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Supplementary Material Available: Listings of elemental

analysis (Table I), mass spectral data of 4,5,6,7-tetrahydro-pyrido[3,4-*d*]imidazole derivatives (Table II), and infrared data of zinc(II) complexes of amino acid Schiff bases (Table V) (4 pages). Ordering information is given on any current masthead page.

Angular Distortions at the Carbon Bound to Cobalt in Coenzyme B₁₂ Models. Implications with Regard to Co-C Bond Cleavage in Coenzyme B₁₂ and Other Alkylcobalamins

Lucio Randaccio,* Nevenka Bresciani-Pahor, Paul J. Toscano, and Luigi G. Marzilli*

Contribution from the Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy, and the Department of Chemistry, Emory University, Atlanta, Georgia 30322. Received March 30, 1981

Abstract: The crystal and molecular structures of the complexes *trans*-bis(dimethylglyoximate)neopentyl(pyridine)cobalt(III) (I) and *trans*-bis(dimethylglyoximate)((trimethylsilyl)methyl)(pyridine)cobalt(III) (II) are reported. Both compounds crystallize in space group *P*3₁ with *a* = 8.814(8) Å, *c* = 23.57 (1) Å, and *D*_{meas} and *D*_{calcd} = 1.37 and 1.38 g cm⁻³, respectively, for I and *a* = 8.870 (5) Å, *c* = 24.72 (1) Å, and *D*_{meas} and *D*_{calcd} = 1.36 and 1.35 g cm⁻³ respectively, for II. For both, *Z* = 3 and 2780 reflections were measured. The structure of I was solved by conventional Patterson and Fourier methods. Block-diagonal least-squares refinement led to a final *R* value of 0.037. The structure of II was refined similarly to a final *R* value of 0.038 by starting with the coordinates of I and substituting Si. The primary coordination sphere about the Co is pseudooctahedral with the usual arrangement of the dimethylglyoximate (DH) ligands occupying the four equatorial positions and the pyridine and alkyl group trans to each other. The Co(DH)₂ unit is relatively planar. Of particular note, the Co-C-Y angle (Y = C or Si) is 130.3 (4)° in I and 127.7 (3)° in II. These unusual values permit the Y(CH₃)₂ fragment to lie in a plane nearly parallel to the Co(DH)₂ plane. Compound I is the first neopentyl transition-metal compound which has been structurally characterized. Angular distortions are believed to be pronounced in unstable alkylcobalamins, and in the B₁₂ coenzyme this angle is 125°. The implications of the present results are discussed in terms of the factors which affect the trans influence and trans effect of the alkyl group. With the addition of the results on I and II, sufficient data are now available on complexes of the type *trans*-alkylbis(dimethylglyoximate)(pyridine)cobalt(III) to discern a clear distortion in the C-Co-N (equatorial) bond angle. Also the Co-N(pyridine) bond length variation in these compounds can now be compared to spectroscopic trends such as ¹³C NMR shifts. Brief comparisons are made to ligand-exchange reactions.

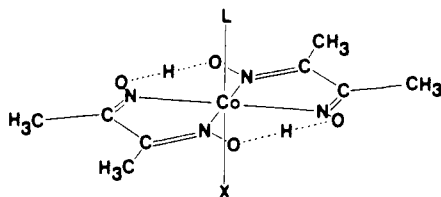
Wider acceptance has recently been accorded to the possibility that a conformational (mechanochemical) change triggers the important Co-C cleavage step in catalytic reactions involving coenzyme B₁₂.¹⁻³ Soluton studies on alkylcobalamins (species in which another alkyl group is substituted for 5'-deoxyadenosine in the coenzyme) have led some investigators to suggest that the Co-C bond length is responsive to steric effects in these organocobalt(III) compounds.⁴⁻⁶ Steric factors are known to be important in destabilizing the Co-C bond in such compounds^{7,8} but the exact nature of the distortions, if any, is uncertain. In model compounds, we have found that the Co-C bond length does indeed respond to steric rather than electronic effects.^{9,10} The bond lengths in structurally characterized complexes vary over a remarkably broad range of ~0.2 Å.¹⁰ Spectroscopic evidence was presented that even longer bonds occur in more sterically hindered systems which have thus far proved to be too unstable for X-ray structural characterization.

