Sulfur Dioxide Insertion into the Co−C Bond in Organocobaloximes: Crystal Structure and Co−C Bond Reactivity† Study

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The insertion of sulfur dioxide into the Co−C bond in $ArCH_2Co(dioxime)_2Py$ forms a mixture of $ArCH_2SO_2Co(dioxime)_2Py$, $ClCo(dioxime)_2Py$, and a neutral trinuclear complex, $[(dpgH)_2PyCo^{III}\text{-}\mu\text{-}SO_3]_2\text{-}Co^{II}(MeOH)_4$. The inserted products 4-CN-$C_6H_4CH_2SO_2Co(dpgH)_2Py$ and $C_6H_5CH_2SO_2Co(gH)_2Py$ and the trinuclear complex have been structurally characterized by X-ray for the first time. The insertion of sulfur dioxide into the Co−C bond affects the orientation of the benzyl group.

Introduction

The recently available crystallographic data on cobalamins suggests that the structural effects of changes in R are similar to those found in cobaloximes and sometimes can be related to their chemical reactivity.[1] Since Co−C bond cleavage is the key step involved in B12-dependent enzymatic or cobaloxime mediated reactions, the strength of the Co−C bond as a function of steric and electronic factors with a wide range of axial ligands in cobaloximes and in related complexes with different chelates have been systematically investigated.[2] The recent results, based on spectral and structural studies, have shown that in addition to the trans effect of the axial base, the cis influence, the effect of the equatorial dioxime on the axial ligands, plays an important role toward the stability of the Co−C bond.[3] Insertion reactions have been used to test the reactivity of M−C bonds in organometallic compounds. Insertion of small molecules such as O_2, SO_2, CO, etc. into a metal−carbon bond is an important reaction and occurs with a remarkably wide range of organometallic compounds;[4] the metal may be one of the transition or main-group elements, and carbon is part of a wide variety of organic ligands. There have been numerous reports on oxygen insertion[5] into Co−C bonds, but the corresponding SO_2 insertion has been relatively little studied.

The early work on the insertion of SO_2 in $RCo^{III}(chelate)_2B$ complexes (chelate = salen, saloph, bae, dmgH; R = alkyl, aryl)[6] has shown that these reactions are very slow (>24 h), occur with great difficulty, and lead to a mixture of products.[7] In contrast, the reaction with allylcobaloxime is facile but becomes complicated with but-3-enyl- and hexenylcobaloximes, where a mixture of products is formed.[7d] Reactions have been carried out under thermal and photochemical conditions with or without solvent. The reaction at the secondary carbon in *cis*- and *trans*-(4-methylcyclohexyl)cobaloxime indicates inversion of configuration at the reacting carbon atom.[8]

The insertion of sulfur dioxide into benzylcobaloxime, $PhCH_2Co(dmgH)_2B$, is the most well-studied system because of the inherently weak Co−C bond. A recent study has shown that the reaction is not true insertion but is an intermolecular process in which the organic group and the metal in the insertion product do not originate from the same molecule of the organometallic substrate.[7,9] Both chain[10a] and nonchain[10b] mechanisms for the insertion of sulfur dioxide in organocobaloximes have been described. In general, the reaction is concerted with the attack of SO_2 at the metal and at the organic group, but in the case of organocobaloximes a dissociative mechanism is operating, where the key step is the cleavage of the Co−C bond.[10] Despite the appreciable amount of work on the kinetics, products, and stereochemistry of these reactions, there is no comprehensive picture of the mechanism. The sulfinato group (Co−S bond) in the inserted product has been identified by IR only,[7,9] and no crystal structure of the inserted product is known to date. The $PyCo(dioxime)_2SO_2Co(dioxime)_2Py$ complex, proposed as one of the termination steps, has never been characterized. A side product, insoluble in most of the organic solvents except methanol, formed in all reactions mentioned above has never been identified. Also, since Co−C bond cleavage is the

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(1) (a) Randaccio, L.; Furlan, M.; Geremia, S.; Slouf, M.; Srnova, I.; Toffoli, D. *Inorg. Chem.* **2000**, *39*, 3403. (b) Randaccio, L.; Geremia, S.; Nardin, G.; Slouf, M.; Srnova, I. *Inorg. Chem.* **1999**, *38*, 4087.

