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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

The Crystal Structure and Reactivity of (η⁵-C₅H₄COOCH₂C₆H₅)Co(CO)I₂

Zhen Pang^a, Xiu-Feng Hou^a, Rui-Fang Cai^a, Xi-Gen Zhou^a, Zu-En Huang^a & Jie Sun^b

^a Department of Chemistry , Fudan University , 220 Handan Road, Shanghai, 200433, P. R. China

^b Shanghai Instituted of Organic Chemistry, Chinese Academy of Sciences, 354 Fengtin Road, Shanghai, 200032, P. R. China Published online: 23 Apr 2008.

To cite this article: Zhen Pang , Xiu-Feng Hou , Rui-Fang Cai , Xi-Gen Zhou , Zu-En Huang & Jie Sun (2000) The Crystal Structure and Reactivity of (η^5 -C₅H₄COOCH₂C₆H₅)Co(CO)I₂ , Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 30:5, 877-895, DOI: <u>10.1080/00945710009351806</u>

To link to this article: http://dx.doi.org/10.1080/00945710009351806

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THE CRYSTAL STRUCTURE AND REACTIVITY OF $(\eta^5-\dot{C}_5H_4COOCH_2C_6H_5)C_0(CO)I_2$

Zhen Pang*, Xiu-feng Hou, Rui-fang Cai, Xi-gen Zhou and Zu-en Huang Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, P. R. China

Jie Sun

Shanghai Instituted of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai, 200032, P. R. China

ABSTRACT

The structure of the title compound $(\eta^5-C_5H_4COOCH_2C_6H_5)Co(CO)I_2$ (1) was determined. The ester carbonyl in the cyclopentadienyl ring substituent of (1) was found at a dihedral angle of 8-10° with the cyclopentadienyl plane and this structural distortion is attributed to the electronic repulsive force from the adjacent C-H bond of the cyclopentadienyl ring and the methylene group of the ring substituent. The redox properties of (1) were also investigated via sodium amalgam and cyclic voltammetry

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INTRODUCTION

Cyclopentadienyl metal complexes are an important class of compounds for both theoretical and applied purposes¹. Considering both aspects, modifying this class of compounds by alternating their ligands and substituents has always been of interest to chemists². By choosing a different valence charge of the metal or alternating the ligands around the metal, large changes can made to the electron density of the metal center of the designed complexes. Functional groups on the substituents of the ligand have a minor influence on the electron density of the metal center. The reactivity of these compounds, influenced by their electronic and geometric features, has been pointed out by many researchers³.

Very recently, we have synthesized some cyclopentadienyl cobalt carbonyl derivatives with various substituents on the cyclopentadienyl ring. The ligands around the metal center have also been alternated⁴. We examined the influence of the ligand and substituents on the metal center by instrumentation analyses. In this paper, we describe the structure of $(\eta^5-C_5H_4COOCH_2C_6H_5)Co(CO)I_2$ (1) and its reactivity towards oxidation and reduction.

EXPERIMENTAL

All operations including column chromatography were carried out under a nitrogen atmosphere utilizing standard Schlenk techniques. Solvents were dried and distilled from calcium hydride under a nitrogen atmosphere. Neutral alumina used in column chromatography had been dried in an oven at 120° C for several days, and then heated at 180° C under reduced pressure on a rotary evaporator to remove residual water and oxygen. The alumina was subsequently deactivated with 5 % (by weight) degassed water.

The X-ray measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) and a 12kW rotation anode generator. Cyclic voltammetry (CV) was carried out in dry CH₂Cl₂ containing 0.2 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte and using a m273A EG&G Princeton Applied Research Potentiostat. The electrochemical cell was a three-electrode system, with a Teflon cap containing a platinum disc electrode with a diameter of 2 mm, a platinum wire acted as an auxiliary electrode and silver/saturated silver acetate (in CH₂Cl₂ solution) was employed as a reference electrode. The potential values are reported with the ferrocenium/ferrocene couple as the internal reference.

The elemental analyses were performed on a Rapid CHN-O 240C Analyzer (Heraeus, Germany) at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. IR spectra were recorded on a Nicolet FT-IR-50-X spectrophotometer. The mass spectrum was measured on a HP 5989A instrument. The UV/Vis spectrum was recorded on Shimadzu UV-240 spectrometer.

