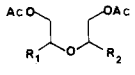
protons in **3** and **5** are axial since the coupling constants are 7.2–9.5 Hz; the C-8 H in **3** and C-2 H in **5**, however, are equatorial as $J_{8,7}$ in **3** and $J_{2,3ax}$ and $J_{2,3eq}$ in **5** are 5–5.5 Hz. Since palytoxin possesses only one $-CH_2O-$ carbon, which is found in unit **1a**, the acetoxyl-bearing CH_2 carbons of **3**, **4**, and **5** are aldehydic carbons in the oxidation products and hydroxyl-bearing methine carbons in palytoxin. All of the –CHOAc– groups correspond to –CHOH– groups in palytoxin since compounds **6**, **7**,[15] and *meso*-**8** are formed instead of **3**, **4**, and **5** if the oxidation period is longer.



6 R_1 = $AcOCH_2CHCH_3CH_2$; R_2 = $CH{=}CHCH_2OAc$

7 R_1 = $AcOCH_2CH{=}CHCH{=}CHCHOAcCH_2$; R_2 = CH_2CH_2OAc

8 $R_1 = R_2 = CH_2CH_2OAc$

Unit **1g** may exist in palytoxin from Okinawan *P. tuberculosa*, but it is not present in the palytoxins from *P. toxica* and the Tahitian *Palythoa* sp. since we have been unable to convert them to the tetraacetate described by Hirata et al.[5] High-frequency ^1H NMR studies[16] indicate the presence of the *trans*-$\dot{C}H$—$CH{=}CH$—$\dot{C}H(CH_3)$– portion of **1g**, however, suggesting that our palytoxins have structural differences in **1g**. Moreover, the NMR signals for the olefinic protons and the methyl group are doubled, signifying that our palytoxins are two-component mixtures and that the components differ in structure **1g**.

Units **1a**–**1f** account for $C_{75}H_{125}O_{31}N_3$ of the palytoxins. If one also considers unit **1g** and the compositions of two other cyclic ether-containing units which we will describe shortly,[16] then at least an additional $C_{48}H_{90}O_{16}$ is accounted for. At this time we do not have enough information to determine the molecular formula of any of the palytoxins; however, there is little doubt that all previously suggested formulas[3-5] are incorrect.

Acknowledgment. This research was supported by Grant No. CA12623-07, awarded by the National Cancer Institute, Department of Health, Education, and Welfare. NMR studies at 360 MHz were carried at the Stanford Magnetic Resonance Laboratory under the auspices of NSF Grant No. GP-23633 and NIH Grant No. RR00711. The 600-MHz NMR studies at Carnegie–Mellon University were supported by NIH Grant No. RR00292. We thank Mr. K. Lee and Professors A. A. Bothner-By and J. Datok for their assistance. We also thank Dr. K. Straub at the University of California Bio-organic, Biomedical Mass Spectrometry Resource (A. L. Burlingame, Director), supported by NIH Grant No. RR00719, for determining the field desorption and high resolution electron ionization mass spectra.

(14) Compound **5**: FDMS, *m/e* 360 (M^+); ^1H NMR (C_6D_6) δ 5.330 (ddd, J = 9.0, 7.2, and 5.0 Hz, C-4 H), 5.061 (t, J = 7.2 Hz, C-5 H), 4.524 (dd, J = −11.9 and 8.7 Hz, C-1 H), 4.40 (m, C-8 H), 4.35 (m, C-8 H), 4.07 (m, C-6 H), 4.037 (br sextet, J = 8.7, 5, 5, and 3.8 Hz, C-2 H), 2.07 (m, C-7 H), 2.02 (m, C-7 H), 1.954 (s, OAc), 1.918 (s, OAc), 1.84 (m, equatorial C-3 H), 1.825 (s, OAc), 1.814 (s, OAc), 1.69 (ddd, J = −14, 9.0, and 5 Hz, axial C-3 H).

(15) The Δ^5-cis double bond in **1e** isomerizes to trans during long-term oxidation.

(16) In collaboration with J. Ford and A. A. Bothner-By, Carnegie-Mellon University, and K. Straub and A. L. Burlingame, University of California.

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Received July 7, 1980

Structural and Spectroscopic Evidence That Cobalt to Carbon Bond Lengths Are Influenced by Conformational Effects in Cobaloximes. The Longest Co–C Bond in a Vitamin B_{12} Model: *trans*-Bis(dimethylglyoximato)(isopropyl)-(triphenylphosphine)cobalt(III)

Sir:

Cobalt–carbon bond cleavage is widely believed to be an essential feature of the mechanism of action of coenzyme B_{12}–enzyme complexes.[1-3] Two fundamental questions which arise are the following: (1) What factors induce or "trigger" the cleavage reaction? (2) What is the nature of the intermediate formed? In secondary alkyl organocobalt compounds of this general type, the organic products of the cleavage reaction are olefins,[4,5] possibly produced either by a concerted β-hydride abstraction (leading to $Co^{III}H$ which eventually gives Co(II) and $^1/_2H_2$) or by a homolytic cleavage, yielding Co(II) and R· with subsequent H abstraction. The specific nature of this important reaction is under active investigation in several laboratories.[4,5]

Conformational changes induced in the coenzyme by the enzymes may be the responsible trigger mechanism. The instability of sterically crowded alkylcobalamins[4] may result either from conformational changes in the corrin ring brought about by the bulky alkyl group or from weakening (lengthening) of the Co–C bond induced by steric crowding or from a combination of both effects. However, even in unstrained environments, the corrin ring system in cobalamins and related compounds deviates quite appreciably from planarity,[6] and an assessment of further distortions may prove difficult.