An additional factor, which may be an important controller of Co-C bond lability, is a distortion of the Co-C-C bond angle away from the normal tetrahedral value.⁵ Indeed, this angle is 125° in the coenzyme.¹¹ Such a distortion could be viewed as altering the degree of carbon s and p character used in the bond to Co. Of the sterically hindered alkyl groups employed in studies of alkylcobalamins,⁴⁻⁶ the neopentyl group frequently exhibited some of the most pronounced effects. However, to our knowledge, no neopentyl organometallic complex has ever been structurally characterized.

We have prepared neopentyl complexes of one class of vitamin B₁₂ coenzyme model compounds which are known as cobaloximes (the trivial name for complexes such as those containing the Co(DH)₂ unit with DH equal to the monoanion of dimethylglyoxime).¹² Cobaloximes have been shown to respond structurally to changes in the electronic and steric properties of axial ligands in pseudooctahedral complexes of the type LCo(DH)₂X, where L equals neutral and X equals negative monodentate ligands, respectively.^{9,10,13-16} (See structure 1).

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* Address correspondence as follows: L.R., Università di Trieste; L.G.M., Emory University.



The following types of structural distortions have been noted: (a) variation in the Co to axial ligating atom distance for both L and X; (b) displacement (always toward L) of the Co atom above the plane defined by the four N's of the (DH)₂ system, the so-called "doming" effect; (c) angular distortions within L and X; and (d) folding of the (DH)₂ system, away from L, to create a dihedral angle between the individually planar DH units. The structural parameters within each DH unit are not significantly dependent on L or X.

Similarly, large variations in reactivity (up to factors of 10⁵)^{17,18} and appreciable variation of spectral properties¹⁸⁻²³ have been found for closely related cobaloximes. This solid-state and solution diversity provides an opportunity to systematically explore structure-reactivity and structure-spectroscopy relationships. Cobaloximes have the further advantage that a remarkably broad range of X ligands (from the hard NO₃ to soft alkyl ligands) and almost as broad a range of L ligands (with ligating atoms equal to C, O, S, N, P, As, and Sb) can be incorporated.^{12,19,20,23,24} The spectroscopic variations observed for cobaloximes correlate, in many cases, extremely well with those found for other metal complexes.^{24,25}

A need for a full appreciation of the effect of X on structural properties has led us to concentrate our structural studies on systems with L equal to H₂O, pyridine, and triphenylphosphine. In this report, we evaluate in detail the effects of CH₂-Y-(CH₃)₃ ligands (Y = C, Si) in (py)Co(DH)₂CH₂-Y-(CH₃)₃ on the structural parameters described above. When Y = C, a rather large Co-C-C bond angle was found and the implication of this finding with regard to Co-C bond cleavage is discussed.

Experimental Section

(a) Synthesis. The complexes, (py)Co(DH)₂CH₂C(CH₃)₃ (I) and (py)Co(DH)₂CH₂Si(CH₃)₃ (II), were prepared via standard procedures¹⁸ by using neopentyl iodide (Tridom) and (trimethylsilyl)methyl chloride (Aldrich) as alkylating agents, respectively.

(b) Crystal Data. Crystals of I and II were obtained by slow crystallization from acetone/H₂O. The compounds were found to be isomorphous, and their cell dimensions were determined from Weissenberg and precession photographs and refined on a Siemens AED single-crystal diffractometer. The results are given in Table I. One check reflection intensity was measured every 100 reflections in the data collections for both crystals. There was no systematic variation throughout the data recordings. The intensities for which $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption.

(c) Solution and Refinement of Structure. The structure of I was solved by conventional Patterson and Fourier methods and refined by the block-diagonal anisotropic least-squares method to a final *R* value of 0.037. The structure of II was refined in the same way, starting from the atomic positions of I after exchange of C(10) by Si, to a final *R* value of 0.038. The contribution of hydrogen atoms was held constant ($B = 5 \text{ \AA}^2$) in both of the structures.

In the final refinements, the weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 8.6$ (I) and 11.4 (II) and $B = 0.017$ 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 were those given in Ref 26.