X-ray Structure Determination

Compound (1) was prepared and characterized as previously described⁴. Black crystals of (1) were grown in hexane solution under N₂ atmosphere at -10° C. It should be kept from light to prevent the loss of CO. A suitable crystal having the approximate dimensions of $0.20 \times 0.20 \times 0.30$ mm was sealed in a nitrogenfilled, thin-walled glass capillary mounted on a glass fiber. Data were collected at a temperature of $20 \pm 1^{\circ}$ C using the ω -2 θ scan technique to a maximum 2 θ value of 50.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.05° with a take-off angle of 6.0°.

Of the 1625 reflections which were collected, 1506 were unique ($R_{int} = 0.030$). The intensities of three representative reflections were measured after every 200 reflections. Over the course of the data collection, the standards increased by 1.0%. A linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 3.61894e-7).

The structure was solved by direct methods (SAPI91) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically with full-matrix least-squares. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corporation⁵. Relevant data concerning the crystal, data collection and structure solution are recorded in Table I.

Reaction of Compound (1) with Na-Hg

Compound (1) (0.280 g, 0.518 mmol) and Na-Hg (Na, 35.8 mg, 1.56 mmol, 1%) were mixed in 60 mL of tetrahydrofuran (THF) at -60° C. The mixture was stirred and the temperature was allowed to rise slowly. When the temperature reached about -42° C, the color of the solution turned from deep violet to redbrown. The reaction mixture was then stirred at that temperature for half an hour, and then filtered through a glass frit. The solvent of the filtrate was removed in vacuo at -20° C. The residue was dissolved in a small amount of CH₂Cl₂, placed on an alumina-packed column and eluted with a 1:1:4 CH₂Cl₂: ether : petroleum ether mixture below -20° C. The red band was collected. The eluent was evaporated in vacuo. The resulted solid was recrystallized in a mixture of CH₂Cl₂ and petroleum ether (1 to 1 ratio) to afforded a red brown solid (0.121 g, yield 51%). The solid product characterized colbaltocene was as (C5H4COOCH2C6H5)2Co. MS: 457 (M⁺,100). Mp: 140° C. Calculated for C26H22O4Co (formula weight 457.4): C, 68.28; H, 4.85 %. Found: C, 67.18; H, 4.73 %. IR (KBr pellet, in cm⁻¹): 1731 s (C=O), 1497 w (C=C of phenyl ring),

Formula	$C_{14}H_{11}O_{3}Col_{2}$
Formula Weight	539.98
No. of Reflections Used for Unit Cell	
Determination (20 range)	25 (16.0 - 28.7)
Crystal system	monoclinic
Lattice Parameters	a = 7.332(6) Å
	b = 10.915(4) Å
	c = 10.105(5) Å
	$\beta = 95.90(5)^{\circ}$
	$V = 804.5(8) Å^3$
Space Group	P2 ₁ (#4)
Z value	2
Dcale	2.229 g/cm ³
μ(ΜοΚα)	49.08 cm ⁻¹
Scan Rate (°/min)	16.0
2θmax (°)	50.0
No. of observations $(l > 2.50\sigma(l))$	1461
No. of variables	181
P factor	0.03
R; Rw	0.044; 0.057
Goodness of fit indicator	2.78

Table I. Crystal Data and Structure Refinement for (1).

 $R = \Sigma ||Fo| - |Fc||/\Sigma|Fo|$ $Rw = \sqrt{\Sigma W (|Fo| - |Fc|)^2 / \Sigma W Fo^2)}$



Fig. 1. (a) PRTEP Diagram of Compound (1). (b)A Depiction of Compound (2) According to Reference 8.



Fig. 2. A Projected View of Molecule (1) over the Cyclopentadienyl Plane.

1469 m, 1384 m, 1272 s, 1131 s. CV (in CH₂Cl₂, with 0.2 M TBAP): $E_{1/2} = -0.32 V^6$.

RESULTS AND DISCUSSION

Discussion of the Structure

Crystals of compound (1) consist of discrete molecules, separated by normal

van der Waals distances. Its ORTEP view is given in Fig. 1(a) with the atoms numbered for clarity. Fig. 2 is a view of the molecule (1) projected from the cyclopentadienyl plane. Selected bond lengths and bond angles are given in Table II.

