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Further Evidence for Quantitation of Relationships among Structure, NMR Spectra, and Kinetics in B_{12} Models Containing Planar N-Donor Ligands. Synthesis and Structural Characterization of 1,2-Dimethylimidazole–Alkylcobaloximes with Alkyl = CCl_2CN, CH_2CN, Me, and *i*-Pr

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The synthesis and three-dimensional structures of $Me_2ImCo(DH)_2R$ complexes where Me_2Im = 1,2-dimethylimidazole, DH = the monoanion of dimethylglyoxime and R = CCl_2CN (I), CH_2CN (II), Me (III), and *i*-Pr (IV) are reported. Crystallographic details follow. I: $CoCl_2O_4N_7C_{15}H_{22}$, monoclinic $P2_1/c$, a = 9.074 (2) Å, b = 14.280 (2) Å, c = 16.997 (4) Å, β = 105.86 (2)°, D(calcd) = 1.55 g cm^{-3}, Z = 4, R = 0.048 for 3042 independent reflections. II: $CoO_4N_7C_{15}H_{24}$, monoclinic $P2_1/c$, a = 9.055 (2) Å, b = 9.165 (2) Å, c = 22.713 (3) Å, β = 93.15 (1)°, D(calcd) = 1.50 g cm^{-3}, Z = 4, R = 0.042 for 2862 independent reflections. III: $CoO_4N_6C_{14}H_{25}$, monoclinic $C2/c$, a = 10.080 (1) Å, b = 15.452 (2) Å, c = 23.651 (3) Å, β = 92.36 (1)°, D(calcd) = 1.44 g cm^{-3}, Z = 8, R = 0.034 for 3571 independent reflections. IV: $CoO_4N_6C_{16}H_{29}$, monoclinic $P2_1/c$, a = 8.309 (2) Å, b = 29.177 (4) Å, c = 9.028 (1) Å, β = 116.22 (1)°, D(calcd) = 1.45 g cm^{-3}, Z = 4, R = 0.042 for 3244 independent reflections. The axial Co–C and Co–N bond lengths increase with the increase of the bulk and of the σ-donating ability of the R group, respectively. The Co–C distances range from 2.001 (2) (III) to 2.096 (3) Å (IV) and the Co–N distances from 2.025 (3) (I) to 2.121 (2) Å (IV). A previously proposed method for measuring the σ-donating ability of the R groups by using the EP parameter, derived from NMR data for the $pyCo(DH)_2R$ series, is revisited and extended to series containing other axial neutral ligands. Comparison with kinetic and structural data indicates that the EP values rationalize the observed trends in these properties. However, steric effects appear to have a detectable influence.

Introduction

Organocobalt compounds, modeled after coenzyme B_{12} (5'-deoxyadenosylcobalamin), are of intense interest for understanding the relationships between solution properties of these compounds and their structures.[1-8] It is widely believed that structural and conformational changes in coenzyme B_{12} lead to an acceleration in Co–C bond cleavage rates[9-11] (by a factor of 10^{10}–10^{15}) when the coenzyme binds to an enzyme and its holoenzyme is activated by substrates in B_{12}-dependent processes. However, although some progress has been made in crystallizing B_{12} enzyme systems,[12] these materials are so large that at the present time it is difficult to investigate precisely structural changes. Therefore, we have emphasized relating solution and X-ray crystallographic data on cobalamins and very small models such as cobaloximes, $LCo(DH)_2L$ (DH = monoanion of dimethylglyoxime and L = neutral ligand).[1,3,8]

This interest has led to a great diversity and abundance of information on the dependence of ligand dissociation rates, Co–axial bond lengths, etc., on the nature of the alkyl (R) groups bound to the cobalt.[1-4,7,8,13,14] Nevertheless, the empirical relationships have not been fully understood, and several anomalies were noted[15] and persisted in the literature for some time. Recently, two observations appear to hold promise as means of quantitatively predicting the relationships between rates, structures, and spectra of diverse and as yet unsynthesized organocobalt compounds.[13,14]

In a first set of observations, some of us developed an approach whereby kinetic and spectral results for $LCo(DH)_2CH_2Y$ compounds could be fit by using a dual substituent parameter (dsp) approach.[13] This type of result suggests that $n \rightarrow \sigma$ conjugation[16] can be quantitatively treated by using the inductive and π-delocalization substituent constants (σ_I, $\sigma_R{}^{\circ}$, $\sigma_R{}^{+}$) derived from correlations in organic benzenoid systems.[17]

In a second set of observations,[14] some of us noted that in $LCo(DH)_2R$ compounds (L = py) the differences of ^{13}C NMR shifts with respect to the R = CH_3 derivative, $\Delta C(Y^1Y^2Y^3)$ = $\delta[^{13}C(CH_3)] - \delta[^{13}C(CY^1Y^2Y^2)]$, were additive. Thus, using the chemical shifts of the γ-^{13}C of pyridine, we defined the differences $\delta[^{13}C(CH_3)] - \delta[^{13}C(CH_2Y)]$ as ΔY. Having obtained such constants ΔY^1, ΔY^2, and ΔY^3 for three substituents Y^1, Y^2, and Y^3, their sum was defined as the electronic parameter, EP, of the $CY^1Y^2Y^3$ group:

$$EP = \Delta Y^1 + \Delta Y^2 + \Delta Y^3 \tag{1}$$

The good agreement between the EP parameters are the observed $\Delta C(Y^1Y^2Y^3)$ values confirms the validity of eq 1. The EP values also correlate well with structure and rate information on this class of compounds.[14]

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Table I. Crystallographic Data and Details of Refinements for Compounds I–IV, $Me_2ImCo(DH)_2R$[a]

	I	II	III	IV
R	CCl_2CN	CH_2CN	Me	*i*-Pr
formula	$CoCl_2O_4N_7C_{15}H_{22}$	$CoO_4N_7C_{15}H_{24}$	$CoO_4N_6C_{14}H_{25}$	$CoO_4N_6C_{16}H_{29}$
fw	494.3	425.4	400.4	428.4
a, Å	9.074 (2)	9.055 (2)	10.080 (1)	8.309 (2)
b, Å	14.280 (2)	9.165 (2)	15.452 (2)	29.177 (4)
c, Å	16.997 (4)	22.713 (3)	23.651 (3)	9.028 (1)
β, deg	105.86 (2)	93.15 (1)	92.36 (1)	116.22 (1)
V, Å^3	2119 (1)	1882 (1)	3681 (1)	1963 (1)
D(calcd), g cm^{-3}	1.55	1.50	1.44	1.45
D(measd), g cm^{-3}	1.55	1.49	1.44	1.44
Z	4	4	8	4
F(000)	1016	888	1680	904
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
μ(Mo Kα), cm^{-1}	11.0	9.4	9.6	9.0
no. of measd reflcns	5452	4892	4691	5094
no. of indep reflcns with $I \geq 3\sigma(I)$	3042	2862	3571	3244
no. of params refined	262	244	226	244
R	0.048	0.042	0.034	0.042
R_w	0.065	0.056	0.049	0.055

[a] All data were collected at 18 °C by using graphite-monochromated MoKα radiation (λ = 0.7107 Å); $2\theta_{max}$ = 56°.