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Table I. Crystallographic Data for Compounds I and II

	I	II
formula	CoO ₄ N ₅ C ₁₈ H ₃₀	CoSiO ₄ N ₅ C ₁₇ H ₃₀
mol wt	439.5	455.5
<i>a</i> , Å	8.814 (8)	8.870 (5)
<i>c</i> , Å	23.57 (1)	24.72 (1)
<i>D</i> _{measd.} , g cm ⁻³	1.37	1.36
<i>D</i> _{calcd.} , g cm ⁻³	1.38	1.35
<i>Z</i>	3	3
space group	<i>P</i> 3 ₁	<i>P</i> 3 ₁
μ , cm ⁻¹	7.8	8.8
cryst dimens, cm ³	0.08 × 0.06 × 0.08	0.03 × 0.06 × 0.06
no. of reflctns measd	2780	2780
no. of independent reflctns	2062	1836
max 2 θ , deg (Mo K α)	28	28
<i>R</i>	0.037	0.038

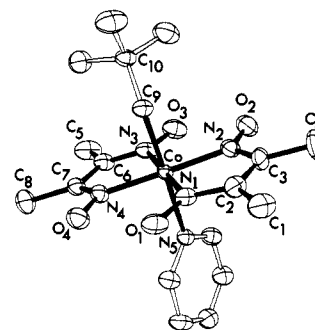


Figure 1. ORTEP drawing and numbering scheme for (py)Co(DH)₂CH₂C(CH₃)₃ (I).

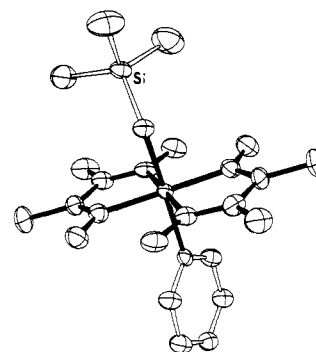


Figure 2. ORTEP drawing for (py)Co(DH)₂CH₂Si(CH₃)₃ (II). Numbering scheme is the same as that in Figure 1, except C(10) is replaced by Si.

Final nonhydrogen positional parameters are collected in Table II. Hydrogen positional parameters, anisotropic thermal parameters, and a list of final calculated and observed structure factors have been deposited. All calculations were done by using the computer programs from X-RAY 72.²⁷

Results and Discussion

Structure. ORTEP drawings of crystallographically independent molecules of I and II with the atom numbering scheme are depicted in Figures 1 and 2, respectively. Bond lengths and selected bond angles are listed in Table III.

The four N atoms of the (DH)₂ unit are coplanar within ± 0.018 Å (I) and ± 0.012 Å (II). The cobalt atom is displaced 0.002 Å (I) and 0.004 Å (II) from their mean plane. The deviation from planarity of the Co(DH)₂ unit is very small in both molecules; the interplanar angles α , β and γ are -5.2 , -1.5 , and -3.5° (I) and -1.2 , 1.5 , and -2.7° (II), respectively, where α is the angle between the two DH units and β and γ are the angles between

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Table II. Nonhydrogen Atom Positional Parameters ($\times 10^4$)