(2) (a) Toscano, P. J.; Swider, T. F.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3416 and references therein. (b) Bresciani-Pahor, N.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1. (c) Randaccio, L.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225. (d) Randaccio, L. *Comments Inorg. Chem.* **1999**, *21*, 327.

(3) Gupta, B. D.; Mandal, D. *Organometallics* **2005**, *24*, 1501 and references therein.

(4) (a) Jacobson, S. E.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *72*, 113. (b) Cámpora, J.; López, J. A.; Palma, P.; del Rio, D.; Carmona, E. *Inorg. Chem.* **2001**, *40*, 4116. (c) Cooney, J. M.; Depree, C. V.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1996**, *515*, 109.

(5) (a) Gupta, B. D.; Vijaikanth, V.; Singh, V. *J. Organomet. Chem.* **1998**, *570*, 1. (b) Gupta, B. D.; Roy, M.; Das, I. *J. Organomet. Chem.* **1990**, *397*, 219. (c) Gupta, B. D.; Roy, S. *Inorg. Chim. Acta* **1985**, *108*, 261.

(6) Abbreviations: salen = *N*,*N*′-ethylenebis(salicylideneiminato), saloph = *N*,*N*′-phenylenebis(salicylideneiminato), bae = *N*,*N*′-ethylenebis(acetylacetonyliminato), dmgH = dimethylglyoximato, dpgH = diphenylglyoximato, gH = glyoximato.

(7) (a) Cozens, R. J.; Deacon, G. B.; Felder, P. W.; Murray, K. S.; West, B. O. *Aust. J. Chem.* **1970**, *23*, 481. (b) Murray, K. S.; Cozens, R. J.; Deacon, G. B.; Felder, P. W.; West, B. O. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 705. (c) Johnson, M. D.; Lewis, G. J. *J. Chem. Soc. A* **1970**, 2153. (d) Cooksey, C. J.; Dodd, D.; Gatford, C.; Johnson, M. D.; Lewis, G. J.; Titchmarsh, D. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 655.

(8) Cotton, J. D.; Crisp, G. T. *J. Organomet. Chem.* **1980**, *186*, 137.

(9) (a) Gupta, B. D.; Roy, S.; Roy, M. *Tetrahedron Lett.* **1987**, *28*, 1219. (b) Gupta, B. D.; Roy, M.; Oberoi, M.; Dixit, V. *J. Organomet. Chem.* **1992**, *430*, 197.

(10) (a) Johnson, M. D.; Crease, A, E. *J. Am. Chem. Soc.* **1978**, *100*, 8013. (b) Johnson, M. D.; Derenne, S. *J. Organomet. Chem.* **1985**, *286*, C47.

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Table 1. Elemental Analysis Data for the Compounds 1a−9a

		found (calcd)			
no.	formula	C	H	N	S
1a	$C_{40}H_{34}CoN_5O_6S$	62.88 (62.26)	4.45 (4.41)	9.14 (9.08)	4.20 (4.15)
2a	$ClC_{40}H_{33}CoN_5O_6S$	60.23 (59.63)	4.13 (4.10)	8.59 (8.70)	4.04 (3.98)
3a	$C_{41}H_{33}CoN_6O_6S$	62.72 (61.81)	4.12 (4.15)	10.51 (10.55)	4.05 (4.02)
4a	$C_{38}H_{32}CoN_5O_6S_2$	58.10 (58.69)	4.17 (4.12)	8.93 (9.01)	8.17 (8.24)
5a	$C_{16}H_{16}CoN_5O_6S$	41.67 (41.29)	3.48 (3.44)	15.28 (15.05)	6.83 (6.88)
6a	$C_{20}H_{24}CoN_5O_6S$	46.58 (46.07)	4.67 (4.61)	13.54 (13.44)	6.08 (6.14)
7a	$ClC_{20}H_{23}CoN_5O_6S$	42.80 (43.24)	4.18 (4.14)	12.48 (12.61)	5.85 (5.77)
8a	$C_{21}H_{23}CoN_6O_6S$	46.60 (46.15)	4.16 (4.21)	15.55 (15.38)	5.92 (5.86)
9a	$C_{36}H_{32}CoN_5O_6S$	60.51 (59.92)	4.46 (4.44)	9.78 (9.71)	4.50 (4.44)