The exciting prospect of these observations is that a unified set of constants may eventually be derived for predicting the properties of a diverse range of organometallic compounds, not only those relevant to coenzyme B_{12}. Although the first approach has the advantage of transferring to organometallic chemistry substituent constants from organic chemistry, at the present it is limited to alkylcobaloximes with R = CH_2Y. On the contrary, the EP approach may be applied not only to any axial alkyl but also to acid ligands such as N_3^- or Cl^-. Furthermore, we have found that chemical shifts, rate constants, and axial bond lengths for the series $LCo(DH)_2R$ with several L ligands are linearly related to the corresponding data for the series with L = py, as it will be described in the Discussion. This finding has suggested the opportunity to test the validity of the EP approach by using a more extended set of L ligands. Therefore, we have recently studied the structural and solution properties for a series of alkylcobaloximes with L = 1,5,6-trimethylbenzimidazole (Me_3Bzm).[18,19] We report now the synthesis and the crystal structure of four complexes with the bulkier ligand 1,2-dimethylimidazole (Me_2Im), namely those with R = CCl_2CN (I), CH_2CN (II), Me (III), and *i*-Pr (IV). The structures of those with R = CH_2NO_2 and $(CH_2)_3CN$ have been already determined.[20] It is worthwhile to note that compound I represents the cobaloxime with the strongest electron-withdrawing group so far reported. On the other hand, the Me_2Im ligand is expected to have a size intermediate between those of py (or Me_3Bzm) and $2\text{-}NH_2py$ so that properties of Me_2Im derivatives should fit those already available for the above planar ligands.

Experimental Section

Preparation of the Complexes. All the reagents were from Aldrich and were used as received. All the complexes were characterized by X-ray crystal structure analysis.

$Me_2ImCo(DH)_2CCl_2CN$. A 3.10-g (7.14-mmol) sample of $Me_2ImCo(DH)_2Cl$[21] was suspended in 300 mL of methanol, and the resulting mixture was kept under nitrogen at room temperature and with vigorous stirring. Then, an aqueous NaOH solution (three pellets in 5 mL of H_2O) was prepared and added. Meanwhile, 0.56 g (14.8 mmol) of $NaBH_4$ was suspended in 5 mL of H_2O. Once the starting cobalt complex had dissolved, 2 mL of the previously prepared $NaBH_4$ suspension was added dropwise. When the gas evolution had finished, 3 mL (29.9 mmol) of CCl_3CN was poured in, followed by the remaining $NaBH_4$ solution, which was also added dropwise. The resulting mixture was stirred at room temperature for an additional 15 min, and then 30 mL of acetone was added to quench the $NaBH_4$ excess and the N_2 bubbling was stopped. The stirring was kept at room temperature for half an hour and then the undissolved materials were removed by filtration. The filtrate was concentrated on a rotary evaporator until a solid formed and then set aside to allow complete precipitation of the compound. The brownish product was collected by vacuum filtration, washed with 2 × 10 mL of H_2O, and air-dried. (Yield: 58%.)

$Me_2ImCo(DH)_2CH_2CN$. To a solution containing 0.30 g (0.90 mmol) of $H_2OCo(DH)_2CH_2CN$[22] in 20 mL of methylene chloride was added 90.0 μL (1.01 mmol) of Me_2Im. The reaction mixture was stirred at room temperature for 1 h. During this period, its color changed from red-brown to bright orange. The desired compound was then precipitated by adding petroleum ether until the solution became turbid (ca. 15 mL) and setting the solution aside at 4 °C overnight. The solid formed was collected and air-dried. (Yield: 71.4%.)

$Me_2ImCo(DH)_2Me$. To a suspension containing 0.42 g (1.37 mmol) of $H_2OCo(DH)_2Me$[23,24] in 50 mL of CH_2Cl_2 was added 150 μL (1.69 mmol) of Me_2Im, and the resulting solution was stirred at room temperature for 20 min. The solid formed after the addition of 15 mL of petroleum ether was collected, washed with 2 × 5 mL of H_2O, and air-dried. (Yield: 79.4%.)

$Me_2ImCo(DH)_2$-*i*-Pr. First, 1.5 g (3.44 mmol) of 4-CNpyCo$(DH)_2$-*i*-Pr[21] was suspended in 75 mL of a methanol-water mixture (80:20). Then 1.5 g of strong acidic cation-exchange resin (Dowex 50-X8-100) was added. The resulting mixture was stirred at room temperature for 1 h and filtered out. Concentration of the filtrate on a rotary evaporator produced a red solid, $H_2OCo(DH)_2$-*i*-Pr, which was filtered out and air-dried. Substitution of the aquo ligand by the Me_2Im was carried out as follows: 0.75 g (2.14 mmol) of $H_2OCo(DH)_2$-*i*-Pr was suspended in 50 mL of CH_2Cl_2, and then 0.2 mL of Me_2Im (2.25 mmol) was added. The mixture was stirred at room temperature until the aquocompound had dissolved. Petroleum ether was added to the orange solution till it turned cloudy, and then it was set aside at ca. 4 °C for 24 h. The solid formed was removed by vacuum filtration and air-dried. (Yield: 43%.)

Crystal Data. Cell dimensions, determined from Weissenberg and precession photographs, were refined on a CAD4 Enraf-Nonius single-crystal diffractometer. The results are given in Table I. The intensity data were collected by the $\omega/2\theta$ scan technique by using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Three check reflections measured every 60 min showed no intensity decay during the data collections. Reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects and for anomalous dispersion. No absorption and extinction corrections were applied. Some details of the intensity data collections are summarized in Table I.

Solution and Refinement of the Structures. All of the structures were solved by conventional Patterson and Fourier methods and refined by the full-matrix anisotropic least-squares method. In the final cycles, the contribution of hydrogen atoms at calculated positions (held constant at

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Table II. Atomic Positional Parameters of Non-Hydrogen Atoms with Esd's in Parentheses of $Me_2ImCo(DH)_2CCl_2CN$ (I)[a]

