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Intramolecular C–H Bond Activation: Preparation, Structure, and Properties of a Unique Cobalt(III) Complex, $K[Co^{III}(dacoda)(SO_3)]\cdot 5H_2O$, Containing a Weak Agostic Interaction in Aqueous Solution

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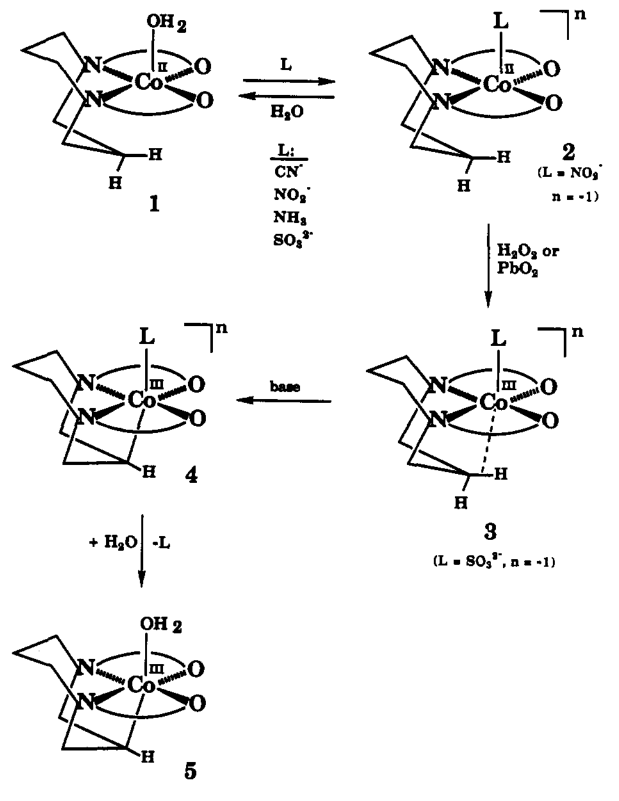
Oxidation of $[Co^{II}(dacoda)(H_2O)]$ (dacoda = 1,5-diazacyclooctane-*N,N'*-diacetate) with PbO_2 in the presence of 1 equiv of SO_3^{2-} affords the classically five-coordinate Co(III) complex $K[Co^{III}(dacoda)(SO_3)]\cdot 5H_2O$ (3), which contains a three-center, two-electron Co⋯HC (agostic) interaction in the sixth coordination position. 3 crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.500$ (2) Å, $b = 16.5469$ (15) Å, $c = 30.978$ (4) Å, $\beta = 89.91$ (2)°, $V = 3844$ (1) Å^3, with $Z = 8$, and a final unweighted R value of 0.051. The structural and spectroscopic results indicate that a *weak* agostic interaction exists between the Co center and the C(2)–H(2a) bond. The agostic Co(1)–H(2a) and Co(1)–C(2) distances were found to be 2.31 (5) and 2.531 (4) Å, respectively. ^{13}C NMR studies reveal that the agostic C(2)–H(2a) group shows only a slightly reduced coupling constant, $J(^{13}C-^{1}H) = 122$ Hz, versus the value of 129 Hz observed for similar methylene C–H groups within the metal complex. The ligand field parameter, Dq, of the "agostic ligand" is calculated to be only ~600 cm^{-1}, reflecting the weakness of the agostic interaction. The weakness of the Co⋯HC interaction and the reason for the surprising stability of 3 in aqueous solution are attributed to the strong trans influence of the sulfite ligand. However, this complex can be deprotonated in methanol to form the Co–alkyl complex $[Co^{III}(dacoda\text{-}C(2))(H_2O)]$, where dacoda-*C*(2) refers to dacoda coordinated in a quinquedentate fashion with the C(2) carbon of the daco portion of the ligand directly bonded to the cobalt center. These results demonstrate the activation of a C–H bond via electrophilic attack of Co(III) in a relative simple but sterically constrained molecule, which may be inherent to C–H activation in enzymes.

Introduction

The quadridentate macrocyclic ligand dacoda (1,5-diazacyclooctane-*N,N'*-diacetic acid) forms square-pyramidal five-coordinate $[M^{II}(dacoda)(H_2O)]$ complexes with M = Ni, Co, and Zn as a result of the unique stereochemical requirements of the chelated ligand.[1] A crystal structure of the Ni(II) complex,[1b] which is isomorphous to the Co(II) and Zn(II) complexes, demonstrated that the chair-boat conformation of the chelate rings formed by the daco (1,5-diazacyclooctane) backbond results in the placement of a β-methylene C–H group over an axial coordination site, thus sterically enforcing five-coordination (see **1**, Scheme I). An interesting consequence of the five-coordinate nature of the Co(II) complex, $[Co^{II}(dacoda)(H_2O)]$ (**1**), is its stability to oxidation. Unlike typical cobalt(II) poly(amino carboxylate) complexes, neither oxygen nor hydrogen peroxide will oxidize **1**.[1a,c] This is presumably due to the strong propensity for Co(III) to form six-coordinate octahedral metal complexes in water. However, we reasoned that oxidation to Co(III) would be possible if a very strong axial ligand field were supplied by substitution of the coordinated water with a ligand such as CN^-. We anticipated that this would lead to stabilization of classically five-coordinate Co(III) through a two-electron, three-center Co⋯HC (agostic)[2] interaction in the sixth position or to some type of C–H activation.[3]

We have reported[4] just such an example of C–H bond activation; oxidation of **1** with H_2O_2 in the presence of CN^- results in a unique Co(III)–alkyl complex, $[Co^{III}(dacoda\text{-}C(2))(H_2O)]\cdot 2H_2O$ (**5**), where dacoda-*C*(2) refers to dacoda coordinated in a quinquedentate fashion with the C(2) carbon of the daco portion of the ligand directly bonded to the cobalt center (see **5**, Scheme I). The Co–alkyl complex was proposed to have been produced via the electrophilic attack of low-spin Co(III) on the proximal β-methylene C–H bond of the coordinated dacoda ligand, resulting in heterolytic cleavage of the C–H bond and the formation of a direct Co–C bond.[4] This mechanism centers on the intermediacy of a classically five-coordinate Co(III) species containing an agostic interaction in the sixth coordination position (Scheme I). We reported[4] in preliminary form an example of this type of complex, $K[Co^{III}(dacoda)(SO_3)]\cdot 5H_2O$ (**3**), which to our knowledge is the first illustration of an agostic interaction in a classical coordination complex. We now report the synthesis,

Scheme I



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characterization, and properties of this unusual, formally coordinatively unsaturated 16-electron Co(III) complex, including a single-crystal X-ray structural analysis. In addition further characterization of the deprotonated Co–C-bonded product **5** is presented.

