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Organocobalt Complexes with Exceptionally Poor Electron-Donating Alkyl Groups. Extension and Quantitation of the Relationship between Structure and NMR Spectra in B_{12} Models

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The crystal and molecular structures of the complex *trans*-bis(dimethylglyoximato)(chlorocyanomethyl)(pyridine)cobalt(III), $(py)Co(DH)_2CH(CN)Cl$ (I), are reported. I crystallizes in space group $P2_1/n$ of the monoclinic system with a = 15.688 (4) Å, b = 12.714 (2) Å, c = 9.513 (3) Å, β = 93.12 (4)°, V = 1894.6 Å^3, Z = 4, D_{measd} = 1.53 g cm^{-3}, and D_{calcd} = 1.55 g cm^{-3}; R = 0.040 for 3007 independent reflections. The Co–N bond length in I of 2.017 (2) Å is the shortest such bond found thus far for a $(py)Co(DH)_2R$ compound. The Co–C bond length of 2.015 (3) Å is the shortest bond to Co from an α-C-disubstituted alkyl group found thus far in a B_{12} model. Other compounds, $LCo(DH)_2R$ with R = cyano-substituted alkyl groups and L = py, 4-CNpy, $PhNH_2$, and $P(OMe)_3$, were also prepared. The crystal and molecular structures of $(py)Co(DH)_2CH_2CH_2CN$ (II) were determined. II crystallizes in space group $P2_12_12_1$ of the orthorhombic system with a = 9.546 (3) Å, b = 12.615 (3) Å, c = 16.082 (3) Å, V = 1936.8 Å^3, Z = 4, D_{measd} = 1.45 g cm^{-3}, and D_{calcd} = 1.45 g cm^{-3}; R = 0.042 for 1606 independent reflections. The rate constants, k_1, for dissociation of 4-CNpy from $(4\text{-}CNpy)Co(DH)_2R$ with R = $CH(CN)Cl$, $CH(CN)CH_2CN$, $CH(Me)CN$, and CH_2CH_2CN were determined. Trends in ^1H, ^{13}C, and ^{31}P NMR spectra were examined for several series of $LCo(DH)_2R$ complexes and compared with the large body of rate, structural, and spectroscopic data available for related $LCo(DH)_2R$ compounds. On the basis of the ^{13}C NMR data for the γ-C in $pyCo(DH)_2R$ compounds, we derived a scale of substituent constants, $\Delta(Y_i)$, for all substituents Y_i on the α-C of R. Good correlations were found between $\sum_{i=1}^{3}\Delta(Y_i)$ and Co–N bond length, log k_1, ^{13}C NMR shifts, and ^{31}P NMR shifts. It was concluded that the influence of Y_i on the properties evaluated is mainly electronic (electronic trans influence). The steric effect of Y_i affects primarily the Co–C bond length (steric cis effect). The series of $\Delta(Y_i)$ values in the order of increasing electron donation was NO_2, CN, CF_3, I $\approx$ CO_2Me, Br, Cl $\approx$ CH_2CN, $C(Me)(CO_2Et)_2$, H, $Si(CH_3)_3$, Ph, Me, Et and larger hydrocarbon groups, OMe.

Introduction

The organocobalt compounds known as cobaloximes were originally studied as models for vitamin B_{12} and for the B_{12} coenzymes.[1] However, these simple compounds, which usually contain two equatorial dimethylglyoximato ligands (DH), now represent the most extensively studied class of metal compounds with both organometallic members, such as $LCo(DH)_2R$, and nonorganometallic members, such as $LCo(DH)_2X$, where L = neutral ligand and R and X are mononegative alkyl and non-alkyl ligands, respectively.[1]

As part of a program aimed at assessing the interrelationship between steric and electronic effects on properties of these compounds, particularly as such properties may relate to those in cobalamins, we report here a study of cobaloxime complexes containing alkyl groups with the strongly electron-withdrawing CN substituent. Such groups serve to close the gap which currently exists between the properties of $LCo(DH)_2X$ and $LCo(DH)_2R$ compounds. With the additional information collected on these compounds, we have been able to derive some quantitative relationships between structural, rate, and NMR spectroscopic trends with the ^{13}C NMR shift in $pyCo(DH)_2R$ and $pyCo(DH)_2X$ compounds. Specifically, it is found that there is additivity for the substituent effects of Y_i for $-CY_1Y_2Y_3$ alkyl groups.

Experimental Section

Reagents. Dichloroacetonitrile was purchased from Fairfield Chemical. All other reagents were from Aldrich and used without further purification.

Instrumentation. NMR spectral measurements were made with Nicolet NB-360 (360 MHz, ^1H), Varian CFT-20 (20 MHz, ^{13}C), and IBM WP-200SY (81.01 MHz, ^{31}P) spectrometers. Ligand substitution reactions were monitored spectrophotometrically with a Perkin-Elmer LAMBDA-3B instrument equipped with a Perkin-Elmer C570-0701 digital temperature controller thermostated at 25.00 ± 0.04 °C.

Rate Measurements. For each compound, the visible spectrum of a methylene chloride solution was recorded and then compared with the visible spectrum obtained after addition of a calculated excess (>20:1) of entering ligand (L′ = $P(OMe)_3$) and allowing sufficient time (estimated by ^1H NMR) for reactions to reach completion. Suitable wavelengths to monitor the exchange reaction were selected in the range 420–435 nm for solutions (0.0015–0.0045 M) of the complexes studied. The data were analyzed as previously described[4,5] and yield classical S_N1 LIM behavior.

Preparations. The complexes were prepared by standard methods[1,4] except for the following.