atom	*x*	*y*	*z*	*B*,[a] Å^2
Co	0.28424 (5)	0.27495 (3)	0.39341 (3)	2.742 (9)
Cl1	0.5803 (1)	0.2245 (1)	0.33164 (9)	7.04 (4)
Cl2	0.3443 (2)	0.0836 (1)	0.30389 (8)	6.11 (3)
O1	0.5824 (3)	0.3098 (3)	0.5007 (2)	5.52 (8)
O2	0.0876 (4)	0.1185 (2)	0.3934 (2)	5.31 (8)
O3	−0.0085 (4)	0.2378 (2)	0.2851 (2)	4.98 (7)
O4	0.4828 (3)	0.4278 (2)	0.3915 (2)	4.95 (7)
N1	0.4605 (4)	0.2507 (3)	0.4809 (2)	4.03 (8)
N2	0.2210 (4)	0.1612 (2)	0.4309 (2)	4.09 (8)
N3	0.1064 (4)	0.3000 (3)	0.3089 (2)	3.46 (7)
N4	0.3452 (4)	0.3898 (2)	0.3573 (2)	3.43 (7)
N5	0.2042 (3)	0.3484 (2)	0.4749 (2)	2.91 (6)
N6	0.0856 (4)	0.4038 (3)	0.5609 (2)	3.70 (7)
N7	0.2706 (6)	0.2687 (3)	0.1683 (3)	6.4 (1)
C1	0.5776 (7)	0.1559 (5)	0.6011 (4)	8.7 (2)
C2	0.4541 (5)	0.1800 (4)	0.5256 (3)	5.0 (1)
C3	0.3133 (6)	0.1252 (3)	0.4959 (3)	4.9 (1)
C4	0.2776 (9)	0.0374 (4)	0.5339 (4)	8.6 (2)
C5	−0.0278 (7)	0.4076 (4)	0.2017 (4)	6.6 (1)
C6	0.1025 (5)	0.3790 (3)	0.2714 (3)	4.01 (9)
C7	0.2436 (5)	0.4329 (3)	0.3010 (2)	3.81 (9)
C8	0.2716 (7)	0.5261 (4)	0.2681 (3)	6.3 (1)
C9	0.3781 (4)	0.2082 (3)	0.3121 (3)	3.63 (8)
C10	0.3137 (5)	0.2439 (3)	0.2244 (3)	4.4 (1)
C11	0.0782 (4)	0.3427 (3)	0.4998 (3)	3.42 (8)
C12	0.2239 (5)	0.4506 (3)	0.5763 (3)	3.97 (9)
C13	0.2942 (5)	0.4162 (3)	0.5236 (2)	3.61 (8)
C14	−0.0570 (5)	0.2809 (4)	0.4692 (3)	5.9 (1)
C15	−0.0252 (5)	0.4158 (4)	0.6090 (3)	5.3 (1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Atomic Positional Parameters of Non-Hydrogen Atoms with Esd's in Parentheses of $Me_2ImCo(DH)_2CH_2CN$ (II)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Co	0.30813 (5)	0.20807 (5)	0.13613 (2)	2.115 (7)
O1	0.0144 (3)	0.1308 (3)	0.1645 (1)	3.38 (5)
O2	0.4650 (3)	0.4699 (3)	0.1655 (1)	4.16 (6)
O3	0.6097 (3)	0.2775 (3)	0.1181 (1)	3.92 (6)
O4	0.1580 (3)	−0.0622 (3)	0.1160 (1)	3.18 (5)
N1	0.1182 (3)	0.2369 (3)	0.1642 (1)	2.60 (5)
N2	0.3344 (3)	0.3985 (3)	0.1663 (1)	2.95 (6)
N3	0.5026 (3)	0.1755 (3)	0.1125 (1)	2.83 (6)
N4	0.2845 (3)	0.0138 (3)	0.1106 (1)	2.49 (5)
N5	0.2515 (3)	0.2991 (3)	0.0556 (1)	2.34 (5)
N6	0.1454 (3)	0.3741 (4)	−0.0280 (1)	3.00 (6)
N7	0.2807 (7)	0.2554 (6)	0.3056 (2)	8.2 (1)
C1	−0.0504 (5)	0.4012 (5)	0.2136 (2)	4.27 (9)
C2	0.0910 (4)	0.3630 (4)	0.1870 (1)	2.91 (7)
C3	0.2201 (4)	0.4599 (4)	0.1877 (2)	3.18 (7)
C4	0.2219 (6)	0.6097 (5)	0.2130 (2)	4.8 (1)
C5	0.6790 (4)	−0.0009 (5)	0.0747 (2)	4.35 (9)
C6	0.5296 (4)	0.0461 (4)	0.0922 (2)	2.81 (7)
C7	0.4011 (4)	−0.0497 (4)	0.0910 (2)	2.81 (7)
C8	0.4054 (5)	−0.2058 (5)	0.0724 (2)	4.10 (8)
C9	0.3736 (5)	0.1237 (5)	0.2154 (2)	4.13 (9)
C10	0.3240 (5)	0.1978 (5)	0.2661 (2)	4.35 (9)
C11	0.1341 (4)	0.2833 (4)	0.0184 (1)	2.50 (6)
C12	0.2739 (4)	0.4511 (5)	−0.0197 (2)	3.88 (8)
C13	0.3385 (4)	0.4040 (5)	0.0317 (2)	3.41 (7)
C14	0.0034 (5)	0.1894 (5)	0.0250 (2)	4.17 (8)
C15	0.0409 (5)	0.3870 (6)	−0.0792 (2)	4.8 (1)

[a] See footnote *a* is Table II.

Table IV. Atomic Positional Parameters of Non-Hydrogen Atoms with Esd's in Parentheses of $Me_2ImCo(DH)_2Me$ (III)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Co	0.28713 (3)	0.08510 (2)	0.13538 (1)	2.163 (5)
O1	0.3425 (2)	0.2580 (1)	0.16947 (8)	4.05 (4)
O2	0.3324 (2)	0.0050 (1)	0.02936 (6)	3.28 (3)
O3	0.2586 (2)	−0.09287 (9)	0.10457 (7)	3.28 (3)
O4	0.2556 (2)	0.1617 (1)	0.24408 (7)	3.89 (4)
N1	0.3409 (2)	0.2008 (1)	0.12665 (8)	3.01 (4)
N2	0.3381 (2)	0.0791 (1)	0.05989 (8)	2.61 (3)
N3	0.2468 (2)	−0.0329 (1)	0.14569 (7)	2.45 (3)
N4	0.2455 (2)	0.0890 (1)	0.21219 (7)	2.72 (3)
N5	0.0906 (2)	0.1064 (1)	0.10792 (7)	2.42 (3)
N6	−0.1164 (2)	0.1463 (1)	0.08979 (8)	2.89 (3)
C1	0.4303 (3)	0.3119 (2)	0.0639 (1)	4.66 (6)
C2	0.3820 (2)	0.2226 (2)	0.0773 (1)	3.18 (4)
C3	0.3801 (2)	0.1502 (2)	0.0375 (1)	3.07 (4)
C4	0.4257 (3)	0.1555 (2)	−0.0215 (1)	4.47 (6)
C5	0.1708 (3)	−0.1459 (2)	0.2095 (1)	4.35 (6)
C6	0.2074 (2)	−0.0552 (1)	0.19503 (9)	2.70 (4)
C7	0.2071 (2)	0.0174 (1)	0.23477 (9)	2.77 (4)
C8	0.1711 (3)	0.0093 (2)	0.2953 (1)	4.12 (5)
C9	0.4744 (2)	0.0574 (2)	0.1604 (1)	3.74 (5)
C10	−0.0003 (2)	0.1655 (1)	0.11837 (9)	2.54 (4)
C11	−0.0979 (2)	0.0703 (2)	0.0606 (1)	3.08 (4)
C12	0.0285 (2)	0.0469 (2)	0.07168 (9)	2.88 (4)
C13	0.0132 (3)	0.2416 (2)	0.1566 (1)	3.77 (5)
C14	−0.2413 (3)	0.1932 (2)	0.0911 (2)	4.78 (6)

[a] See footnote *a* in Table II.