atom	x	y	z
(a) (py)Co(DH) ₂ CH ₂ C(CH ₃) ₃ (I)			
Co	449 (1)	2349 (1)	1500 (1)
O(1)	2446 (5)	2595 (6)	527 (2)
O(2)	400 (6)	5097 (6)	2128 (2)
O(3)	-1661 (5)	2086 (6)	2450 (2)
O(4)	529 (6)	-401 (6)	898 (2)
N(1)	2080 (5)	3466 (6)	920 (2)
N(2)	1130 (6)	4687 (6)	1693 (2)
N(3)	-1233 (5)	1220 (6)	2080 (2)
N(4)	-210 (5)	24 (5)	1327 (2)
N(5)	-1544 (5)	2164 (5)	979 (2)
C(1)	4184 (9)	6294 (10)	470 (3)
C(2)	2851 (7)	5205 (8)	914 (3)
C(3)	2270 (8)	5899 (7)	1363 (3)
C(4)	2900 (11)	7808 (8)	1432 (4)
C(5)	-3540 (9)	-1550 (11)	2481 (3)
C(6)	-2107 (6)	-494 (7)	2069 (2)
C(7)	-1463 (7)	-1193 (7)	1629 (2)
C(8)	-2141 (11)	-3118 (8)	1538 (3)
C(9)	2539 (6)	2530 (7)	1948 (2)
C(10)	2694 (7)	2180 (7)	2575 (2)
C(11)	2478 (11)	3456 (10)	2962 (3)
C(12)	1479 (9)	295 (9)	2759 (3)
C(13)	4574 (9)	2516 (12)	2657 (3)
C(14)	-2675 (7)	2650 (7)	1160 (2)
C(15)	-4036 (7)	2493 (8)	833 (3)
C(16)	-4296 (7)	1775 (8)	306 (3)
C(17)	-3145 (8)	1249 (8)	110 (2)
C(18)	-1787 (7)	1465 (8)	466 (2)
(b) (py)Co(DH) ₂ CH ₂ Si(CH ₃) ₃ (II)			
Co	325 (1)	2392 (1)	1487 (1)
O(1)	2230 (6)	2550 (7)	533 (2)
O(2)	428 (7)	5202 (7)	2081 (2)
O(3)	-1581 (6)	2223 (7)	2429 (2)
O(4)	286 (7)	-427 (6)	906 (2)
N(1)	1904 (6)	3455 (7)	897 (2)
N(2)	1073 (7)	4744 (7)	1656 (2)
N(3)	-1242 (6)	1328 (7)	2059 (2)
N(4)	-388 (7)	32 (6)	1323 (2)
N(5)	-1700 (6)	2210 (6)	1007 (2)
C(1)	4085 (10)	6175 (11)	468 (3)
C(2)	2732 (8)	5164 (9)	887 (3)
C(3)	2208 (8)	5910 (8)	1322 (3)
C(4)	2900 (13)	7848 (10)	1395 (4)
C(5)	-3464 (11)	-1430 (13)	2481 (4)
C(6)	-2101 (8)	-393 (9)	2066 (3)
C(7)	-1563 (8)	-1129 (8)	1635 (3)
C(8)	-2249 (13)	-3049 (9)	1563 (4)
C(9)	2415 (7)	2569 (8)	1882 (2)
Si	2560 (2)	2072 (2)	2606 (1)
C(11)	2275 (18)	3530 (17)	3080 (4)
C(12)	1096 (13)	-263 (12)	2808 (4)
C(13)	4855 (11)	2506 (16)	2678 (4)
C(14)	-2791 (8)	2727 (8)	1188 (3)
C(15)	-4168 (8)	2579 (9)	878 (3)
C(16)	-4449 (7)	1867 (8)	372 (3)
C(17)	-3347 (9)	1308 (9)	181 (3)
C(18)	-1978 (8)	1519 (9)	510 (3)

each of these units and the coordination plane.²⁸ Bond lengths and angles of the Co(DH)₂ moiety are quite normal in both compounds.¹³⁻¹⁶

The R-Co-py fragment is characterized in both structures by a large Co-C(9)-Y angle (Y = C(10) in (I) and Si in (II)), which is 130.3 (4) and 127.7 (3)° in (I) and (II), respectively. These

(28) The angle α very approximately reflects the sum of β and γ . When both β and γ are positive (each DH ligand is displaced toward X), α is defined as positive and the intersection is above (toward L) the equatorial plane defined by the four N atoms. Therefore α is negative when both β and γ are negative. When β and γ have opposite signs, the intersection of the planes occurs on the side of the four N plane which is defined by the largest absolute value of β and γ . In II, α is negative but the intersection of the planes is above the four N plane, the typically observed situation. Such an analysis is somewhat crude because the planes of the DH ligands could be tilted with respect to each other.

Table III. Bond Lengths (Å) and Selected Bond Angles (Deg) for (py)Co(DH)₂CH₂C(CH₃)₃ (I) and (py)Co(DH)₂CH₂Si(CH₃)₃ (II)