Experimental Section

Synthesis. Daco·2HBr. The dihydrobromide salt of daco was prepared by previously reported procedures[5,6] with modifications. A mechanical stirrer, a reflux condenser, and a 200-cm^3 dropping funnel were fitted to a 3-L three-necked flask equipped with a heating mantle. Six moles of anhydrous hydrazine (200 g = ca. 200 cm^3) were added to 1 dm^3 of ethanol, and the resulting solution was brought to a gentle reflux, with stirring. Two moles of 1,3-dibromopropane (400 g = ca. 200 cm^3) were added to the solution over a period of 4 h. Faster addition resulted in a significant reduction of the yield of daco·2HBr. During the reaction, hydrazine monohydrobromide settled out in an oily layer. The reflux was continued for an additional 1 h, after which the reaction mixture was transferred into a 2-dm^3 beaker and stored in a refrigerator at 4 °C overnight. The resulting white mass of hydrazine monohydrobromide was filtered off and washed with ethanol (200 cm^3). The washings were combined with the filtrate, and the pH of the solution was adjusted to ca. 3 with 48% hydrobromic acid. Benzaldehyde (120 cm^3) and water (600 cm^3) were added to the solution, resulting in a yellow color. After several hours of cooling at 4 °C, yellow crystalline benzalazine deposited, which was removed by filtration. The filtrate was extracted with approximately an equal volume of ether to remove dissolved benzalazine. The volume of the aqueous phase was reduced by rotary evaporation until the solution became very syrupy. With vigorous shaking, 500 cm^3 of ethanol and added to the syrup, resulting in the precipitation of white fluffy material. The precipitate was filtered off, washed with ethanol until the washings were colorless, and then washed with ether. The average yield was 30 g.

Ba(dacoda)·2H_2O. Dacoda was isolated as the barium salt by a modification of previously reported procedures.[5,6] A small three-necked flask was fitted with a thermometer and a dropping funnel, purged with argon, and mounted in an ice/salt bath. Chloroacetic acid (5.12 g) was added to the flask and dissolved in 4 cm^3 of degassed H_2O. Sodium hydroxide (1.74 g) was dissolved in 2 cm^3 of degassed H_2O and added slowly, dropwise, to the stirred solution while the temperature was maintained below 10 °C. Daco·2HBr (5.52 g) and NaOH (3.2 g) were dissolved in 10 cm^3 of degassed H_2O and added to the chloroacetate solution dropwise over a 15-min period. The resulting solution was heated at 50–60 °C for 2 h. The solution was cooled, and a concentrated aqueous solution of $BaCl_2·2H_2O$ (4.84 g) was added, resulting in the precipitation of a white mass of Ba(dacoda)·2H_2O. (If no precipitation occurs, concentrated NaOH is added to make the solution basic enough for precipitation.) Ba(dacoda)·2H_2O was filtered off and washed with cold water, ethanol, and then ether. Yield: 5.5 g (75%).

Na[Co^{II}(dacoda)(NO_2)]·0.5H_2O (2). Solid sodium nitrite (0.42 g, 6 mmol) was added to a solution of **1**[1c] (1.3 g, 4 mmol) in 40 cm^3 of water. The solution was rotary evaporated until syrupy, dissolved in 20 cm^3 of methanol, and then evaporated to dryness. The resulting orange powder was recrystallized from a minimum amount of methanol by addition of acetone. Anal. Calcd for $NaCoC_{10}H_{17}N_3O_{6.5}$: C, 32.89; H, 4.69; N, 11.51. Found: C, 32.79; H, 4.70; N, 11.24. Magnetic moment at room temperature: $\mu_{eff} = 4.5\ \mu_B$.

K[Co^{III}(dacoda)(SO_3)]·5H_2O (3). A solution of K_2SO_3 (0.32 g, 2 mmol) in 1 cm^3 of water was added to a solution of **1** (0.65 g, 2 mmol) in 20 cm^3 of H_2O. The pH of the mixture was adjusted to 6 with dilute acetic acid. Lead dioxide (0.5 g, 2 mmol) was added to the solution, and the suspension was stirred at room temperature under a nitrogen blanket. After 0.5 h, the insoluble material was filtered off. The blue filtrate was concentrated to ca. 3 cm^3 by rotary evaporation. Ethanol (2 cm^3) was added to the solution. Blue needles were obtained after cooling the solution at 4 °C, which were collected by filtration and then air dried. Yield: 0.30 g (30%). Anal. Calcd for $KCoC_{10}H_{26}N_2O_{12}S$: C, 24.20; H, 5.64; N, 5.28. Found: C, 24.10; H, 5.64; N, 5.24. UV–vis (H_2O) [absorption maximum $\sigma/10^3/cm^{-1}$ (log $\epsilon/mol^{-1}\ cm^3\ cm^{-1}$): 16.9 (2.26), 21.4 (1.66), 25.4 (2.40), 27.9 (2.06), 35.6 (4.12), 39.4 (3.77), 46.1 (4.10).

3 was deprotonated in methanol with sodium methoxide to give **5** as follows: **3** (0.050 g) was dissolved in 25 cm^3 of methanolic sodium methoxide (0.1 M) under nitrogen. This solution was stirred for ca. 20 min while the color of the solution changed from dark blue to pink. The solution was concentrated to ca. 5 cm^3 and chromatographed with QAE-Sephadex and Dowex ion-exchange resins as described below for **5**. The spectral properties of the pink eluate were identical with those of **5**.

[Co^{III}(dacoda-*C*(2))(H_2O)]·2H_2O (5). A mixture of KCN (0.27 g, 4 mmol) and 10% H_2O_2 (0.7 cm^3, 2 mmol) in 20 cm^3 of H_2O was dripped into a solution of **1** (1.3 g, 4 mmol) in 40 cm^3 of H_2O. The resulting dark brown solution was warmed at 50–60 °C for 1 h while the color of the reaction mixture gradually turned dark red. This dark red solution was poured onto a QAE-Sephadex column (Cl^- form: 4 cm × 20 cm). A pink band was eluted off with water, leaving some anionic species[7] on the top of the column. The pink eluate was then passed over a Dowex column (50W-X8, H^+ form: 4 cm × 10 cm) using water as an eluent. The eluate was evaporated to ca. 5 cm^3 by rotary evaporation at 40 °C, and 100 cm^3 of acetone was added to precipitate crude pink material. This solid was dissolved in a small amount of water, and the pH of the solution was adjusted to 2 by an addition of a dilute HCl. The solution was left to evaporate at room temperature. After a few days, red crystals deposited, which were harvested and air dried. Yield: 570 mg (43%). Anal. Calcd for $CoC_{10}H_{21}N_2O_7$: C, 35.30; H, 6.22; N, 8.23. Found: C, 35.33; H, 6.28; N, 8.24. UV–vis (H_2O) [absorption maximum $\sigma/10^3\ cm^{-1}$ (log $\epsilon/mol^-\ dm^3\ cm^{-1}$)]: 19.6 (2.19), 23.0 (1.51), 26 (2.1) sh, 29.5 (2.23), 39 (3.6) sh, 46.7 (4.20).

The same compound was obtained by using PbO_2 instead of H_2O_2. Nitrite and ammonia, as well as cyanide, were also found to have catalytic activity in the preparation of **5**. The reaction employing nitrite or ammonia, however, proceeded more efficiently in methanol rather than in water.