Table V. Atomic Positional Parameters of Non-Hydrogen Atoms with Esd's in Parentheses of $Me_2ImCo(DH)_2$-*i*-Pr (IV)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Co	0.29590 (5)	0.13161 (1)	0.12979 (4)	2.047 (7)
O1	0.5255 (3)	0.19796 (9)	0.3564 (3)	3.89 (6)
O2	0.2980 (3)	0.09992 (9)	−0.1694 (3)	3.55 (5)
O3	0.0594 (3)	0.06755 (8)	−0.1028 (3)	3.58 (6)
O4	0.2874 (3)	0.16587 (9)	0.4211 (3)	3.91 (6)
N1	0.4827 (3)	0.17497 (9)	0.2141 (3)	2.58 (5)
N2	0.3726 (3)	0.12853 (9)	−0.0373 (3)	2.43 (5)
N3	0.1023 (3)	0.09057 (9)	0.0393 (3)	2.81 (6)
N4	0.2141 (3)	0.13730 (9)	0.2923 (3)	2.86 (6)
N5	0.4644 (3)	0.07511 (9)	0.2484 (3)	2.40 (5)
N6	0.6479 (3)	0.0236 (1)	0.4164 (3)	2.98 (6)
C1	0.7091 (5)	0.2191 (1)	0.1692 (5)	4.5 (1)
C2	0.5656 (4)	0.1838 (1)	0.1255 (4)	2.92 (7)
C3	0.4994 (4)	0.1564 (1)	−0.0248 (4)	2.84 (7)
C4	0.5647 (5)	0.1616 (2)	−0.1527 (4)	4.76 (9)
C5	−0.1454 (5)	0.0529 (2)	0.0692 (6)	5.2 (1)
C6	0.0102 (4)	0.0846 (1)	0.1226 (4)	3.35 (7)
C7	0.0760 (4)	0.1126 (1)	0.2714 (4)	3.40 (7)
C8	−0.0070 (5)	0.1140 (2)	0.3885 (5)	5.34 (9)
C9	0.1097 (4)	0.1828 (1)	0.0005 (4)	3.15 (7)
C10	0.0405 (6)	0.1799 (2)	−0.1839 (5)	4.7 (1)
C11	0.1647 (7)	0.2301 (2)	0.0636 (6)	6.5 (1)
C12	0.5827 (4)	0.0665 (1)	0.4031 (4)	2.73 (6)
C13	0.5677 (4)	0.0035 (1)	0.2624 (4)	3.21 (7)
C14	0.4564 (4)	0.0355 (1)	0.1610 (4)	2.82 (7)
C15	0.6384 (5)	0.0976 (2)	0.5455 (4)	4.6 (1)
C16	0.7785 (5)	0.0008 (2)	0.5645 (5)	4.6 (1)

[a] See footnote *a* in Table II.

$B = 5$ Å^2) was included. The final weighting scheme was $w = 1/(\sigma^2(F) + (pF)^2 + 1)$ with $p = 0.03$ for I and II and 0.02 for III and IV, chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta)/\lambda$. The final R and R_w values are given in Table I. Final non-hydrogen positional parameters are given in Tables II–V. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of calculated and observed structure factors are available as supplementary material.

All calculations employed the SDP CAD4 programs on a PDP11/44 computer.

Results and Discussion

Description of the Structures. The ORTEP drawings for non-hydrogen atoms of I–IV with the atom numbering scheme are depicted in Figures 1–4. In all of the structures, the DH ligands occupy the four equatorial positions of a distorted octahedron around Co. The geometry of the equatorial moiety in these complexes is very similar with the exception of the displacement, *d*, of Co out of the mean plane passing through the four N equatorial donors and the dihedral angle, α, between the planes passing through the two approximately planar DH units. The

Table VI. Relevant Geometric Parameters for $Me_2ImCo(DH)_2R$ Complexes

R	Co–N, Å	Co–C, Å	N–Co–C, deg	Co–C–Y, deg	C–Y, Å	Co–N–C-(Me), deg	Co–N–C, deg	d,[a] Å	α,[a] deg	φ, deg
CCl_2CN[b]	2.025 (3)	2.047 (4)	175.6 (1)	114.1 (2) 114.1 (2) 112.6 (3)	1.789 (4) 1.804 (5) 1.532 (7)	133.5 (2)	120.5 (2)	−0.02	−8.5	7.0
CH_2NO_2[c]	2.049 (3)	1.999 (3)	174.0 (1)	114.5 (1)	1.456 (4)	132.2 (2)	122.2 (2)	+0.03	+3.4	13.8
CH_2CN[b]	2.049 (3)	2.018 (4)	177.1 (2)	116.5 (3)	1.432 (6)	132.5 (2)	121.2 (2)	+0.06	+6.0	4.1
$(CH_2)_3CN$[c]	2.083 (2)	2.023 (3)	174.2 (1)	119.4 (2)	1.488 (5)	133.9 (2)	120.7 (2)	+0.06	+5.9	3.0
Me[b]	2.086 (1)	2.001 (2)	176.62 (8)			134.9 (1)	119.1 (1)	+0.06	+3.4	4.1
i-Pr[b]	2.121 (2)	2.096 (3)	174.5 (1)	113.8 (2) 114.9 (2)	1.504 (2) 1.484 (5)	134.0 (2)	120.4 (2)	+0.04	+7.3	2.5

[a] Positive α and d values indicate bending of the equatorial ligand toward R and displacement of Co toward Me_2Im. [b] Present work. [c] Reference 20.

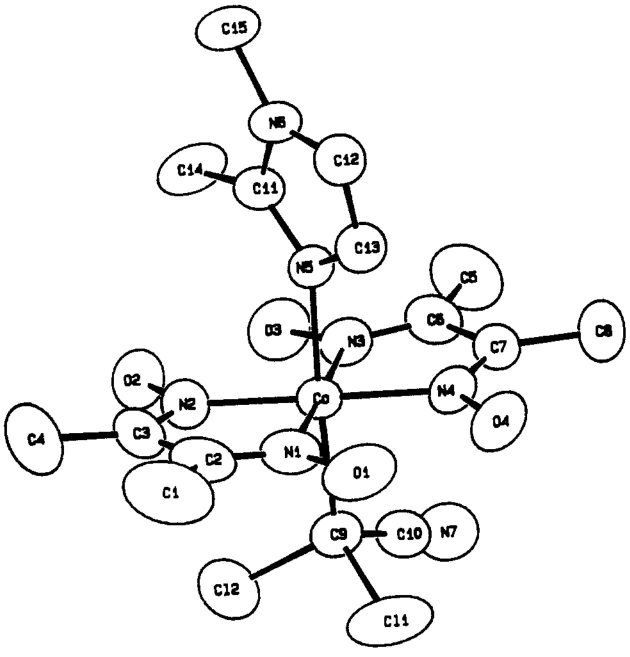

Figure 1. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for the non-hydrogen atoms of I.