The cyclopentadienyl ring and the phenyl ring are planar with a difference of The dihedral angle between the cyclopentadienyl plane and the phenyl 0.01 Å. The eclipsed C-C bonds in the cyclopentadienyl ring are plane is 96.68°. obviously longer than the non-eclipsed C-C bonds but are still in the normal range. This phenomenon was also found in other molecules with a cyclopentadienyl ligand⁷. The average distance of Co to the ring carbon is 2.067 Å, slightly shorter than 2.095 Å as found in its analogue diiodo(η^5 : η^1 -1-[2-(N,N-dimethylamino) ethyl]-2,3,4,5-tetramethylcyclppentadienyl cobalt(III) (2) [see Fig. 1 (b)]⁸. This difference is attributed to the opposite electronic properties of their ligand and ring Since the ester group in the ring substituent of (1)substituent in (1) and (2). is electron withdrawing in nature and the terminal carbonyl is a strong π -acceptor, both reduce the electronic density of the metal center. On the other hand, the four methyl groups on the cyclopentadienyl ring in (2) are electron releasing in nature and the chelated amino nitrogen is a strong σ donor. But the differences of the Co-I bond length (2.557 Å for (1) and 2.622 Å for (2)) in these two compounds are larger compared to that of their metal-ring distances. Although the ester group in the ring substituent of (1) is expected to be coplanar with the cyclopentadienyl ring through their strong interaction in a conjugated π system⁴, a dihedral angle of 8-10° between the two planes is observed. The bond angle of C6-C5-H4 is 135° while that of C4-C5-H4 is 115.8°. The C5-H4 bond obviously bends away from the ester carbonyl double bond from an ideal angle of 126° as we found in the rest of the ring C-H bonds. The bond length of C5-H4 is significantly longer than the other ring C-H bonds. Abnormal bond angles and bond lengths are also observed

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)		
I(1)	Со	2.558(2)	C(2)	H(1)	0.93		
l(2)	Co	2.557(2)	C(3)	H(2)	0.94		
Со	C(1)	1.86(2)	C(4)	H(3)	0.94		
Со	C(2)	2.08(1)	C(5)	H(4)	1.02		
Со	C(3)	2.07(1)	C(8)	H(5)	0.88		
Со	C(4)	2.06(1)	C(8)	H(6)	1.16		
Со	C(5)	2.07(1)	C(10)	H(7)	0.92		
Со	C(6)	2.05(1)	C(11)	H(8)	0.98		
C(2)	C(3)	1.39(2)	C(12)	H(9)	0.96		
C(3)	C(4)	1.47(2)	C(13)	H(10)	0.97		
C(4)	C(5)	1.38(2)	C(14)	H(11)	0.87		
C(5)	C(6)	1.44(2)	C(2)				
C(2)	C(6)	1.45(2)	C(2)				
O(2)	C(7)	1.20(1)	C(2)				
Atoms		Angles (°)) A	toms	Angles (°)		
O(2)-C	C(7)-C(6)-C((2) -169(1)	O(3)-0	C(8)-H(5)	93.6		
O(3)-C	c(7)-C(6)-C((2) 10(1)	O(3)-0	C(8)-H(6)	115.1		
O(3)-C	(7)-C(6)-C(5) -172(1)	C(9)-C	C(8)-H(5)	124.0		
C(7)-O	(3)-C(8)-C(9) -78(1)	C(9)-C	C(8)-H(6)	104.5		
O(2)-C	(7)-O(3)-C((8) 4(1)	C(6)-C	C(5)-H(4)	135.0		
O(3)-C((8)-C(9)-C(14) -24(2)	C(4)-C	C(5)-H(4)	115.8		

Table II. Selected Bond Distances (Å) and Angles (°).