Scheme 1

$$\underset{\mathbf{1-10}}{RCH_2Co^{III}(dioxime)_2B} + SO_2(g) \xrightarrow[0\ ^\circ C,\ CH_2Cl_2]{h\nu} \underset{\mathbf{1a-10a}}{RCH_2SO_2Co^{III}(dioxime)_2B} + \underset{\mathbf{11}}{ClCo^{III}(dioxime)_2B}$$

dioxime = dpgH; B = Py;
RCH_2 = benzyl (**1**), 4-chlorobenzyl (**2**), 4-cyanobenzyl (**3**), 2-thienylmethyl (**4**)

dioxime = gH; B = Py; RCH_2 = benzyl (**5**)

dioxime = gH; B = 4-^{t}BuPy; RCH_2 = benzyl (**6**), 4-chlorobenzyl (**7**), 4-cyanobenzyl (**8**)

dioxime = dpgH; B = Py; RCH_2 = allyl (**9**), 3-methylallyl (**10**)

$ClCo(dioxime)_2B$; dioxime = dpgH; B = Py (**11**)

$[(dpgH)_2PyCo^{III}\text{-}\mu\text{-}SO_3]_2Co^{II}(MeOH)_4$ (**12**)

key feature of these reactions and the reactivity of the Co−C bond depends on the equatorial ligands (cis influence),[3] it would be appropriate to study this reaction by varying the equatorial dioxime ligand to see if it leads to any change in the product distribution and also to see if it is possible to correlate the molecular structure with the spectral data.

In this work we report our findings of sulfur dioxide insertion in $RCH_2Co(dioxime)_2Py$ (dioxime = dpgH, gH) complexes (Scheme 1). We also report the first crystal structure of a sulfur dioxide inserted product. The side product (termed as methanol fraction) has been characterized by X-ray and FAB mass and is a neutral trinuclear complex, $Co^{III}-Co^{II}-Co^{III}$ (**12**). The spectral data have been correlated with the molecular structures.

Experimental Section

$ClCo(dioxime)_2Py$ (dioxime = dpgH, gH), $RCH_2Co(dioxime)_2Py$ (dioxime = gH, dpgH; RCH_2 = benzyl, 4-chlorobenzyl, 4-cyanobenzyl, 2-thienylmethyl), and $RCH_2Co(gH)_2$-4-^{t}BuPy were either synthesized by the literature procedure[11] or were available from our laboratory from a different study. The synthesis work was carried out in subdued light and under a blanket of argon or nitrogen. Silica gel (100−200 mesh) and distilled solvents were used in all chromatographic separations. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-JNM LAMBDA 400 spectrometer in $CDCl_3$. For ^{1}H and ^{13}C NMR spectra, TMS was used as an internal reference. Elemental analysis was carried out using a Thermoquest CE instruments CHNS-O elemental analyzer. The FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV, and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol (NBA) was used as the matrix unless specified otherwise. The peaks at *m*/*z* 136, 154, 289, and 307 are the matrix peaks. Elemental analysis data for compounds **1a**−**9a** are given in Table 1.

X-ray Structural Determination and Refinement. Orange crystals were obtained by slow evaporation of the solutions of **3a** and **6a** in a dichloromethane, *n*-hexane, and benzene mixture and by that of **12** in methanol. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from ref 12. The data integration and reduction were processed with SAINT[13] software. An empirical absorption correction was applied to the collected reflections with SADABS[14] using XPREP.[15] The structure was solved by direct methods using SIR-97[16] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[17] program package. All non-hydrogen atoms were refined anisotropically in the structures. The hydrogen atoms of the OH group of oxime were located on difference maps and were constrained to those difference map positions. The hydrogen atom positions or thermal parameters were not refined but were included in the structure factor calculations. The pertinent crystal data and refinement parameters are compiled in Table 2.

SO_2 Insertion: **General Procedure.** A solution of benzylcobaloxime (**1**; 0.09 g, 0.196 mmol) in 10 mL of dry dichloromethane was purged with a stream of dry nitrogen gas to remove all traces of oxygen. It was irradiated with a 200 W tungsten lamp placed at about 10 cm from the reaction vessel. The temperature was maintained at 0 °C by a Julabo refrigerator circulator, and dry sulfur

(11) (a) Gupta, B. D.; Roy, S. *Inorg. Chim. Acta* **1988**, *146*, 209. (b) Gupta, B. D.; Qanungo, K. *J. Organomet. Chem.* **1997**, *543*, 125. (c) López, C.; Alvarez, S.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **1991**, *414*, 245.