***trans*-Ca[Co^{III}(SO_3)(1,3-pdda)(H_2O)]Cl·4H_2O.** Cobalt nitrate hexahydrate (1.5 g, 5 mmol) and 1,3-pddaH_2·2HCl (1,3-PddaH_2 = 1,3-propanediamine-*N*,*N*′-diacetic acid)[8,9] (1.3 g, 5 mmol) were dissolved in 50 cm^3 of water, and the pH of the mixture was adjusted to 6 with dilute KOH. Potassium sulfite (0.8 g, 5 mmol) was added with stirring, followed by 23 cm^3 of 10% H_2O_2 (6 mmol). After the solution was stirred at 50–60 °C for 0.5 h, the insoluble product was filtered off. The filtrate was diluted to 3 dm^3 with water and charged on a QAE-Sephadex column (Cl^- form: 4 cm × 30 cm). After the column was washed with water, the adsorbed band was eluted with dilute $CaCl_2$ solution (1 g/dm^3, 0.01 M). The eluate from the broad red band was collected and evaporated to ca. 20 cm^3 by a rotary evaporator at 30 °C. A mixture of ethanol/acetone/ether (2:2:1) was added to the solution to precipitate the crude material. The crude product was purified by chromatography. The product, which was isolated from the subsequent eluate, was recrystallized from a minimum amount of water by addition of ethanol. Yield: 0.16 g (7%). Anal. Calcd for $CaCoC_7H_{22}N_2O_{12}SCl$; C, 17.06; H, 4.50; N, 5.68. Found: C, 17.23; H, 4.45; N, 5.56.

The elemental analysis suggests that the compound crystallized as a double salt that consists of the complex anion and chloride. Free chloride was confirmed by the observation that precipitation of silver chloride occurred without any color change when silver nitrate was added to a solution of the compound. UV–vis (H_2O) [absorption maximum $\sigma/10^3\ cm^{-1}$ (log $\epsilon/mol^{-1}\ dm^3\ cm^{-1}$)]: 19.8 (2.32), 23.5 (1.46), 27 (2.2) sh, 36.0 (4.21), 39.5 (3.89), 46.7 (4.26). The geometrical configuration of the complex was determined to be trans via ^1H NMR spectroscopy.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The electronic absorption spectra were recorded on a Cary 219 spectrophotometer (Varian Instruments). The ^1H and ^{13}C NMR data were obtained by using a Nicolet NT-200 spectrometer in ^2H_2O. The MCD spectrum was recorded in a magnetic field of 1.5 T with a JASCO MOE-1 spectropolarimeter. Powder magnetic susceptibility measurements were made at room temperature with a PAR vibrating-sample magnetometer. Corrections for the diamagnetic background and core diamagnetism were made.[10] Electrochemical studies were performed with a Hokuto Denki potentiogalvanostat, Model HA-201, and linear scanner, Model HB-103. An electrolysis cell was used with a glassy-carbon working electrode, a 3.33 mol dm^{-3} calomel reference electrode (0.25 V vs NHE at 25 °C), and a Pt-wire counter electrode.

X-ray Structure of K[Co^{III}(dacoda)(SO_3)]·5H_2O. Diffraction-quality crystals were obtained by addition of ethanol to a concentrated aqueous

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Table I. Crystallographic Data for **3**

chem formula: $C_{10}H_{26}N_2O_{12}SKCo$
a = 7.500 (2) Å
b = 16.547 (2) Å
c = 30.978 (4) Å
β = 89.91 (2)°
V = 3844 (1) Å^3
Z = 8
T = 22 °C

fw: 496.41
space group: $P2_1/c$
λ = 0.71069 Å
ρ_{calc} = 1.72 g cm^{-3}
μ = 12.65 cm^{-1}
transm coeff = 0.648–0.967
$R(F_o)$ = 0.051
$R_w(F_o)$ = 0.047

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (A^2 × 10^3) for **3**

atom	x	y	z	U_{eq}
Co(1)	3942 (1)	3159 (1)	650 (1)	22 (1)
N(1)	3072 (6)	2993 (3)	63 (1)	28 (2)
N(2)	4858 (6)	2064 (3)	680 (1)	24 (1)
C(1)	4812 (7)	2995 (4)	−187 (1)	37 (2)
C(2)	6404 (6)	2882 (4)	110 (1)	38 (2)
C(3)	6466 (7)	2131 (3)	390 (2)	33 (2)
C(4)	3664 (8)	1400 (3)	537 (2)	32 (2)
C(5)	3018 (8)	1476 (4)	76 (2)	38 (2)
C(6)	2015 (8)	2244 (4)	−23 (2)	36 (2)
C(7)	1999 (8)	3714 (3)	−52 (2)	36 (2)
C(8)	2706 (8)	4438 (3)	192 (2)	33 (2)
C(9)	5443 (7)	1918 (3)	1137 (2)	28 (2)
C(10)	5846 (7)	2703 (3)	1351 (2)	26 (2)
O(1)	3615 (5)	4270 (2)	533 (1)	30 (1)
O(2)	2385 (6)	5130 (2)	72 (1)	48 (2)
O(3)	5323 (4)	3346 (2)	1152 (1)	25 (1)
O(4)	6611 (5)	2721 (2)	1706 (1)	36 (1)
O(5)	1659 (5)	2390 (2)	1309 (1)	37 (1)
O(6)	1645 (5)	3855 (2)	1323 (1)	39 (1)
O(7)	4 (5)	3128 (3)	769 (1)	43 (2)
S(1)	1547 (2)	3134 (1)	1055 (1)	28 (1)
Co(2)	8728 (1)	7385 (1)	1889 (1)	24 (1)
N(11)	9491 (6)	8484 (3)	1783 (1)	27 (2)
N(12)	7887 (6)	7650 (3)	2464 (1)	29 (2)
C(11)	11133 (7)	8534 (4)	2065 (2)	37 (2)
C(12)	11173 (4)	7842 (4)	2388 (2)	36 (2)
C(13)	9631 (8)	7749 (4)	2707 (2)	38 (2)
C(14)	6712 (8)	8381 (3)	2516 (2)	39 (2)
C(15)	7603 (9)	9147 (4)	2357 (2)	44 (2)
C(16)	8173 (8)	9139 (3)	1890 (2)	40 (2)
C(17)	10009 (8)	8549 (3)	1320 (2)	34 (2)
C(18)	10605 (7)	7733 (3)	1164 (2)	32 (2)
C(19)	6926 (8)	6924 (3)	2634 (2)	35 (2)
C(20)	7655 (8)	6173 (3)	2427 (2)	38 (2)
O(11)	10135 (5)	7127 (2)	1403 (1)	30 (1)
O(12)	11423 (6)	7660 (2)	821 (1)	45 (2)
O(13)	8549 (5)	6297 (2)	2076 (1)	33 (1)
O(14)	7379 (6)	5502 (2)	2579 (1)	55 (2)
O(15)	6492 (6)	6488 (2)	1291 (1)	49 (2)
O(16)	6343 (5)	7926 (2)	1179 (1)	49 (2)
O(17)	4798 (5)	7319 (3)	1790 (1)	50 (2)
S(11)	6321 (2)	7269 (1)	1494 (1)	34 (1)

solution of **3** and cooling to 5 °C. A suitable needle (0.4 mm × 0.2 mm × 0.12 mm) was attached to a glass fiber with epoxy and mounted on a Nicolet R3m/E four-circle diffractometer equipped with a Mo Kα X-ray source and a graphite monochromator. Twenty-five well-dispersed high-angle reflections were accurately centered, and the lattice parameters as well as crystal orientation were optimized by a least-squares procedure. Full listings of the data collection parameters,[11] cell parameters, and details of the crystallographic analysis core given in the supplementary material. A summary of crystallographic parameters is given in Table I. Intensity data were collected by ω scans, and three strong well-separated reflections were measured every 100 reflections to check for crystal movement or decomposition. Absorption corrections were applied by an empirical method using ψ-scan data about six reflections near χ = 90°.