$PhNH_2Co(DH)_2R$ (R = $CH(CN)CH_2CN$, $CH(Me)CN$). To a solution of $PhNH_2Co(DH)_2Cl$ (3 g) in 90:10 CH_3OH/H_2O (200 mL) under N_2 at −20 to −40 °C was added slowly a solution of $NaBH_4$ (0.55 g in 5 mL of H_2O). Gas was evolved, and the color

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Table I. Crystallographic Data for Compounds I and II[a]

	I	II
formula	$CoClO_4N_6C_{15}H_{20}$	$CoO_4N_6C_{16}H_{23}$
M_r	442.8	422.4
a, Å	15.688 (4)	9.546 (3)
b, Å	12.714 (2)	12.615 (3)
c, Å	9.513 (3)	16.082 (3)
β, deg	93.12 (4)	
V, Å^3	1894.6	1936.8
D_{measd}, g cm^{-3}	1.53	1.45
D_{calcd}, g cm^{-3}	1.55	1.45
Z	4	4
space group	$P2_1/n$	$P2_12_12_1$
μ, cm^{-1}	10.8	9.2
cryst dimens, cm^3	0.02 × 0.02 × 0.03	0.01 × 0.02 × 0.02
no. of reflects measd	5031	2657
no. of indep reflects ($I > 3\sigma(I)$)	3007	1606
R	0.040	0.042
R_w	0.051	0.050

[a] Esd's are given in parentheses.

of the solution changed from brown to green. The gas evolved in this and subsequent reactions is probably H_2, and special caution should be exercised if the reaction is scaled up. The olefin (fumaronitrile, 2.3 g for R = $CH(CN)CH_2CN$ and acrylonitrile, 2.4 mL for R = CH(Me)CN) was then added. After 4 h (for R = $CH(CN)CH_2CN$) or 1 h (R = CH(Me)CN), the temperature of the now reddish orange solution was slowly raised to room temperature and the N_2 purging stopped. The volume was reduced with a rotary evaporator (30 °C) until precipitation began. When left standing at 5 °C overnight, the solution yielded a brownish orange crystalline product. It was collected by vacuum filtration, washed with water, and air-dried. Yields: R = $CH(CN)CH_2CN$, 2.40 g (73%); R = CH(Me)CN, 2.5 g (80%). $PhNH_2Co(DH)_2CH(Me)CN$ was also obtained by using 2-chloropropionitrile (2.7 mL) instead of acrylonitrile.

(py)Co(DH)$_2$R (R = CH(CN)CH$_2$CN, CH(Me)CN). A mixture of $(py)Co(DH)_2Cl$ (3 g) and CH_3OH (300 mL) was stirred under N_2. Dissolution of the starting material occurred upon addition of an aqueous KOH solution (ca. 0.8 g in 5 mL of H_2O). The olefin (fumaronitrile, 2.9 g for R = $CH(CN)CH_2CN$, and acrylonitrile, 2.1 mL for R = CH(Me)CN) was then added, followed by a solution of $NaBH_4$ (0.3 g in 5 mL of H_2O). Gas evolved and the brown solution became wine red. As soon as the gas evolution ceased, acetone (10 mL) was added and the N_2 purging stopped. The volume of the solution was reduced to ~50 mL on a rotary evaporator (30 °C). H_2O (100 mL) was added. The solution (pH ~12) was neutralized to pH 7 with concentrated HCl. $(py)Co(DH)_2CH(CN)CH_2CN$ precipitated immediately as a golden yellow solid. For R = CH(Me)CN, more H_2O (50 mL) was added and the solution when maintained at 5 °C overnight afforded a yellow-orange crystalline compound. The solid material was collected by vacuum filtration, washed with water, and dried. Yields: R = $CH(CN)CH_2CN$, 1.70 g (51%); R = CH(Me)CN, 0.85 g (27%).

(4-CNpy)Co(DH)$_2$R (R = CH(CN)CH$_2$CN, CH(Me)CN). $PhNH_2Co(DH)_2R$ (1 g) was dissolved in warm CH_3OH (50 mL). H_2O (10 mL) and Dowex 50-X8-100 cation-exchange resin (1 g) were added. The mixture was heated at reflux for 1 h. Upon removal of the resin by filtration, 4-CNpy (2.0 g) was added to the warm solution. The resulting solution was set aside, and crystallization occurred after a few days. The deep reddish orange crystals were collected by vacuum filtration, washed with water, and air-dried. Yields: R = $CH(CN)CH_2CN$, 0.63 g (59%); R = CH(Me)CN, 0.40 g (39%).

P(OMe)$_3$Co(DH)$_2$R (R = CH(CN)CH$_2$CN, CH(Me)CN, CH(CN)Cl). $PhNH_2Co(DH)_2R$ (0.5 g) was suspended in CH_2Cl_2 (25 mL) ($CHCl_3$ for R = CH(CN)Cl). $P(OCH_3)_3$ (1.6 mL) was added and the suspension stirred until dissolution occurred (~30 min, R = CH(Me)CN; ~10 h, R = $CH(CN)CH_2CN$; ~24 h, R = CH(CN)Cl). The resulting solution was taken to dryness on a rotary evaporator. The yellow residue was collected by vacuum filtration, washed with absolute diethyl ether, and air-dried. Yields: R = $CH(CN)CH_2CN$, 0.45 g (87%); R = CH(Me)CN, 0.35 g (66%); R = CH(CN)Cl, 0.50 g (94%).

Elemental Analyses. C, H, N analyses performed by Atlantic Microlabs, Inc. (Atlanta, GA), were satisfactory for all new compounds (supplementary material).

Crystal Data. Crystals of I and II were obtained by slow crystallization from CH_3OH/H_2O at room temperature. The unit cell parameters were refined and intensities collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation. Crystal data are given in Table I. Three check reflections intensities were measured after every one hundred reflections. During the data collection for both I and II, no systematic variations were observed. Intensity data were corrected for Lorentz and polarization effects, but not for absorption due to the small size of the crystal used and the low value of μ. Anomalous dispersion corrections for Co and Cl were applied.

Structure Determination and Refinement. The structures were solved by conventional Patterson and Fourier methods and refined by the full-matrix anisotropic least-squares method to final R and R_w values of 0.040 and 0.051 for I and 0.042 and 0.050 for II, respectively. The contribution of hydrogen atoms (held constant, B = 5 Å^2) was included in the final refinement. The hydrogen atom coordinates were fixed at their calculated positions (sp^2, sp^3 hybridization). The parameters of the hydrogen atoms were not refined. The final weighting scheme was $w = 1/\sigma^2(F) + (pF)^2 + q$), where p = 0.02 and q = 1.0 were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin \theta)/\lambda$. Final positional parameters are given in Tables II and III. Atomic scattering factors were those given in ref 2. All the calculations were done by using the Enraf-Nonius CAD4-SDP programs.[3] Tables of anisotropic thermal parameters, calculated and observed structure factors, hydrogen atom fractional coordinates, and a full list of bond lengths and angles are available as supplementary material.

