Inorg. Chem. **2005**, *44*, 9902–9913

Inorganic Chemistry
Article

X-ray Structures and Homolysis of Some Alkylcobalt(III) Phthalocyanine Complexes

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Received June 29, 2005

The first crystallographic data for σ-bonded alkylcobalt(III) phthalocyanine complexes are reported. A single-crystal X-ray structure of $CH_3CH_2Co^{III}Pc$ (Pc = dianion of phthalocyanine) reveals that the solid consists of centrosymmetric face-to-face dimers in which the $CH_3CH_2Co^{III}Pc$ units retain their square pyramidal geometry. The structure appears to be the first one reported for a five-coordinate RCo(III)(chelate) complex with an electron-deficient equatorial system. The Co–C bond in $CH_3CH_2Co^{III}Pc$ (2.031(5) Å) is the longest found in five-coordinate RCo^{III}(chel) complexes (R = simple primary alkyl group). Another X-ray study demonstrates that $CH_3Co^{III}Pc$(py) has a distorted octahedral geometry with axial bonds of very similar length to those in methylcobalamin. The axial bonds are shorter than those in its octaethylporphyrin analogue, in accordance with a weaker trans axial influence in six-coordinate complexes containing an electron-deficient phthalocyanine equatorial ligand. A different trend has been observed for five-coordinate RCo^{III}(chel) complexes: electron-rich equatorial systems seem to make the Co–C axial bond shorter. Kinetic data for the homolysis of $RCo^{III}Pc$ complexes (R = Me, Et) in dimethylacetamide are also reported. Homolysis of ethyl derivatives is faster. The Co–C bond dissociation energies (BDEs) for the pyridine adducts of the methyl and the ethyl derivative are 30 ± 1 and 29 ± 1 kcal/mol, respectively. The BDE for CH_3CoPc(py) is considerably lower than that for MeCbl despite the very similar lengths of the axial bonds in the two complexes. The results of this work do not support any correlation between the Co–C bond length and the bond strength as defined by BDE.

Introduction

Very few five-coordinate alkylcobalt(III) complexes have been structurally characterized so far.[2−7] Not surprisingly, none of these has as an electron-deficient[8] equatorial ligand. This work provides the first structural data for such complex. As demonstrated by recent equilibrium studies of trans axial ligation, also by cyclic voltammetry, alkyl-$Co^{III}Pc$ complexes clearly can be categorized as electron-poor models of methylcobalamin.[9] The electrophilic nature of the five-coordinate $CH_3Co^{III}Pc$ species has been the rationale behind its exceptional S_N2 methyl-transfer reactivity. Consequently, the considerable Lewis acidic strength of the Co center seems to leave little hope for obtaining a solid consisting of the five-coordinate units, especially since reasonable solubility of these compounds can only be attained in binding solvents. However, phthalocyanines are known for their strong propensity for π-stacking, which may prevent trans axial ligation in the solid.[10] The geometry of the coordination sphere in

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(1) Abbreviations: Pc, dianion of phthalocyanine; $MeCbi^+$, methylcobinamide; MeCbl, methylcobalamin; OEP, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; NPc, dianion of naphthalocyanine; TPP, dianion of 5,10,15,20-tetraphenylporphyrin; TTP, dianion of 5,10,15,20-tetratolylporphyrin; DH, monoanion of dimethylglyoxime; (DO)(DOH)pn, anion of $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine-3-oxime); salen, dianion of bis(salicydene)ethylenediamine; saloph, dianion of bis(salicylidene)-*o*-phenylenediamine; TC, tropocoronand; acacen, dianion of bis(acetylacetone)ethylenediimine; py, pyridine; *N*-MeIm, *N*-methylimidazole; DMA, dimethylacetamide; DMSO, dimethyl sulfoxide; TEMPO, 2,2,6,6-tetramethyl-1-piperidinyloxy.

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10.1021/ic051078p CCC: $30.25

five-coordinate (or pseudo-five-coordinate) $RCo^{III}Pc$ units in a face-to-face dimer is of interest with regard to the S_N2 reactivity of alkylcobalt(III) phthalocyanine complexes.

The structural data for σ-bonded alkyl-Co(III) octaethylporphyrins reported by Stolzenberg et al.[6,7] set the stage for interesting comparisons with their phthalocyanine congeners. While phthalocyanine complexes have the most electron-deficient equatorial arrangement among porphyrinic models, the octaalkylporphyrin compounds are just the opposite. Octaalkylporphyrins (H_2P) are ~15 pK_a units less acidic than phthalocyanines.[11] Another striking feature of phthalocyanine complexes, consistent with their electron deficiency, are their redox potentials, which are considerably less negative than those for octaalkylporphyrins. For instance, Co(II)/Co(I) potentials are −0.2 or −0.35 [12] and −0.95 V[13] vs SCE for phthalocyanine and octaethylporphyrin compounds, respectively. Bond length and strength of the axial system in alkylcobalt(III) complexes are a central problem in bioinorganic chemistry. It appears that long Co−C bonds coincide with a long trans $Co-N_{ax}$ bond. This unique feature of the alkyl-Co−N axial system, known as inverse trans influence, has recently gained much interest. Molecular mechanics studies,[14] as well as DFT calculations,[15] aimed at reproducing the structural data, and with less success, the BDEs have been mostly conducted on corrinoids having various axial ligands. The cis influence of the equatorial system has received less attention. Riordan and Halpern noted that, in closely related organoiron porphyrin complexes, the metal−carbon bond dissociation is faster when the equatorial ligand is less basic.[16] Similar conclusions were derived by Qiu and Sawyer from their electrochemical studies on iron and cobalt porphyrins.[17] No correlation of these observations with the bond distances could be attempted because the needed structural data are not available. A comparison of the structural data for five-coordinate RCo(OEP) and RCoPc complexes with equatorial ligands of sharply contrasting basicity, as well as pyridine adducts with CH_3CoPc and $CH_3Co(OEP)$, should provide some insight into the scale of the possible cis electronic influence.

Most of the literature data on the homolysis of the Co−C bond relate to bulky axial alkyls, relevance to adenosylcobalamine chemistry being an obvious reason. Excessively large bond dissociation energies (BDEs) and the resulting inconveniently slow rates may have been another reason for the scarcity of data on the homolytic cleavage of the Co−(primary alkyl) systems, with simple primary alkyls such as methyl or ethyl. In addition, β-hydrogen-containing alkyls, such as ethyl, could have been avoided because of possible in-cage β-H elimination. For the methyl−cobalt system, apart from BDE values for the homolysis of MeCbl[18] and its popular model, $CH_3Co(DH)_2(py)$,[19] and some kinetic data on $CH_3Co[TC-(4,4)]$,[5] there is probably only one report on the homolysis of σ-bonded methylcobalt(III) porphyrinic model[20] and one regarding the thermolysis of $CH_3Co^{III}Pc$ under aerobic conditions.[21]

A variety of alkylcobalt model complexes have been synthesized and extensively studied. The phthalocyanine model of MeCbl is unique in its outstanding methyl donor ability. It is interesting to see if this atypical reactivity will be reflected to any appreciable extent in the structural parameters of the coordination sphere as well in the Co−C bond dissociation energies. As follows from Marcus theory, small BDEs should contribute to lowering the intrinsic free-energy barrier for methyl (CH_3^+) transfer. [22] Hence, a comparison of the BDE values for inactive methyl donors, such as methylcobaloxime or MeCbl, and reactive CH_3CoPc is of interest.

The alkyl group effect (Me > Et) has been demonstrated to be a characteristic feature of the S_N2 reactions of $RCo^{III}Pc$ complexes,[9] in (anticipated) contrast to Et > Me, for the homolytic cleavage. In this work, the faster homolysis of $CH_3CH_2Co^{III}Pc$ than that of $CH_3Co^{III}Pc$ is documented. The homolysis data are also of interest because of the possible correlation between structural parameters of the axial system and the rates of homolysis. Rigid porphyrinic models,[23,24] with nonbulky axial alkyl groups, in which steric trans influence is minimal and electronic effects can be more easily observed, have not attracted as much attention as they deserve. Further studies of these systems seem warranted.

Experimental Section

Materials. $CH_3Co^{III}Pc$ and $CH_3CH_2Co^{III}Pc$ were prepared as described earlier,[9] and their solutions were handled at dim light. All chemicals were purchased from Aldrich. Pyridine and toluene were purified by standard methods. Double-distilled *N*-methylimidazole was used as received. Dimethylacetamide (DMA) was purified and handled as described elsewhere.[9]

Crystal Growth. X-ray quality crystals of $CH_3CH_2Co^{III}Pc$ were obtained by ethanol vapor infusion into a DMA solution of the complex, which had been flash chromatographed on a SiO_2-packed column using DMA as the eluant. All manipulations were

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performed in dim light, but the presence of air was irrelevant. $CH_3Co^{III}Pc(py)$ crystals were obtained by slow evaporation of a mixed toluene/pyridine solution that had been chromatographed on a SiO_2-packed column using the toluene/pyridine solution as the eluant. Numerous attempts to grow crystals of $CH_3Co^{III}Pc$, $CH_3Co^{III}Pc(DMA)$, $CH_3CH_2Co^{III}Pc(py)$, or $CH_3CH_2Co^{III}Pc$(N-MeIm) suitable for X-ray investigations proved to be unsuccessful.[25]

X-ray Crystallography. Dark blue crystals of $CH_3CH_2Co^{III}Pc$ and $CH_3Co^{III}Pc(py)$ were used for structure determination. Crystal, data collection, and refinement parameters are summarized in Table 2.