The structure of **3** was solved by direct methods and Fourier techniques using the SHELXTL-84 program,[12] followed by least-squares refinements. Atomic scattering factors were taken from a standard source,[13]. All hydrogens were located on a ΔF map. The hydrogen atoms attached to carbon atoms were included in calculated idealized positions (C–H = 0.96 Å) with isotropic thermal parameters set at ca. 20% larger than the corresponding carbon atom, except for the hydrogens on the agostic carbon, which were refined isotropically. The water hydrogen positional parameters were refined, but the isotropic thermal parameters were fixed at 6.0 Å^2. All heavy atoms were included with anisotropic thermal parameters. Final agreement factors are R = 0.051 and R_w = 0.047.

Table III. Selected Bond Distances and Angles for **3**

	Bond Lengths (Å)		
Co(1)–N(1)	1.953 (4)	Co(2)–N(11)	1.935 (4)
Co(1)–N(2)	1.940 (4)	Co(2)–N(12)	1.940 (4)
Co(1)–O(1)	1.890 (3)	Co(2)–O(11)	1.887 (4)
Co(1)–O(3)	1.895 (3)	Co(2)–O(13)	1.896 (4)
Co(1)–S(1)	2.191 (2)	Co(2)–S(11)	2.190 (2)
Co(1)–C(2)	2.531 (4)	Co(2)–C(12)	2.517 (4)
Co(1)–H(2a)	2.31 (5)	Co(2)–H(12a)	2.22 (5)
C(2)–H(2a)	0.90 (5)	C(2)–H(12a)	1.06 (5)
	Bond Angles (deg)		
N(1)–Co(1)–N(2)	91.9 (2)	N(11)–C(2)–N(12)	92.3 (2)
N(1)–Co(1)–O(1)	85.1 (2)	N(11)–Co(2)–O(11)	84.9 (2)
N(2)–Co(1)–O(3)	85.4 (2)	N(12)–Co(2)–O(13)	84.9 (2)
O(1)–Co(1)–O(3)	93.9 (1)	O(11)–Co(2)–O(13)	94.0 (2)
N(1)–Co(1)–S(1)	104.8 (1)	N(11)–Co(2)–S(11)	103.3 (1)
N(2)–Co(1)–S(1)	104.2 (1)	N(12)–Co(2)–S(11)	105.4 (1)
O(1)–Co(1)–S(1)	91.2 (1)	O(11)–Co(2)–S(11)	89.7 (1)
O(3)–Co(1)–S(1)	88.9 (1)	O(13)–Co(2)–S(11)	91.7 (1)
N(1)–Co(1)–O(3)	166.2 (2)	N(11)–Co(2)–O(13)	164.9 (2)
N(2)–Co(1)–O(1)	164.6 (2)	N(12)–Co(2)–O(11)	164.9 (2)
Co(1)–N(1)–C(1)	100.7 (3)	Co(2)–N(11)–C(11)	101.2 (3)
Co(1)–N(2)–C(3)	100.6 (3)	Co(2)–N(12)–C(13)	101.5 (3)
Co(1)–N(1)–C(6)	117.4 (3)	Co(2)–N(11)–C(16)	116.4 (3)
Co(1)–N(2)–C(4)	117.5 (3)	Co(2)–N(12)–C(14)	118.0 (3)
N(1)–C(1)–C(2)	111.6 (4)	N(11)–C(11)–C(12)	110.8 (4)
N(2)–C(3)–C(2)	112.2 (4)	N(12)–C(13)–C(12)	110.2 (4)
S(1)–Co(1)–H(2a)	173 (1)	S(11)–Co(2)–H(12a)	169 (1)
Co(1)–H(2a)–C(2)	93 (1)	Co(2)–H(12a)–C(12)	93 (1)

Table IV. Comparison of Selected Bond Angles (deg) and Bond Distances (Å) in Structurally Similar Metal–Dacoda Complexes

	Co(dacoda-*C*(2))-(H_2O) (**5**)	Co(dacoda)-(SO_3)$^-$ (**3**)	Ni(dacoda)-(H_2O) (**6**)
M–N(1)–C(1)	91.4 (2)	100.7 (3)	106.7 (6)
M–N(2)–C(3)	91.1 (2)	100.6 (3)	105.9 (6)
N(1)–C(1)–C(2)	101.3 (3)	111.6 (4)	111.8 (8)
N(1)–C(3)–C(2)	101.2 (3)	112.2 (4)	111.6 (8)
C(1)–C(2)–C(3)	119.3 (3)	118.6 (4)	116.4 (8)
M–C(2)	1.941 (4)	2.531 (4)	2.72 (1)
M–H(2a)		2.31 (5)	2.51 (9)

Table V. ^{13}C NMR Spectral Data for **3** and **5**

chem shift, ppm from TMS		C atom assgnt	chem shift, ppm from TMS		C atom assgnt
3	**5**		**3**	**5**	
182.9	182.2	C(8), C(10)	53.0	51.7	C(4), C(6)
67.6	69.5	C(7), C(9)	21.7	22.9	C(5)
58.2	64.1	C(1), C(3)	18.6	−9.2	C(2)

Results

We have prepared a classicallly five-coordinate Co(III) complex containing an agostic interaction in the sixth coordination position, **3**, by oxidation of **1** with PbO_2 in the presence of 1 equiv of SO_3^{2-}. The structure of **3** has been determined by X-ray crystallography. Final positional parameters are listed in Table II, and selected bond lengths and bond angles are provided in Table III. There are two crystallographically independent but structurally nearly identical complex anions in the asymmetric unit. An ORTEP

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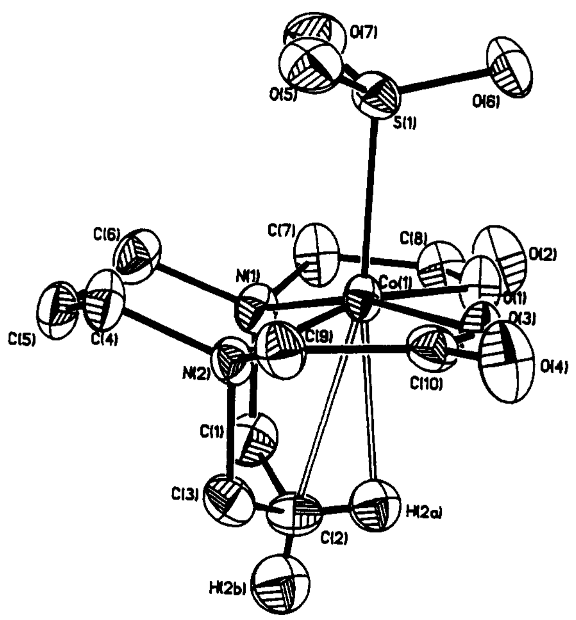

Figure 1. ORTEP drawing of the monoanion $[Co^{III}(dacoda)(SO_3)]^-$ in **3**, showing 50% ellipsoids and the atom-labeling scheme. The hydrogen atoms except for H(2a) and H(2b) have been omitted for clarity.