(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(13) SAINT+, version 6.02; Bruker AXS, Madison, WI, 1999.

(14) Sheldrick, G. M. SADABS, Empirical Absorption Correction Program; University of Göttingen, Göttingen, Germany, 1997.

(15) XPREP, version 5.1; Siemens Industrial Automation Inc., Madison, WI, 1995.

(16) Sheldrick, G. M. *SHELXTL Reference Manual: Version 5.1*; Bruker AXS: Madison, WI, 1997.

(17) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

Table 2. Crystal Data and Structural Refinement Details for 3a, 6a, and 12

	4-CN-$C_6H_4CH_2SO_2Co(dpgH)_2Py\cdot 2C_6H_6$ (**3a**)	$[C_6H_5CH_2SO_2Co(gH)_2(4\text{-}^tBuPy)]_2\cdot 2CH_2Cl_2\cdot C_6H_6\cdot H_2O$ (**6a**)	$[(dpgH)_2PyCo^{III}\text{-}\mu\text{-}SO_3]_2\text{-}Co^{II}(MeOH)_4$ (**12**)
empirical formula	$C_{53}H_{45}CoN_6O_6S$	$C_{48}H_{64}Cl_4Co_2N_{10}O_{13}S_2$	$C_{70}H_{70}Co_3N_{10}O_{18}S_2$
formula wt	952.94	1312.87	1580.28
temp (K)	100(2)	100(2)	100(2)
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimens			
a (Å)	13.285(2)	10.9123(8)	10.0213(10)
b (Å)	13.854(2)	16.2234(12)	11.1220(11)
c (Å)	14.562(2)	17.2569(13)	17.4143(16)
α (deg)	93.985(2)	101.9630(10)	89.046(2)
β (deg)	90.190(3)	90.1680(10)	76.351(2)
γ (deg)	115.726(2)	91.1730(10)	67.463(2)
V (Å^3)	2407.0(6)	2988.0(4)	1736.2(3)
Z	2	2	1
ρ(calcd), Mg/m^3	1.315	1.459	1.511
μ (mm^{-1})	0.456	0.871	0.848
F(000)	992	1360	817
cryst size (mm^3)	0.31 × 0.25 × 0.22	0.27 × 0.20 × 0.19	0.38 × 0.28 × 0.23
index ranges	$-17 \le h \le 8$, $-17 \le k \le 18$, $-18 \le l \le 19$	$-14 \le h \le 14$, $-19 \le k \le 21$, $-22 \le l \le 15$	$-9 \le h \le 13$, $-13 \le k \le 14$, $-23 \le l \le 21$
no. of rflns collected	15 642	20 188	11 703
no. of indep rflns	11 311	14 273	8280
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
GOF on F^2	1.053	1.035	1.025
final R indices ($I > 2\sigma(I)$)	R1 = 0.1093	R1 = 0.0744	R1 = 0.0774
	wR2 = 0.2955	wR2 = 0.1825	wR2 = 0.2094
R indices (all data)	R1 = 0.1491	R1 = 0.1011	R1 = 0.1007
	wR2 = 0.3214	wR2 = 0.1975	wR2 = 0.2259
no. of data/restraints/params	11 311/62/604	14 273/0/718	8280/0/468

