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Novel Chemistry of Carbon Bound to Cobalt in Organocobalt Complexes Related to B12

Suzette M. Polson, Lory Hansen, and Luigi G. Marzilli*

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322

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Abstract: A rare Co−N−C three-membered ring has been formed by a novel pathway involving a facile interligand nucleophilic addition of an equatorial nitrogen donor to a ligated axial carbon in some organocobalt complexes. The highly distorted structure of a typical resulting complex provides clear experimental evidence useful in assessing hypotheses and computations concerning Co−C bond activation in B12 chemistry. Treatment of R = $-CH_2X$ (X = halogen) derivatives of imine/oxime B12 models of the type $[LCo((DO)(DOH)pn)R]^+$ with base afforded major products with striking NMR spectral features in common, e.g., two one-proton olefinic doublets ($J \approx 3$ Hz) and two one-proton singlets. The X-ray structure for the pyridine (py) derivative $[pyCo(N\text{-}CH_2\text{-}CHEL)]^+$ (**1**) reveals two unexpected features: a three-membered metallocycle containing an η^2-aminomethylene group, and an enamine ($N-C{=}CH_2$) in place of one imine moiety ($N{=}C-CH_3$). The C−Co−N ring angle is acute (43.7°) with the distortion of the coordination sphere concentrated in the Co−C and the Co−N ring linkages, which move away from the normal pseudooctahedral positions. Studies of the formation of the aqua analog of **1**, $[H_2OCo(N\text{-}CH_2\text{-}CHEL)]^+$ (**3**), in aqueous solution suggest that the initial intermediate formed is deprotonated at one imine methyl. Ring closure in the short-lived deprotonated intermediate is facile. Published calculations predict that such ring closure could occur and that, of two processes which could facilitate Co−C bond cleavage (θ-bending of the N−Co−C angle and ϕ-bending of the Co−C−C angle), the latter factor should be more significant in weakening the Co−C bond. There is large θ-bending in **1**; thus, the new metallocyclic B12 analogs afford the first experimental test of these calculations. Our findings that the Co−C bond in **1** is short and that the bond did not readily cleave support the predictions of the calculations.

Introduction

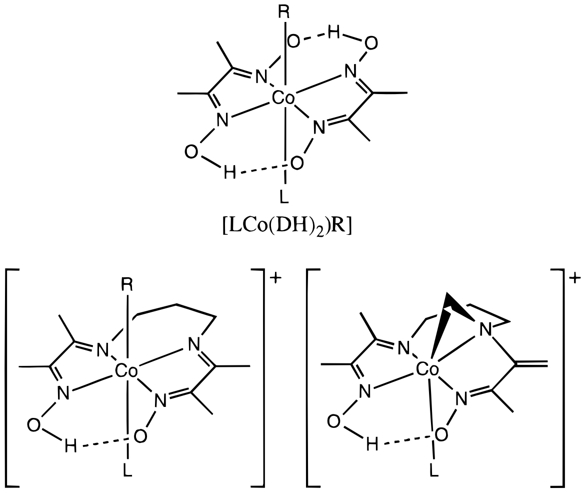
The enzymatic reactions involving B12 cofactors are still poorly understood and difficult to model. Organocobalt B12 and B12 model complexes with diverse alkyl derivatives are necessary for elucidating the fundamental relationships between structure and spectra,[1−3] relationships helpful in understanding structural and/or ligating group changes that may occur in B12-dependent processes.

Although ligands with diverse properties have been readily incorporated into the alkylcobaloxime class of B12 models, $LCo(DH)_2R$ (Chart 1), a comparable range of ligands cannot be introduced so readily into other models or into B12 (cobalamins). Even the closely related imine/oxime models, such as $[LCo((DO)(DOH)pn)R]^+$ complexes (Chart 1),[4] pose greater synthetic challenges.[4,5] Therefore, we are exploring in more detail the reasons for the difficulty in extending the apparently straightforward chemistry of cobaloximes. For example, the synthesis of $Co-CH_2OCH_3$ complexes by reaction 1 has been limited to the cobaloximes.

$$Co-CH_2Br + CH_3O^- \rightarrow Co-CH_2OCH_3 + Br^- \qquad (1)$$

Previous attempts to prepare $[LCo((DO)(DOH)pn)CH_2OCH_3]^+$ derivatives by this route had failed.