(η⁵-C₅H₄COOCH₂C₆H₅)Co(CO)I₂

for the methylene group in the ring substituent, which is on the other side of the ester carbonyl. The bond angles of O3-C8-H5 and O3-C8-H6 are 93.6° and 115.1°, respectively. Both deviate significantly from the ideal bond angle of 109.48° for sp³ hybridization. A shorter bond length for C8-H5, which is close to and faces O2 of the ester carbonyl, and a longer bond length for C8-H6, which is pointing away from O2, are also observed compared to the normal C-H bond length. Although the exact C-H bond lengths are not certain (we did not refine the hydrogen atoms in our structural solution), the existence of the repulsive force between the ester carbonyl double bound and the C5-H4 bond as well as the carbon hydrogen bond of the methylene group seems to lead to these structural distortions in the crystal. This static electronic repulsion among the ester carbonyl double bond, C5-H4 bond and the methylene C-H bonds might force the ester carbonyl out of the cyclopentadienyl ring plane. The dihedral angle of 8-10° between the cyclopentadienyl ring plane and the ester plane should be a balance between the repulsion and the conjugation effect. Such an electronic repulsive effect can also be found for the C14-H11 bond, which points to the terminal metal carbonyl. The electronic repulsive force seems to push H11 away from the terminal metal carbonyl as the ester carbonyl does to H5, since a shorter bond length of C14-H11 is observed than the other C-H bonds in the phenyl ring. This phenomenon might hint that there is significant electron density around the hydrogen atoms in the alkane and alkene protons. The nuclei of these hydrogen atoms are effectively shielded by the electron density around it. The distance between H4 and H5 to O2 is 3.055 Å and 2.450 Å, respectively. The distance of O1 to H11 is 3.034 Å. H1 has a distance of 4.10 Å from O2 and the C2-H1 bond does not show any geometrical distortion.

Reduction of Compound (1) with Na-Hg

The reduction with sodium amalgam of trivalent compounds of the type

 $Cp^{R}Co(CO)I_{2}$ ($Cp^{R} = \eta^{5}-C_{5}H_{5}$ or $\eta^{5}-C_{5}H_{4}R$) was reported to form the monovalent intermediate Cp^RCo(CO), which may be trapped by intramolecular coordination if R is a chelatable substituent, or trapped by a ligand to form $Cp^{R}Co(CO)L^{9}$. In our case, a divalent compound, $(Cp')_2Co$ ($Cp' = \eta^5 - C_5H_4COOCH_2C_6H_5$), was formed instead of a Co(1) compound. We also used sodium amalgam to reduce (η^{5} -C₅H₄COOCH₂C₆H₅)Co(PPh₃)I₂, an analogue of compound (1), and (Cp')₂Co was The v(C=O) band of the product is at 1731 cm⁻¹, about 6 cm⁻¹ also obtained. blue-shifted compared to that of compound (1), but the v(C=C band of phenyl ring)remains the same. We can expect a more electron rich metal center for $(Cp')_2Co$ that will feed back its electron density to its ligand Cp', making the C-H bond and ester carbonyl more electron-rich, and a larger static electronic repulsion might resulting. The dihedral angle between the cyclopentadienyl ring plane and ester plane might increase due to this repulsion. Thus, a less π -conjugated ester carbonyl, which has a blue-shift in its IR stretching frequency, might be a reasonable result.

It was reported that when reduced by sodium amalgam, $Cp^RCo(CO)_2$ formed a radical compound that may result in a metal dimer and cyclopentadienide¹⁰. When the substituent on the cyclopentadienyl is an electron-withdrawing group such as $-CO_2CH_3$, 80-85 % of cyclopentadienide was formed during the reduction¹¹. This result may account for the formation of cobaltocene, Cp'_2Co , in our case: $-COOCH_2C_6H_5$ is a strong electron withdrawing group which favors the formation of the cyclopentadienide and Cp'Co(CO) which was then trapped by Cp' and resulting in $(Cp')_2Co$.

Electrochemical Oxidation

Fig. 3 illustrates the cyclic voltammetric response of compound (1) in CH_2Cl_2 solution with 0.2 M TBAP as supporting electrolyte under nitrogen atmosphere.



Fig. 3. Cyclic Voltammogram of (1) in Methylene Chloride with 0.2 M TBAP, Showing the Dissociation of the Oxidation Product of (1).

There is a quasi-reversible redox peak I corresponding to a Co(III)/Co(IV) couple in dichloromethane solution. Its redox potential is at $E_{1/2} = 0.19$ V which was calculated from the average of the anodic Epa = 0.36 V and cathodic Epc = 0.01 V, with the peak to peak separation of 348 mV: The redox potential of ferrocene ($E_{1/2} = 0.40$ V vs. SCE) was used as the internal reference with the peak separation of 266 mV under the same condition. The large peak separation is normal for a reversible couple in an organic solvent due to the high resistance¹². Two consecutive oxidation peaks, II and III, follow the quasi-reversible peak located at 0.66 V and 0.77 V and no reduction response was observed. When the cyclic voltammogram of (1) was run in the reduction mode from 1.4 V to -0.2 V, same result as Fig. 3 was obtained. Increasing the scan rate from 50 to 2000 mV/s, the quasi-reversible peak I is reduced in size while peaks II and III increased and moved towards E higher values. This corresponds to the decomposition of the oxidation product of compound (1). The current of peak I is linearly proportional to the square root of the scan rate, indicating a diffusion controlled process of the quasi-reversible oxidation. The redox process may be expressed by the following equation:

$$Cp^{R}Co^{III}(CO)I_{2} \xrightarrow{-c} Cp^{R}Co^{IV}(CO)I_{2} \xrightarrow{-c} Decomposition$$