X-ray data collections were carried out with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using a KUMA KM4CCD diffractometer[26] equipped with an Oxford Cryosystems low-temperature device. Data were corrected for Lorentz-polarization and absorption effects.[27] The structures were solved by direct methods with SHELXS97[28] and refined by full-matrix least-squares against F^2 using SHELXL97.[29] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in calculated positions and refined as a riding model, and the isotropic displacement parameters for the hydrogen atoms were set at 1.2× the U_{eq} values for the appropriate carrier atoms. The ethyl group in $CH_3CH_2Co^{III}Pc$ is disordered over two alternative positions, with site occupation factors of 0.60(1) and 0.40(1). In the crystal structure of $CH_3Co^{III}Pc(py)$, the disordered molecule of solvent−pyridine was found; this molecule shows no specific interactions with the $CH_3Co^{III}Pc(py)$ molecules. This solvent molecule was refined isotropically with one common U_{iso} value and subjected to weak geometric constraints.

Kinetic Measurements. Rates for homolysis of $RCo^{III}Pc$ complexes were measured spectroscopically in dilute solutions of the organocobalt substrate under limiting trapping conditions. First-order rate law was obeyed by the kinetic data for the disappearance of the organocobalt substrate. The end-point method was used in most cases. The end points of these slow reactions were determined by anaerobic photolysis. The homolysis rates were zero-order in [TEMPO] over the concentration range of 0.005−0.1 M. Poor solubility of the $Co^{II}Pc$ product sets certain limitations on the kinetic measurements. If the disappearance of the substrate is to be followed spectrophotometrically, low concentrations of RCoPc ($<2 \times 10^{-5}$ M) are required, otherwise precipitation of $Co^{II}Pc$ may occur. Kinetic measurements in toluene are not viable unless an N-donor ligand is added, which not only prevents precipitation of the $Co^{II}Pc$ product but also eliminates cleavage of the phthalocyanine system.

Table 1. Yields (%) of the Products of Thermolysis of $RCo^{III}Pc$ in DMA

R		[py] (M)	[TEMPO] (M)	CH_4	C_2H_4	CH_3CH_3	Co^IPc^-
Me	60 h, 100 °C	0	0	100	0	2	0
Me	70 h, 100 °C	0.7	0	92	0	2.3	75
Me	70 h, 100 °C	0.7	0.02	0.92	0	0.35	0
Et	24 h, 60 °C	0	0	0	65	28	+ n.d.[a]
Et	6h, 80 °C	0	0	0	66	30	+ n.d.[a]
Et	15h, 70 °C	0	0	0	69	27	+ n.d.[a]
Et	15h, 70 °C	0.7	0	0	69	28	7.5
Et	15h, 70 °C	0	0.02	0	21	0.4	0
Et	15h, 70 °C	0.7	0.02	0	22	0.2	0
Et	15h, 60 °C	0.7	0.02	0	20	0.3	0
Et	6h, 80 °C	0.7	0.02	0	19	0.2	0

[a] Observed but not quantified.

In kinetic runs, usually, a deaerated solution of $RCo^{III}Pc$, containing TEMPO (0.02 M) and an N-donor ligand (where applicable) in a 25 mL flask was heated under Ar in an oil-circulating bath. The temperature was maintained constant within ± 0.1 °C. Periodically, an aliquot from the reaction mixture was quenched to room temperature in a 1 cm cell, and after equilibration at 25 °C, a UV−visible spectrum in an HP 8452A spectrometer was taken. In the absence of an N-donor, a small volume of 0.5 M sodium cyanide was added to the samples to turn unreacted $RCo^{III}Pc$ and the $Co^{II}Pc$ product into $RCoPc(CN)^-$ and $Co^{III}Pc(CN)_2^-$, respectively, and the spectrum was recorded. The rates calculated from the spectra of the original samples or from those with cyanide added agreed well, but the latter were more precise. Spectral changes at several wavelengths, usually the maxima of the difference spectra, were used for calculations (see Figure S2). (In the absence of added N-donor, they were 332, 646, and 664 nm, or when cyanide was added to the sample, they were 348, 428, 508 (methyl), 528 nm (ethyl), and 682 nm; see Figure S4.) The rate constants determined at various wavelengths agreed within 10%. The averaged values are reported.

In some cases, at 60 and 70 °C, the kinetic measurements were also performed in spectrophotometric cell under Ar. The results were consistent with those of sampling. Control runs in air in the absence of TEMPO yielded similar rates, although aerobic thermolyses of $CH_3CH_2Co^{III}Pc$ in DMSO-d_6 also produced small amounts of $CH_3CH_2OOCo^{III}Pc$, as suggested by the appearance of ethyl resonances in the ^1H NMR spectrum: δ −1.31 (3H, t, 7 Hz), −0.883 (2H, q, 7 Hz), downfield shifted from those of CH_3CH_2CoPc.[9] (A similar downfield shift was observed upon oxygen insertion into the Co−C bond in alkylcobalt(OEP) complexes.)[30]

Product Studies. Product studies were carried out in (i) DMA, (ii) DMA in the presence of pyridine, and (iii) DMA in the presence of pyridine and radical-trap TEMPO. Two exemplary procedures are described below and the results are collected in Table 1. GC analysis was performed as described earlier.[9]

$CH_3Co^{III}Pc$ Thermolysis in DMA in the Presence of 0.7 M Pyridine. A solution of $CH_3Co^{III}Pc$ (12 mg, 0.02 mmol) and pyridine (300 μL, 0.7 M) in 10 mL of DMA was sealed in a vial under Ar. In the course of a 70 h incubation at 100 °C, the solution turned yellow-green. The gas phase over the solution was subjected GC analysis for light hydrocarbons. Methane (92%) and ethane (2.3%) were found. A small portion of the yellow-green solution was transferred under Ar into a 0.1 mm cell, and a visible spectrum of Co^IPc^- was obtained (75% yield).

$CH_3CH_2Co^{III}Pc$ Thermolysis in DMA in the Presence of TEMPO. A solution of $CH_3CH_2Co^{III}Pc$ (12 mg, 0.02 mmol) and TEMPO (27 mg, 0.173 mmol) in 10 mL of DMA was sealed in a vial under Ar. In the course of a 15 h incubation at 70 °C, a nearly colorless solution was obtained in which a fine dark solid was suspended. A GC analysis for light hydrocarbons yielded ethylene (21%) and ethane (0.4%).

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(25) Growing an X-ray quality crystal of a phthalocyanine complex is not an easy task, as can be seen from the scarcity of structural data. Difficulties were encountered in earlier intense efforts to grow a suitable $CH_3Co^{III}Pc$ crystal from a THF solution (ref 21), where the solid consisted prevalently of six-coordinate $CH_3Co^{III}Pc(THF)$ molecules, but a good refinement could not be achieved because the THF was lost during the X-ray irradiation. Clearly the stronger ethyl labilizer and protic medium, in which the strength of O-donor ligands is considerably reduced, allowed dimeric $CH_3CH_2Co^{III}Pc$ to be obtained.

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Table 2. Experimental Data for the X-ray Diffraction Studies of $CH_3CH_2Co^{III}Pc$ and $CH_3Co^{III}Pc(py)$

	CH_3CH_2CoPc (100K)[a]	CH_3CH_2CoPc (ambient temperature)[a]	$CH_3CoPc(py)$
formula	$C_{34}H_{21}CoN_8$	$C_{34}H_{21}CoN_8$	$C_{38}H_{24}CoN_9 \cdot 1/2C_6H_5N$
fw	600.52	600.52	705.14
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	10.290(2)	10.425(1)	10.530(2)
b (Å)	11.003(2)	11.153(1)	14.977(3)
c (Å)	12.728(2)	12.805(1)	20.736(4)
α (deg)	78.81(1)	78.466(8)	90
β (deg)	72.65(1)	72.39(1)	104.36(3)
γ (deg)	69.08(1)	69.28(1)	90
V (Å^3)	1278.6(4)	1311.7(2)	3168.1(1)
Z	2	2	4
ρ_{calc} (g/cm^3)	1.560	1.521	1.479
temp (K)	100(1)	ambient	100(1)
θ range (deg)	3.33−25.00	3.51−22.50	3.38−25.00
reflns collected	8237	12697	15858
independent refls (R_{int})	4407 (0.047)	4587 (0.059)	5542 (0.033)
GOF on F^2	1.038	1.010	1.13
R1 ($I > 2\sigma(I)$)	0.0544	0.0458	0.0589
all data	0.1035	0.0653	0.0805
wR2 ($I > 2\sigma(I)$)	0.0901	0.0864	0.1351
all data	0.1028	0.0967	0.1468
largest diff peak and hole (e Å^3)	0.468 and −0.410	0.545 and −0.349	1.321 and −1.023

[a] Two different specimens were used to determine the low and ambient temperature structures.

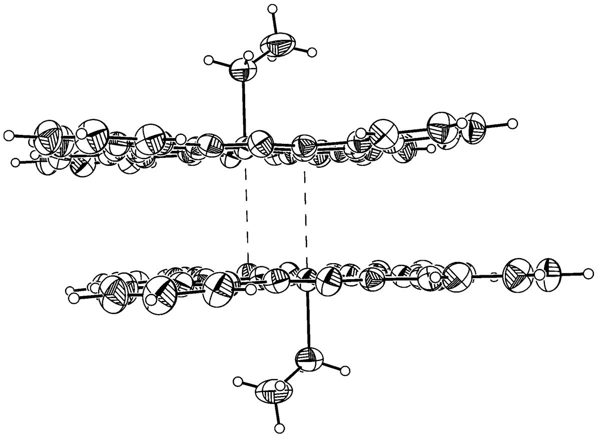

Figure 1. Side view of $(CH_3CH_2CoPc)_2$. The dashed lines link cobalt atoms with their N_{iso}' counterparts.