Chart 1



$[LCo(DH)_2)R]$

$[LCo((DO)(DOH)pn)R]^+$ $[LCo(N\text{-}CH_2\text{-}CHEL)]^+$

We now report that attempts to carry out reaction 1 with some organocobalt complexes led to an unexpected outcome: A rare Co−N−C three-membered ring was formed through a novel pathway involving a remarkably facile interligand nucleophilic addition of an equatorial nitrogen donor to a ligated axial carbon. The highly distorted structure of a typical resulting complex provides clear experimental evidence useful in assessing hypotheses and computations concerning Co−C bond activation in B12 chemistry.

Experimental Section

X-ray Methods. Crystal Data. Crystals of $[pyCo(N\text{-}CH_2\text{-}CHEL)]ClO_4$ (**1**, py = pyridine; N-CH_2-CHEL = modified (DO)(DOH)pn macrocycle as shown in Chart 1 and described below) were obtained

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Table 1. Crystallographic Data for **1**

empirical formula	$C_{17}H_{25}ClCoN_5O_6$
space group	$P2_1/c$
a (Å)	10.557(2)
b (Å)	14.115(2)
c (Å)	14.784(2)
β (deg)	102.30(2)
volume (Å^3)	2152.3(6)
Z	4
formula weight	489.8
density (calc) (mg/m^3)	1.51
abs coeff (mm^{-1})	0.965
radiation	Mo Kα (λ = 0.71073 Å)
temp (K)	298
min/max transmission	0.43/0.46
final R indices (%)	
R	5.29
R_w	7.59

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

Bond Lengths (Å)			
Co−N(1)	1.886(5)	Co−N(4)	1.878(6)
Co−N(2)	1.943(5)	Co−N(5)	2.068(5)
Co−N(3)	1.895(5)	Co−C(12)	1.927(5)

Bond Angles (deg)			
N(1)−Co−N(2)	82.8(2)	N(5)−Co−C(12)	150.9(2)
N(2)−Co−N(3)	97.3(2)	Co−N(1)−C(1)	118.2(4)
N(1)−Co−N(4)	96.6(2)	Co−N(2)−C(3)	108.7(4)
N(3)−Co−N(4)	81.3(2)	Co−N(2)−C(5)	120.6(4)
N(1)−Co−N(5)	92.6(2)	Co−N(2)−C(12)	67.5(3)
N(2)−Co−N(5)	107.1(2)	Co−N(3)−C(7)	120.6(5)
N(3)−Co−N(5)	91.7(2)	Co−N(3)−C(8)	115.0(4)
N(4)−Co−N(5)	99.6(2)	Co−N(4)−C(10)	117.7(4)
N(1)−Co−C(12)	85.8(2)	Co−N(5)−C(13)	121.5(4)
N(2)−Co−C(12)	43.8(2)	Co−N(5)−C(17)	121.2(5)
N(3)−Co−C(12)	91.2(2)	Co−C(12)−N(2)	68.7(3)
N(4)−Co−C(12)	109.5(2)		

by recrystallization from CH_2Cl_2/Et_2O. An orange crystal (0.3 × 0.3 × 0.4 mm) was used for data collection. Intensity data were collected at 25 °C on a Siemens P4 instrument. The crystal system and high-angle cell constants were determined by automatic reflection selection, indexing, and least-squares refinement (XSCANS Version 2.0). Three check reflections were measured every 97 reflections; there was no significant deviation in intensity.

Solution and Refinement of the Structure. Intensity data were corrected for Lorentz and monochromator polarization and absorption (semiempirical method based on azimuthal scans). The structure of **1** was solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedures using SHELXTL IRIS. The oxime H-atom was observed in the difference map and was included in the refinement. The C(4) H-atoms were also located from difference maps. All other H-atoms were generated at calculated positions (d(C−H) = 0.96 Å). All H-atoms were constrained using a riding model with isotropic thermal parameters fixed at 0.08. Crystal data and refinement parameters are presented in Table 1. Selected bond lengths and bond angles are reported in Table 2.

Reagents and Characterization. Sodium and Dowex resin were from Aldrich. Sodium iodide and all solvents were from Fisher. The 300 MHz ^{1}H NMR spectral data (GE QE-300) in $CDCl_3$ or DMSO-d_6 (CIL) and elemental analyses (Atlantic Microlabs, Atlanta, GA) are tabulated in the supporting information.