Results

Description of the Structures. ORTEP drawings of the crystallographically independent molecules of I and II with the atom numbering scheme are shown in Figures 1 and 2, respectively.

The four N atoms of the $(DH)_2$ unit are coplanar within ±0.03 Å in I and ±0.07 Å in II. In I, Co is displaced (d)

Table II. Positional Parameters and Their Estimated Standard Deviations of I

atom	x	y	z	atom	x	y	z
Co	0.26753 (3)	0.08136 (3)	0.48830 (4)	C3	0.1813 (2)	0.0214 (3)	0.7152 (3)
Cl	0.30309 (7)	−0.16927 (8)	0.5462 (1)	C4	0.1530 (3)	0.0121 (4)	0.8625 (4)
O1	0.1391 (2)	−0.0457 (2)	0.3538 (3)	C5	0.4619 (2)	0.2819 (3)	0.3696 (4)
O2	0.2974 (2)	0.1233 (2)	0.7817 (2)	C6	0.3920 (2)	0.2032 (3)	0.3815 (4)
O3	0.3916 (2)	0.2184 (2)	0.6219 (3)	C7	0.3498 (2)	0.1501 (3)	0.2603 (3)
O4	0.2448 (2)	0.0307 (2)	0.1958 (2)	C8	0.3743 (3)	0.1678 (3)	0.1127 (4)
N1	0.1706 (2)	−0.0066 (2)	0.4758 (3)	C9	0.3485 (2)	−0.0416 (3)	0.5036 (4)
N2	0.2474 (2)	0.0734 (2)	0.6819 (3)	C10	0.4203 (2)	−0.0246 (3)	0.6087 (4)
N3	0.3614 (2)	0.1757 (2)	0.4997 (3)	C11	0.1877 (2)	0.2837 (3)	0.5593 (4)
N4	0.2895 (2)	0.0882 (2)	0.2952 (3)	C12	0.1367 (3)	0.3707 (3)	0.5436 (4)
N5	0.1893 (2)	0.2066 (2)	0.4634 (3)	C13	0.0827 (3)	0.3801 (3)	0.4256 (4)
N6	0.4699 (2)	−0.0121 (3)	0.6809 (4)	C14	0.0831 (2)	0.3023 (3)	0.3256 (4)
C1	0.0593 (3)	−0.0953 (3)	0.6065 (5)	C15	0.1368 (2)	0.2175 (3)	0.3466 (4)
C2	0.1357 (2)	−0.0273 (3)	0.5938 (4)				

Table III. Positional Parameters and Their Estimated Standard Deviations of II

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.2509 (1)	0.11989 (5)	0.24162 (4)	C4	−0.1376 (7)	0.2072 (5)	0.1411 (5)
O1	0.3701 (5)	0.2581 (3)	0.1201 (3)	C5	0.3895 (8)	−0.0655 (6)	0.4396 (4)
O2	−0.0388 (4)	0.0760 (4)	0.2717 (3)	C6	0.3718 (7)	0.0037 (5)	0.3656 (4)
O3	0.1314 (5)	−0.0109 (4)	0.3657 (3)	C7	0.4854 (7)	0.0562 (5)	0.3220 (4)
O4	0.5393 (4)	0.1720 (4)	0.2174 (3)	C8	0.6362 (7)	0.0414 (6)	0.3468 (5)
N1	0.2517 (6)	0.2158 (3)	0.1519 (3)	C9	0.2287 (8)	0.2377 (5)	0.3240 (4)
N2	0.0559 (5)	0.1287 (4)	0.2237 (3)	C10	0.255 (2)	0.3404 (7)	0.3064 (6)
N3	0.2498 (6)	0.0272 (3)	0.3337 (3)	C11	0.245 (2)	0.4073 (7)	0.3844 (6)
N4	0.4445 (5)	0.1158 (4)	0.2632 (3)	C12	0.3667 (9)	−0.0112 (6)	0.1051 (4)
N5	0.2695 (6)	−0.0071 (4)	0.1629 (3)	C13	0.387 (1)	−0.0982 (7)	0.0536 (5)
N6	0.222 (1)	0.4576 (5)	0.4391 (4)	C14	0.299 (1)	−0.1846 (6)	0.0637 (5)
C1	0.1117 (7)	0.3192 (5)	0.0524 (4)	C15	0.203 (1)	−0.1836 (6)	0.1243 (6)
C2	0.1318 (7)	0.2407 (4)	0.1212 (3)	C16	0.1866 (9)	−0.0921 (6)	0.1716 (5)
C3	0.0130 (6)	0.1895 (5)	0.1640 (4)				

Table IV. First-Order Rate Constants (s^{-1}) for L Exchange of $LCo(DH)_2R$ with $P(OMe)_3$ in CH_2Cl_2 at 25 °C

R	$PhNH_2Co(CH)_2R$	(4-CNpy)$Co(DH)_2R$	(py)$Co(DH)_2R$
CH(CN)Cl		$(1.38 \pm 0.03) \times 10^{-5}$	
CH_2CN		$(3.0 \pm 0.3) \times 10^{-5}$[a]	
$CH(CN)CH_2CN$	$(2.53 \pm 0.02) \times 10^{-4}$	$(3.4 \pm 0.1) \times 10^{-5}$	
CH(Me)CN	$(2.06 \pm 0.02) \times 10^{-2}$	$(1.321 \pm 0.006) \times 10^{-3}$	$(7.0 \pm 0.1) \times 10^{-5}$
CH_2CH_2CN		$(2.57 \pm 0.06) \times 10^{-2}$	
Me	1.51 ± 0.04[a]	$(4.1 \pm 0.3) \times 10^{-2}$[b]	$(8.0 \pm 0.8) \times 10^{-3}$[c]

[a] From ref 6. [b] From ref 4. [c] From ref 2, p 82.