Table 3. Selected and Average Bond Lengths (Å) and Angles (deg) for $CH_3CH_2Co^{III}Pc$[a]

Co−C(11)	2.031(3)	C(11)−C(12A)	1.428(7)
Co−N_{iso}	1.914(3)	C(11)−C(12B)	1.428(12)
N_{iso}−C_a	1.376(5)	Co−C_t	0.086(1)
C_a−N_{aza}	1.327(3)	C_b−C_c	1.391(3)
C_a−C_b	1.449(6)	C_c−C_d	1.378(4)
C_b−C_b	1.387(5)	C_d−C_d	1.395(5)
Co−C(11)−C(12A)	119.0(3)	C_a−N_{aza}−C_a	122.1(2)
Co−C(11)−C(12B)	120.8(5)	N_{aza}−C_a−C_b	121.8(2)
N_{iso}−Co−C(11)	92(2)	N_{iso}−C_a−C_b	110.5(1)
cis-N_{iso}−Co−N_{iso}	89.9(3)	C_a−C_b−C_b	106.3(3)
Co−N_{iso}−C_a	126.7(2)	C_b−C_b−C_c	121.2(2)
N_{iso}−C_a−N_{aza}	127.7(2)	C_b−C_c−C_d	117.4(4)
C_a− N_{iso}− C_a	106.4(1)	C_c−C_d−C_d	121.4(4)
N−Co−C(11)−C(12A)	−10.2(5)	N−Co−C(11)−C(12B)	−76.7(9)

[a] Data for the ambient temperature structure.

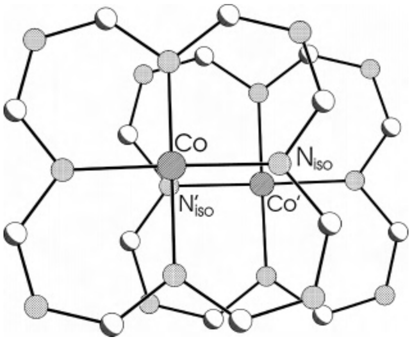

Figure 2. Perspective view of the $(CH_3CH_2CoPc)_2$ central fragment perpendicular to the coordination planes.

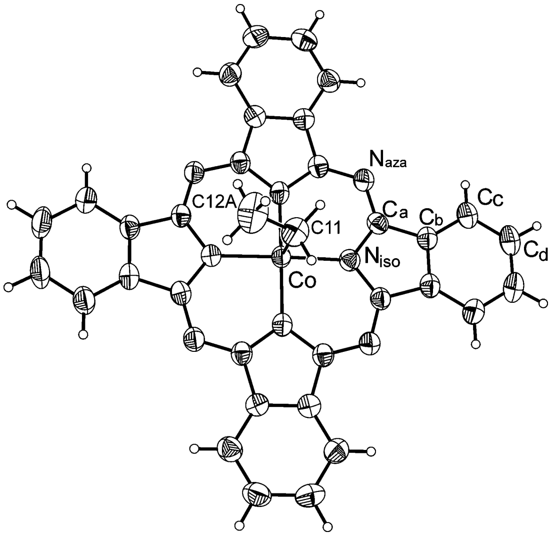

Figure 3. ORTEP drawing and numbering scheme for CH_3CH_2CoPc. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are depicted as spheres with arbitrary radii. For clarity, only one orientation of the ethyl group is shown.

Results and Discussion

Description of Structures. $(CH_3CH_2Co^{III}Pc)_2$ The crystal consists of centrosymmetric dimers (Figure 1). The cobalt atom of $CH_3CH_2Co^{III}Pc$ is five-coordinate and has a distorted square-pyramidal coordination geometry (Figure 3). The equatorial ligand planes of the two CH_3CH_2CoPc molecules are parallel with a 1.913 Å shift in the Co−N_{iso} direction from the eclipsed configuration (Figure 2). The distance between the two mean planes of four isoindole atoms (N_{iso}) is 3.21(3) Å, while the separation between benzo groups of one molecule and the N_4 plane of the other varies from 2.99 to 3.6 Å. The interplanar separation is thus characteristic of π stacking. Packing forces and intermolecular interactions cause some peripheral deformations in the essentially planar phthalocyanine ligand. The most out-of-N_4-plane benzo group (dihedral angle of ∼7°) is bent toward an ethyl group of another "dimer". The cobalt atom of one phthalocyanine faces an isoindole N atom of the other, N_{iso}', at a separation of 3.303 Å, an arrangement different from that of the β form of $Co^{II}Pc$, where an azamethine atom of the neighboring molecule at a 3.219[31] or 3.154 Å [32] distance is the closest contact. The straight line determined by Co and N_{iso}' is

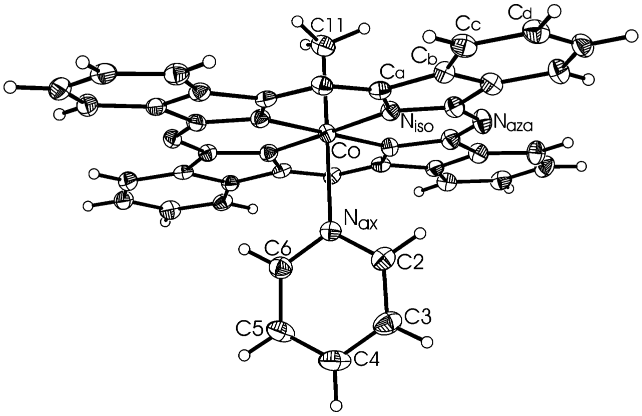

Figure 4. ORTEP drawing and numbering scheme for $CH_3CoPc(py)$. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are depicted as spheres with arbitrary radii.

Table 4. Selected and Average Bond Lengths (Å) and Angles (deg) for $CH_3Co^{III}Pc(py)$

Co−C(11)	1.993(4)	Co−N_{ax}	2.177(3)
Co−N_{iso}	1.922(3)	Co−C_t	−0.0052(14)
N_{iso}−C_a	1.373(4)	C_c−C_d	1.381(5)
C_a−N_{aza}	1.322(5)	C_d−C_d	1.394(6)
C_a−C_b	1.453(4)	N_{ax}−C2 (py)	1.342(3)
C_b−C_b	1.391(6)	C2−C3 (py)	1.379(3)
C_b−C_c	1.389(4)	C3−C4 (py)	1.374(4)
N_{iso}−Co−C(11)	89.8(7)	C_a−N_{aza}−C_a	121.5(1)
cis-N_{iso}−Co−N_{iso}	90.0(2)	N_{aza}−C_a−C_b	122.2(4)
N_{iso}−Co−N_{ax}	90.1(8)	N_{iso}−C_a−C_b	110.0(3)
		C_a−C_b−C_b	106.4 (3)
Co− N_{iso}−C_a	126.4 (3)	C_b−C_b−C_c	121.3 (6)
N_{iso}−C_a−N_{aza}	127.8 (2)	C_b−C_c−C_d	117.4 (4)
C_a−N_{iso}−C_a	107.2 (2)	C_c−C_d−C_d	121.4 (3)
C2py−N_{ax}−C6py	117.1(3)	py rotation[a]	29.2
N_{ax}−C2py−C3py	123.1(1)	py cant[b]	88.8(1)
C2py−C3py−C4 py	119.2(1)	C3py−C4py−C5 py	118.4(4)

[a] Dihedral angle between the pyridine plane and an N_{iso}−Co−N_{ax} plane. [b] Dihedral angle between pyridine plane and the mean plane of the four N_{iso} atoms.

inclined to the plane of four N_{iso} atoms at an angle of 87.7°. The four isoindole nitrogen atoms that form the basal plane are coplanar within ± 0.004 Å. The cobalt atom is displaced 0.0857(14) Å from the mean $(N_{iso})_4$ plane toward the ethyl group. The average Co−N_{iso} bond length, 1.916(3) Å, is virtually identical to that found in the β form of $Co^{II}Pc$.[33] The cis N_{iso}−Co−N_{iso} angles average 89.9(3)°. The axial Co−C bond is 2.031(3) Å long and is tipped slightly, 2.3°, from the normal to the mean plane of four N_{iso} atoms. The axial ethyl group is disordered (see the Experimental Section). There are two arrangements in which the CH_2−CH_3 bond and a Co−N_{iso} bond are nearly eclipsed (torsion angles N_{iso}−Co−C(11)−C(12) = 10.5(6) and 76.2 (10)°). The corresponding Co−C(11)−C(12) angles are 119.2(4) and 121.1(5)°, respectively. The disorder did not disappear when the structure was determined at 100 K. The torsion angle N_{iso}−Co−C(11)−C(12) of 10.5° is similar to the analogous angle in $CH_3CH_2Co(OEP)$.[7] The average bond lengths and angles of the phthalocyanine macrocycle are typical.

Thermal motion was held responsible for the extremely short CH_3−CH_2 distance of 1.39(1) Å observed for the otherwise normal ethyl group in the ambient temperature structure of the six-coordinate complex $CH_3CH_2Co(saloph)(py)$.[3] Two independent determinations of the $CH_3CH_2Co^{III}Pc$ structure, one of them carried out at 100 K and the other at ambient temperature, gave essentially identical results. This makes the thermal motion explanation for the shortening of the C(11)−C(12) bond in $CH_3CH_2Co^{III}Pc$ less plausible. Also, the shortening of the CH_3−CH_2 distance in other σ-bonded ethylcobalt(III) complexes appears to be real. For instance, should thermal motion be the only reason for the apparent shortening of the Cα−Cβ bond in the propyl group of *n*-PrCo[TC-(3,3)],[4] then the Cβ−Cγ bond would be shorter than Cα−Cβ one, which is not the case (Table 5).