	I	II
(a) Bond Lengths		
Co-N(1)	1.867 (4)	1.914 (5)
Co-N(2)	1.891 (5)	1.892 (6)
Co-N(3)	1.893 (2)	1.873 (4)
Co-N(4)	1.874 (5)	1.903 (6)
Co-N(5)	2.081 (4)	2.091 (5)
Co-C(9)	2.060 (6)	2.031 (6)
N(1)-O(1)	1.341 (7)	1.330 (8)
N(2)-O(2)	1.352 (7)	1.352 (9)
N(3)-O(3)	1.332 (7)	1.339 (9)
N(4)-O(4)	1.353 (7)	1.352 (8)
N(1)-C(2)	1.330 (7)	1.314 (8)
N(2)-C(3)	1.297 (7)	1.312 (8)
N(3)-C(6)	1.309 (7)	1.322 (9)
N(4)-C(7)	1.301 (6)	1.291 (7)
C(1)-C(2)	1.508 (9)	1.498 (10)
C(2)-C(3)	1.438 (10)	1.455 (11)
C(3)-C(4)	1.494 (9)	1.519 (11)
C(5)-C(6)	1.492 (8)	1.498 (10)
C(6)-C(7)	1.459 (9)	1.450 (11)
C(7)-C(8)	1.506 (9)	1.505 (10)
C(9)-C(10)[Si]	1.529 (7)	1.863 (6)
C(10)[Si]-C(11)	1.531 (12)	1.854 (15)
C(10)[Si]-C(12)	1.521 (8)	1.880 (9)
C(10)[Si]-C(13)	1.543 (10)	1.883 (11)
N(5)-C(14)	1.337 (9)	1.338 (10)
N(5)-C(18)	1.324 (7)	1.339 (8)
C(14)-C(15)	1.374 (9)	1.392 (10)
C(15)-C(16)	1.360 (9)	1.367 (10)
C(16)-C(17)	1.388 (11)	1.381 (12)
C(17)-C(18)	1.395 (9)	1.394 (11)
O(1)···O(4)	2.476 (6)	2.499 (6)
O(2)···O(3)	2.470 (6)	2.488 (7)
(b) Bond Angles		
N(1)-Co-N(2)	82.0 (2)	81.8 (2)
N(1)-Co-N(3)	179.0 (2)	179.2 (2)
N(1)-Co-N(4)	98.9 (2)	97.9 (2)
N(1)-Co-N(5)	90.4 (2)	89.6 (2)
N(1)-Co-C(9)	85.0 (2)	85.1 (2)
N(2)-Co-N(3)	97.9 (2)	98.8 (3)
N(2)-Co-N(4)	178.5 (2)	178.9 (3)
N(2)-Co-N(5)	91.3 (2)	91.4 (2)
N(2)-Co-C(9)	90.5 (2)	90.3 (3)
N(3)-Co-N(4)	81.3 (2)	81.5 (2)
N(3)-Co-N(5)	88.6 (2)	89.9 (2)
N(3)-Co-C(9)	96.0 (2)	95.4 (2)
N(4)-Co-N(5)	89.9 (2)	89.7 (2)
N(4)-Co-C(9)	88.4 (2)	88.6 (3)
N(5)-Co-C(9)	174.7 (2)	174.1 (2)
Co-C(9)-C(10)[Si]	130.3 (4)	127.7 (3)
C(9)-C(10)[Si]-C(11)	111.8 (6)	113.1 (5)
C(9)-C(10)[Si]-C(12)	114.2 (4)	115.1 (3)
C(9)-C(10)[Si]-C(13)	106.1 (5)	103.8 (4)
C(11)-C(10)[Si]-C(12)	110.8 (5)	110.0 (5)
C(11)-C(10)[Si]-C(13)	107.5 (6)	108.0 (6)
C(12)-C(10)[Si]-C(13)	106.0 (6)	106.3 (6)
Co-N(5)-C(14)	121.5 (3)	121.6 (4)
Co-N(5)-C(18)	120.6 (5)	120.7 (5)

values, which are unusual for an sp³ C atom, allow the nonhydrogen atoms of the Y(CH₃)₂ grouping to lie in a plane nearly parallel to that of the equatorial ligands. The orientation of the C(CH₃)₃ and Si(CH₃)₃ groups with respect to the Co(DH)₂ plane is illustrated in Figures 3 and 4.

There are no X-ray structures of neopentyl complexes with which we can compare our results. Large Cr-C-C angles of 119-126° were found in Cr(CH₂C(CH₃)₂C₆H₅)₄,²⁹ but these are all significantly smaller than the Co-C-C angle in I.

By contrast, several structural studies have been reported for (trimethylsilyl)methyl transition-metal complexes and M-C-Si

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Table IV. NMR and Structural Data for (py)Co(DH)₂R Compounds