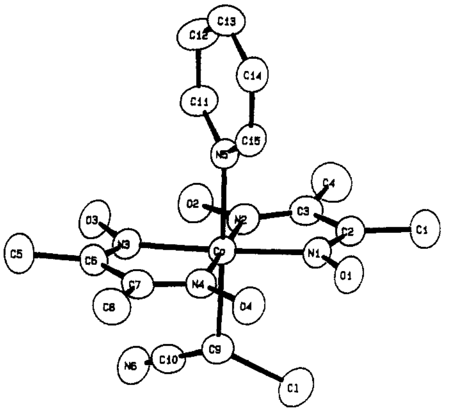

Figure 1. ORTEP drawing and labeling scheme for non-hydrogen atoms of I (thermal ellipsoids, 50% probability).

by 0.02 Å from their mean plane toward the axial alkyl group. The dihedral angle, α, between the planes passing through the two DH units is −7.0°, which is due partly to a bending toward py and partly to a twist of the two planes. In II, Co is displaced towards py with d = 0.04 Å, and the binding of the two DH units is toward CH_2CH_2CN with α = +2.7°.

The py–Co–CH(CN)Cl axial fragment is characterized by Co–N and Co–C distances, which are 2.017 (2) and 2.015 (3) Å, respectively, with a Co–Co–N angle of 177.0 (1)°. The CH(CN)Cl group has Co–C–Cl, Co–C–CN and Cl–C–CN angles of 117.0 (2), 112.9 (2), and 105.8 (2)°, respectively, and the C–Cl and C–CN bond lengths are 1.827 (3) and 1.481 (5) Å, respectively. The py–Co–CH_2CH_2CN fragment in II is characterized by Co–N and Co–C distances of 2.050 (5) and 2.002 (7) Å, respectively, with a C–Co–N angle of 176.4 (3)°. The Co–C–C, CH_2–CH_2–C, and CH_2–C–N angles and CH_2–CH_2, CH_2–C, and C–N distances are limited somewhat in accuracy by the large thermal motion of C(10), C(11), and N(6) (Table III).

The geometry of the Co–CH(CN)Cl group, especially Co–C(9)–X angles, indicates that the bonding to Co does not require strong deformations in the substituted alkyl group, as was found in CH_2CMe_3 and *i*-Pr analogues.[1]

Solution Studies. The results of the rate and NMR spectroscopic measurements, obtained as described in the Experimental Section, are summarized in Tables IV and VI. Also contained in these tables are relevant crystallographic information (Table V), a number of each R to be used in the figures below (Table VI), and the value of the EP (electronic parameter) for each R to be defined below (Table VI).

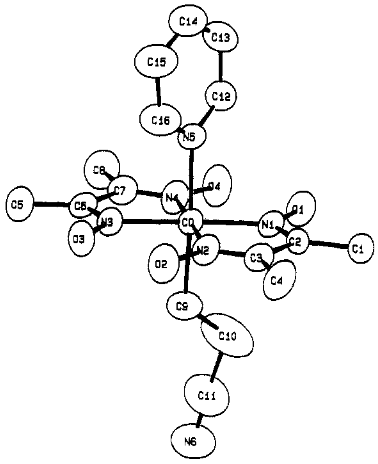

Figure 2. ORTEP drawing and labeling scheme for non-hydrogen atoms of II (thermal ellipsoids, 50% probability).

Discussion

Structural Comparisons. The Co–C bond length of 2.002 (7) Å in II is comparable to that of the Me analogue (1.998 (5) Å).[1] The Co–N distance of 2.050 (5) Å is only slightly shorter than that of 2.068 (3) Å reported for the Me derivative. These data suggest that the steric interaction of CH_2CH_2CN with the equatorial ligands as well as its electronic trans influence is comparable to that of (py)$Co(DH)_2Me$. It is of interest to compare the geometry of the axial fragment of II with that of the analogous complex (py)$Co(PH)_2CH_2CH_2CN$, where the Co–C and

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(6) Summers, M. F.; Bayo, F., unpublished results.

(7) Bresciani-Pahor, N.; Marzilli, L. G.; Randaccio, L.; Toscano, P. J.; Zangrando, E. *J. Chem. Soc., Chem. Commun.* **1984**, 1508.

(8) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Summers, M. F.; Ramsden, J. H.; Marzilli, P. A.; Marzilli, L. G. *Organometallics* **1985**, *4*, 2086.

Table V. γ-^{13}C NMR Shifts (ppm) and Axial Bond Lengths for $LCo(DH)_2R$ Complexes[a]

	γ-^{13}C NMR				
R	L = 4-*t*-Bupy	L = py	Co–N(py), Å	Co–C, Å	α, deg
CH(CN)Br		138.64			
$CH(CN)CH_2CN$	163.27	138.62			
CH(CN)Cl		138.60	2.017	2.015	-7.0
CH_2NO_2	163.09	138.48	2.028	2.002	0.2
CH_2CN		138.25			
$CHBr_2$	162.87				
CH(Me)CN		138.17	2.047	2.053	
CH_2CF_3	162.50	138.03	2.041[c]	2.010	1.0
CH_2CO_2Me	162.45	137.97	2.039	2.024	
CH_2Br	162.37	137.96			
CH_2I		137.98			
CH_2CH_2CN		137.80	2.050	2.002	2.7
DDT	162.26	137.79			
$CH(CO_2Me)Me$			2.058	2.083	
$CH{=}CH_2$	162.06	137.72			
$CH_2C(Me)(CO_2Et)_2$		137.53	2.075	2.047	-12.3
Me	161.84	137.48	2.068	1.998	3.2
CH_2Ph	161.73	137.40[b]			
CH_2SiMe_3	161.67	137.42	2.091	2.031	-1.2
Et	161.59	137.34	2.081[d]	2.035	9.1
CH_2-*i*-Pr		137.32			
CH_2CMe_3	161.53	137.29	2.081	2.060	-5.2
CH_2OMe		137.24			
i-Pr	161.37	137.21	2.099	2.085	4.0
CH(Me)Et		137.17			
c-C_6H_{11}		137.15			
$CHEt_2$		137.10			
CH(Me)(*i*-Pr)		137.10			
adamantyl		137.00	2.102[e]	2.160	-10.2

[a] From ref 1 (p 54) or this work, except as indicated. [b] Reference 6. [c] L = 4-CNpy. [d] L = 4-N(H)=C(OMe)py. [e] L = $4\text{-}Me_2Npy$, unpublished result.