Supplemental Material

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition number 112936. Tables of the atomic coordinates, thermal parameters, nonessential bond distances and angles are available from the author.

ACKNOWLEDGMENTS

Project 29771008 was supported by the National Natural Science Foundation of China. A Research Grant from the State Educational Committee of China and a Fudan University Faculty Research Grant for partial support of this work are greatly acknowledged. This project was also supported by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences and by the State Key Laboratory of Coordination Chemistry, Nanjing University.

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Received: 27 May 19999 Accepted: 24 January 2000 Referee I: D. J. Casadonte, Jr. Referee II: D. J. Caudle

Atom	x	У	Z	B(eq)
I (1)	0.1388(1)	0.1941	0.4727(1)	4.64(2)
l(2)	-0.3254(1)	0.2440(2)	0.58631(9)	5.40(3)
Co	-0.1951(2)	0.1760(2)	0.3729(2)	2.80(3)
O(1)	-0.172(2)	0.433(1)	0.298(2)	7.6(4)
O(2)	0.117(1)	0.037(1)	0.117(1)	4.7(2)
O(3)	-0.072(1)	0.185(1)	0.0272(8)	4.0(2)
C(1)	-0.181(2)	0.341(2)	0.327(2)	4.6(4)
C(2)	-0.345(1)	0.129(1)	0.194(1)	3.1(2)
C(3)	-0.431(2)	0.085(1)	0.300(2)	4.2(3)
C(4)	-0.304(2)	0.003(1)	0.380(1)	3.7(3)
C(5)	-0.144(2)	-0.003(1)	0.319(1)	3.1(2)
C(6)	-0.162(2)	0.076(1)	0.205(1)	2.8(2)
C(7)	-0.022(2)	0.095(1)	0.114(1)	3.0(2)
C(8)	0.049(2)	0.209(2)	-0.078(1)	4.3(3)
C(9)	0.215(2)	0.280(1)	-0.032(1)	3.4(3)
C(10)	0.364(2)	0.280(1)	-0.106(1)	4.1(3)
C(11)	0.511(2)	0.356(2)	-0.074(1)	4.5(3)
C(12)	0.516(2)	0.433(2)	0.035(2)	4.8(4)
C(13)	0.372(3)	0.432(2)	0.110(2)	5.5(4)
C(14)	0.221(2)	0.360(2)	0.079(1)	4.9(4)
H(1)	-0.3938	0.1834	0.1286	5.6
H(2)	-0.5505	0.1039	0.3208	5.2
H(3)	-0.3291	-0.0399	0.4568	4.5
H(4)	-0.0384	-0.0491	0.3703	4.8
H(5)	0.0506	0.1317	-0.1024	7.9
H(6)	-0.0182	0.2625	-0.1691	4.6
H(7)	0.3593	0.2182	-0.1690	3.1
H(8)	0.6203	0.3497	-0.1231	6.3
H(9)	0.6189	0.4860	0.0580	5.2
H(10)	0.4106	0.4900	0.1795	8.7
H(11)	0.1240	0.3817	0.1169	2.1