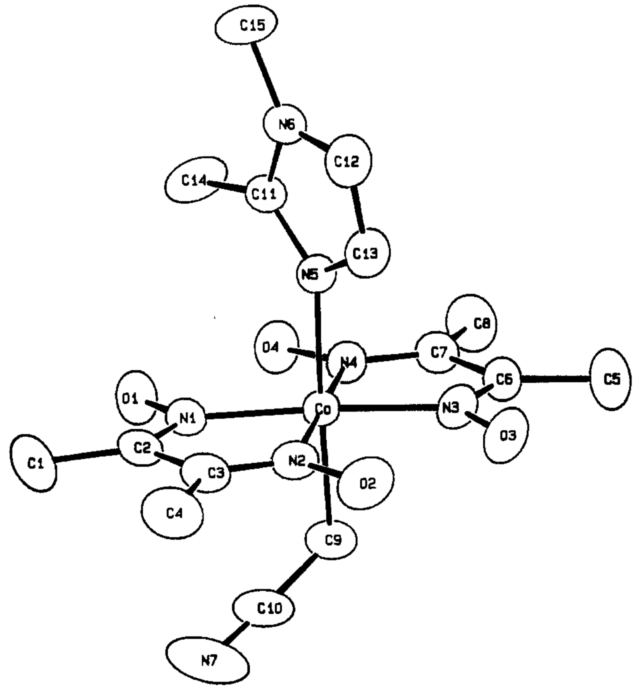

Figure 2. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for the non-hydrogen atoms of II.

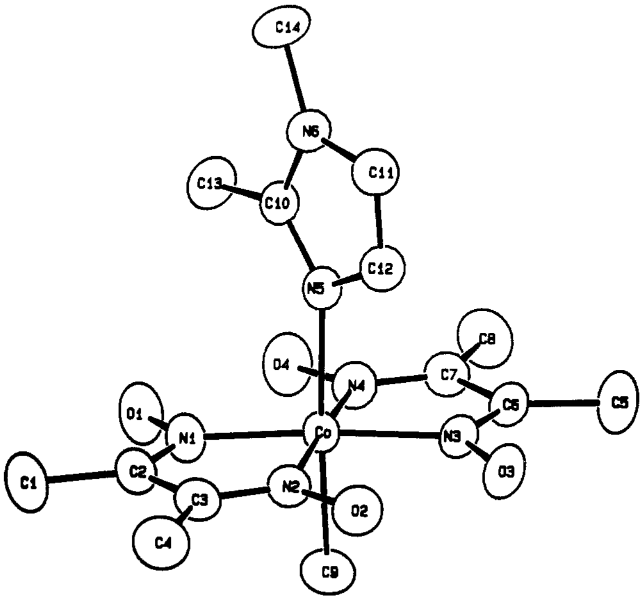

Figure 3. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for the non-hydrogen atoms of III.

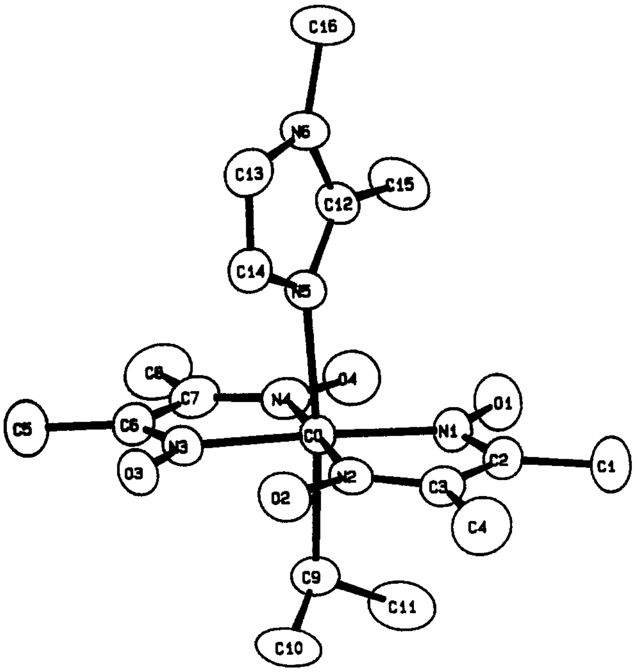

Figure 4. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for the non-hydrogen atoms of IV.

corresponding values, together with selected bond lengths and angles that characterize the axial fragment Me_2Im–Co–R, are given in Table VI. For comparison, the corresponding data for $Me_2ImCo(DH)_2R$ with R = CH_2NO_2 and $(CH_2)_3CH$ are also reported. As expected, the alkyl σ-donor power mainly influences the Co–N axial distances, which increase with the increasing

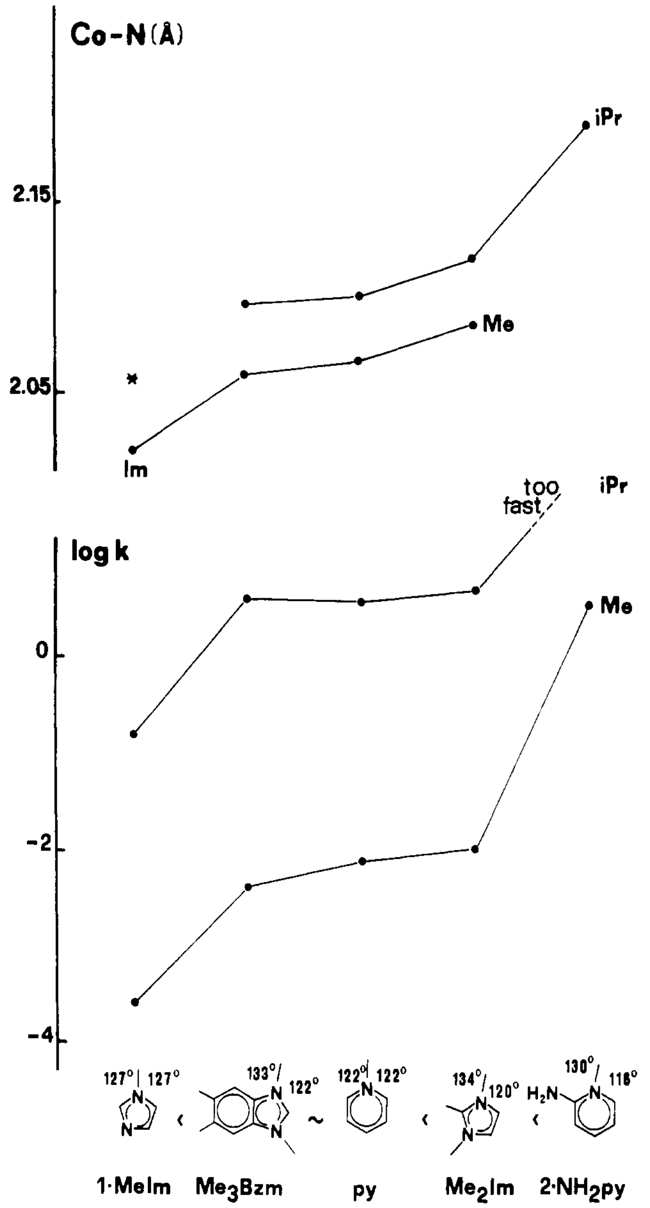

Figure 5. Trends of axial Co–N distances and of log *k* in $LCo(DH)_2R$ complexes with R = Me and *i*-Pr and different planar L ligands. The starred point refers to the Co–N bond length in $1\text{-MeImCo(DH)}_2\text{Me}$ with a different orientation of the neutral ligand. The values of the Co–N–C angles are reported in the formula at the bottom of the figure.