Table VI[a]

alkyl	EP	log k_1	$\delta[^{13}C(P(OMe)_3)]$	$\delta[^{31}P(P(OMe)_3)]$
1. CH(CN)Cl	-1.10	-4.85	53.89[b]	115.74[b]
2. $CH(CN)CH_2CN$	-1.07	-4.47	53.88[b]	116.20[b]
3. CH_2NO_2	-0.98	-5.37	53.75	
4. $CH(Br)_2$	-0.88	-3.28	53.62	
5. CH_2CN	-0.75	-4.52	53.40	122.2
6. $CH(Cl)_2$	-0.70		53.41	122.4
7. CH(Me)CN	-0.63	-2.88	53.36[b]	122.48[b]
8. CH_2CF_3	-0.55	-3.57	53.19	121.9
9. CH_2I	-0.50	-2.79	52.95	
10. CH_2CO_2Me	-0.49	-3.57	53.10	
11. CH_2Br	-0.44	-2.58	52.87	126.3
12. $CH(CO_2Me)Me$	-0.37			
13. CH_2Cl	-0.35	-2.51	52.77	126.5
14. CH_2CH_2CN	-0.32	-1.59	52.71[b]	123.80[b]
15. $CH_2C(Me)(CO_2Et)_2$	-0.05	-0.51		
16. Me	0	-1.39	52.24	128.96[b]
17. CH_2SiMe_3	+0.06	-0.37	52.54	
18. CH_2Ph	+0.08	-0.48	52.46	
19. Et	+0.12	-0.02	52.16	131.1
20. *n*-Pr	+0.18	0.08	52.20	
21. CH_2CMe_3	+0.19	1.04	52.36	
22. CH_2-*i*-Pr	+0.20	0.15	52.25	130.6[c]
23. *i*-Pr	+0.24	1.43	52.18	131.9
24. CH_2OMe	+0.24	1.38		
25. CH(Me)Et	+0.30	1.60	52.16	
26. cyclohexyl	+0.32	1.59	52.20	
27. $CH(Et)_2$	+0.36	2.00	52.22	
28. CH(Me)(*i*-Pr)	+0.38	1.92		
29. adamantyl	+0.48		52.27[c]	136.7[c]

[a] $CDCl_3$ was the solvent for NMR studies; ^{13}C and ^{31}P chemicals shifts were referenced to internal Me_4Si and external H_3PO_4, respectively. [b] From the present work; other data come from ref 1, p 62, except as indicated. [c] Reference 8.

Co–N(py) distances are 2.005 (5) and 2.094 (4) Å, respectively.[9] The PH ligand differs from DH in having two phenyl groups instead of two methyl groups. The larger Co–N bond length in this compound compared to that in II could be due to a larger steric interaction of the py moiety with the two phenyl groups of the equatorial moiety than that with the methyl groups in II.

In contrast to the relatively normal distances in II, the Co–C bond length of 2.015 (3) Å in I is the shortest dis-

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[9] Uchida, A.; Ohashi, Y.; Sasada, Y.; Ohgo, Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 25.

Table VII. $\Delta'(Y)$ **and** $\Delta(Y)$ **Values of Y Groups Bonded to C for L = 4-*t*-Bupy and py**

Y	$\Delta'(Y)$	$\Delta(Y)$
NO_2	−1.25	−0.98
CN		−0.75[a]
CF_3	−0.66	−0.55
CO_2Me	−0.61	−0.49
Br	−0.52[a]	−0.44[a]
I		−0.50
Cl		−0.35
CH_2CN		−0.32
$C(Me)(CO_2Et)_2$		−0.05
H	0	0
$SiMe_3$	+0.17	+0.06
Ph	+0.11	+0.08
Me	+0.24[a]	+0.12[a]
i-Pr		+0.16
CH_2–		+0.16[b]
Et		+0.18
CMe_3	+0.31	+0.19
OMe		+0.24

[a] Mean values. [b] Mean value calculated from the following equations: $\Delta(c\text{-}C_6H_{11}) = 2\Delta(CH_2\text{–})$ and $\Delta(\text{adamantyl}) = 3\Delta(CH_2\text{–})$.

tance so far reported for a disubstituted alkyl group bound to cobalt. Furthermore, the Co–N bond length of 2.017 (2) Å (the lowest value so far observed for alkylcobaloximes) indicates that the σ-donor power of the carbon atom bonded to Co is significantly decreased by the electron-withdrawing substituents Cl and CN, approaching that of a poor σ-donor non-alkyl ligand such as N_3. In $(py)Co(DH)_2N_3$, the Co–py distance is 1.973 (1) Å, which should be compared with that of 2.099 (2) Å in $(py)Co(DH)_2$-*i*-Pr.[1]

A Scale of Electronic Parameters for Octahedral Cobaloximes. The short Co–N distance in $(py)Co(DH)_2CH(CN)Cl$ was expected, based on the py γ-C ^{13}C NMR shift and our previous findings on this series of compounds.[10] We showed that the Co–N(py) bond length is clearly sensitive to the electronic nature of the substituents at the α-C bonded to cobalt. Thus, the Co–N bond lengthens with the increasing electron-donating ability of these substituents: e.g., for R = CH_2NO_2 the Co–N(py) distance of 2.028 (3) Å is shorter than that of 2.091 (5) Å for R = CH_2SiMe_3. On the other hand, we have also shown that ^{13}C NMR shifts, particularly of nuclei remote from Co, reflected this bond length trend.[11] In fact, a fairly linear relationship was found between Co–N(py) distances and γ-^{13}C NMR shifts of the corresponding 4-*t*-Bupy analogues.[1]

Since then, we have gathered more ^{13}C NMR and crystallographic data (Table V). Therefore, a more complete analysis of the $LCo(DH)_2CY_1Y_2Y_3$ series (where Y_1, Y_2, and Y_3 are the substituents on the α-carbon of the alkyl) seemed warranted. We find that (i) the γ-^{13}C NMR shifts for L = py linearly correlate with those for L = 4-*t*-Bupy for all the $CY_1Y_2Y_3$ groups and (ii) the difference, $\Delta(CY_1Y_2Y_3)$, between the shift of the Me derivative and that of the $CY_1Y_2Y_3$ group in the py series could be related by a simple relation:

$$\Delta(CY_1Y_2Y_3) = \Delta(Y_1) + \Delta(Y_2) + \Delta(Y_3) \qquad (1)$$

Using data from Table V, we have calculated the $\Delta(Y_i)$ values and also the related $\Delta'(Y_i)$ values for 4-*t*-Bupy complexes (Table VII). When it was possible to apply relation 1 to more than one compound, mean values for $\Delta(Y_i)$ and $\Delta'(Y_i)$ were obtained.