R	γ - ¹³ C ^a	Co-N(py), Å	Co-C, Å	<i>d</i> , ^b Å	α , ^c deg	\angle Co-C-R, deg
<i>i</i> -C ₃ H ₇ ⁹	161.37	2.099 (2)	2.085 (3)	0.02	4.0	114.2 (2)
CH ₂ Si(CH ₃) ₃	161.67	2.091 (5)	2.031 (6)	0	-1.2	127.7 (3)
neo-C ₃ H ₇ ¹¹	161.53	2.081 (4)	2.060 (6)	~0	-5.2	130.3 (4)
CH=CH ₂ ³⁷	162.06	2.073 (3)	1.966 (6)	0.04	6.3	
CH ₃ ³⁶	161.84	2.068 (3)	1.998 (5)	0.04	3.2	
DDTA ³⁵	162.26	2.043 (10)	1.970 (13)			
CH ₂ COOCH ₃ ³⁴	162.45	2.040 (6)	2.040 (6)			
CH ₂ NO ₂ ¹⁴	163.09	2.028 (3)	2.002 (3)	0.02	0.2	113.7 (2)
N ₃ ³⁸	163.85	1.973 (5)		0.02	2.9	

^a Shift (ppm) of the γ -C of (4-*tert*-butylpyridine)Co(DH)₂R. ^b The displacement of Co above the plane defined by the four (DH)₂N atoms. ^c See second paragraph of results and ref 28 for a definition.

Table V. Comparison of Bond Angles at Co between the Co Bound C and the Dioxime Equatorial N atoms^a

C(9)-Co-N angle	CH ₂ C(CH ₃) ₃	CH ₂ Si(CH ₃) ₃	CH ₂ NO ₂ ¹⁴	CH ₂ CO ₂ CH ₃ ³⁴	<i>i</i> -C ₃ H ₇ ⁹	CH ₃ ³⁶
N(1)	85.0 (2)	85.1 (2)	85.1 (1)	84.6 (3)	86.7 (1)	87.4 (2)
N(2)	90.5	90.3	89.6	89.4	86.4	88.5
N(3)	96.0	95.4	94.2	94.9	92.1	89.3
N(4)	88.4	88.6	88.7	87.8	92.1	88.3

^a The substituent lies near N(3) for the primary alkyl compounds. Numbering scheme is the same as in Figure 1.

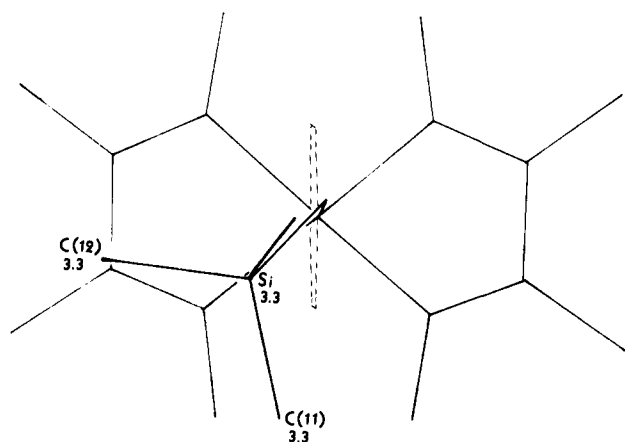


Figure 3. Orientation of CH₂Si(CH₃)₃ and pyridine with respect to equatorial plane defined by the dioxime ligands in (py)Co(DH)₂CH₂Si(CH₃)₃ (II).

angles larger than the tetrahedral angles were noted for an octahedral complex, *cis*-[Cr(CH₂Si(CH₃)₃)₂(bpy)₂]I (127.9, 128.3°),³⁰ a five-coordinated compound, MoCl(CH₂Si(CH₃)₃)₃-P(CH₃)₃ (122.2, 122.8, 121.2°),³¹ and the square-planar complexes, *trans*-PtCl(CH₂Si(CH₃)₃)₂(P(CH₃)₂C₆H₅)₂ (116.1°)³² and *trans*-Ni(CH₂Si(CH₃)₃)Cl(P(CH₃)₃)₂ (112.1°).³³

The Co-N(py) distances are essentially the same in I (2.081 (4) Å) and II (2.091 (5) Å), as well as the C(9)-Co-N(py) angles of 174.7 (2)° (I) and 174.1 (2)° (II). On the contrary, the Co-C(9) distances of 2.060 (6) Å in I and 2.031 (6) Å in II appear significantly different. This is probably due to the different steric interaction of the alkyl groups with the equatorial ligands. The C(10)-C and Si-C bond lengths have the expected values, while large deviations from tetrahedral geometry are observed in the C(9)-Si-C and C(9)-C(10)-C bond angles (Table III).

Finally, the pyridine ligand (planar within ± 0.007 Å in both I and II has the usual orientation^{9,14} with respect to the equatorial plane (Figure 3).