Table I. Positional Parameters and B(eq)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
I(1)	Со	l(2)	94.02(6)	C(4)	Со	C(6)	67.8(5)
l(1)	Со	C(1)	87.1(5)	C(5)	Со	C(6)	40.9(5)
l(1)	Со	C(2)	139.4(3)	C(7)	O(3)	C(8)	117(1)
I(1)	Со	C(3)	155.6(4)	Со	C(1)	O(1)	178(2)
i(1)	Со	C(4)	114.7(4)	Со	C(2)	C(3)	69.9(7)
l (1)	Со	C(5)	89.1(3)	Co	C(2)	C(6)	68.5(6)
I(1)	Со	C(6)	[00.2(3)	C(3)	C(2)	C(6)	107(1)
l(2)	Со	C(1)	87.9(5)	Со	C(3)	C(2)	70.9(7)
I(2)	Со	C(2)	126.5(3)	Со	C(3)	C(4)	68.8(7)
l(2)	Со	C(3)	93.8(4)	C(2)	C(3)	C(4)	109(1)
I(2)	Co	C(4)	93.3(4)	Co	C(4)	C(3)	69.5(8)
I (2)	Со	C(5)	126.0(4)	Co	C(4)	C(5)	71.0(7)
l(2)	Со	C(6)	159.8(3)	C(3)	C(4)	C(5)	108(1)
C(1)	Co	C(2)	93.4(6)	Со	C(5)	C(4)	69.8(8)
C(1)	Со	C(3)	116.3(7)	Со	C(5)	C(6)	68.9(6)
C(1)	Со	C(4)	158,1(6)	C(4)	C(5)	C(6)	108(1)
C(1)	Со	C(5)	146.1(6)	Со	C(6)	C(2)	70.3(7)
C(1)	Со	C(6)	107.0(6)	Co	C(6)	C(5)	70.2(7)
C(2)	Со	C(3)	39.2(5)	Со	C(6)	C(7)	126.7(8)
C(2)	Со	C(4)	68.4(5)	C(2)	C(6)	C(5)	108(1)
C(2)	Со	C(5)	68,6(5)	C(2)	C(6)	C(7)	127(1)
C(2)	Со	C(6)	41.1(5)	C(5)	C(6)	C(7)	125(1)
C(3)	Со	C(4)	41.8(6)	O(2)	C(7)	O(3)	125(1)
C(3)	Co	C(5)	67.7(5)	O(2)	C(7)	C(6)	125(1)
C(3)	Co	C(6)	67.5(5)	O(3)	C(7)	C(6)	110(1)
C(4)	Co	C(5)	39,1(5)	O(3)	C(8)	C(9)	114(1)
C(8)	C(9)	C(10)	120(1)	C(8)	C(9)	C(14)	122(1)
C(10)	C(9)	C(14)	118(1)	C(9)	C(10)	C(11)	121(1)
C(10)	C (11)	C(12)	120(1)	C(11)	C(12)	C(13)	119(1)
C(12)	C(13)	C(14)	122(2)	C(9)	C(14)	C(13)	120(1)

Table II. Intramolecular Bond Angles Involving the Nonhydrogen Atoms. Angles are in Degrees. Estimated Standard Deviations in the Least Significant Figure are given in Parentheses.

Table III.Intramolecular Bond Angles Involving the Hydrogen Atoms.Angles arein Degrees.Estimated Standard Deviations in the Least Significant Figure are givenin Parentheses.

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Со	C(2)	H(1)	126.38	C(9)	C(8)	H(5)	124.02
C(3)	C(2)	H(1)	126.58	C(9)	C(8)	H(6)	104.52
C(6)	C(2)	H(1)	126.26	H(5)	C(8)	H(6)	106.27
Со	C(3)	H(2)	125.31	C(9)	C(10)	H(7)	113.64
C(2)	C(3)	H(2)	126.81	C(11)	C(10)	H(7)	125.01
C(4)	C(3)	H(2)	124.45	C(10)	C(11)	H(8)	119.75
Со	C(4)	H(3)	126.45	C(12)	C(11)	H(8)	119.58
C(3)	C(4)	H(3)	126.05	C(11)	C(12)	H(9)	120.29
C(5)	C(4)	H(3)	126.13	C(13)	C(12)	H(9)	120.66
Со	C(5)	H(4)	118.82	C(12)	C(13)	H(10)	102.28
C(4)	C(5)	H(4)	115.76	C(14)	C(13)	H(10)	135.54
C(6)	C(5)	H(4)	134.99	C(9)	C(14)	H(11)	123.60
O(3)	C(8)	H(5)	93.59	C(13)	C(14)	H(11)	114.57
O(3)	C(8)	H(6)	115.12				

Table IV. Intramolecular Distances Involving the Nonhydrogen Atoms. Distances are in Angstroms. Estimated Standard Deviations in the Least Significant Figure are given in Parentheses.