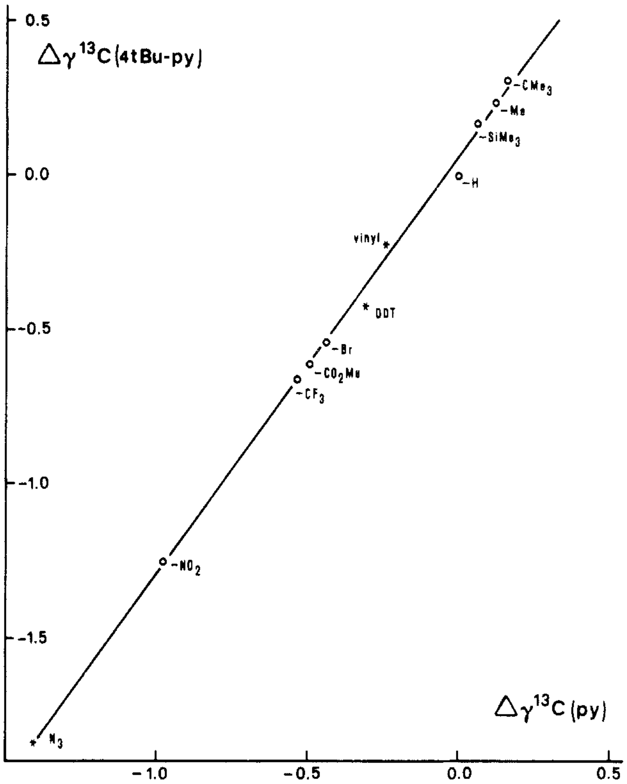

Figure 3. Δ_γ-^{13}C NMR (4-*t*-Bupy) ($\Delta'(Y)$) vs. Δ_γ-^{13}C NMR (py) ($\Delta(Y)$) shifts for different CH_2X substituents. Points with an asterisk correspond to non-alkyl groups (DDT:$C(Cl){=}CPh_2$).

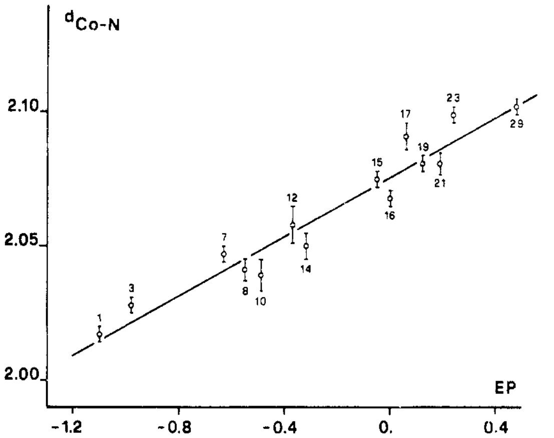

Figure 4. Co–N distances (Å) vs. electronic parameters, EP. Numbers correspond to alkyl groups in Table VI.

Point i is clearly illustrated in Figure 3 where the $\Delta'(Y_i(\Delta_\gamma\text{-}^{13}C))$ for 4-*t*-Bupy are plotted against $\Delta(Y_i(\Delta_\gamma\text{-}^{13}C))$ for py. The linear regression gives the following equation

$$\Delta'(Y_i) = 0.050 + 1.322\Delta(Y_i) \text{ with } r = 0.9983 \ (n = 9) \qquad (2)$$

This relationship appears to hold also for groups other than alkyls as shown by the starred points in Figure 3 and the excellent linear correlation for the 11 points in this figure.

If additivity also holds for Co–N bond lengths (D(Co–N)), the latter should be expressed by the simple relationship

$$D(\text{Co–N}(\text{–}CY_1Y_2Y_3)) = a + K(\Delta(Y_1) + \Delta(Y_2) + \Delta(Y_3)) = a + K(\text{EP}) \qquad (3)$$

where a should be the value of the Co–N distance in the methyl analogue.

The sum $\sum_{i=1}^{3}\Delta(Y_i)$ is called the electronic parameter (EP) because our past studies have revealed that the Co–N

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[10] Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347.

[11] See ref 1, p 104.

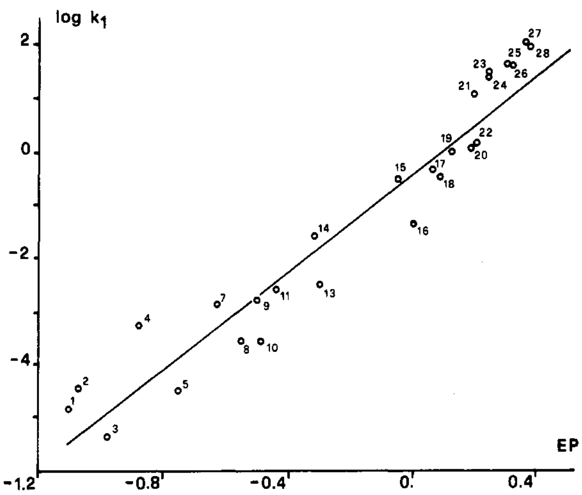

Figure 5. Log k_1 for the displacement of 4-CN-py from (4-CNpy)Co(DH)$_2$R vs. EP. Numbers correspond to alkyl groups in Table VI.

bond length is mainly dependent on the electronic character of the alkyl groups. The DCo–N values in Table V are plotted against EP in Figure 4. In some cases, we have found that the equatorial ligand system is distorted with a "butterfly" type bending defined by the dihedral angle α. A negative α value is a bending toward the neutral L ligand. Although this steric effect on bond length is of secondary importance, in the (py)Co(DH)$_2$CH$_2$C(Me)(CO$_2$Et)$_2$ ($\alpha = -12.3°$) and the adamantyl ($\alpha = -10.2°$) derivatives where the α values are larger, the steric trans influence may have contributed significantly to the lengthening of the Co–N bonds. However, when the data for the complexes with these two alkyl groups are included, a linear regression calculation gives D(Co–N) = 2.076 + 0.055EP ($r = 0.967$ with $n = 14$). Thus, we conclude that steric factors are not significant in the analysis and eq 3 is valid.