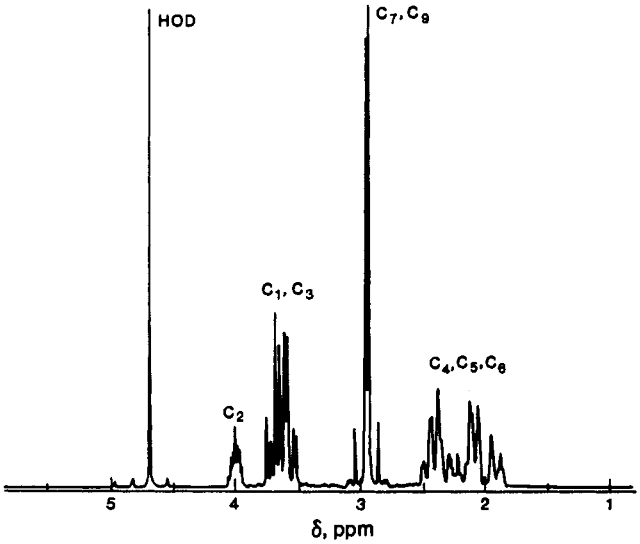

Figure 2. ^1H NMR spectrum of **5** in ^2H_2O. C_1–C_9 refer to the carbon atom to which the observed protons are attached. The labeling scheme is the same as for **3**, shown in Figure 1.

drawing of one of these is shown in Figure 1. The numbering scheme for the other unique complex anion is the same except the number of each non-metal atom has been increased by 10 (i.e. C(1) corresponds to C(11).

The transformations observed in this work are summarized in Scheme I. In addition, we have studied the spectroscopic properties of **3** and **5**. The results of ^{13}C and ^1H NMR studies are presented in Figures 2 and 3 as well as Table V. Results of electronic absorption studies are presented in Figures 4 and 5. The results of these studies will be introduced at appropriate sections which follow.

Discussion

General Synthetic and Mechanistic Considerations. The preparation of the Co(III)–alkyl complex, $[Co^{III}(dacoda\text{-}C\text{-}(2))(H_2O)]$ (**5**), was proposed to proceed via the C–H activation mechanism shown in Scheme I.[4] This is a general reaction as far as the oxidant and the additional ligand L is concerned. **5** is produced in significant yields when either H_2O_2 or PbO_2 is added to an aqueous solution of **1** containing an additional strong field ligand L, such as CN^-, NO_2^-, or NH_3. The presence of a *strong*

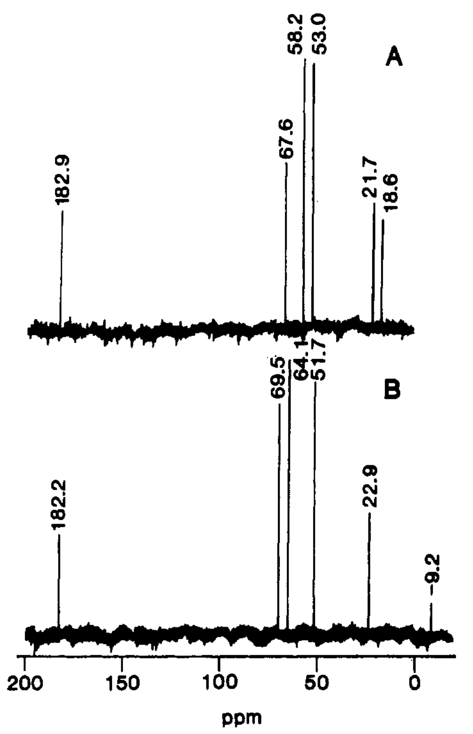

Figure 3. ^{13}C NMR spectra of **3** (A) and **5** (B) in ^2H_2O.

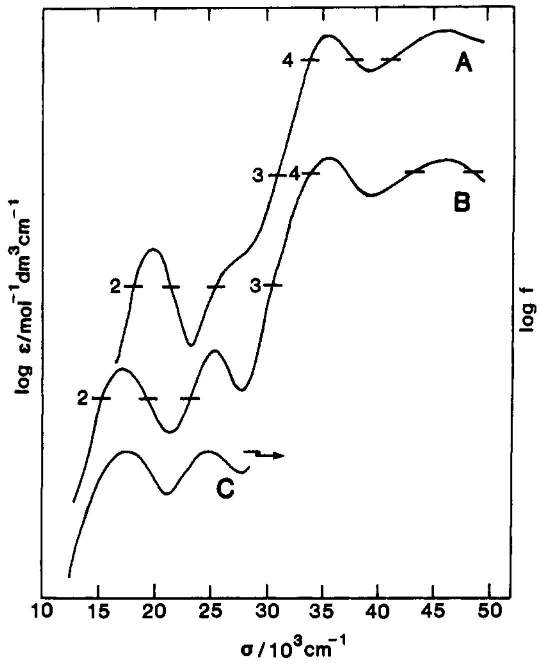

Figure 4. Electronic absorption spectra of *trans*-$[Co^{III}(1,3\text{-pdda})(SO_3)(H_2O)]^-$ in H_2O (A) and **3** in H_2O (B) and the diffuse reflectance spectrum of **3** (C).

field ligand is essential though, since no production of **5** was detected when the reaction was carried out with weaker field ligands such as Cl^-, SCN^-, or H_2O. The role of the additional ligand is 2-fold. First, coordinated stronger field ligands should ease the oxidation step depicted in Scheme I. Cyclic voltammetric studies of **1** and $[Co^{II}(NO_2)(dacoda)]^-$ (**2**) in dimethyl sulfoxide support this hypothesis. The $E_{1/2}$ value of the quasi-reversible wave corresponding to the Co(III)/Co(II) redox couple was found to shift from 0.55 V (vs NHE) for **1** to 0.46 V (vs NHE) for **2**. Second, the strong field axial ligand serves to ensure that the Co(III) agostic intermediate is low-spin, leaving the d_{z^2} orbital empty and available for the three-center, two-electron bond.[4]

Another, albeit subtle, role of the additional ligand is apparent if one considers that the isolation of an agostic intermediate when

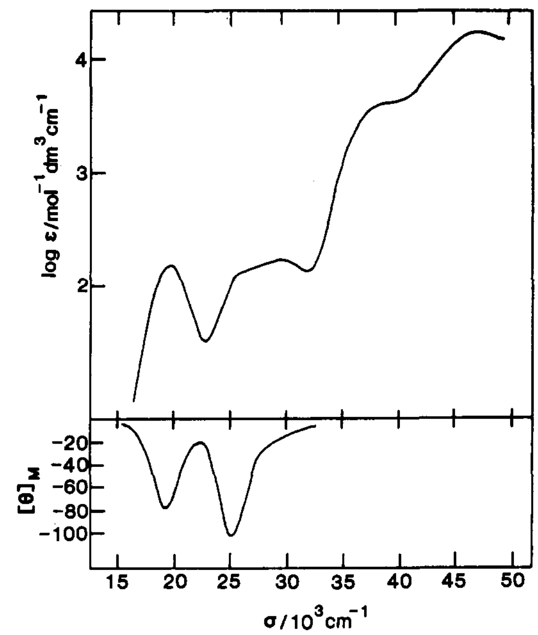

Figure 5. Electronic absorption and MCD spectra of **5** in H_2O.