Cobaloximes (the trivial name for complexes with the bis(dimethylglyoximato)cobalt unit, $Co(DH)_2$) have a relatively planar $Co(DH)_2$ unit in both $pyCo(DH)_2CH_3$ and $pyCo(DH)_2$-*i*-C_3H_7.[7] The Co–C bond length in the latter compound is ~0.1 Å longer than in the former. In this report, we investigate the influence of conformational distortion of the $Co(DH)_2$ unit on Co–C bond lengths and provide evidence that such a distortion does lead to increased Co–C bond lengths and that the basis of the effect is steric and not electronic. The compound *trans*-bis(dimethylglyoximato)(isopropyl)(triphenylphosphine)cobalt(III) (**1**) has by far the longest Co–C bond length discovered to date. Spectroscopic data (^1H NMR) are presented for this and related compounds which we interpret as suggesting that even longer Co–C bond lengths probably exist. However, these latter compounds have so far proved to be too unstable to obtain satisfactory crystals.

1, prepared by standard procedures,[7] crystallizes from acetone/H_2O (in the dark) in the monoclinic space group $P2_1$ with a = 10.536 (8), b = 15.918 (9), c = 8.906 (7) Å, β = 100.6 (1)° (Mo Kα), and Z = 2 formula units of $CoPO_4N_4C_{29}H_{36}$; observed and calculated densities are 1.34 and 1.35 g cm^{-3}, respectively. Three-dimensional X-ray diffraction data were collected on an automated SIEMENS-AED diffractometer by using Mo Kα radiation and a θ–2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by the least-squares method with anisotropic temperature factors for Co, P, N, and O atoms to a final conventional R value of 0.058. The hydrogen atoms of the dioxime bridges were refined isotropically, while those belonging to the DH units and $(C_6H_5)_3P$ ligand were included with constant contribution (B = 5.0 Å^2). No attempt to locate the isopropyl hydrogen atoms was made owing to the high thermal motion of the ligand.[8] A total of 1147 independent reflections having $\theta_{max} \leq 25°$ and $I > 3\sigma(I)$ was used in the final calculations, since all crystals examined exhibited a significant falling off of intensities with increasing Bragg angle. No absorption correction was applied (μ(Mo Kα) = 9 cm^{-1}, 0.01 < r < 0.02 cm).

The crystals consist of discrete $(C_6H_5)_3PCo(DH)_2$(*i*-C_3H_7) units (Figure 1). The Co–C bond length of 2.22 (2) Å is even longer

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(8) The strong thermal motion of *i*-C_3H_7, especially its methyl groups, affects the accuracy of the Co(*i*-C_3H_7) fragment. However, the C–Me bond lengths of 1.49 (3) and 1.58 (5) Å and the bond angles Co–C–Me of 112 (2)° and 118 (2)° as well as the Me-C-Me angle of 113 (2)° are in agreement within experimental error with the values reported for $pyCo(DH)_2$-*i*-C_3H_7.[7]

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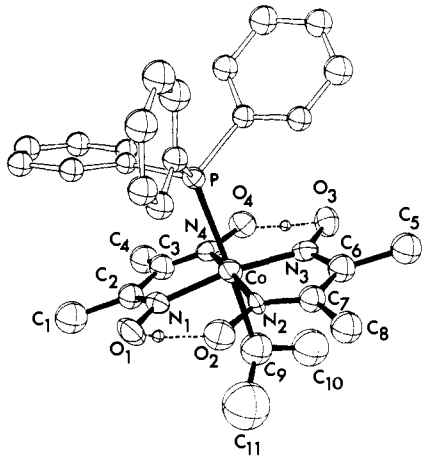

Figure 1. Molecular structure of **1**.