σ-donating ability of R. On the other hand, the R size mainly influences the Co–C bond lengths, the Co–C–Y angles and the α and *d* values, which increase with the increasing bulk of R. The geometry of Me_2Im (which deviates from planarity not more than 0.03 Å) and its orientation with respect to the equatorial ligand are very similar in all the complexes of Table VI. The mean plane passing through Me_2Im makes an angle, φ, with the ideal symmetry mirror plane referring the two DH units that does not exceed 14° in all the complexes. The φ values, measured as the torsion angle (Me)C–N(5)–Co–N*, where N* is the midpoint between N(1) and N(4), are given in Table VI. Although the Co–N(5) axial bond lengths are different, the values of the bond angles around N(5) are very similar in all the structures. The side Me group in position 2 provokes the nonequivalence of the two Co–N(5)–C angles, which differ by more than 10°. This effect is similar to that found in Me_3Bzm derivatives.[18,19]

Discussion of the Structures. The axial Co–N bond lengths for several $LCo(DH)_2R$ complexes reported in Table VII show a clear influence of the bulk of the L ligand (steric *cis* influence). For the same alkyl group with different planar N-donor ligands, the order of increasing Co–N(axial) distance is shown in Figure 5. This order is the same as that for the dissociation rate of L, also shown in Figure 5. This trend of Co–N distances and log *k*

Table VII. Comparison of Axial Co–N Distances (Å) in $LCo(DH)_2R$ Complexes

L	R = CH_2NO_2	R = Me	R = *i*-Pr	R = adamantyl
Im		2.019 (3)[a]		
1-MeIm		2.058 (5)[b,c]		2.065 (4)[d]
Me_3Bzm	2.013 (3)[e]	2.060 (2)[e]	2.097 (2)[e]	2.137 (4)[f]
py	2.028 (3)[b]	2.068 (3)[b]	2.099 (2)[b]	2.102 (3)[g,h]
Me_2Im	2.049 (3)[i]	2.086 (1)[j]	2.121 (2)[j]	
$2\text{-NH}_2\text{Py}$			2.194 (4)[b]	

[a] Pattabhi, V.; Nethaji, M.; Gabe, E. J.; Lee, F. L.; Le Page, Y. *Acta Crystallogr.* **1984**, *C40*, 1115. [b] Reference 1. [c] The orientation of L corresponds to φ = 66.1° in contrast to φ ≈ 0° in other compounds. [d] Bresciani Pahor, N.; Marzilli, L. G.; Randaccio, L.; Toscano, P. J.; Zangrado, E. *J. Chem. Soc., Chem. Commun.* **1984**, 1508. [e] Reference 18. [f] Reference 19. [g] Reference 29. [h] L = $4\text{-Me}_2\text{Npy}$. [i] Reference 20. [j] Present work.

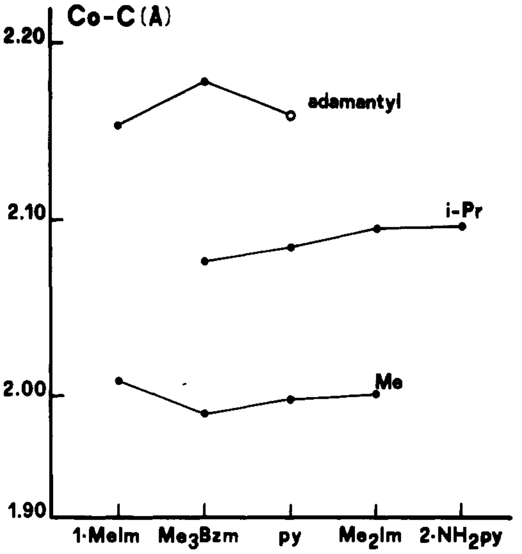

Figure 6. Trend of axial Co–C bond lengths in $LCo(DH)_2R$ complexes with R = Me, *i*-Pr, and adamantyl and different planar L ligands. The open circle for adamantyl refers to the L = $4\text{-Me}_2\text{Npy}$ derivative.

$$\text{Im} \le 1\text{-MeIm} < \text{py} \approx \text{Me}_3\text{Bzm} \le \text{Me}_2\text{Im} < 2\text{-NH}_2\text{py} \qquad (1a)$$

has been attributed to the combined influence of the opening of internal Cα–N(axial)–Cα angle and of the presence of non-hydrogen side substituents on the α-carbon atoms of the planar ligand.[2,18] The Me_2Im ligand occupies the expected position in that trend. The somewhat high value of the Co–N axial distance found in $1\text{-MeImCo(DH)}_2\text{Me}$ (starred point in Figure 5), has been attributed[20] to the different orientation (φ = 66.1°) of the 1-MeIm ligand plane with respect to the equatorial moiety. Since the log *k* values for 1-MeIm do not show irregularity, it may be concluded that the "anomalous" orientation of this ligand is a consequence of the crystal packing.

It is worthwhile to note that the bulk of the neutral planar ligand is mainly reflected in distortions of the coordination of N to Co. In fact, there is no significant variation of the trans Co–R bond length when L varies from 1-MeIm to $2\text{-NH}_2\text{py}$ (Figure 6). The only apparent effect transmitted from L to R is the electronic trans influence, not detected by Co–C bond length measurements but revealed[25] by Co–C bond dissociation energy (BDE) for $LCo(DH)_2CH(Me)Ph$ complexes. In the latter series, the Co–C BDE increases linearly with the increase of the pK_a of L = 4-Xpy with X = CN, H, Me, NH_2. This result confirms the previous conclusion by Geno and Halpern[26] that the equatorial ligand acts as

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(25) Ng, T. T.; Rempel, G. L.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 621.

(26) Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238.

Table VIII. Values of a_1 and b_1 for the Linear Regressions $d_{\text{Co-N}}(\text{py}) = a_1 + b_1\, d_{\text{Co-N}}(\text{L})$, $\log k(\text{4-CNpy}) = a_2 + b_2 \log k(\text{L})$, and $\Delta C(Y^1Y^2Y^3)(\text{py}) = a_3 + b_3\, \Delta C(Y^1Y^2Y^2)(\text{L})$, Together with the Correlation Factor, *r*, and the Number of Observables, *n*[a]

	L	a_1	b_1	*r*	*n*
$d_{\text{Co-N}}$	Me_3Bzm	0.200 (5)	0.90 (7)	0.992	5
	Me_2Im	−0.236 (8)	1.10 (14)	0.985	4
log *k*	Me_3Bzm	0.90 (10)	0.909 (16)	0.999	10
	1-MeIm	2.17 (16)	0.94 (4)	0.995	8
	$2\text{-}NH_2py$	−1.95 (20)	1.03 (5)	0.994	8
$\Delta C(Y^1Y^2Y^3)$	4-*t*-Bupy, γ-C	−0.06 (3)	0.753 (15)	0.998	12
	Me_3Bzm, B5	−0.04 (3)	1.32 (3)	0.998	11

[a] *n* also specifies the number of R groups included in each regression.

a rigid "barrier" shielding the Co–R bond from steric perturbations of the planar N-donor ligands not able to bend the $(DH)_2$ moiety toward R enough to weaken sensibly the Co–C bond. Therefore, all the steric distortions will be reflected in the Co–L bonding. On the contrary, the bending of the $(DH)_2$ moiety induced by the bulkier phosphines is reflected in a weakening of the trans Co–C bond.[26,27] However, more rigid equatorial ligands such as octaethylporphyrins are not distorted even by phosphines,[26] and again the electronic trans influence is the more apparent effect. Thus, both the relative rigidity of the equatorial ligand and the relative bulk of the L ligand are important in defining the main detected effect.