L = SO_3^{2-} is unique, since no such intermediate was observed or isolated when the reaction was carried out with L = CN^-, NO_2^-, or NH_3.[4] We have rationalized this observation and the surprising stability of **3** in aqueous solution by considering the relative trans influence of these ligands; as the trans influence of the ligand opposite the C–H bond increases, the strength of the agostic interaction decreases, and thus the acidity of the agostic hydrogen decreases. Thus, sulfite, which has the largest trans influence of the four ligands thus far shown to affect the reaction sequence,[35] must weaken the agostic interaction sufficiently such that the deprotonation step shown in Scheme I is not facile in aqueous solution, rendering **3** isolable. This proposal is supported by an ab initio MO study of the role of the agostic interaction in β-eliminations,[34] wherein optimized geometries obtained from calculations on $[Pd(C_2H_5)(H)(PH_3)]$ isomers indicated that a much weaker M⋯HC interaction was obtained when hydride rather than PH_3 was trans to the agostic C–H group.

The most compelling evidence for the existence of an agostic interaction in **3** and the validity of the mechanism shown in Scheme I, which was proposed earlier[4] for the general preparation of **5**, is the observation that the C(2)–H(2a) bond is sufficiently acidic such that it can be deprotonated in methanol with sodium methoxide to give the Co–alkyl complex, **5**.

Crystal Structure of K[Co^{III}(dacoda)(SO_3)]·5H_2O. Inspection of the bond distances and angles for **3** shows that the cobalt center is found in a *classically* five-coordinate, distorted square-pyramidal coordination geometry with the agostic C(2)–H(2a) bond occupying the sixth coordination site, as shown in Figure 1. Therefore, the complex formally has an *octahedral* distribution of ligands. The cobalt atom is located 0.244 Å above the mean plane formed by N(1), N(2), O(1), and O(3) in the direction of the sulfite ligand. The axial hydrogen atom, H(2a), is found nearly directly opposite the sulfite sulfur atom, with an S(1)–Co(1)–H(2a) angle of 172.7 (3)°. The Co(1)–H(2a) distance was found to be 2.31 (5) Å. This distance and the Co(1)–C(2) distance of 2.531 (4) Å strongly support the existence of a two-electron, three-center bonding interaction in this complex when compared with the corresponding metrical parameters in the structure of [Ni^{II}(dacoda)(H_2O)]·2H_2O[1b] (**6**), which is isomorphous with [Co^{II}(dacoda)(H_2O)]·2H_2O[1c] (**1**) and has the same basic conformation of the coordinated dacoda ligand but no agostic interaction.[14] The Ni–H (2.51 (9) Å) and Ni–C (2.72 (1) Å) distances were found to be significantly longer, as expected. Moreover, the Co–H and Co–C distances in the other independent anion of **3** are even shorter: Co(2)–H(12a) = 2.22 (5) Å and Co(2)–C(12) = 2.517 (4) Å. The difference between the two independent anions of **3** is most likely a crystal-packing phenomenon. In addition, the Ni center in the five-coordinate complex **6** is found significantly farther above the basal coordiantion plane (0.364 (1) Å), in the direction opposite the C–H bond, than the Co is in the present complex (vide infra).

Further evidence for the agostic interaction is found by comparison of the conformation of the boat chelate ring containing the agostic C–H group in **3** with the conformations of the corresponding boat chelate rings in the structurally similar metal–dacoda complexes **5** and **6**, which are summarized in Table IV. A significant interaction between the metal center and the C(2)–H(2a) bond should induce strain in the boat chelate ring, with the extreme limit being a direct metal–carbon bond and thus a severely strained four-membered chelate ring system as seen in **5**. The M–N–C angles in **3** are much more acute than the analogous angles in **6** but are not as severe as the nearly 90° M–N–C angles seen in **5**. The remaining angles in the boat chelate rings compare favorably between **3** and **6**, whereas the N–C–C angles in **5** give further testimony of the distortion induced by the formation of the Co–C bond. The distorted geometry about the coordinated nitrogens in **3** is consistent with a significant interaction between the Co center and the C(2)–H(2) bond, effectively pulling C(1)–C(3) toward the Co center. Additional structural evidence for strain induced by the agostic interaction is found by examining the geometry about the metal center: within **3** the S(1)–Co(1)–O(1) and S(1)–Co(1)–O(3) angles are 91.2 (1) and 88.9 (1)°, respectively, whereas the S(1)–Co(1)–N(1) and S(1)–Co(1)–N(2) angles are 104.8 (1) and 104.2 (1)°, respectively. The corresponding angles in **6** are much more symmetrical: O(H_2O)–Ni–N = 100.2 (3) and 102.4 (3); O(H_2O)–Ni–O = 97.2 (3) and 102.1 (3)°.

Generally, agostic C–H bond distances are found to be 5–10% longer than analogous nonbridging C–H bonds.[2] The C(2)–H(2a) and C(12)–H(12a) bond lengths in **3** were found to be 0.90 (5) and 1.06 (5) Å, respectively. The average of these, 0.98 Å, is slightly longer than the normal, optimal (X-ray determined) C–H distance of 0.95 Å,[15] but due to the uncertainty of these distances this difference is not considered statistically significant.

Spectroscopic Properties. ^1H NMR Spectra. Figure 2 shows the 200-MHz ^1H NMR spectrum of **5** in ^2H_2O. The resonances are well resolved and therefore are easily assigned (see Figure 2) on the basis of intensity ratios and coupling modes. The multiplet, which is centered at 3.99 ppm, corresponding to one proton, can be assigned to the resonance of the H(2) proton. It should be noted that the chemical shift of the H(2) proton occurs at relatively low field in comparison with values typically found for Co–alkyls. For example, the methine proton of the isopropyl group in [Co(DH)$_2$(*i*-pro)(py)] (DH = dimethylglyoximato) is found at 2.12 ppm.[16] This low-field shift will be discussed later in relation to the results from the ^{13}C NMR spectrum.

A high-resolution 200-MHz ^1H NMR spectrum of **3** in ^2H_2O was obtained, confirming the low-spin (d^6) electronic configuration for this Co(III) complex. However, a distinct high-field resonance was not observed for the agostic proton, despite the fact that agostic protons typically display high-field shifts.[2] Nevertheless, this observation is consistent with the presence of a weak agostic interaction. Definitive assignment of the H(2a) (agostic) proton was not possible due to overlapping resonances; however, from integration data and by comparison with the ^1H NMR spectrum of **5** this resonance was determined to be part of a multiplet that occurs between 2.9 and 3.5 ppm. The possibility that the agostic proton had exchanged with the ^2H_2O solvent has been ruled out by virtue of the observation of a proton-coupled ^{13}C resonance for the agostic C(2) carbon (see next section). In addition,

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(14) The minimal requirement for an agostic interaction is that the metal center have a suitably oriented, low-energy, empty orbital available to receive the two electrons of the C–H bond.[2] For [Ni^{II}(dacoda)(H_2O)] the appropriate orbital is the d_{z^2} orbital, which is occupied.

