon.

be possible to obtain σ_I, σ_R^+, and σ_R^0 values for the CHCHOHCHOHCH(Ade)O moiety. Likewise, with adequate data bases, we should be able to determine values for σ_I, σ_R^+, and σ_R^0 for additional Y substituents by using the ρ_R and ρ_I parameters determined in this study.

Bonding Implications of the New DSP Approach. Our modified DSP approach gives good to excellent fits with constants derived from organic aromatic systems with these substituents. Orbitals on the substituents can conjugate with π orbitals on the aromatic ring. Likewise, orbitals on the substituent can conjugate with orbitals on the metal.

Perhaps the best qualitative view of such interactions can be gained by extending the concepts developed by Traylor's laboratory in studies on the effects of metal substituents on the properties of R groups.[32] The effect of an organometallic substituents, such as CH_2SnMe_3, on the properties of organic moieties is about the same as an amino group. Therefore, the M–C bond is about as polarizable as an amino group lone pair.

Extending these concepts to the cobaloximes, the possibility exists for n → σ conjugation between Y lone pairs and the Co–C bond. Such conjugation could explain, for example, the large effect of the OMe substituent on rates, ^{13}C spectra, and Co–N bond length. Apparently, σ_R constants are reasonable quantitative empirical measures of this conjugation, and σ_I constants are a good measure of the inductive effect of the substituent in these organocobalt compounds. Thus, since σ_I and σ^* are directly related, the previous limited success of the σ^* only analysis undoubtedly arose from a neglect of the n → σ conjugation and, possibly, from steric effects. Although R = CH_2OMe compounds were not studied in published reports utilizing the σ^* approach,[16,17] the large negative value for σ_R^+ for OMe leads to the large discrepancy we found using the σ^* analysis.

Evidence has been presented that ligand exchange is a dissociative process with a considerable degree of Co–L bond breaking at the transition state.[37] Therefore, the Co center becomes electron deficient. The DSP approach gives negative values for ρ_R^+ (Figure 4). Thus, "resonance" donating substituents such as OMe will stabilize the transition state relative to the ground state. There are parallels to organic chemistry in which σ_R^+ constants are useful in correlating reactions leading to electron-deficient centers. The correlation of the ^{13}C results with σ_R^0 also has parallels in organic chemistry since ^{13}C shifts reflect ground-state properties and no changes in charge are involved.

Summary. We believe we have clearly established the utility of treating R groups as CH_2Y substituents. This approach explains long-standing anomalies in the effects of R groups on the properties of organocobalt species and calls into question quantitative conclusions based solely on σ^* values for the R groups. The concepts developed by physical organic chemists to explain the significance of σ_I, σ_R^+, and σ_R^0 are relevant to these organocobalt systems. Qualitatively, the effect of the Y substituent may be the consequence of n → σ conjugation involving the polarizable Co–C bond. The effects of R groups on several types of organocobalt compounds are closely related,[2,3] and the findings should apply to B_{12} systems.[20] Analysis of the effects of ligands on the properties of metal complexes reveals that cobaloximes are representative,[11,12,38] and thus it is conceivable that organic substituent constants could be transferred to other organometallic systems by our approach. Finally, since the effects of substituents appear to be additive,[35] it is likely that this approach can be generalized to R derivatives other than CH_2Y compounds. Although such prospects of a general scale to correlate the properties of very diverse compounds are exciting, the definition of the utility and limitations of the method require further work.

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Supplementary Material Available: Tables of elemental analyses, ^{13}C shifts, rate constants, complete DSP approach results, anisotropic thermal parameters, hydrogen atom coordinates, and complete bond lengths and bond angles (21 pages); listing of final calculated and observed structure factors (40 pages). Ordering information is given on any current masthead page.

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