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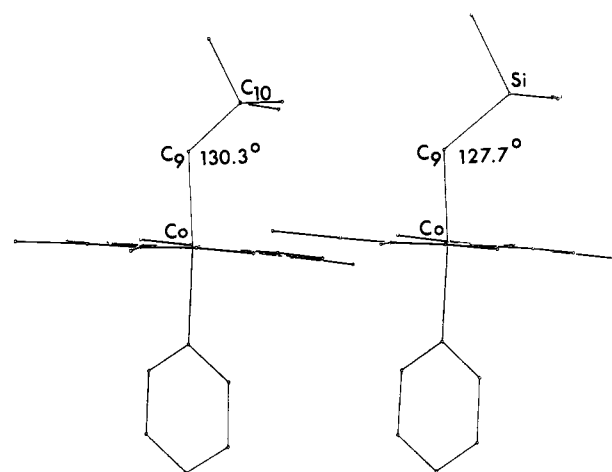


Figure 4. Side-on views of I and II. Molecules are oriented so that the Co-C(9)-Y angle (Y = C(10), Si) is in the plane of the paper.

Comparison of Structures. In compounds I and II, the similar Co-N(pyridine) bond lengths are not significantly different from the 2.099 (2) Å in (py)Co(DH)₂*i*-C₃H₇.⁹ There is, however, a regular increase in the Co-N(py) distances from 2.028 (3) to 2.099 (2) Å in the series of (py)Co(DH)₂R compounds in the order R = CH₂NO₂,¹⁴ CH₂COOCH₃,³⁴ DDTA,³⁵ CH₃,³⁶ CHCH₂,³⁷ neo-C₃H₇,¹¹ CH₂Si(CH₃)₃, and *i*-C₃H₇.⁹ This trend suggests that the *trans* Co-N(py) bond length is influenced by the nature of the alkyl group.

We have already suggested that the lengthening of the Co-C bond by ~ 0.1 - 0.15 Å in LCo(DH)₂*i*-C₃H₇ as compared to that in LCo(DH)₂CH₃ (L = py,³⁶ (C₆H₅)₃P¹³) is mainly due to the steric interaction of the bulky *i*-C₃H₇ group with the rigid equatorial ligands.^{9,10} The results obtained here show that lengthening of the Co-C bond may not be the only consequence of this interaction; a large bending of the Co-C-R angle may also be observed (Table IV). In the *i*-C₃H₇ complex, a large Co-C-CH₃ angle is not favored because the resulting small C-C-C bond

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angle would lead to the mutual repulsion of the two methyl groups. Therefore a lengthening of the Co-C bond results. In the $\text{CH}_2\text{C}(\text{CH}_3)_3$ and $\text{CH}_2\text{Si}(\text{CH}_3)_3$ compounds, both stretching of the Co-C bond and widening of the Co-C-Y (Y = C, Si) angle occur, while for CH_2NO_2 ,¹⁴ little or no deformations occur owing to the relatively small bulk of the NO_2 group. However, with the addition of the present results, a clear trend has emerged for the C(9)-Co-N (equatorial) bond angles (Table V). Clearly, for the primary alkyl compounds, one angle is larger and one smaller, apparently in response to steric strain, even in the $-\text{CH}_2\text{NO}_2$ compound.

Structure-Spectroscopy and Structure-Reactivity Relationships.

An interesting observation is that the Co-N(py) distances correlate fairly well with the ^{13}C chemical shifts of the γ -carbon of coordinated 4-*tert*-butylpyridine in the corresponding (4-*t*-Bupy)Co(DH)₂R complexes¹⁹ (Table IV). These chemical shifts are felt to reflect the electronic effect of the ligand trans to 4-*t*-bupy.¹⁹ The correlation coefficient for the comparison is -0.974 , indicating the correlation is significant. This result cannot be generalized when pyridine is replaced by a bulkier ligand such as $(\text{C}_6\text{H}_5)_3\text{P}$ or $(\text{c-C}_6\text{H}_{11})_3\text{P}$ since a "trans steric influence" may become important.³⁹ Thus, the Co-P bond length has nearly the same value in $(\text{C}_6\text{H}_5)_3\text{PCo}(\text{DH})_2\text{CH}_3$ (2.418 (1) Å)¹³ and $(\text{C}_6\text{H}_5)_3\text{PCo}(\text{DH})_2\text{-}i\text{-C}_3\text{H}_7$ (2.412 (4) Å).¹⁰ Nevertheless, in the closely analogous neopentyl and (trimethylsilyl)methyl compounds studied here, the trend in ^{13}C shifts is opposite to that expected from σ^* values of R.⁴⁰ The shifts are, however, not significantly divergent from the trends exhibited by the measured Co-N bond lengths.