Relationship between Structure and Solution Properties: The EP Parameter. In order to test the EP approach[14] described in the Introduction, we extend it to available data for the $LCo(DH)_2R$ series with L ligands other than py.[28] This extension can be done since axial Co–N distances, log *k*'s for the L displacement, and $\Delta C(Y^1Y^2Y^3)$ in the series $pyCo(DH)_2R$ (4-CNpy for log *k*) with several R groups are linearly related to the corresponding properties of the analogous alkylcobaloximes containing the N-donor planar ligands as specified in the following equations:

$$d_{\text{Co-N}}(\text{py}) = a_1 + b_1\, d_{\text{Co-N}}(\text{L})$$
$$\text{L} = Me_3Bzm,\ Me_2Im$$

$$\log k(\text{4-CNpy}) = a_2 + b_2 \log k(\text{L})$$
$$\text{L} = Me_3Bzm,\ \text{1-MeIm},\ 2\text{-}NH_2py$$

$$\Delta C(Y^1Y^2Y^3)(\text{py}) = a_3 + b_3\, \Delta C(Y^1Y^2Y^3)(\text{L})$$
$$\text{L} = \text{4-}t\text{-Bupy},\ Me_3Bzm$$

The a_1 and b_1 values are given in Table VIII together with the correlation factor, *r*, and the number of observables, *n*. The good quality of these correlations indicates that the above properties are influenced by the change of the trans-R group in the same way in all the series independently upon the L ligand. Therefore, by using these relationships, the $d_{\text{Co-N}}$, log *k*, and $\Delta C(Y^1Y^2Y^3)$ values for each series (with the same L and various R) were scaled on those of pyridine derivatives (see supplementary material). Then for each R group, the scaled data were averaged to obtain the mean values reported in Table IX. The mean $\Delta C(Y^1Y^2Y^3)$ values were utilized to obtain the ΔY constants for several Y substituents through a least-squares procedure (see supplementary material). Entering these ΔY's into relation 1 allows us to obtain the EP parameters, reported in the last column of Table IX, for several $CY^1Y^2Y^3$ groups. They differ little from those already reported,[14] and the excellent agreement with the observed $\Delta C(Y^1Y^2Y^3)$ values indicates that the previously observed additivity holds. The convention for the sign of the EP parameters is the same used in the previous paper;[14] i.e., negative values denote electron-withdrawing groups.

Table IX. Mean Values of $d_{\text{Co-N}}$ (Å), log *k*, $\Delta C(Y^1Y^2Y^3)$, and the EP Parameter

no.	R	$d_{\text{Co-N}}$	log *k*	$\Delta C(Y^1Y^2Y^3)$	EP
1	CCl_2CN	1.992			−1.48
2	CHClCN	2.019	−4.85	−1.09	−1.13
3	$CH(CH_2CN)CN$	2.039	−4.47	−1.12	−1.12
4	CH_2NO_2	2.023	−5.42	−0.96	−0.96
5	$CHBr_2$		−3.28	−0.80	−0.82
6	CH_2CN	2.016	−4.52	−0.77	−0.78
7	$CHCl_2$	2.047	−2.95		−0.70
8	CHMeCN	2.047	−2.88	−0.66	−0.63
9	CH_2CF_3	2.041	−3.56	−0.53	−0.53
10	CH_2I		−2.79	−0.47	−0.47
11	CH_2CO_2Me	2.039	−3.57	−0.46	−0.46
12	CH_2COMe		−3.23	−0.45	−0.44
13	CH_2Br		−2.68	−0.43	−0.41
14	CH_2Cl		−2.43	−0.38	−0.35
15	CH_2CH_2CN	2.050	−1.59	−0.33	−0.34
16	$CHMeCO_2Me$	2.058			−0.31
17	$CH{=}CH_2$	2.073	−1.65	−0.20	−0.20
18	$CH_2C(CO_2Et)_2Me$	2.075	−0.54	−0.02	−0.02
19	Me	2.064	−1.31	0.00	0.00
20	CH_2Ph		−0.48	0.08	0.08
21	CH_2SiMe_3	2.091	−0.49	0.10	0.10
22	Et	2.081	0.00	0.16	0.15
23	CH_2-*i*-Pr		0.19	0.18	0.18
24	CH_2CMe_3	2.081	1.00	0.18	0.18
25	CH_2CH_2Me		0.08	0.19	0.20
26	CH_2OMe		1.38	0.27	0.27
27	*i*-Pr	2.098	1.43	0.31	0.30
28	CHMeEt		1.55	0.34	0.34
29	cyclohexyl	2.106	1.61	0.36	0.35
30	$CHEt_2$		2.00	0.41	0.40
31	adamantyl	2.134	2.57	0.51	0.51

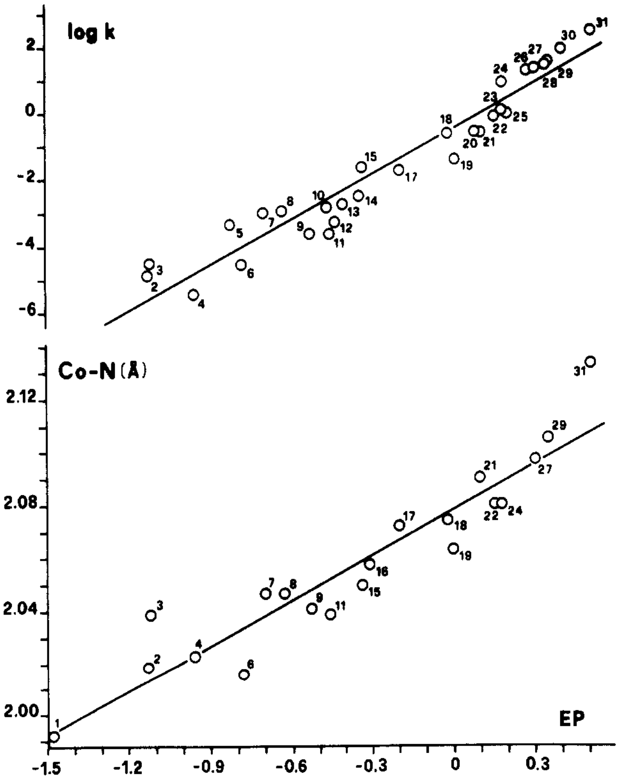

Figure 7. Plots of log *k* and Co–N distances against EP. The linear regressions include all data of Table IX and the numbers correspond to alkyl groups in the same table.