Similar relationships should be valid for other properties of these complexes. In fact, if log k_1 for the displacement reaction of 4-CNpy ligand in the (4-CNpy)Co(DH)$_2$CY$_1$Y$_2$Y$_3$ series is plotted against its EP value, the linear relationship of Figure 5 is obtained. Its equation is

$$\log k_1 = -0.318 + 4.691\mathrm{EP} \text{ with } r = 0.9652\ (n = 26)$$

A linear relationship is also obtained when ^{13}C NMR shifts of the P(OMe)$_3$ group in the series P(OMe)$_3$Co(DH)$_2$CY$_1$Y$_2$Y$_3$ are plotted against EP parameters. The corresponding equation is

$$\delta(^{13}\mathrm{C\ NMR}) = 52.50 - 1.185\mathrm{EP} \text{ with } r = 0.9745\ (n = 25)$$

The following relationship

$$\delta(^{31}\mathrm{P\ NMR}) = 129.77 + 12.067\mathrm{EP} \text{ with } r = 0.9818\ (n = 14)$$

was obtained by plotting (Figure 6) the ^{31}P NMR shifts of P(OMe)$_3$ in the series of complexes against the EP values. On the contrary, for the ^{31}P NMR shifts for the Ph$_3$PCo(DH)$_2$CY$_1$Y$_2$Y$_3$ series,[12] only a poor linear relationship is observed, although the same general trend as in the other series is observed.

The values of EP for acido ligands (NO$_2$, CN, Cl, etc.) can be obtained from the ^{13}C NMR shift of the γ-C of the 4-t-Bupy series and eq 2. (The shifts for the γ-C of the py series are not available for most X.) The EP values, which in the case for X ligands represent the total effect of the ligand and not a summation of substituent effects, were as follows: NO$_3$ (−1.927); Cl (−1.56); Br (−1.46); I (−1.30); N$_3$ (−1.43); NO$_2$ (−1.53); CN (−1.58); p-CH$_3$PhSO$_2$ (−1.13); P(O)(OMe)$_2$ (−0.73); P(O)(Ph)$_2$ (−0.45); DDT (−0.36); p-C$_6$H$_4$Br (−0.35); CH$_2$CH (−0.20). Thus, the EP values range from ~−2 to ~0.5 with an overlap of ~0.6 unit between alkyl and non-alkyl compounds. Most of the non-alkyl ligands are incapable of promoting L dissociation at reasonable rates, and the most extensive comparison is possible for the ^{13}C NMR shift of P(OMe)$_3$ in the P(OMe)$_3$Co(DH)$_2$ (R or X) series.[13-15] For the 38 compounds where a comparison is possible, the relationship is

$$\delta(^{13}\mathrm{C\ NMR}) = 52.47 - 1.473\mathrm{EP} \text{ with } r = 0.969$$

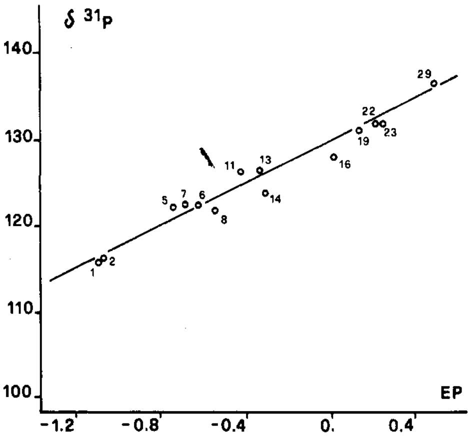

Figure 6. ^{31}P NMR shifts of P(OMe)$_3$Co(DH)$_2$R vs. electronic parameters, EP. Numbers correspond to alkyl groups in Table VI.

Thus, in all cases, the results support the utility of the EP concept and indicate that there is no particular difference between the organometallic and non-organometallic compounds except that the organometallic compounds are, in general, better electron donors. Although the correlations we have found can be considered good, clearly they are not excellent. For example, steric effects may influence rates.[16] Since reaction rates are also influenced by the nature of the transition state, it could be that different substituent parameters may be necessary, in the final analysis, to account for NMR data and for rate data. Furthermore, we have focused on ^{13}C signals for C atoms fairly remote from the Co center. This is because the Co heavy-atom effect (Co anisotropy) can influence shifts of nuclei in coordinated ligands. This effect decreased severely with increasing distance of the resonating nucleus from Co, as suggested by the dipole model.[14,17-22]

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Interpretation of shifts of signals closer to the metal center is even more complex.[22] No doubt, because of this complexity, we know of no successful extensive correlations of the types described here in other organometallic systems. Clearly, more work is needed particularly in view of the initial success in correlating shifts of ^{1}H, ^{31}P, and ^{13}C shifts of alkylcobalamins with changes in their structure and thermodynamic properties.[19,22]

In conclusion, we have shown that, particularly with regard to ^{13}C NMR shifts, the effects of substituent Y on the α-C of an alkyl group appear to have an additive effect. The substituent effects can be quantitated and the analysis gives a substituent constant, ΔY. With these constants, a second constant (EP) for the entire ligand can be calculated. The EP values can be extended with ^{13}C NMR data to acido ligands.