For displacement by other ligands of H_2O (in H_2O) from $\text{H}_2\text{OCo}(\text{DH})_2\text{R}$, plots of $\log k_{\text{obsd}}$ vs. σ^* were found to be non-linear.^{21,22} This nonlinearity was interpreted as resulting from the existence of a solvated five-coordinate $\text{Co}(\text{DH})_2\text{R}$ in equilibrium with the hexacoordinate aquo complex. Steric factors were dismissed.

Insufficient structural data exist on cobaloximes which have been studied kinetically for as full an analysis of trends as described above for ^{13}C shifts. However, comparison of kinetic data⁴¹ for four alkyl groups (CH_3 , $\text{CH}_2\text{C}(\text{CH}_3)_3$, $\text{CH}_2\text{Si}(\text{CH}_3)_3$, and $i\text{-C}_3\text{H}_7$) with Co-N bond lengths reveal no clear trend. In contrast, there is a correlation with Co-C bond lengths. We speculate that if steric factors are important in ligand substitution reactions and that if, as we strongly suspect, the Co-C bond length reflects such steric factors, then such a correlation could be expected. The unexpectedly 20-fold greater reactivity of the neopentyl vs. (trimethylsilyl)methyl complexes could be a reflection of this steric

effect. The long C-Si bonds limit the steric effects in II. With use of the data in Table V as a guide, steric factors appear unimportant only for the CH_3 compound. It is therefore of some interest to note that, in the $\log k_{\text{obsd}}$ vs. σ^* plots discussed above, the point for CH_3 had to be discarded.^{21,22}

Based on an evaluation of reactivity and spectroscopic patterns of alkylcobalamins, Chemaly and Pratt⁴⁻⁶ predicted the following order of Co-C bond lengths for cobalamins: $\text{CH}_3 \approx \text{C}_3 < \text{C}_2\text{H}_5 \approx n\text{-C}_3\text{H}_7 < i\text{-C}_4\text{H}_9 < i\text{-C}_3\text{H}_7 \approx \text{C}_5 \approx \text{C}_6 \approx \text{CH}_2\text{C}(\text{CH}_3)_3$ (where C_3 , C_5 , C_6 are cyclopropyl etc.). The actual order for cobaloximes is CH_3 , $\text{CH}_2\text{C}(\text{CH}_3)_3$, $i\text{-C}_3\text{H}_7$. However, it was suggested that the long Co-C bond for neopentyl is a consequence of the interaction of the neopentyl ligand with side groups in the corrin ring and such an interaction is not likely to occur in simple model compounds. However, distortion of the bond angles at C(9) was felt to be important in influencing Co-C bond lability. It was suggested that this distortion occurred in cobalamins but not significantly in models, accounting for the stability of neopentyl model compounds. The present results clearly show that large distortions do occur in models. It is also of some interest that the relative Co-C bond strengths in $(\text{py})\text{Co}(\text{saloph})\text{R}$ (where saloph = salicylaldehyde-*o*-phenylenediimine) have been estimated as follows: $n\text{-C}_3\text{H}_7 > i\text{-C}_3\text{H}_7 > \text{CH}_2\text{C}(\text{CH}_3)_3$.⁴²

We pointed out above that the C(9)-Co-N bond angles reflected steric strain. It is of some interest that, in the coenzyme,¹¹ an analogous distortion exists.⁴³ In the cobaloximes, the atom attached to C(9) lies preferentially almost over one of the equatorial N's (N(3), Table V). In the coenzyme, the substituent lies between two corrin N's. It is premature to speculate as to the relevance of such angular correlations on the Co-C bond cleavage mechanism. It would be of some interest if the estimates of Co-C bond strengths such as those previously reported^{42,44-46} could be performed for compounds which have been structurally characterized such as those studies here.

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Supplementary Material Available: A listing of structure factors and tables of anisotropic temperature factors and hydrogen atom parameters for I and II (21 pages). Ordering information is given on any current masthead page.

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