Plots of distances and log *k*'s against the EP values are given in Figure 7. The best fit equations are

$$\log k = -0.4\ (6) + [4.6\ (2)]\text{EP} \qquad r = 0.965 \qquad n = 29 \tag{2a}$$

$$d_{\text{Co-N}} = 2.08\ (1) + [0.058\ (4)]\text{EP} \qquad r = 0.943 \qquad n = 20 \tag{2b}$$

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(27) Randaccio, L.; Bresciani Pahor, N.; Zangrando, E. *Recl. Trav. Pays-Bas* **1987**, *106*, 344.

(28) Data of axial Co–N bond lengths, log *k*, and ^{13}C NMR shifts for the series $LCo(DH)_2R$ with L = py, 4-CNpy, 4-*t*-Bupy, Me_3Bzm, Me_2Im, 1-MeIm, $2\text{-}NH_2py$ are available as supplementary material. For the Me_3Bzm series, the ^{13}C NMR shifts refer to the B5 carbon atom of Me_3Bzm^2, for the py and 4-*t*-Bupy series, they refer to the γ-C of py.

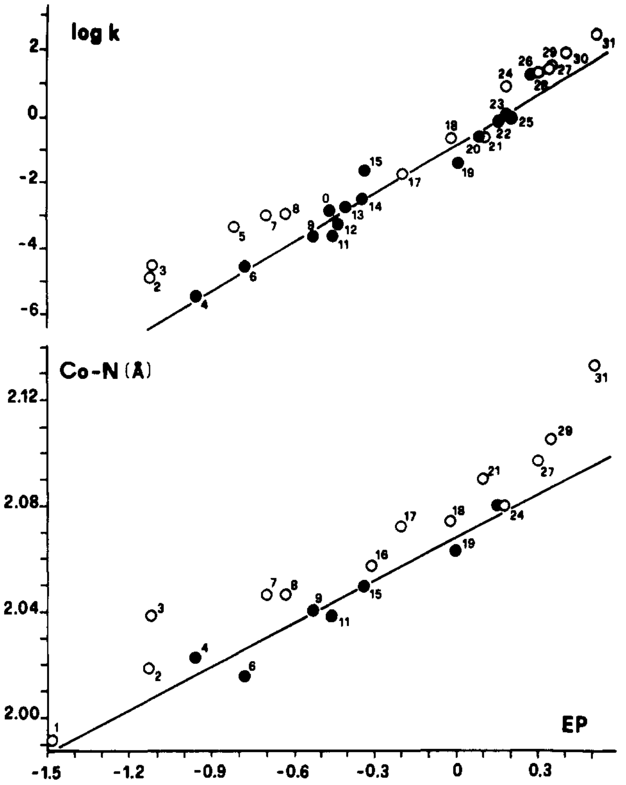

Figure 8. Plots of log k and Co–N distances against EP. The linear regressions include only data relative to derivatives of Table IX with less bulky alkyl groups (solid circles). Open circles represent data not included in the linear regressions. Numbers correspond to alkyl groups in Table IX.

These relationships indicate that both the trans influence (distances) and the trans effect (log k's) reflect the σ-donor ability of R in a similar way. However, significant deviations are observed, especially at the extreme "sides" of the EP values, i.e. for strong σ-donating and σ-withdrawing groups. With a few exceptions, these R groups have more than one substituent at the C atom bonded to Co and presumably they have a larger bulk. This suggests that other effects, mainly steric in origin, may play a role within the general trend. In fact, in the series with L = $P(OMe)_3$, py, Me_3Bzm, and alkyl groups in a limited range of σ-donating ability, i.e. Me, Et, *i*-Pr, and adamantyl, the analysis of Co–N distances and log k's as a function of EP suggested that the steric effect on rates is reflected significantly in the transition state mainly for the adamantyl derivative.[29] This observation is consistent with the present analysis. In fact, when the linear regressions in (2) are limited to those cobaloximes of Table IX having alkyl groups presumably with little or negligible bulk, i.e. CH_2Y groups where Y is not bulky, the following equations are obtained:

$$\log k = -0.7\ (4) + [5.0\ (3)]\mathrm{EP} \qquad r = 0.979 \qquad n = 15 \tag{3a}$$

$$d_{\mathrm{Co-N}} = 2.068\ (6) + [0.055\ (6)]\mathrm{EP} \qquad r = 0.967 \qquad n = 7 \tag{3b}$$

Compared with eq 2, they indicate an improvement of the linear relationship. The corresponding diagrams are given in Figure 8, where points relative to all the alkyl groups are reported. Those relative to data included in the regressions in (3) are marked by a solid circle; the remaining points are denoted by an open circle. Both for distances and log k's, it is apparent that all the points representative of bulky alkyl groups lie above the best line passing through the points relative to the less bulky R and the displacement above the line increases with the increase of the absolute value of EP (Figure 8), i.e. with a general increase of the bulk of R. The trends represented in Figure 8 are a clear indication that EP is a good measure of the σ-donor power of R and that contribution from steric influences can be evidentiated, at least qualitatively. Furthermore, the displacement of $d_{\mathrm{Co-N}}$ values from the line are relatively larger than those of log k for the same alkyl group. This suggests that the influence of the bulk, when significant, should affect both the ground and the transition states.

In conclusion, the EP parameter seems to be an acceptable measure of the electronic effects transmitted from one to the other axial ligand throughout the metal center. However, the following point should be stressed, taking into account the intrinsic nature of the properties that are compared. EP parameters, derived from chemical shifts, may be influenced by Co anisotropy effects and possibly by steric factors; bond lengths can be affected by steric influence; and log k's can be influenced by steric effects in both the ground and the transition states. The present analysis has shown clearly that steric influences play a role, but no indication is available as to the EP parameter "disturbance". Therefore, we are extending our studies to analogous complexes containing Rh instead of Co, where the metal anisotropy should be negligible and the steric effects probably less important.

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Registry No. I, 125227-63-6; II, 125249-49-2; III, 125227-64-7; IV, 125227-65-8; $Me_2ImCo(DH)_2Cl$, 110294-32-1; CCl_3CN, 545-06-2; $H_2OCo(DH)_2CH_2N$, 58079-60-0; $H_2OCo(DH)_2Me$, 25360-55-8; 4-$CNpyCo(DH)_2$-*i*-Pr, 52970-67-9; $H_2OCo(DH)_2$-*i*-Pr, 30974-89-1.

Supplementary Material Available: Tables of complete crystal data, anisotropic thermal parameters, hydrogen atom coordinates, and complete bond lengths and angles for compounds I–IV and tables of axial Co–N bond lengths, log k, ^{13}C NMR shifts, $\Delta C(Y^1Y^2Y^3)$, and their scaled values (see text) for the series $LCo(DH)_2R$ with L = py, 4-CNpy, 4-*t*-Bupy, Me_3Bzm, Me_2Im, 1-MeIm, and 2-NH_2py (16 pages); tables of structure factors for compounds I–IV (28 pages). Ordering information is given on any current masthead page.

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