Preparation of Complexes. [*N*-MeImdCo((DO)(DOH)pn)CH_2Br]ClO_4 (*N*-MeImd = *N*-methylimidazole) and [H_2OCo((DO)(DOH)pn)-*neo*-C_5H_{11}]ClO_4 were prepared as previously reported.[4] Complexes of the type [*N*-MeImdCo((DO)(DOH)pn)CH_2X]ClO_4 (X = Cl, I) were made similarly to the X = Br analog,[4] except that one-third of the $NaBH_4$ solution was added before, and the rest shortly after, the addition of the alkylating agent. [H_2OCo((DO)(DOH)pn)CH_2X]ClO_4 (X = Cl, I) were made by the method for X = Br.[4]

[*N*-MeImdCo(*N*-CH$_2$-CHEL)]ClO$_4$ (2). [*N*-MeImdCo((DO)(DOH)pn)CH_2Br]ClO_4[4] (1.10 g, 1.92 mmol) was added to a solution of sodium (0.22 g, 9.6 mmol) in MeOH (200 mL) under N_2. After being purged for 10 min, the mixture was stirred overnight under N_2. The volume of the solution was reduced to ∼60 mL. A dark orange powder was collected and washed with cold H_2O and Et_2O. Yield: 0.48 g (51%).

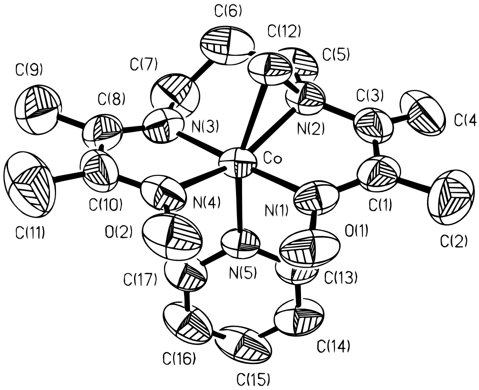

Figure 1. Perspective drawing of **1** with 50% probability for the thermal ellipsoids.

[H$_2$OCo(*N*-CH$_2$-CHEL)]ClO$_4$ (3). Dowex 50×8-100 exchange resin (0.36 g) was added to **2** (0.24 g, 0.56 mmol) in 4:1 MeOH−H_2O (32 mL). After the mixture was stirred for 2 days, the resin was filtered, and the solvent was removed. The orange solid remaining was washed quickly with cold water and dried under vacuum. Yield: 0.084 g (35%).

[pyCo(*N*-CH$_2$-CHEL)]ClO$_4$ (1). **3** (0.10 g, 0.23 mmol) was suspended in CH_2Cl_2 (50 mL) and py (0.021 mL, 0.26 mmol) was added. The mixture was stirred overnight to give a cloudy yellow solution, which was filtered through a fine frit. The solvent was removed. The resulting orange oil was dissolved in a minimum of CH_2Cl_2, and an equal amount of ether was added. From the clear solution, kept in the freezer overnight, a red solid was collected, washed with ether, and vacuum dried. Yield: 0.085 g (74%).

ICo(*N*-CH$_2$-CHEL). To an aqueous suspension of **3** (0.061 g in 20 mL) was added NaI (0.40 g, 3.5 mmol). The resulting solution was extracted with CH_2Cl_2. The dark red organic layer was dried over Mg_2SO_4. The solvent was removed, and the residue was redissolved in MeOH. The MeOH was removed under reduced pressure to give a dark red solid. Yield: 0.060 g (98%).

ICo((DO)(DOH)pn)*neo*-C$_5$H$_{11}$. This compound was prepared in the same manner as ICo(*N*-CH$_2$-CHEL), by using $CHCl_3$ in place of CH_2Cl_2. Yield: 0.030 g (40%).

Results and Discussion

Treatment of [LCo((DO)(DOH)pn)CH_2X]$^{+}$[4] derivatives (X = halogen, Chart 1) with base afforded major products with the same striking NMR spectral features, e.g., two one-proton olefinic doublets ($J \approx 3$ Hz) and two one-proton singlets.[6] These features and the elemental analyses indicate that reaction 1 did not occur. The NMR results provide evidence for low-symmetry complexes, although the *trans* ligand (L) signals have typical shifts.