Table I. Comparisons of Conformational Effects in Organocobaloximes

	$(C_6H_5)_3PCo(DH)_2CH_3$[a]	$pyCo(DH)_2CH_3$[b]	$(C_6H_5)_3PCo(DH)_2(i\text{-}C_3H_7)$[c]	$pyCo(DH)_2(i\text{-}C_3H_7)$[d]
Co-C, Å	2.026 (6)	1.998 (7)	2.22 (2)	2.085 (3)
Co-P(N), Å	2.418 (1)	2.068 (3)	2.412 (4)	2.099 (2)
C-Co-P(N), deg	175.4 (2)	178.0 (2)	170.3 (6)	175.4 (1)
d, Å[e]	0.11	0.04	0.17	0.02
α, deg[f]	14	4	14	4

[a] Reference 10. [b] Reference 12. [c] Present work. [d] Reference 8. [e] In all cases the displacement of Co is on the opposite side of the alkyl group. [f] The bending is always toward the alkyl group.

than the value of 2.085 Å found for $pyCo(DH)_2$-i-C_3H_7.[7] This difference appears statistically significant, being over six times the highest estimated standard deviation. Conversely the Co–P bond length of 2.412 (4) Å does not differ from that of 2.418 (1) Å found in $(C_6H_5)_3PCo(DH)_2CH_3$.[9] The apparently similar trans influence of CH_3 and i-C_3H_7 may be attributed to a secondary steric effect;[10] that is, steric hindrance prevents the i-C_3H_7 group from being a much better electron donor than CH_3.

The $Co(DH)_2$ unit exhibits steric strain, although bond lengths and angles within each DH unit are quite normal.[7,9,11] The cobalt atom is displaced by 0.17 Å out of the plane of the N donors (coplanar within ±0.01 Å) toward the phosphine ligand, whereas the two DH units, both coplanar with ±0.06 Å, make an interplanar angle of 14°. Finally, the C–Co–P angle of 170.3 (6)° is narrower than the analogous angle of 175.4 (2)° found in the methyl derivative. It is of interest to compare some structural data of the two pairs of complexes, $(C_6H_5)_3PCo(DH)_2R$ and $pyCo(DH)_2R$, in which R = CH_3, i-C_3H_7 (Table I). These results suggest that the increase in bulkiness from pyridine to $(C_6H_5)_3P$ provokes a lengthening of the Co–C bond, which appears mainly due to the increased distortion of the $Co(DH)_2$ moiety by the ligand trans to the alkyl group. This is shown by the larger values of C–Co–L angle, the out-of-plane distance of cobalt atom, d, and the interplanar angle, α, between the two DH units found in the $(C_6H_5)_3P$ complexes.

We believe that this lengthening is probably not a consequence of the effect of the conformational distortion on the electronic properties of the Co center, since in $LCo(DH)_2CH_3$ compounds with L = $(CH_3O)_3P$,[12] $(C_6H_5)_3P$,[9] and $(c\text{-}C_6H_{11})_3P$,[13] the Co–C bond lengths are very similar even though there are conformational changes in the $Co(DH)_2$ unit as the bulk of L is increased. This finding is in keeping with the known instability of cobaloximes containing secondary alkyl groups.[4,14]

Table II. Dependence of the Chemical Shift (^{1}H NMR) of the Isopropyl Methyl Groups in $LCo(DH)_2$-i-C_3H_7 on the Bulk of L[a]

N-donor L	shift	P-donor L	shift
1-ethyl-2-methylbenzimidazole	0.06	$(c\text{-}C_6H_{11})_3P$	0.16
2-methylpyridine	0.10	$(i\text{-}C_3H_7)_3P$	0.28
1,2-dimethylimidazole	0.32	$(C_6H_5)_3P$	0.41
pyridine	0.46	$(CNCH_2CH_2)_3P$	0.52
5,6-dimethylbenzimidazole	0.50	$(CH_3O)_3P$	0.54
1-methylimidazole	0.50	$(n\text{-}C_4H_9)_3P$	0.54

[a] In ppm downfield from $(CH_3)_4Si$, $CDCl_3$, JEOL MH-100.

The ^{1}H NMR spectra of nonalkylcobaloximes are sensitive to conformational distortions induced by bulky ligands.[15] A useful measure of such distortions is the length of the Co–P bond when the bulky ligand is a phosphine.[16] We now find that organocobaloximes exhibit similar effects, as illustrated for $LCo(DH)_2$-i-C_3H_7 compounds in Table II. The data in Table II clearly reflect primarily the bulk of the ligand L and suggest that some ligands such as $(c\text{-}C_6H_{11})_3P$ and 1-ethyl-2-methylbenzimidazole induce greater conformational distortions than does $(C_6H_5)_3P$. Thus, it is very likely that, since we have demonstrated here a relationship between steric distortion and Co–C bond length, even longer Co–C bond lengths would be observed if crystals of sufficient stability could be prepared.

Acknowledgment. This research was supported in part by a NATO grant (to L.G.M. and L.R.), a grant (to L.R.) from C.N.R. (Rome Italy), and NIH Grants No. GM 25906 and 29225 (to L.G.M.).

Supplementary Material Available: A listing of structure factors, atomic parameters, hydrogen atom coordinates, and bond lengths and angles of $(C_6H_5)_3PCo(DH)_2$-i-C_3H_7 (8 pages). Ordering information is given on any current masthead page.

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Received March 10, 1980

Occurrence of a 1,2 Shift during Enzymatic and Chemical Oxidation of a Terminal Acetylene

Sir:

Evidence that acetylenic moieties can be oxidatively metabolized has remained sufficiently oblique for the very existence of this transformation to remain in doubt.[1] Scattered reports of acetylene group metabolism, generally based on in vivo studies, are am-

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