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fluxional behavior is not expected in this system, although an equilibrium between agostic and nonagostic structures due to C(1)–C(3) bending away from the metal is plausible.

^{13}C NMR Spectra. Figure 3 shows the proton-decoupled ^{13}C NMR spectra of 3 and 5 in ^2H_2O. The observed resonances were assigned by comparison of these two spectra and by reference to the assigned resonances of 1,3-pdda–Co(III) complexes[17] and are presented in Table V.

The assignment of the C(2) carbon of 3 to the resonance at 18.6 ppm was confirmed by the observation of this resonance as a symmetrical quartet with $J(^{13}C(2)-^{1}H(2a))$ of 122 Hz and $J(^{13}C(2)-^{1}H(2b))$ of 129 Hz in the proton-coupled spectrum. In contrast, the resonances of the central methylene carbon of the chair backbone, C(5), and all the other daco backbone methylene carbons were observed as triplets with $J(^{13}C-^{1}H)$ of 129 and 141 Hz, respectively. The uniqueness of the C(2) carbon, as evidenced by the reduced ^{13}C(2)–H(2a) coupling constant, is consistent with the presence of an agostic interaction, but as noted by Brookhart and Green,[2] typical values of $J(^{13}C-^{1}H)$ for M··HC bridged systems are 75–100 Hz. In addition, agostic carbons are typically shifted to higher fields in ^{13}C spectra, which is not observed for 3. We interpret these observations as that the present system displays a weak agostic interaction.

The assignment of the C(2) carbon of 5 to the resonance at −9.2 ppm was confirmed by the observation of a doublet with $J = 164$ Hz in the proton-coupled spectrum. The weakness of this resonance is consistent with the smaller nuclear Overhauser enhancement expected due to the loss of a proton. In addition, it is generally known that the ^{13}C resonance for a carbon atom which is coordinated directly to a cobalt center is weak and sometimes undetectable.[18]

The C(2) resonance of 5 is found at a relatively high field in comparison with that of the corresponding carbon in organocobalt(III) complexes with unsaturated equatorial ligands, e.g., 11–50 ppm for $[Co(DH)_2(R)py]$ (R = alkyl)[18] and 2–14 ppm for methyl corrinoids.[19,20] This difference in chemical shift suggests that the equatorial ligand system effects considerable influence on the nature of the coordinated carbon and is an indication that the cobalt–carbon bond in 5 has less covalent character than in alkyl–cobaloximes and alkyl–corrinoids. This is consistent with the relatively low-field shift observed for the C(2) proton, indicating significant ionic character in the cobalt–carbon bond.

The difference in the nature of the cobalt–carbon bond between the present complex and other organocobalt(III) complexes may be explained by Pearson's hard-soft concept[21] or Jorgensen's optical electronegativity[22] on equatorial ligand systems. That is, the softness of unsaturated ligands, such as dimethylglyoxime and corrin, may favor covalent cobalt–carbon bonds, while the hardness of the poly(amino carboxylate) ligand favors ionic character in the cobalt–carbon bond.

Electronic Absorption Spectra. The electronic absorption spectrum of 3 is shown in Figure 4B, together with that of *trans*-$[Co^{III}(SO_3)(1,3\text{-pdda})(H_2O)]^-$ (Figure 4A) for comparison. The visible spectrum of 3 is typical of an *octahedral* cobalt(III) complex, showing two bands in the visible–near-UV region, which is somewhat surprising given the classically five-coordinate geometry of this complex. In addition, the UV spectrum is virtually identical with that of the related complex *trans*-$[Co^{III}(SO_3)(1,3\text{-pdda})(H_2O)^-$; the charge-transfer (CT) transition due to SO_3^{2-} was observed at ca. 36 000 cm^{-1}, and that due to the poly(amino carboxylate) moiety, at ca. 46 000 cm^{-1}. The position of the former CT transition is typical of S-coordinated mono(sulfito)cobalt(III) complexes.[23]

Figure 4C shows the diffuse reflectence spectrum of 3. Taking into consideration band broadening due to a solid-state effect, it can be concluded that 3 shows the same d–d spectrum both in the solid state and in solution. Therefore, it is reasonable to assume that the solid-state structure is preserved in solution.

Under the assumption of the additivity of axial fields, 3 can be approximated as having D_{4h} symmetry with respect to the coordinating ligands.[24,25] In this approximation the broad first band (Figure 4B) corresponds to a superposition of the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions. A ligand field analysis[24,25] of the first band reveals that the ligand field strength (*Dq*) of the agostic interaction is ~600 cm^{-1}. This is a very small *Dq* value, reflecting the weakness of the agostic interaction; for comparison, the *Dq* values for the very weak field ligands N_3^- and I^- are 1076 and 971 cm^{-1}, respectively.[25]

The electronic spectra of alkylcobalt(III) complexes have been widely studied for coenzyme B_{12} and related complexes,[26-29] with particular interest in the ligand field strength of alkyl groups and the position of the charge-transfer transition due to the cobalt–carbon bond. However, the complexes that contain unsaturated equatorial ligands, such as dimethylglyoxime and salen, display a charge-transfer transition in the visible region, which makes the assignment of the d–d transitions ambiguous. Relatively few examples of alkylcobalt(III) complexes with saturated equatorial ligands have been reported to date[30-32] although Bacac and Espenson[31] recently reported a general method for the preparation of $[Co^{III}([14]aneN_4)(H_2O)(R)]^{2+}$ (R = alkyl, benzyl) complexes.

Figure 5 shows the electronic absorption and MCD spectra of 5. The MCD spectrum was used to confirm band assignments. The spectral features are typical of a Werner-type cobalt(III) complex with the lowest energy band assigned to the first d–d transition, which allows *Dq* of the alkyl ligand to be estimated. Interestingly, the absorption maximum of the first d–d transition of 5 is very similar to that for *trans*-$[Co^{III}(SO_3)(1,3\text{-pdda})(H_2O)]^-$. Furthermore, since the ligand field strength of dacoda can be regarded to be the same as that of 1,3-pdda and the aqua ligand is found opposite the alkyl and SO_3^{2-} groups in the respective complexes, it can be concluded that the ligand field strength of the alkyl group is very similar to the value for SO_3^{2-}, 2430 cm^{-1}.[25,33] This value is consistent with those previously obtained for alkyl ligands of Co(III)–tetraazamacrocyclic complexes.[26]

Summary and Conclusions

The results presented here demonstrate that 3 is a square-pyramidal *classically* five-coordinate Co(III) complex with a weak two-electron, three-center Co··HC (agostic) interaction occupying

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the sixth coordination site, which to our knowledge is the first example of an agostic C-H interaction in a classical coordination complex. NMR studies of **3** are consistent with a weak agostic interaction, since only a slightly reduced ^{13}C-H coupling constant is observed for the agostic C-H group. The weakness of the Co⋯HC interaction and the reason for the surprising stability of **3** in aqueous solution is attributed to the strong trans influence of the sulfite ligand. Nevertheless, the agostic interaction in **3** activates the C(2)-H(2a) bond sufficiently such that it can be deprotonated in methanol to give Co-alkyl complex **5**. This demonstrated activation of a C-H bond via electrophilic attack of Co(III) strongly supports the mechanism shown in Scheme I, which was proposed earlier[4] for the general preparation of **5**. It is intriguing that a relatively simple but sterically constrained molecule can exhibit C-H activation in an aqueous environment. Such specificity may be inherent to C-H activation in enzymes.