$CH_3Co^{III}Pc(py)$. The cobalt atom of $CH_3Co^{III}Pc(py)$ has distorted octahedral geometry. The four isoindole nitrogen atoms that form the basal plane are coplanar within ±0.0056 Å. The cobalt atom is displaced by at most a trivial amount, 0.0054(12) Å, from this plane toward the nitrogen atom of the axial pyridine ligand. The Co−C bond is 1.990(3) Å long and is perpendicular to the plane. The average Co−N_{iso} bond length is 1.920(4) Å, and that of Co−N_{ax} is 2.174(2) Å. The N_{iso}−Co−N_{iso} angles depart trivially from the idealized 90°.

The plane of the pyridine ring is inclined at an angle of 88.8° with respect to the equatorial nitrogen mean plane and is rotated 29.1° from an N_{iso}−Co−N_{ax} plane. The latter angle is significantly smaller than 45°, the value corresponding to the orientation with minimal nonbonded contacts between the pyridine ortho hydrogen atoms and the phthalocyanine core. It is close to the 28.6(2)° value found in $Co^{II}Pc(py)_2$, where nonbonded interactions are unlikely because of the very long Co−N_{ax} bonds,[34] and it is larger than the 14.3° rotation angle in relevant $CH_3Co(OEP)(py)$. The average bond lengths and angles of the phthalocyanine macrocycle are unremarkable.

Five-Coordinate Structure of $CH_3CH_2Co^{III}Pc$ in Solid Form. The pseudo-five-coordinate structure of relatively electron-deficient $CH_3CH_2Co^{III}Pc$ can be observed in the solid only because the attracting interaction between two large aromatic systems is stronger than the binding energy of trans axial O-donor ligand in the protic medium (the solvents in which the crystals are grown). Packing effects may also favor the dimeric structure of $CH_3CH_2Co^{III}Pc$ in the solid, since in dilute solutions, in nonbinding solvents, the complex exists in monomeric form,[9] which attests to the weakness of Co−N_{iso}' interaction in the dimer. The weakness of the interaction between the Co atom and N_{iso}' is also evident from (i) the long Co−N_{iso}' distance, which is ca. 1.2 Å larger than the 2.05 Å Co(III)−N(sp^2) coordination distance calculated by Little and Ibers,[35] (ii) the negligible 0.014 Å displacement of the N_{iso}' atom toward facing Co, and (iii) the fact that the cobalt remains significantly

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(31) Mason, R.; Williams, G. A.; Fielding, P. E. *J. Chem. Soc., Dalton Trans.* **1979**, 676.

(32) Williams, G. A.; Figgis, B. N.; Mason, R.; Mason, S. A.; Fielding, P. E. *J. Chem. Soc., Dalton Trans.* **1980**, 1688.

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(35) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4440.

Table 5. Comparison of the Geometry of Five-Coordinate R-Cobalt(III) Complexes with Primary Alkyl Axial Group R

complex	Co−C (Å)	Cα−Cβ (Å)	Cβ−Cγ (Å)	Co−C−C (deg)	Co−N$_{eq}$^{a} (Å)	Co−C$_t$^{c} (Å)	ref
CH_3CH_2CoPc[b]	2.031(3)	1.428(7) 1.428(12)	−	120.8(5) 119.0(3)	1.914(3)	0.086(1)	this work
$CH_3CH_2Co(OEP)$	1.988(2)	1.503(3)	−	114.2(1)	1.970(8)	0.103(1)	7
$CH_3CH_2Co[TC\text{-}(3,3)]$	1.963(6)	1.496(9)	−	116.7(4)	1.890(4)	0.213(1)	5
n-PrCo[TC-(3,3)]	1.976(7)	1.49(1)	1.53(1)	117.7(5)	1.894(9)	0.185(1)	5
$CH_3Co^{III}(saloph)$[d]	1.957(13)	−	−	−	1.868(5)	0.105(2)	3
$CH_3Co^{III}(OEP)$	1.973 (6)	−	−	−	1.966(14)	0.094 (3)[e] 0.105(3)[f]	6
$CH_3Co[TC\text{-}(4,4)]$	1.940 (8)	−	−	−	1.90[g]	0.107(1)	5
$CH_3Co(acacen)$	1.952 (18)	−	−	−	1.873(12)	0.12	2

[a] Average value. [b] In this table ambient temperature data are given, but the less well-resolved low-temperature structure is not significantly different. [c] Displacement of Co atom from the least-squares plane of the four equatorial donors. [d] Molecule B. [e] Molecule 1. [f] Molecule 2. [g] Average value for a molecule where two pairs of different length Co−N$_{eq}$ bonds are observed.

displaced toward the ethyl group from the mean N_4 plane, while in six-coordinate complexes it is virtually in-plane. The Co−C$_t$ displacement in $CH_3CH_2Co^{III}Pc$ is merely 0.017(2) Å smaller than it is in its strictly monomeric OEP congener. In the X-ray structures of some RCo^{III}(chel)dimers, considerably shorter distances between Co and a facing donor (usually oxygen atom, O′) have been found, such as the 2.34 Å Co−O′ distance in $(EtCo(salen))_2$[36]or the 2.435 Å Co−O′ distance in one of $CH_3Co(saloph)$ dimers,[9] and the donor atoms are visibly displaced from their equatorial moiety toward the Co atom. These cannot be regarded truly five-coordinate complexes.

Further discussion on this point would not be necessary if it were not for the fact that the weak axial interactions in β-$M^{II}Pc$ have been held responsible for changes in the ground electronic state between the monomeric tetragonal molecules and the β phase,[37,38] where each cobalt atom interacts with two N_{aza} atoms at distant (∼3.2 Å) axial positions. It should be noted that in present case we have only one interaction of this type per one CH_3CH_2CoPc molecule. Furthermore, the interaction is probably weaker than those in the β form. According to Figgis et al., in a $Co^{II}Pc$ molecule, a considerable positive charge (+1.88) resides on the cobalt atom, and N_{aza} is more negatively charged than N_{iso}.[37] Face-to-face interactions and charge distribution over the planar system in CH_3CH_2CoPc are not expected to be very different. In the β form and in the $Co^{II}Pc$ dimer, van der Waals forces are the main contributor to binding energy, while electrostatic interactions are believed to determine the orientation of the two planes.[39] Therefore, the preference for N_{aza} over N_{iso} atoms in the β conformer, also present in the structure of $Co^{II}NPc(py)$,[40] can be accounted for by both the larger Co−Co distance and the increased negative charge on N_{aza}. The fact that this preference is not manifested in $(CH_3CH_2CoPc)_2$ and in the α conformer of $Co^{II}Pc$,[41] where there is no N atom in the axial position, underlines the weakness of this type of interactions.[42] Even though the CH_3CH_2CoPc molecules in the solid are not separated as ideal, and it would be unwise to disregard the interaction between Co and N_{iso}' completely, it seems justified to view the structure as essentially five-coordinate.

Comparison of the Structures. Comparisons with other σ-bonded alkyl-Co(III) phthalocyanine complexes are not possible because none have been structurally characterized prior to this report. Despite intense efforts, a complete series of structures needed for the investigation of structural effects relevant to homolytic Co−C bond disruption, such as five-coordinate $RCo^{III}Pc$, $RCo^{III}Pc(L)$ and $Co^{II}Pc(L)$,[43] is not available. Also the alkyl group effect on the structure cannot be directly studied in either the $RCo^{III}Pc$ or $RCo^{III}Pc(L)$ series.

Factors influencing the length (and strength) of Co−C bond have gained much interest recently, and a great deal of theoretical work has been done to explain the so-called inverse trans effect. On the other hand, it should be recognized that alkylcobalt chemistry may exemplify a fundamental rule of chemistry that the length of a single bond between a given pair of atoms is remarkably independent of the identity of a molecule in which these atoms reside.[49] Small variations in the Co−C distances, in particular for complexes with same axial alkyl group, should be considered from this perspective, especially since the accuracy of the X-ray determinations is often low compared to the observed changes in bond lengths.

$CH_3CH_2Co^{III}Pc$ appears to be the most electron-deficient five-coordinate alkylcobalt(III) model among the few structurally characterized complexes of this type. The Co−C bond in $CH_3CH_2Co^{III}Pc$, 2.031(5) Å, is the longest found in five-

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(37) Reynolds, P. A.; Figgis, B. N. *Inorg. Chem.* **1991**, *30*, 2294.

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(41) Ballirano, P.; Caminiti, R.; Ercolani, C.; Maras, A.; Orru, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 12798.

(42) It should be also noted that in the structure of $MgPc(H_2O)(py)_2$ dimer N atoms of the phthalocyanine moiety are not even the closest contacts of the central metal atoms. Fischer, M. S.; Templeton, D. H.; Zalkin, A.; Melvin, C. *J. Am. Chem. Soc.* **1971**, *93*, 2622.

(43) No X-ray structures of strictly five-coordinate $Co^{II}Pc$(N-donor) complexes are known.

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(47) Zou, X.; Brown, K. L. *Inorg. Chim. Acta* **1998**, *267*, 305.