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Registry No. I, 103751-75-3; II, 28136-56-3; (py)Co(DH)$_2$CH(CN)CH$_2$CN, 14783-94-9; (py)Co(DH)$_2$CH(Me)CN, 28136-55-2; (4-CNpy)Co(DH)$_2$CH(CN)CH$_2$CN, 103751-60-6; (4-CNpy)Co(DH)$_2$CH(Me)CN, 103881-18-1; P(OMe)$_3$Co(DH$_2$)CH(CN)CH$_2$CN, 103751-61-7; P(OMe)$_3$Co(DH)$_2$CH(Me)CN, 103751-62-8; P(OMe)$_3$Co(DH)$_2$CH(CN)Cl, 103751-63-9; PhNH$_2$Co(DH)$_2$Cl, 23575-27-1; (py)Co(DH)$_2$Cl, 23295-32-1; PhNH$_2$Co(DH)$_2$CH(CN)Cl, 103751-64-0; (4-CNpy)Co(DH)$_2$CH(CN)Cl, 103751-65-1; (4-CNpy)Co(DH)$_2$CH$_2$CN, 103751-66-2; (4-CNpy)Co(DH)$_2$CH$_2$CH$_2$CN, 103751-67-3; (4-*t*-Bupy)Co(DH)$_2$CH(CN)CH$_2$CN, 103751-68-4; (4-*t*-Bupy)Co(DH)$_2$CH$_2$NO$_2$, 103751-69-5; (4-*t*-Bupy)Co(DH)$_2$CHBr$_2$, 55886-72-1; (4-*t*-Bupy)Co(DH)[2CH$_2$CF$_3$, 103751-70-8; (4-*t*-Bupy)Co(DH)$_2$CH$_2$CO$_2$Me, 103751-71-9; (4-*t*-Bupy)Co(DH)$_2$CH$_2$Br, 55886-76-5; (4-*t*-Bupy)Co(DH)$_2$DDT, 103751-72-0; (4-*t*-Bupy)Co(DH)$_2$CH=CH$_2$, 103751-73-1; (4-*t*-Bupy)Co(DH)$_2$Me, 51194-36-6; (4-*t*-Bupy)Co(DH)$_2$CH$_2$Ph, 55886-75-4; (4-*t*-Bupy)Co(DH)$_2$CH$_2$SiMe$_3$, 55886-77-6; (4-*t*-Bupy)Co(DH)$_2$Et, 55886-79-8; (4-*t*-Bupy)Co(DH)$_2$CH$_2$CMe$_3$, 103751-74-2; (4-*t*-Bupy)Co(DH)$_2$Pr-*i*, 55886-80-1; (py)Co(DH)$_2$CH(CN)Br, 81853-27-2; (py)Co(DH)$_2$CH$_2$C(Me)(CO$_2$Et)$_2$, 57620-61-8; (py)Co(DH)$_2$CH$_2$NO$_2$, 73202-88-7; (py)Co(DH)$_2$CH$_2$CN, 56498-36-3; (py)Co(DH$_2$CH$_2$CF$_3$, 41659-66-9; (py)Co(DH)$_2$CH$_2$CO$_2$Me, 27902-04-1; (py)Co(DH)$_2$CH$_2$Br, 35654-77-4; (py)Co(DH)$_2$CH$_2$I, 35654-78-5; (py)Co(DH)$_2$Pr-*i*, 30974-90-4; (py)Co(DH)$_2$DDT, 103751-76-4; (py)Co(DH)$_2$CH=CH$_2$, 56710-86-2; PhNH$_2$Co(DH)$_2$CH(CN)CH$_2$CN, 103751-59-3; PhNH$_2$Co(DH)$_2$CH(Me)CN, 14637-49-1; (py)Co(DH)$_2$Me, 23642-14-0; (py)Co(DH)$_2$CH$_2$SiMe$_3$, 42934-31-6; (py)Co(DH)$_2$Et, 25360-57-0; (py)Co(DH)$_2$CH$_2$-*i*-Pr, 29131-79-1; (py)Co(DH)$_2$CH$_2$CMe$_3$, 54631-04-8; (py)Co(DH)$_2$CH$_2$OMe, 35654-83-2; (py)Co(DH)$_2$CH(Me)Et, 54712-55-9; (py)Co(DH)$_2$Cl$_6$H$_{11}$-c, 28206-03-3; (py)Co(DH)$_2$CHEt$_2$, 103751-77-5; (py)Co(DH)$_2$CH(Me)(*i*-Pr), 103751-78-6; (py)Co(DH)$_2$R (R = adamantyl), 65466-85-5; (4-N(H)=C(OMe)py)Co(DH)$_2$Et, 103881-19-2; (4-CNPy)Co(DH)$_2$CH$_2$CF$_3$, 86942-05-4; (4-Me$_2$Npy)Co(DH)$_2$R (R = adamantyl), 103751-79-7; fumaronitrile, 764-42-1; acrylonitrile, 107-13-1; 2-chloropropionitrile, 1617-17-0.

Supplementary Material Available: Tables of elemental analyses, bond lengths and angles, and hydrogen atom coordinates (9 pages); a listing of structure factors (20 pages). Ordering information is given on any current masthead page.

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Mixed Germylenes from (Pentamethylcyclopentadienyl)germanium Chloride and (Pentamethylcyclopentadienyl)germanium Tetrafluoroborate

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(Pentamethylcyclopentadienyl)germanium chloride, Me$_5$C$_5$GeCl (**1**), undergoes replacement of chlorine by various nucleophiles. Nucleophiles also react with the (pentamethylcyclopentadienyl)germanium cation of Me$_5$C$_5$Ge$^+$BF$_4^-$ (**2**) to give new germylene compounds. Reactions with silyl-substituted cyclopentadienides yield unsymmetrical germanocenes Me$_5$C$_5$GeC$_5$H$_{5-n}$(SiMe$_3$)$_n$ (**3**, $n = 1$; **4**, $n = 2$; **5**, $n = 3$), which show no ligand symmetrization reactivity. The germylenes **1** and **2** react with lithium bis(trimethylsilyl)amide, lithium 2,2,6,6-tetramethylpiperidide, and [bis(trimethylsilyl)methyl]lithium to produce substituted germylenes Me$_5$C$_5$GeN(SiMe$_3$)$_2$ (**6**), Me$_5$C$_5$GeNC$_9$H$_{18}$ (**7**), and Me$_5$C$_5$GeCH(SiMe$_3$)$_2$ (**8**). Although they can be considered as redistribution products of decamethylgermanocene with other well-known diorganogermylenes, these unsymmetrically substituted germylenes show no tendency to rearrange into the symmetrical compounds. X-ray structural investigations on **8** show a monomeric species in which the electron deficiency at the Ge center is adjusted by η^2-bonding of the cyclopentadienyl ring. Crystals of **8** are monoclinic, space group $P2_1/a$, with $a = 8.844$ (5) Å, $b = 15.530$ (6) Å, $c = 15.916$ (6) Å, $\beta = 102.37$ (4)°, $V = 2135.3$ Å^3, and $Z = 4$. Refinement using 2485 observed diffractometer data converged at $R = 0.052$ and $R_w = 0.046$.

Introduction

Carbene-analogous, and therefore electron-deficient, compounds of the heavier group 4B (14[30]) elements can be stabilized either kinetically, by using the steric hindrance of bulky ligands, or thermodynamically, by means of additional intramolecular electron donation by the ligands. Of the few stable monomeric diorganogermanium(II) compounds known, most belong to one or another of two groups. The first comprises those species with the germanium linked to highly substituted nitrogen, oxygen, and