Although similar products were obtained with several different *trans* L, we chose to investigate the X-ray structure of [pyCo(*N*-CH$_2$-CHEL)]ClO$_4$ (**1**) (Figure 1, Chart 1). The structure reveals an unexpected feature, a methylene bridge from the cobalt to an equatorial ligand N, forming a three-membered metallocycle containing an η^2-aminomethylene group. The ring is formed at the expense of altering the symmetrical imine/oxime-type macrocyclic ligand to one containing an enamine

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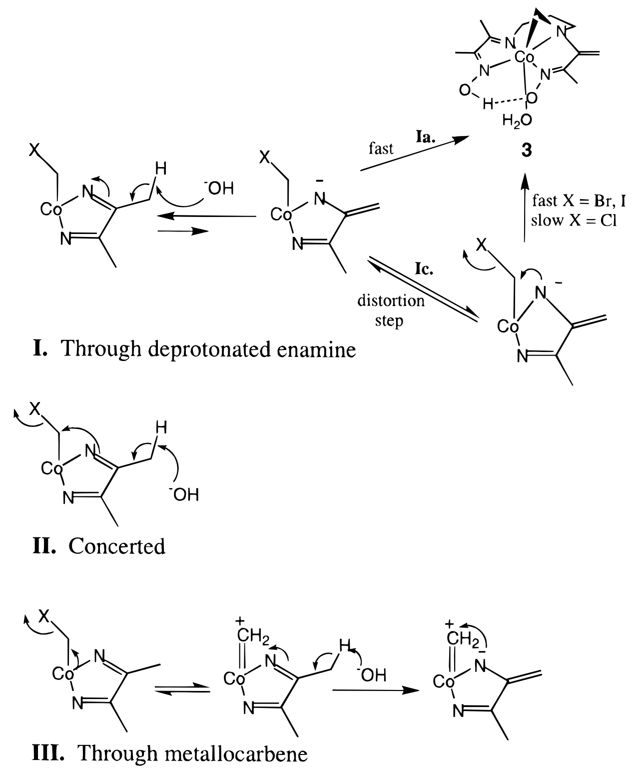
(6) For $CDCl_3$, the two one-proton singlets at δ 3.15 and 4.09 arise from the methylene bridge from the Co to the N. The more upfield singlet is from the ring proton over the unsaturated equatorial ligand. The imine methyl that was converted to an enamine gives rise to the olefin doublets at δ 5.41 and 5.83, and the three remaining imine methyls give rise to signals in the normal shift range (δ 2.04, 2.28, and 2.41). The lower symmetry increases the number of propylene bridge signals.

Scheme 1. Possible Mechanisms for the Formation of **3**



($N{-}C{=}CH_2$) in place of an imine moiety ($N{=}C{-}CH_3$). The structural features will be considered below. First, we will discuss the mechanism of ring closure. Our investigation was prompted by the ease with which this strained ring formed, given that the η^2-aminomethylene group C−N distance is 1.44 Å in **1**, a value ~1.3 Å smaller than the distance between these atoms in the starting complex.

Mechanistic Studies. In the only two previous reports of an η^2-aminomethylene−Co(III) ring, the ring was formed by an intramolecular Co alkylation;[7,8] in contrast, the ring in **1** was formed by an intramolecular N alkylation. In one previous case, *trans*-$[Co(HL^1)Cl_2]^+$ (HL^1 = *N*-methyl N_4 macrocycle)[7] formed $[Co(L^1)Cl]^+$ (L^1 = N_4C chelate) at elevated temperatures or low pH via Co alkylation by the *N*-methyl group. In the other case, photolysis of $[O_2CCH_2NH_2Co(bpy)_2]^{2+}$ led to extrusion of CO_2 to form $[\eta^2\text{-}NH_2CH_2Co(bpy)_2]^{2+}$.[8]

We investigated the formation of the aqua (**3**) and *N*-MeImd (**2**) analogs of **1** in protic solvents. **3** formed from $[H_2OCo((DO)(DOH)pn)CH_2Br]ClO_4$[4] in high yield in mildly basic aqueous solution at ambient temperature. The rate of metallocycle formation increased with basicity, but limited aqueous solubility and decomposition at higher pH's made continuous monitoring of the reaction impractical. The CH_3O^- treatment of [*N*-MeImdCo((DO)(DOH)pn)CH_2Br]PF_6 in CH_3OD under typical harsh preparative conditions afforded **2** with nearly complete deuterium exchange of the three methyl groups but *no* deuteration in the olefinic moiety.