(48) Ouyang, L.; Rulis, P.; Ching, W. Y.; Nardin, G.; Randaccio, L. *Inorg. Chem.* **2004**, *43*, 1235.

(49) The difference in the bond distance between probably extreme cases of *i*-$PrCo(DH)_2(py)$ (Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754) and CF_3Cbl (Table 6) appears to be significant, 0.22 Å.

Table 6. Bond Distances for the Coordination Sphere of Selected $CH_3Co^{III}(chel)(py)$ Complexes and Some Alkylcobalamins

complex	Co−C (Å)	$Co-N_{ax}$ (Å)	ref	BDE (kcal/mol)
$CH_3Co^{III}(DH)_2(py)$	1.998 (2)	2.068 (3)	44	33 ± 2[a]
$[CH_3Co(DO)(DOH)pn(py)]PF_6$	2.003 (3)	2.106 (3)	4	
$CH_3Co^{III}Pc(py)$	1.990 (3)	2.174 (2)	this work	30 ± 1
$CH_3Co^{III}OEP(py)$	2.018 (12)	2.214 (9)	6	
$CH_3Co(acacen)(py)$	1.99 (1)	2.16 (1)	45	
MeCbl	1.979 (4)	2.162 (4)	46	37 ± 3[b]
CF_3Cbl	1.878 (12)	2.049 (1)	47	
AdoCbl	2.030 (3)	2.237 (3)	48	31.5 ± 1.3[c]

[a] Ref 19. [b] Ref 18. [c] Ref 48.

coordinate complexes with a simple primary alkyl axial group (Table 5). It is as long as the bonds in $CH_3(CO)CH_2Co$-(TPP), 2.028(3) Å,[50] or (*i*-Pr)Co(saloph)·$1.5H_2O$, 2.031(8) Å.[51] Such an elongated Co−C bond distance in a 16-electron complex with an "electron-deficient" equatorial system (electron density outflow from the axial system) is perhaps consistent with increased electrophilic character of the α carbon, in accordance with the outstanding S_N2 reactivity of the five-coordinate $RCo^{III}Pc$ complexes.[9]

As is apparent from Table 5, the short CH_3-CH_2 bond and the large Co−C−C angle of ~120° are in the range of values characteristic of alkylcobalt(III) complexes. The simultaneous decrease of the $C\alpha-C\beta$ bond distance and opening of the Co−C−C angle, with a virtually unchanged Co−C bond length, were observed by Marzilli et al. upon increasing the bulk of the trans axial ligand in ethyl−cobaloxime models.[52] It is interesting that, in CH_3CH_2CoPc, the largest angle coincides with the shortest $C\alpha-C\beta$ bond of those for the five-coordinate structures shown in Table 5. In view of the long Co−C bond in the phthalocyanine model, it seems unlikely that the difference in the structural parameters for the ethyl group in complexes containing equatorial ligands of similar geometry, CH_3CH_2CoPc and $CH_3CH_2Co(OEP)$, is caused by steric interactions.

The Co−C bond lengths have been claimed to be insensitive to the nature of the equatorial ligand but dependent on the bulk and electron-donor properties of the axial alkyl ligand.[51] This rule seems to be followed by the six-coordinate complexes as seen, for instance, in Table 6, but the first part of it is not quite observed by few structurally characterized five-coordinate complexes, where the Co−C bonds tend to be shorter in the electron-rich models than they are in the electron-poor models (Table 5). The Co−C bond in $CH_3CH_2Co^{III}Pc$ is 0.043(4) Å longer than that in $CH_3CH_2Co^{III}(OEP)$. When the small variance in the Co−C bond distances is taken into account, especially among complexes with same axial alkyl group, the difference seems to be significant.[53] As an example, it is comparable to the Co−C bond elongation in AdoCbl, calculated for drastic compression of the trans $Co-N_{ax}$ bond.[14]

Apart from electronic cis influence, there is another potential reason for the elongated Co−C bond in the phthalocyanine complex: it seems that the Co atom is held tighter (lower $Co-C_t$ value) by the rigid phthalocyanine equatorial ligand, which forms shorter bonds to the central metal atom than those formed by the porphyrin ligands. (The length of $Co-N_{eq}$ bonds in phthalocyanine complexes are closer to those formed by more flexible ligands (Table 6).) The reduced displacement of the cobalt atom from the equatorial ligand plane, $Co-C_t$, may force expansion of the Co−C bond to avoid nonbonded interactions of the alkyl group with the equatorial moiety. However, as a dominant factor, this is incompatible with the fact that in the OEP model the sum of the Co−C and $Co-C_t$ distances is still 0.026 Å less than that in the phthalocyanine complex (Table 5).

Short Co−C bonds in five-coordinate tropocoronand models (Table 5), 0.068 Å shorter in $CH_3CH_2Co[TC-(3,3)]$ than those in CH_3CH_2CoPc, are striking. The tropocoronand compounds must be extremely electron-rich, as shown by the lack of any trans-axial ligation, even by good N-donor ligands,[5] and large negative Co(II)/Co(I) potentials.[54] Despite their short length, the Co−C bonds in the tropocoronand models are not particularly strong.[5]

In the presence of two axial ligands, including a strong alkyl labilizer, a strong electron-donating equatorial system may exert a destabilizing effect causing an increase in both axial bond distances. In practice, the lengths of relatively weak $Co-N_{ax}$ bonds are far more sensitive than the Co−C distances to changes in the equatorial system (Table 6). It seems that in methylcobalt porphyrinic complexes the steric interactions of (nonbulky) axial N-donor ligands with the equatorial moiety are of secondary importance. Hence, the $Co-N_{ax}$ distance in $CH_3Co(OEP)(py)$, larger than those in MeCbl[55] and $CH_3CoPc(py)$, is likely to reflect, mostly, a stronger electron donation from OEP than that from Pc or corrin.[56] The $Co-N_{ax}$ bond length could be considered to be a measure of the combined inductive effects of the axial alkyl ligand and the equatorial system. This superposition of trans and cis influences would appear to be similar in MeCbl and $CH_3CoPc(py)$, in which both axial bond distances are very similar (Table 6). We could try to use the $Co-N_{ax}$ distances in complexes with same alkyl and N-donor axial ligands to characterize the electron deficiency of the equatorial system. By this criterion, phthalocyanine falls between the Costa-type models and the porphyrins (Table 6), an order consistent with that of the formation constants for CH_3Co^{III}-(chel)(py) complexes.[9] However, the $Co-N_{py}$ bond length in $CH_3Co(acacen)(py)$, thought to be one of the most electron-rich B_{12} models,[51] does not fit into the trend.

The long $Co-N_{ax}$ bond in $CH_3CoPc(py)$, 2.174(2) Å, compared to 2.068(3) Å in $CH_3Co^{III}(DH)_2(py)$ (Table 6),

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(50) Kastner, M. E.; Scheidt, W. R. *J. Organomet. Chem.* **1978**, *157*, 109.

(51) Marzilli, L. G.; Summers, M. F.; Bresciani-Pahor, N.; Zangrando, E.; Charland, J.-P.; Randaccio, L. *J. Am. Chem. Soc.* **1985**, *107*, 6880.

(52) Marzilli, L. G.; Summers, M. F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Am. Chem. Soc.* **1986**, *108*, 4830.

(53) The comparison is meaningful because of the similar steric requirements of the two complexes, at least in the vicinity of the Co center.

(54) Doerrer, L. H.; Bautista, M. T.; Lippard, S. J. *Inorg. Chem.* **1997**, *36*, 3578.

(55) The Dmbz ligand causes some upward folding of the corrin ring but with minimal effect on the Co−C bond when the ligand is CH_3 (ref 51b).

(56) The elongation of the Co−C bond in $CH_3Co(OEP)$ on pyridine binding is real but because of the lower resolution of the $CH_3Co(OEP)py$ structure the extent of this expansion is less certain.

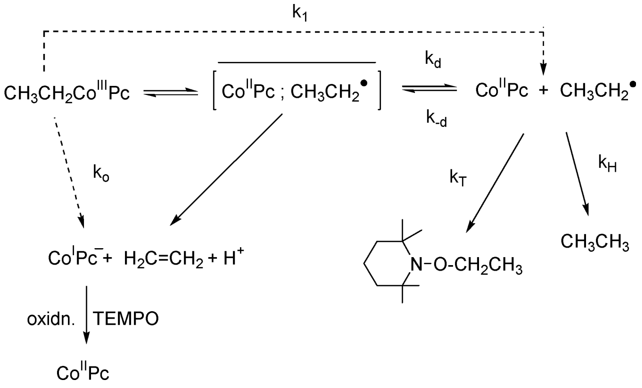
agrees well with the observation that $RCo^{III}Pc$ (N-donor) compounds are kinetically labile for complexes with an electron-deficient equatorial system.[9,57] The increased lability of the long $Co-N_{ax}$ bonds has been observed by Marzilli et al.[58]

Contradiction Between Cis Electronic Influences in Five- and Six-Coordinate Complexes. It should be emphasized that, while the Co−C bond in $CH_3CH_2Co^{III}Pc$ is longer than that in $CH_3CH_2Co^{III}(OEP)$, both axial bonds in $CH_3Co^{III}Pc(py)$ are shorter than those in its OEP analogue. The seemingly contradictory trends in the cis effect on the length of the Co−C bond in the five- and six-coordinate complexes are noteworthy, especially in view of the similar steric requirements of the OEP and Pc complexes, at least in the vicinity of the coordination center. The changes in the Co−C bond distance in the three five-coordinate ethylcobalt(III) compounds of Table 5 parallel the order of Co(II)/Co(I) redox potentials for the corresponding Co^{II}(chel): −0.35,[12] −0.95,[13] and ca. −1.6 V[59] vs SCE for the phthalocyanine, octaethylporphyrin, and tropocoronand complexes, respectively.