Acknowledgment. We are grateful to Don Appel for assistance in obtaining the NMR spectra. We also wish to thank Professor Hisahiko Einaga of University of Tsukuba and Professor Nobuko Matsuoka of Osaka University for technical assistance. The Nicolet X-ray diffractometer was acquired with the aid of NSF Grant CHE-8408407 and The Boeing Corp. In addition, The Boeing Corp. is gratefully acknowledged for assistance in obtaining the Nicolet 200-MHz NMR spectrometer.

Supplementary Material Available: For **3**, tables of complete positional and thermal parameters including those of H atoms, anisotropic thermal parameters, bond distances and bond angles, and data collection and refinement parameters (10 pages); a listing of F_o and F_c values (24 pages). Ordering information is given on any current masthead page.

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Synthesis, Structural Characterization, and Photoinduced Hydrogenation of $[PPN]_2[Re_6C(CO)_{19}]$

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Treatment of $[PPN]_3[Re_7C(CO)_{21}]$ with 2 equiv of ferrocenium ion in the presence of excess triphenylphosphine and a carbon monoxide atmosphere provided $[PPN]_2[Re_6C(CO)_{19}]$, which was isolated as a crystalline solid in 90% yield. The coproduct was identified as $[Re(CO)_4(PPh_3)_2]^+$. $[Et_4N]_2[Re_6C(CO)_{19}]$ was prepared in similar yield. The compound $[PPN]_2[Re_6C(CO)_{19}]$ crystallizes in the monoclinic space group $I2/a$ with $a = 23.943$ (10) Å, $b = 14.907$ (6) Å, $c = 26.164$ (9) Å, $\beta = 93.75$ (3)°, and $Z = 4$ (at $T = -125$ °C). The octahedral Re_6C core has crystallographically imposed C_2 symmetry. There are 18 terminal carbonyl ligands, three coordinated to each metal atom. Two unique positions exist for the 19th carbonyl ligand: one is symmetrically edge bridging, and the second is nearly terminal but with weak bridging interactions to the adjacent two rhenium atoms defining a triangular face. Solution ^{13}C NMR spectra of $[PPN]_2[Re_6{}^{13}C(^{13}CO)_{19}]$ (ca. 50% ^{13}C) showed complete scrambling of the carbonyl ligands even at -85 °C. The averaged ^{13}C-^{13}C coupling between the carbide ligand and the carbonyl ligands was observed as $^2J = 2.6$ Hz. Sunlamp irradiation of $[PPN]_2[Re_6C(CO)_{19}]$ in the presence of hydrogen gas gave $[PPN]_2[H_2Re_6C(CO)_{18}]$ in high yield.

Introduction

In 1985 Beringhelli et al.[1] reported that oxidation of the capped-octahedral[2] rhenium cluster $[Re_7C(CO)_{21}]^{3-}$ with a stoichiometric amount of iodine (acetonitrile, room temperature, CO atmosphere) resulted in removal of the capping $Re(CO)_3$ unit to give $[Re_6C(CO)_{19}]^{2-}$ and that excess iodine provided the novel species $[Re_4C(CO)_{15}I]^-$ in low yield. A footnote to this paper mentioned a preliminary X-ray crystallographic analysis of $[Re_6C(CO)_{19}]^{2-}$ that showed the complex was "an octahedral cluster, centered by the carbide, bearing one doubly-bridging and eighteen terminal CO groups, three for each Re atom." However, no further preparative or structural details regarding $[Re_6C(CO)_{19}]^{2-}$ have been published. As part of our interest in the formation and interconversion of large rhenium carbonyl clusters,[3,4] we have developed a new synthesis of $[Re_6C(CO)_{19}]^{2-}$. In this paper, we report that the reaction of $[Re_7C(CO)_{21}]^{3-}$ with ferrocenium ion (Cp_2Fe^+) in the presence of excess triphenylphosphine and carbon monoxide provides $[Re_6C(CO)_{19}]^{2-}$ in 90% isolated yield together with an identified mononuclear coproduct (eq 1). The structure of $[PPN]_2[Re_6C(CO)_{19}]$ has been fully defined by a low-temperature single-crystal X-ray crystallographic study. Furthermore, we describe the unique photoreactivity of $[Re_6C(CO)_{19}]^{2-}$, which in the presence of hydrogen gas gives the previously known[3,5] dihydrido complex $[H_2Re_6C(CO)_{18}]^{2-}$ (eq 2).

$$[Re_7C(CO)_{21}]^{3-} \xrightarrow[PPh_3,\ CO]{2\ Cp_2Fe^+} [Re_6C(CO)_{19}]^{2-} + [Re(CO)_4(PPh_3)_2]^+ \quad (1)$$

$$[Re_6C(CO)_{19}]^{2-} + H_2 \xrightarrow{h\nu} [H_2Re_6C(CO)_{18}]^{2-} + CO \quad (2)$$

Experimental Section

General Procedures. All operations were conducted by using standard Schlenk techniques. The $[(Ph_3P)_2N]^+$ (PPN^+) and $[Et_4N]^+$ salts of $[Re_7C(CO)_{21}]^{3-}$ were prepared as described previously.[3] Triphenylphosphine and $[Cp_2Fe][PF_6]$ were obtained commercially and were used without further purification. Acetone, dichloromethane, and THF were distilled under nitrogen from anhydrous potassium carbonate, calcium hydride, and sodium/benzophenone, respectively. Triglyme was dried by stirring over sodium at 120 °C under nitrogen for 2 days and was distilled before use. Infrared (IR) spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Elemental analyses were determined in the Microanalytical Laboratory of the School of Chemical Sciences. Fast atom bombardment (FAB) mass spectra were obtained in the School Mass Spectrometry Laboratory; the matrix used was "Magic Bullet" (dithioerythritol-dithiothreitol). ^{13}C NMR spectra were recorded in acetone-d_6 and are referenced to the carbonyl resonance at δ 206.0. High-resolution spectra were obtained on a General Electric GN-500 spectrometer at 125 MHz by using a 128 K data set, which corresponds to a digital resolution of 0.54 Hz/point. Variable-temperature spectra were measured on a General Electric QE-300 spectrometer at 75 MHz.

Preparation of $[PPN]_2[Re_6C(CO)_{19}]$. To a flask containing $[PPN]_3[Re_7C(CO)_{21}]$ (169 mg, 0.0480 mmol), $[Cp_2Fe]PF_6$ (35 mg, 0.11 mmol), and triphenylphosphine (512 mg, 1.95 mmol) was added acetone (50

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