These early observations and the nature of the product suggested initially that deprotonation of an imine methyl group to yield a key deprotonated enamine intermediate preceded the metallocycle formation step (Ia, Scheme 1). Later experiments, described below, led us to consider several variants of this first mechanism.

In a second mechanism (II, Scheme 1), ring closure and deprotonation occur in a concerted slow step. The rate of a concerted process should reflect the deprotonation rate. The half-life for D exchange of one imine methyl H in the $[H_2OCo((DO)(DOH)pn)R]ClO_4$ ($R = CH_2CF_3$) was ~2.5 h at pH 10 in D_2O.[9] The electron donor ability of this R group is similar to that of $-CH_2X$ (X = Cl, Br, I). Although ring closure complicated a similar measurement with the series $R = -CH_2Br$ and $-CH_2I$, the half-lives for a single H to D exchange for starting material were measured to be ~3 h for all three $-CH_2X$ compounds.[9] Thus, the rates of exchange were in the range expected from the data on the CH_2CF_3 compound. A concerted process (II, Scheme 1) is unlikely since the ring formation would have been faster than the exchange rate for the $R = CH_2Br$ and CH_2I compounds. For these two compounds, the data show that exchange is competitive with ring closure.

A third mechanism considered (III, Scheme 1) features a fast equilibrium in which the $Co{-}CH_2X$ complex loses X^- to form a $Co{=}CH_2^+$ intermediate complex prior to the rate-determining deprotonation. However, treatment of [*N*-MeImdCo((DO)(DOH)pn)CH_2X]$^+$ in CH_3OH overnight with LiCl (140 mM; X = Br) or NaI (160 mM; X = Br) or NaBr (85 mM; X = I) resulted in no halogen exchange, which is easily detectable by NMR. There is no fast prior equilibrium, thus ruling out mechnism III.

We believe that the only viable mechanisms involve a deprotonated intermediate formed prior to ring closure, mechanisms Ia−c. Factors that must be considered in assessing these mechanisms are (i) the lifetime of the deprotonated forms and (ii) the extent to which the rate of formation of **3** reflects the relative leaving group ability of X, e.g., Cl:Br:I = 1:14:91.[10] Since the methyl groups have relatively low acidity, reprotonation must be rapid and the intermediate must have a relatively short half-life. For example, in THF the half-life of reprotonation of the free benzyl carbanion by methanol was determined to be $\sim 1.2 \times 10^{-7}$ s.[11]

In the simplest version of the first mechanism (Ia, Scheme 1), the deprotonated short-lived intermediate is formed in a slow step followed by a very fast metallocycle formation step. If Ia were an adequate mechanism, all three $[H_2OCo((DO)(DOH)pn)CH_2X]ClO_4$ complexes would have formed **3** at about the same rate and without the observed competitive deuteration of the imine methyl of the equatorial ligand. The ring closure rate at pH 10.0 showed only a slight dependence on the leaving halogen for Br and I ($t_{1/2}$ = 3 h). For X = Cl, no ring closure could be detected under comparable conditions, even after longer time periods. Thus, mechanism Ia does not account for the halogen dependence.

There are two variants of the first mechanism: (i) the deprotonated species could be formed in a distorted conformation poised for C−N bond formation (Ib, not shown), or (ii) it could distort in a subsequent fast step, which is followed by a fast C−N bond-forming step (Ic, Scheme 1). Since ring closure rates for $[H_2OCo((DO)(DOH)pn)CH_2X]ClO_4$ (X = Br, I) are similar and competitive with deuteration of the imine methyl, the ring closure process cannot be influenced by C−X bond breaking and must be facile, occurring within a time period comparable to the half-life for reprotonation. If the distortion occurred as the intermediate formed, ring closure, which should be faster for X = I than for X = Br, would be the only step

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[9] A 1.4 mM solution of each compound in 50 mM pH 10.0 buffer ($NaHCO_3/NaOH$) was neutralized with HNO_3 after 6 h. NMR spectroscopy was used to estimate the extent of reaction.