The inverse trend between the Co−C bond length and the equatorial ligand basicity observed for five-coordinate $CH_3CH_2Co^{III}$(chel) complexes is based on a few well-resolved structures. More structural data in support of this proposal are certainly needed. Unfortunately, because of large uncertainties of the Co−C distances in some of the five-coordinate CH_3Co^{III}(chel) compounds of Table 6 and the lack of data for a structure with a strongly electron-deficient equatorial ligand, the trend, if existent, hardly could be observed in the methyl−Co(III) system.

As was pointed out by one of reviewers for this work, the trend may seem counterintuitive. Indeed, if we view the Co−C bond as formed by an "electrostatic" interaction of Co^{3+} with a negatively charged alkyl ligand, then the strong alkyl donor should be pulled more tightly in a complex with a less-donating equatorial system. However, it has been noted on many occasions that the Co−C bond is a normal covalent bond, as witnessed by homolytic cleavage of the bond, and the cobalt should not be considered to be true Co^{3+}.[60] The fact that nucleophilic attack on the C atom is possible, at least in some cases, suggests that the axial system is electron deficient,[61] and there is evidence that the five-coordinate form is the reactive species in these S_N2 reactions.[9] The hypothesis of the longer Co−C bonds in five-coordinate complexes with less electron-donating equatorial ligands is viable if the Co−C bond is considered as essentially covalent. In five-coordinate complexes with strong equatorial donors, an electron-density shift into the axial bond would be possible making it shorter. The trend would not be held in six-coordinate complexes, where the trans axial ligand exerts a destabilizing influence (4 electrons total in the axial system).

Scheme 1. Thermolysis of the Co−C Bond in $CH_3CH_2Co^{III}Pc$



The $Co-N_{ax}$ bonds in the five-coordinate porphyrinic complexes of Co(II) do not follow the trend described above. The $Co-N_{py}$ distances are remarkably invariant in $Co^{II}(TPP(CF_3)_4)(py)$,[62] 2.166(3) Å, Co^{II}TPP(3,5-lutidine),[63] 2.166 Å, and Co^{II}(NPc)(py), 2.167(9) Å.[40] A shorter $Co-N_{ax}$ distance was expected in $Co^{II}(TPP(CF_3)_4)(py)$ because of the presence of electron-withdrawing CF_3 groups,[62] and steric interactions in this severely distorted molecule were invoked to explain why it was not. The longest bond in compounds of this type, 2.191(2) Å, was found in $Co^{II}(OEP)(4\text{-}Me_2N\text{-}py)$, where, notably, no substantial steric interactions are present.[6] Thus, it appears that in 17-electron five-coordinate complexes of Co(II) with an unpaired electron in the $3d_{z^2}$ orbital, the trend is not held: strong electron-donating equatorial ligands make the axial bond, if anything, longer.

Homolysis of the Co−C Bond in $RCo^{III}Pc$. When $CH_3Co^{III}Pc$ is thermolyzed in DMA in the absence of TEMPO, regardless of the presence of pyridine ligand, methane is evolved almost quantitatively (Table 1). Apparently there is a sufficient amount of H-donors in the medium. As expected, the fate of the methyl radical is different in the presence of a radical trap such as TEMPO: low yields of methane show that the scavenging by ca. 0.02 M TEMPO is much faster than the interception by H-donors. At this TEMPO concentration, the trapping of free (out-of-cage) radicals usually exhibits saturation.[64] Thermolysis of $CH_3CH_2Co^{III}Pc$ yields a β-H-elimination product, ethylene, in 69 and 21% yield in the absence and presence of the TEMPO trap, respectively (Table 1), consistent with ethylene being produced in a cage reaction (Scheme 1).

The yields of ethylene found in this study are fairly large compared to some other systems,[65] but the thermolysis of cyclopentylmethyl-B_{12} produced still larger amounts of the

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(57) Galezowski, W. *Inorg. Chem.* **2005**, *44*, 5483.

(58) Parker, W. O., Jr.; Zangrando, E.; Bresciani-Pahor, N.; Marzilli, P. A.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1988**, *27*, 2170.

(59) Reported as approximately −2.1 V vs Fc^+/Fc in THF in ref 52. A typical shift between SCE and Fc^+/Fc of 0.5 V is assumed (see ref 12).

(60) Stadlauber, E. A.; Holland, R. J.; Lamm, F. P.; Schrauzer, G. N. *Bioinorg. Chem.* **1974**, *4*, 67. (b) A rather extreme view that alkylcobalt(III) complexes have considerable Co(I) character has been presented in Andriuniow, T.; Zgierski, M. Z.; Kozlowski, P. M. *J. Phys. Chem. B* **2000**, *104*, 10921 and also in (c) De Ridder, D. J. A.; Zangrando, E., Bürgi, H.-B. *J. Mol. Struct.* **1996**, *474*, 63.

(61) The Mulliken charges calculated for the MeCbl-like structure in Jensen, K. P.; Ryde, U. *J. Am. Chem. Soc.* **2003**, *125*, 13970 are −0.01 on CH_3 and +0.54 on Co.

(62) Terazono, Y.; Patrick, B. O.; Dolphin, D. H. *Inorg. Chim. Acta* **2003**, *346*, 265.

(63) Scheidt, W. R.; Ramanuja, J. A. *Inorg. Chem.* **1975**, *14*, 2643.

(64) Stolzenberg, A. M.; Cao, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9078.

(65) Tsou, T.-T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623 and references therein.

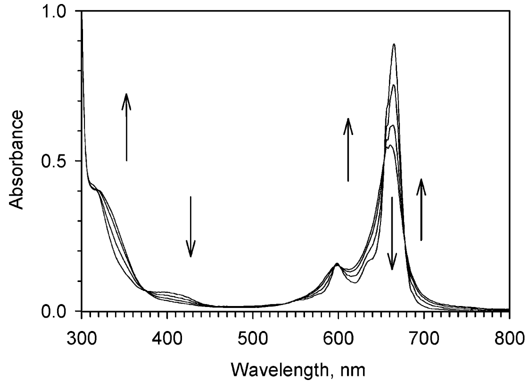

Figure 5. Spectral changes upon homolysis of $CH_3Co^{III}Pc(py)$ in DMA (80 °C) at 0, 6, 15, and 24 h. [py] = 2 M.

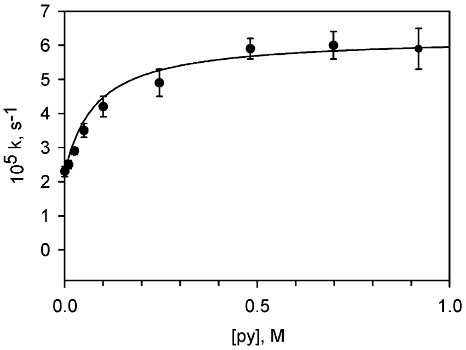

Figure 6. Effect of pyridine on the rates of thermolysis of CH_3CH_2CoPc in DMA (60 °C), [TEMPO] = 0.02 M. The curve was calculated for $K_{py} = 12.5\ M^{-1}$, $k_{py} = 6.2 \times 10^{-5}\ s^{-1}$, and $k_{DMA} = 2.3 \times 10^{-5}\ s^{-1}$.

β-H-elimination product.[66] In the absence of an effective radical trap, in concentrated solutions of $CH_3CH_2Co^{III}Pc$, recombination of the ethyl free radicals with $Co^{II}Pc$ clearly plays a role, leading to an increased yield of ethylene. It appears that the putative second step of β-H elimination, hydrogen atom transfer from the caged ethyl radical, is extremely rapid, only about 4 times slower than separation of the geminate radical pair. Such fast β-H eliminations are not unprecedented and have been shown to be consistent with a nonconcerted mechanism via a cobalt hydride,[67] an intermediate that was frequently postulated but rarely detected. The $Co^{I}Pc^{-}$ product observed when concentrated $CH_3CH_2Co^{III}Pc$ is thermolyzed anaerobically in the absence of TEMPO agrees well with this mechanism, since in DMA, because of the extremely low basicity of $Co^{I}Pc^{-}$, $HCo^{I}Pc$ would readily dissociate into H^{+} and $Co^{I}Pc^{-}$.[68,69]

As depicted in Figure 6, ligation by pyridine accelerates the homolysis, although the effect is very moderate. The curve shown in Figure 6 was fitted using an independently measured stability constant for $CH_3CH_2Co^{III}Pc(py)$.[9] In kinetic runs performed in the presence of pyridine or *N*-MeIm, the concentration of the ligand was large to enforce saturation regime.

Table 7. Rates for Thermolysis of $CH_3Co^{III}Pc$, k_{obs} ($10^{-6}\ s^{-1}$), in DMA[a]

	ligand added		
temp (°C)	none	pyridine[b]	*N*-MeIm[c]
60		1.8 ± 0.2	
70	2.7 ± 0.1	6.7 ± 0.3	6.3 ± 0.3[d]
80	11.5 ± 0.4	22.4 ± 0.4	13.2 ± 0.3
90	35 ± 1	110 ± 10	38 ± 2
100	160 ± 5	280 ± 20	
110	425 ± 20		

[a] [TEMPO] = 0.02 M [b] [py] = 2 M. [c] [*N*-MeIm] = 0.5 M. [d] In toluene.