 Atom	Atom	Distance	Atom	Atom	Distance	
I (1)	Со	2.558(2)	C(2)	C(6)	1.45(2)	
l(2)	Co	2.557(2)	C(3)	C(4)	1.47(2)	
Со	C(1)	1.86(2)	C(4)	C(5)	1.38(2)	
Со	C(2)	2.08(1)	C(5)	C(6)	1.44(2)	
Со	C(3)	2.07(1)	C(6)	C(7)	1.45(2)	
Со	C(4)	2.06(1)	C(8)	C(9)	1.48(2)	
Со	C(5)	2.07(1)	C(9)	C(10)	1.39(2)	
Со	C(6)	2.05(1)	C(9)	C(14)	1.41(2)	
O(1)	C(1)	1.05(2)	C(10)	C(11)	1.38(2)	
O(2)	C(7)	1.20(1)	C(11)	C(12)	1.39(2)	
O(3)	C(7)	1.35(2)	C(12)	C(13)	1.36(3)	
O(3)	C(8)	1.47(1)	C(13)	C(14)	1.37(2)	
C(2)	C(3)	1.39(2)				

Table V.Intramolecular Distances Involving the Hydrogen Atoms.Distances are inAngstroms. Estimated Standard Deviations in the Least Significant Figure are Given inParentheses.

Atom	Atom	Distance	Atom	Atom	Distance	
C(2)	H(1)	0.931	C(10)	H(7)	0.923	
C(3)	H(2)	0.942	C(11)	H(8)	0.984	
C(4)	H(3)	0.939	C(12)	H(9)	0.962	
C(5)	H(4)	1.018	C(13)	H(10)	0.965	
C(8)	H(5)	0.876	C(14)	H(11)	0.874	
C(8)	H(6)	1.158				

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Table VI.	Torsion or Conformation Angles.	When Looking from Atom 2 to Atom 3,						
a Clock-wise Motion of Atom 1 to Atom 4 has Positive Sign.								

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
l(1) Co		1) 0(1)	88(48)	Со	C(2)	C(6)	C(7)	-122(1)
l(1) Co) C(2	2) C(3)	141.6(7)	Со	C(3)	C(2)	C(6)	58.6(8)
I(1) Co) C(2	2) C(6)	23(1)	Со	C(3)	C(4)	C(5)	-61.0(9)
I(1	.) Co	C (2	3) C(2)	-102(1)	Co	C(4)	C(3)	C(2)	60(1)
I(1) Co	• C(3	3) C(4)	18(1)	Co	C(4)	C(5)	C(6)	-58.2(8)
l(1) Co	• C(*	4) C(3)	-172.0(6)	Co	C(5)	C(4)	C(3)	60.0(9)
l(1) Co) C(•	4) C(5)	-53.7(8)	Co	C(5)	C(6)	C(2)	-60.6(8)
I(1) Co) C(5) C(4)	132.9(7)	Co	C(5)	C(6)	C(7)	122(1)
l(1) Co) C(5) C(6)	-106.9(6)	Со	C(6)	C(2)	C(3)	-59.5(9)
l(1) Co) C(6) C(2)	-165.2(7)	Co	C(6)	C(5)	C(4)	58.8(9)
I(1) Co) C(6) C(5)	76.5(7)	Co	C(6)	C(7)	O(2)	98(1)
I(1) Co	• C(6) C(7)	-43(1)	Co	C(6)	C(7)	O(3)	-82(1)
I(2	2) Co) C(1) O(1)	-177(48)	O(1)	C(1)	Co	C(2)	-51(48)
I(2	c) Co) C(2	2) C(3)	-39(1)	O(1)	C(1)	Со	C(3)	-84(48)
I(2	c) Co) C(2	2) C(6)	-157.9(6)	O(1)	C(1)	Со	C(4)	-84(48)
I(2	2) Co) C(3) C(2)	149.4(8)	O(1)	C(1)	Co	C(5)	4(48)
l(2	c) Co) C(2	3) C(4)	-90.6(7)	O(1)	C(1)	Со	C(6)	-11(48)
I(2	c) Co	• C(•	4) C(3)	92.1(7)	O(2)	C(7)	O(3)	C(8)	4(2)
l(2	c) Co	• C(4	4) C(5)	-149.6(7)	O(2)	C(7)	C(6)	C(2)	-170(1)
I(2	2) Co	• C(:	5) C(4)	38.6(9)	O(2)	C(7)	C(6)	C(5)	8(2)
I(2	c) Co) C(:	5) C(6)	158.8(5)	O(3)	C(7)	C(6)	C(2)	10(2)
ł(2	c) Co	C(0	5) C(2)	61(1)	O(3)	C(7)	C(6)	C(5)	-173(1)
I(2	c) Co	C(0	6) C(5)	-58(1)	O(3)	C(8)	C(9)	C(10)	162(1)
l(2	2) Co	• C(e	6) C(7)	-177.0(6)	O(3)	C(8)	C(9)	C(14)	-25(2)
Co) C(2) C(3) C(4)	-58.5(9)	C(1)	Co	C(2)	C(3)	-129(1)
Co) C(2) C(5) C(5)	60.5(8)	C(1)	Со	C(2)	C(6)	112.2(9)