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Table 3. Geometrical Data for **1** and for the Relevant $[pyCo((DO)(DOH)pn)R]^+$ Complexes[a]

R	Co−C, Å	Co−N(py), Å	C−Co−N(py), deg
		N-CH_2-CHEL	
N-CH_2	1.927(5)	2.068(5)	150.9(2)
		(DO)(DOH)pn	
CH_3	2.003(3)	2.106(3)	178.9(1)
neo-pentyl	2.083(4)	2.121(3)	177.1(2)

[a] From ref 4.

competing with reprotonation; i.e., we would have seen much less deuteration compared to formation of **3** for X = I vs X = Br. Thus, the observation that ring closure and deuteration are competitive suggests that the distortion occurs in a separate fast equilibrium process that follows deprotonation and precedes ring closure, mechanism Ic. This mechanism can account for the small dependence of the rate on the halogen for X = Br and I, if in these two cases the C−N bond formation step is fast compared to the reverse of the distortion step (Scheme 1).

We can also use mechanism Ic to interpret the similarities and the differences in the findings for the $-CH_2Cl$ compound compared to the $-CH_2Br$ and $-CH_2I$ compounds. The three $-CH_2X$ complexes have similar deuteration rates; thus, the rates of the first equilibrium in mechanism Ic should be nearly the same for all three species. The $-CH_2Cl$ group has the smallest bulk; therefore, the forward rate of the distortion equilibrium should be at least as fast for the R = CH_2Cl compound as for the R = CH_2Br or CH_2I compounds. Nevertheless, for the $-CH_2Cl$ compound, we found that C−N bond formation was too slow to be competitive with reprotonation. These observations are explained by mechanism Ic if the C−N bond formation step for the $-CH_2Cl$ compound were very slow compared to the reverse of the distortion step. A slow C−N bond formation step is consistent with the greater strength of the C−Cl bond compared to the C−Br and C−I bonds.

Structural and Spectroscopic Properties. The Co−C and Co−N bonds of **1** are bent ~26° and ~22°, respectively, from the directions normally found for $[LCo((DO)(DOH)pn)R]PF_6$ compounds. Co−C bending (θ-bending angle,[12] ~116° = 26° + 90° in **1**, Chart 2) has been the subject of theoretical studies, see below. The facile distortion that leads to ring closure in the formation of the η^2-aminomethylene group is surprising, considering the resulting highly distorted six-coordinate geometry of **1**. The C−Co−N ring angle is acute (43.7°). N(2) is displaced 0.74 Å out of the plane defined by N(1)−N(3)−N(4) toward C(12), which is displaced 1.73 Å out of this plane. These parameters indicate that the distortion of the coordination sphere is concentrated in the Co−C and the Co−N ring linkages. In addition, some distortion extends in the direction of the *trans* py ligand (Figure 1). The N(2)−Co−N(5) angle is 107.1(2)°, and the N(4)−Co−N(5) angle is 99.6(2)° (the remaining two N−Co−N(5) angles are nearly orthogonal at 91.7(2)° and 92.6(2)°).

Not all structural features for **1** are unusual compared to those of the three py imine/oxime-type compounds we have reported.[4,13] The orientation of the plane of the py ring with respect to the two five-membered chelate rings in **1** is similar to that found in structures of imine/oxime-type compounds.[4,13] The Co−N−C angles involving the axial py (121.2(4)° and 121.2(5)°) are normal; although within the range of reported values, the Co−N(py) bond length, 2.068(5) Å, is significantly shorter in **1** than in some other imine/oxime-type alkyl complexes (see Table 3). This result might indicate that the bridging methylene group has a smaller *trans* influence than a normal alkyl group or that the distorted equatorial ligand has a smaller steric *cis* influence. In addition, the Co−C bond length of 1.927(5) Å is not only shorter than in normal imine/oxime-type structures, but shorter than almost all examples of organocobalt(III) compounds in which the coordinated alkyl is part of a polydentate ligand.[7,14−18]

The two reported structures of compounds with the η^2-aminomethylene−Co(III) ring were not well refined.[7,8] In one case, $[\eta^2\text{-}NH_2CH_2Co(bpy)_2]^{2+}$ (R = 0.128),[8] the η^2-aminomethylene moiety is a simple chelate ligand approximately coplanar with two bpy nitrogen atoms. Thus, apart from the angular distortion of the Co−C−N ring, the pseudooctahedral coordination geometry is relatively undistorted. In the other case, $[Co(L^1)Cl]^+$ (R = 0.096),[7] the distortion imposed by the η^2-aminomethylene−Co(III) ring is centered in the most flexible part of the macrocycle.