Table 8. Rates for Thermolysis of $CH_3CH_2Co^{III}Pc(L)$, k_{obs} ($10^{-6}\ s^{-1}$), in DMA[a]

	ligand added		
temp (°C)	none	pyridine[b]	*N*-MeIm[c]
55		30 ± 2	
60	23 ± 2	62 ± 2	45 ± 2
65		130 ± 6	
70	110 ± 10	250 ± 10	160 ± 10
80	450 ± 30	880 ± 40	510 ± 20
90	1350 ± 50		

[a] [TEMPO] = 0.02 M. [b] [py] = 2 M. [c] [*N*-MeIm] = 0.5 M.

A comparison of the rates for the homolytic cleavage of the Co−C bond in five- and six-coordinate species would be of great interest. Unfortunately, homolysis of five-coordinate $RCo^{III}Pc$ species in toluene is not viable because of a decay process yielding an unknown orange product.[70] This unwanted process seems to be independent of the presence of air. The addition of a good ligand, such as pyridine prevents the bleaching, but then six-coordinate species prevail.[9] Ironically, spectral changes observed in the course of thermolysis of dilute solutions of $RCo^{III}Pc$ (Figure 5) are similar to those of S_N2 reactions in dilute solutions of the organocobalt substrate, where the immediate $Co^{I}Pc^{-}$ product is not observed because of the presence of trace oxidants.[9] Furthermore, thermolysis of concentrated solutions of the organocobalt substrate, in the absence of the TEMPO trap, often yields $Co^{I}Pc^{-}$ (Table 1), the formation of which could be generally viewed as an indication of heterolytic methyl transfer. In the presence of TEMPO, no trace of $Co^{I}Pc^{-}$ is observed.[71] Therefore GC analysis of the gas phase, in the absence of TEMPO, is of great help in distinguishing between the homolytic and displacement mechanisms unambiguously.

Kinetic data for homolysis of RCoPc are collected in Tables 7 and 8. The rates were measured over a range of temperatures to determine activation parameters and bond dissociation energies (BDEs) that are listed in Table 9. Eyring plots are available in the Supporting Information. Under limiting trapping conditions, the k_{obs} for disappearance of CH_3CoPc is simply the rate constant k_1 for homolysis (formation of free radicals). The k_1 values for the ethyl

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(66) Kim, S. H.; Chen, H. L.; Feilchenfeld, N.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3120.

(67) Garr, C. D.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 10440.

(68) In ref 21, we demonstrated that there is no measurable H_2 evolution on addition of excess CF_3COOH to a $Co^{I}Pc^{-}$ solution.

(69) Electron transfer from the ethyl radical to Co(II)Pc followed by deprotonation of ethyl cation is also conceivable.

(70) A reaction similar to the formation of a yellow decay product in DMF observed by others: Rollmann, D.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1455.

(71) The reduction potential of TEMPO is −0.15 V vs SCE: Finke, R. G.; Smith, B. L.; Mayer, B. J.; Molinero, A. A. *Inorg. Chem.* **1983**, *25*, 3677 and references therein. This does suggest an easy oxidation of $Co^{I}Pc^{-}$ by the trap. Oxidative properties of TEMPO were also discussed in Samsel, E.; Kochi, J. *J. Am. Chem. Soc.* **1986**, *108*, 4790.

Table 9. Activation Parameters for Homolytic Cleavage of the Co−C Bond in $RCo^{III}Pc$ Complexes in DMA

R	axial ligand	$\Delta H_1^{\ddagger}$ (kcal/mol)	$\Delta S_1^{\ddagger}$ (cal mol^{-1} K^{-1})	D_{Co-R}[a] (kcal/mol)	temp range (°C)
Me	DMA	32.6 ± 0.8	10 ± 2	32 ± 1	70−110
Et	DMA	32 ± 1	16 ± 3	31 ± 1	60−90
Me	py	31 ± 1	8 ± 3	30 ± 1	60−100
Et	py	30.5 ± 0.3	13 ± 1	29 ± 1	55−80

[a] Co−C bond dissociation energy, calculated as recommended in refs 74 and 20.

system (Scheme 1), used for determination of activation parameters for homolysis (and the BDE), were derived from $k_{obs} = k_1 + k_o$, where k_o is the rate constant for the formation of ethylene, and from the yields of ethylene (Table 1), which under limiting trapping conditions correspond to $k_o/(k_o+k_1)$.[72]

It happens that in this particular case the yields of ethylene depend little on the temperature.[73] Consequently, $k_o \approx 0.2k_{obs}$ and $k_1 \approx 0.8k_{obs}$. As a result, $\Delta H_1^{\ddagger} \approx \Delta H_{obs}^{\ddagger}$, and the value of $\Delta S_1^{\ddagger}$ is about 0.4 cal mol^{-1} deg^{-1} lower than the value of $\Delta S_{obs}^{\ddagger}$. The BDE values in a moderate viscosity solvent DMA were calculated as $(\Delta H_1^{\ddagger} - 1) \pm 1$ kcal/mol.[74,20]

Homolysis of the ethyl derivative is faster than that of CH_3CoPc, in contrast to the S_N2 alkyl transfers from these complexes.[9] Also the activation enthalpies (and BDEs) listed in Table 9 seem to be lower for CH_3CH_2CoPc, although the difference is comparable to the experimental error. The activation enthalpies for the methyl system are at least 6 kcal/mol higher than those determined for S_N2 methyl transfers from CH_3CoPc, while the activation entropies for the two reactions are not very different; this does not allow for an easy distinction of the displacement and homolytic processes.[9]

The previously determined activation parameters for the thermolysis of the methyl system under aerobic conditions[21] are generally in agreement with the BDEs obtained in this study in the presence of TEMPO. Apparently, in dilute solutions of organocobalt substrate, alkyl radical trapping by O_2 is quite effective.

The BDEs of Table 9 should be compared with those for other models with similar primary alkyl ligands, some of which are shown in Table 6. The Co−C bond in $CH_3CoPc(py)$ appears to be weaker than the same length bond in MeCbl (BDE = 37 ± 3[18] or 36 ± 4 kcal/mol),[75] $MeCbi^+$ (37 ± 3 kcal/mol),[75] or $CH_3Co(DH)_2(py)$ (33.1 ± 1.6 kcal/mol).[19] Hence, despite the virtually equal Co−C distances in these complexes, there are visible differences in the BDEs. Conversely, the Co−C bond in $CH_3CoPc(py)$ is of similar strength or weaker than that in AdoCbl, whereas in the latter both axial bonds are significantly longer.

It is noteworthy that the BDE for CH_3CoPc is smaller than those for inactive methyl donors, methylcobaloxime and MeCbl. As follows from Marcus theory, a small BDE decreases the intrinsic free energy barrier for methyl transfer.[22] However, since the variation in the BDEs is not very large, this is not going to be the dominant factor.

A comparison of the homolysis of Pc and OEP complexes, in light of their nearly identical steric requirements, would be of interest. Unfortunately, kinetic data for the thermolysis of $CH_3Co(OEP)(py)$ or $CH_3CH_2Co(OEP)(py)$ are not accessible, possibly because of inconveniently slow rates.[30,76] The BDEs for the $C_6H_5CH_2Co^{III}(OEP)$ complexes are fairly large, 29.3 kcal/mol for $C_6H_5CH_2Co(OEP)PBu_3$,[23] similar to those of the RCoPc(py) complexes, whereas the activation enthalpies of benzyl derivatives are usually several kilocalories per mole lower than those of normal primary alkyl complexes. Consequently, it appears that a 0.03 Å shorter Co−C bond in $CH_3Co^{III}Pc(py)$ is probably weaker (that is, its BDE is smaller) than the longer bond in $CH_3Co^{III}(OEP)(py)$, which is against the notion that a shorter bond should be stronger. On the basis of results obtained with complexes containing flexible equatorial arrangements, the lack of correlation between the Co−C bond length or other properties of this bond in the ground-state, such as the stretching Co−C frequency and BDE, was pointed out by Marzilli et al. two decades ago.[77] As this study demonstrates, these claims are also valid for complexes with more rigid equatorial arrangements, where trans-steric influence is minimized.

Effect of the Equatorial Ligand on BDE. The electrochemical investigations by Qiu and Sawyer suggest an increase in the free energy of Co−C bond dissociation, described as $-\Delta G_{BF}$, with the electron density of the porphyrin ring.[17] This is in agreement with the results of homolytic cleavage studies on organoiron porphyrin complexes, the behavior of which parallels that of RCo^{III}(chel) complexes.[78] The following order for the homolyses of (five-coordinate) PhFe(P) complexes in mesitilene was found: TPP > TTP > OEP. This is in agreement with the Fe^{III}/Fe^{II} potentials or porphyrin basicities, in other words, the BDE increases with the equatorial ligand basicities. Riordan and Halpern concluded that the cis-electronic influence visibly changes the BDEs in a manner analogous to that of the trans electronic effect observed in phosphine adducts with rigid benzyl-Co^{III}(OEP), where the trans-steric influence is offset, or in complexes with flexible equatorial system $RCo^{III}(DH)_2$-(X-py) complexes,[79] where a series of isosteric trans ligands are used. In each case, the "purely electronic effect" seems to be the same, the Co−C bond dissociation rates decrease with increasing ligand basicity. Hence, the homolyses of RCoPc complexes would reasonably be faster than those of their OEP analogues (not reported, but estimated to be very slow). There are, however, observations that do not fit into this scheme. Since Pc precedes TPP in the order of equatorial ligands, one could predict a slower homolysis of RCo(TPP)

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(72) Halpern, J. *Pure Appl. Chem.* **1983**, *33*, 1059.