(continued)

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
C(1)	Со	C(3)	C(2)	60(1)	C(3)	Co	C(5)	C(4)	-39.3(8)
C(1)	Со	C(3)	C(4)	179.9(9)	C(3)	Со	C(5)	C(6)	80.9(8)
C(1)	Co	C(4)	C(3)	0(2)	C(3)	Со	C(6)	C(5)	-81.4(8)
C(1)	Co	C(4)	C(5)	118(2)	C(3)	Co	C(6)	C(7)	159(1)
C(1)	Co	C(5)	C(4)	-144(1)	C(3)	C(2)	Со	C(4)	38.3(9)
C(1)	Со	C(5)	C(6)	-23(1)	C(3)	C(2)	Со	C(5)	80.5(9)
C(1)	Co	C(6)	C(2)	-75.1(9)	C(3)	C(2)	Co	C(6)	119(1)
C(1)	Co	C(6)	C(5)	166.6(8)	C(3)	C(2)	C(6)	C(5)	1(1)
C(1)	Co	C(6)	C(7)	47(1)	C(3)	C(2)	C(6)	C(7)	179(1)
C(2)	Co	C(3)	C(4)	120(1)	C(3)	C(4)	Со	C(5)	-118(1)
C(2)	Со	C(4)	C(3)	-36.1(8)	C(3)	C(4)	Co	C(6)	-80.6(8)
C(2)	Co	C(4)	C(5)	82.2(8)	C(3)	C(4)	C(5)	C(6)	2(1)
C(2)	Co	C(5)	C(4)	-81.8(8)	C(4)	Со	C(2)	C(6)	-80.4(8)
C(2)	Co	C(5)	C(6)	38.5(7)	C(4)	Со	C(5)	C(6)	120(1)
C(2)	Co	C(6)	C(5)	-118(1)	C(4)	Со	C(6)	C(5)	-36.1(7)
C(2)	Co	C(6)	C(7)	122(1)	C(4)	Со	C(6)	C(7)	-156(1)
C(2)	C(3)	Co	C(4)	-120(1)	C(4)	C(3)	Со	C(5)	36.9(7)
C(2)	C(3)	Со	C(5)	-83.0(9)	C(4)	C(3)	Со	C(6)	81.3(8)
C(2)	C(3)	Со	C(6)	-38.6(8)	C(4)	C(3)	C(2)	C(6)	0(1)
C(2)	C(3)	C(4)	C(5)	-1(2)	C(4)	C(5)	Со	C(6)	-120(1)
C(2)	C(6)	Со	C(3)	36.9(8)	C(4)	C(5)	C(6)	C(7)	-180(1)
C(2)	C(6)	Со	C(4)	82.2(8)	C(5)	Co	C(2)	C(6)	-38.3(7)
C(2)	C(6)	Co	C(5)	118(1)	C(5)	Co	C(6)	C(7)	-119(1)
C(2)	C(6)	C(5)	C(4)	-2(1)	C(5)	C(4)	Со	C(6)	37.7(7)
C(3)	Со	C(2)	C(6)	-119(1)	C(6)	C(7)	O(3)	C(8)	-175(1)
C(3)	Co	C(4)	C(5)	118(1)	C(7)	O(3)	C(8)	C(9)	-79(2)
C(8)	C(9)	C(10)	C(11)	172(1)	C(8)	C(9)	C(14)	C(13)	-174(2)
C(9)	C(10)	C(11)	C(12)	2(2)	C(9)	C(14)	C(13)	C(12)	2(3)
C(10)	C(9)	C(14)	C(13)	0(2)	C(10)	C(11)	C(12)	C(13)	0(2)
C(11)	C(10)	C(9)	C(14)	-1(2)	C(11)	C(12)	C(13)	C(14)	-1(3)