Intramolecular N-alkylation of the planar N4 macrocycle by the axial carbon has also been found in iron−carbene porphyrin chemistry.[19,20] However, any three-membered ring formed is transient, with the M−N bond becoming disrupted. The porphyrin denticity is not increased. In contrast, the denticity increases for the imine/oxime complexes, and indeed, a sexadentate chelate is found with the new lariat-imine/oxime-type complexes.[21,22] Only four examples exist in which the η^2-aminomethylene moiety is part of an extended chelated ligand.[7,23−25]

Relevance to MO Calculations. Regardless of the mechanism by which it forms, our analysis shows that the distortion needed for ring closure occurs readily. Computations suggest that, in B12 compounds, Co−C bending (θ-bending angle,[12] Chart 2) will foster an attractive interaction between the axial C and an equatorial N, leading to a lengthening of the Co−N bond.[12] The facile formation of the metallocycle in **1** supports the attractive interaction. The Co−N bond of the η^2-aminomethylene moiety is longer (1.94 Å) than the other equatorial Co−N bonds (range 1.88−1.90 Å).

Probably the most important aspect of the computations is the evaluation of the hypothesis that θ-bending is a possible avenue through which coenzyme−enzyme binding energy could weaken the Co−C bond and thereby facilitate B12-dependent reactions.[12,26] The computations predict that ϕ-bending (bending of the Co−C−C angle, Chart 2) away from tetrahedral is more important than θ-bending in weakening the Co−C bond.

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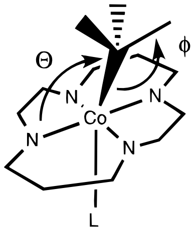
Chart 2. MO Parameters ϕ, Θ



Experimental tests for ϕ-bending exist in the structures of neopentyl derivatives,[4,27−29] and the bond has been shown to be weak.[30]

The compounds presented here provide the first opportunity to gain experimental insight into the likely consequences of θ-bending on the Co−C bond. The computations[12] suggest that θ-bending even as great as found in **1** will have a small effect (∼15% decrease in total overlap population of the Co−C bond). In addition to θ-bending, the strain in the distorted product **1** might contribute to Co−C bond weakening.

We evaluated Co−C bond weakening both by considering the structure and by assessing the ease of Co−C bond cleavage. It is clearly established that weak Co−C bonds are long.[4,13,31,32] However, the Co−C bond length of 1.927(5) Å in **1** is significantly *shorter* than that in undistorted related organocobalt compounds (Table 3).[4] Qualitative observations under conditions for which Co−C bond cleavage is normally observed suggest that **1** is relatively inert. For example, we compared iodo complexes of *N*-CH_2-CHEL and imine/oxime macrocycles. The Co−C bond in ICo(*N*-CH_2-CHEL) (0.27 mM) did not thermally cleave after 2 days in refluxing benzene in the presence of the trap TEMPO[30,33] (27 mM). The imine/oxime analog with the ϕ-bent neopentyl ligand, ICo((DO)(DOH)pn)-$CH_2C(CH_3)_3$, exhibited complete Co−C bond cleavage after only 1 day under similar conditions. Thus, the Co−C bond in compounds such as **1** is relatively strong.[34]

We conclude that ϕ-bending is more likely than θ-bending to be an important means of Co−C bond weakening in B12 reactions. However, the coordination sphere of organocobalt species appears to be readily distorted. The facility of the θ-bending suggests potential biological functions. The θ-bending could allow favorable cofactor−protein contacts or favorable stereochemistry during turnover. Several features of the published computations[12] are well supported by the new experimental results.

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Supporting Information Available: Table of elemental analyses, ^{1}H NMR data, and crystallographic data (anisotropic displacement coefficients, hydrogen atom parameters, complete tables of bond lengths and bond angles, and atomic coordinates with equivalent isotropic displacement coefficients) (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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