(73) The constant k_o/k_1 ratio was observed by Halpern and co-workers, see ref 66.

(74) Garr, C. D.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 4412.

(75) Hung, R. R.; Grabowski, J. J. *J. Am. Chem. Soc.* **1999**, *121*, 1359.

(76) In fact, electrochemical studies by Qiu and Sawyer (ref 17) suggest extremely slow rates for homolysis of n-$BuCo^{III}$(porphyrin) ($-\Delta G_{BF}$ > 36 kcal/mol).

(77) Nie, S.; Marzilli, P. A.; Marzilli, L. G.; Yu, N.-T. *J. Am. Chem. Soc.* **1990**, *112*, 6084 and references therein.

(78) Riordan, C. G.; Halpern, J. *Inorg. Chim. Acta* **1996**, *243*, 19.

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

complexes than that of their phthalocyanine congeners. Contrary to that prediction, the BDEs of the alkyl-Co^{III}TPP complexes are considerably, ~10 kcal/mol, lower.[80] Steric interactions in the TPP system could be held accountable for this, but the very similar BDEs for the methyl and butyl derivatives seem to refute such explanation. In a further twist, the Co−C bond dissociation in tropocoronand complexes, in which the equatorial ligand is strongly basic and the Co−C bond is 0.068 Å shorter, for the ethyl derivative, than that in $CH_3CH_2Co^{III}Pc$, occurs under very mild conditions.[5] At present, it would be hard to reconcile all the facts regarding the cis influence of the equatorial ligand, and it is unlikely that this could be done, at least in some cases, by invoking the varied steric interactions of the (nonbulky) axial alkyl group with the equatorial arrangement.

Effect of the Strength of the Co−N_{ax} Bond on Homolysis. Faced with a lack of correlation of BDE to the Co−C distance in the ground state, Marzilli et al. concluded that the only clear correlation to Co−C BDE values is the Co−N_{ax} bond length[3,81] and also that transition state effects dominate the Co−C cleavage.[77] Consequently, a comparison of the parameters of the Co−N_{ax} bond in the ground state and in the homolysis product, the latter believed to bear similarity to the late transition state of the homolytic process, is of interest.[82] The Co−N_{ax} bond in $CH_3Co^{III}Pc(py)$, 2.174(2) Å, is within 1 σ of being as long as that in $Co^{II}NPc(py)$, 2.167(9) Å,[40] and it is plausible that the Co−N_{ax} bond in the latter would not be much different from that in $Co^{II}Pc(py)$. The Co−N_{ax} bond lengths in the $CH_3Co^{III}(OEP)(py)$ and $Co^{II}(OEP)(4\text{-}Me_2Npy)$ couple, 2.214(9) and 2.191(2) Å, respectively, are the same within 2 σ. The crystal structure of cob(II)alamin shows a relatively short Co−N_{ax} bond length of 2.131 Å,[83] that is, ~0.03 Å shorter than in MeCbl.[46] A simplistic approach, neglecting the fact that bond energy may be distributed over many modes and disregarding the ~0.1 Å displacement of cobalt from the N_4 plane on formation of the five-coordinate Co(II) structure, would indicate that there is no strong stabilization of the transition state by a shorter (stronger) Co−N_{ax} bond in the transition state than in the ground state that could account for a significant base-on effect. An analysis based on a comparison of the formation constants of N-donor adducts with the organocobalt(III) substrate and the Co(II) product, the latter representing properties of the transition state, has been described in detail by Stolzenberg and Summers.[84] One order of magnitude larger association constants of N-donors with Co(II) than RCo(III) complexes have been found for sterically hindered porphyrins, such as those studied by Stolzenberg, and a similar relationship also stems from earlier data on the ligation of TPP complexes (stability constants for $CH_3CH_2Co(TPP)py$ and Co(TPP)py in CH_2Cl_2 are 8.9[85] and 480[86] M^{-1}, respectively). Hence, the phthalocyanine complexes are expected to exhibit similar behavior. Unfortunately, the formation constant for tetragonal $Co^{II}Pc$ with N-donors cannot be conveniently measured because of the π stacking. However, the stability constants for the ring-substituted derivatives that do not self-associate but probably have very similar ligand binding properties as plain $Co^{II}Pc$[87] appear to be larger than those for $CH_3Co^{III}Pc$: the association constants of pyridine with $Co^{II}(t\text{-}Bu_4Pc)$[88] and $CH_3Co^{III}Pc$[9] in CH_2Cl_2 are 30 200 and 3630 M^{-1}, respectively; this value is, again, ~1 order of magnitude in favor of Co(II) complexes. Differences of this magnitude correspond to a 1−2 kcal/mol reduction in the free-energy barrier for Co−C bond dissociation in RCo^{III}(chel)L complexes relative to that of five-coordinate RCo^{III}(chel) complexes. Consequently, in the absence of trans-steric influence, no strong base-on effect is predicted. Also, no significant variation in the rates of homolysis should be expected upon changing the trans ligand, L, in a RCo^{III}(chel)(L) complex, exactly as observed in this work upon replacing very weakly basic DMA with pyridine or *N*-MeIm (Tables 6 and 7) and elsewhere in alkylcobalt and organoiron porphyrins.[78,89]

Conclusions

A long Co−C bond in coordinatively unsaturated CH_3CH_2CoPc, containing an equatorial arrangement known for its electron deficiency, may indicate the electrophilic character of the alpha carbon, in accordance with the enhanced alkyl (cation) transfer reactivity of the phthalocyanine model of MeCbl. Not only the alkyl cation transfer but also the homolytic rupture of the Co−C bond in phthalocyanine models are faster than those in their alkylcorrinoid, OEP, and cobaloxime analogues. In accordance with the Marcus theory, the relatively low BDE for CH_3CoPc contributes to faster rates for methyl transfer from this complex. The differences in the rates of homolysis between $CH_3CoPc(py)$ and MeCbl are not reflected in the structural parameters of the axial systems, which are virtually identical for the two complexes. The faster homolysis of the Pc model than the OEP model is consistent with the value of the BDE increasing with the basicity of the equatorial ligand, but this rule fails for TPP and tropocoronand alkylcobalt(III) complexes. The results of this study reinforce the earlier claim of Marzilli el al. that, even in rare cases where measurable differences in the Co−C bond length are observed, the order of bond strength as defined by BDE cannot be safely

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(80) However, because of the atypical strongly negative $\Delta S_{BD}^{\ddagger}$ value, the value of $\Delta G_{BD}^{\ddagger}$ is only ca. 4 kcal/mol lower than that for $CH_3Co^{III}Pc$.

(81) Summers, M. F.; Toscano, P. J.; Bresciani-Pahor, N.; Nardin, G.; Randaccio, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1983**, *105*, 6259.

(82) In an enzymatic environment, in the absence of diffusion step, there is probably no transition state. Brown, K. L.; Marques, H. M. *THEOCHEM* **2005**, *714*, 209.

(83) Berendsen, H. J. C.; Postma, J. P. M.; Van Gunsteren, W. F.; DiNicola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684. (b) Kräutler, B.; Keller, W.; Kratky, C. *J. Am. Chem. Soc.* **1989**, *111*, 8936.

(84) Stolzenberg, A. M.; Summers, J. S. *Inorg. Chem.* **2000**, *39*, 1518.

(85) Kadish, K. M.; Han, B. C.; Endo, A. *Inorg. Chem.* **1991**, *30*, 4502.

(86) Kadish, K. M.; Botomley, L. A.; Beroiz, D. *Inorg. Chem.* **1978**, *17*, 1124.

(87) This is suggested by the similar ligand binding properties of the CH_3CoPc and $CH_3Co[PcR_4]$ complexes, R = *tert*-butyl or neo-pentoxyl. Galezowski, W. Unpublished results.

(88) Kimura, M.; Sakaguchi, A.; Ohtha, K.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *Inorg. Chem.* **2003**, *42*, 2821.

(89) It should be noted, however, that it has been claimed that the BDE for benzyl-Co(OEP)(L) varies with the basicity of the trans ligand within several kcal/mol (see ref 23).

predicted from the structural parameters of the axial system in the ground state. For rigid porphyrinic complexes with nonbulky axial alkyl groups, this lack of correlation is not likely to be caused by variable steric interactions. A number of observations such as equal length Co−N$_{ax}$ bonds in $CH_3Co^{III}Pc(py)$ and $Co^{II}NPc(py)$ and moderate ratios of the association constants of N-donor ligands with RCo^{III}(chel) and Co^{II}(chel) suggest a weak base-on effect on the Co−C BDEs. The weak dependence of the BDEs on the identity of trans ligand observed in this work for phthalocyanine complexes and elsewhere for iron and cobalt porphyrins is in agreement with above statement.

The trend of decreasing Co−C bond distance in five-coordinate RCo^{III}(chel) complexes with increasing basicity of the equatorial system, tentatively established in this work, needs more experimental support.

Acknowledgment. Support of this work through a grant from the Polish State Committee for Scientific Research (Grant 7 T09A 07421) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files (in CIF format) for CH_3CH_2CoPc (ambient temperature), CH_3CH_2CoPc (100 K), and $CH_3CoPc(py)$. These files have also been deposited with Cambridge Crystallographic Data Centre, CCDC Nos. 234305, 260988, and 23436, respectively. Exemplary kinetic traces for homolytic cleavage of the Co−C bond in CH_3CH_2CoPc measured at several wavelengths and corresponding end-point plots and a figure showing the Eyring plots for homolyses of CH_3CoPc, CH_3CH_2CoPc, and their pyridine adducts, in DMA. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051078P