Table 3. Results of SO_2 Insertion into Organocobaloximes 1−10

R in $RCH_2Co(dioxime)_2Py$	solvent	products	yield, %
benzyl (**1**)[a]	CH_2Cl_2	$C_6H_5CH_2SO_2Co(dpgH)_2Py$ (**1a**)	23
		$ClCo(dpgH)_2Py$ (**11**)	46
4-chlorobenzyl (**2**)	CH_2Cl_2	4-Cl-$C_6H_4CH_2SO_2Co(dpgH)_2Py$ (**2a**)	24
		$ClCo(dpgH)_2Py$ (**11**)	48
	MeCN/$CHCl_3$ (3:1)	4-Cl-$C_6H_4CH_2SO_2Co(dpgH)_2Py$ (**2a**)	30
		$ClCo(dpgH)_2Py$ (**11**)	20
	THF	4-Cl-$C_6H_4CH_2SO_2Co(dpgH)_2Py$ (**2a**)	40
4-cyanobenzyl (**3**)	CH_2Cl_2	4-CN-$C_6H_4CH_2SO_2Co(dpgH)_2Py$ (**3a**)	23
		$ClCo(dpgH)_2Py$ (**11**)	48
2-thienylmethyl (**4**)	CH_2Cl_2	2-thienylmethyl$SO_2Co(dpgH)_2Py$ (**4a**)	24
		$ClCo(dpgH)_2Py$ (**11**)	23
benzyl (**5**)	CH_2Cl_2	$C_6H_5CH_2SO_2Co(gH)_2Py$ (**6a**)	30
benzyl (**6**)[b]	CH_2Cl_2	$C_6H_5CH_2SO_2Co(gH)_2(4\text{-}^tBuPy)$ (**6a**)	40
4-chlorobenzyl (**7**)[b]	CH_2Cl_2	4-Cl-$C_6H_4CH_2SO_2Co(gH)_2(4\text{-}^tBuPy)$ (**7a**)	45
4-cyanobenzyl (**8**)[b]	CH_2Cl_2	4-CN-$C_6H_4CH_2SO_2Co(gH)_2(4\text{-}^tBuPy)$ (**8a**)	30
allyl (**9**)	CH_2Cl_2	$CH_2{=}CHCH_2SO_2Co(dpgH)_2Py$ (**9a**)	20
		$ClCo(dpgH)_2Py$ (**11**)	45
3-methylallyl (**10**)	CH_2Cl_2	$CH_3CH{=}CHCH_2Co(dpgH)_2Py$ (**10a**)	*c*
		$ClCo(dpgH)_2Py$ (**11**)	46

[a] A similar ratio of products is formed in chloroform. [b] Base = 4-^{t}BuPy. [c] Pure product could not be isolated; 10−15% of **12** is formed in most of the reactions.

dioxide gas[18] was bubbled through the solution under a positive pressure of nitrogen.[9] The reaction was continued until all of the starting cobaloxime had disappeared. The progress of the reaction was monitored with TLC on silica gel with a mixture of ethyl acetate and dichloromethane as the eluent. At the end of the reaction the solvent was removed and the products were separated using column chromatography.

Column Details. In dpgH complexes the reaction mixture, a brown powder, dissolved in a minimum amount of dichloromethane was loaded on the silica gel column pre-eluted with dichloromethane. The polarity was increased slowly with ethyl acetate. $ClCo(dpgH)_2Py$ (**11**) eluted out first with 5% ethyl acetate, followed by the inserted product with 10% ethyl acetate (**1a**). The rest of the compound was eluted out with methanol (**12**).

In gH complexes, the column details are same, except that the first fraction is the inserted product and is eluted out with 60% ethyl acetate. The rest of the compound was eluted out with methanol.

Results and Discussion

Benzylcobaloxime (**1**) reacts with sulfur dioxide gas under photolytic conditions to give a mixture of $C_6H_5CH_2SO_2\text{-}Co^{III}(dpgH)_2Py$ (**1a**) and chlorocobaloxime (**11**) in 23% and 46% yields, respectively. A smooth reaction occurs and is complete in about 1.5 h. A similar reaction occurs with substituted benzyl and thienylmethyl cobaloximes (**2**−**4**) (Table 3). Either chlo-

(18) Dry sulfur dioxide gas was generated from sodium sulfite and dilute sulfuric acid and passed through traps of sulfuric acid and anhydrous calcium chloride. The solution of organocobaloxime was kept over molecular sieves during the reaction.

Table 4. ^{1}H NMR Data (ppm) for Complexes 1−9 and 1a−9a[a]

					pyridine			
no.	aromatic	allyl/others	CH_2 (s)	dpgH/gH	α (d)	*β*	*γ* (t)/^{t}Bu (s)	O−H···O
1	6.92−7.35		3.44	*b*	8.85	7.40 (t)	7.79	18.73
1a	6.94−7.69		4.47	*b*	8.84	*b*	7.91	
2	6.92−7.27		3.35	*b*	8.83	7.41 (t)	7.81	18.71
2a	7.15−7.32		4.34	*b*	8.79	7.49 (t)	7.91	18.48
3	6.92−7.27		3.30	*b*	8.89	7.41 (t)	7.82	18.68
3a	7.12−7.50		4.47	*b*	8.84	*b*	7.95	
4	6.83−7.26		3.63	*b*	8.84	7.39 (t)	7.79	18.67
4a	6.77−7.77		4.66	*b*	8.84	*b*	8.00	
5	7.06−7.10		3.01	7.24	8.54	7.35 (t)	7.75	17.67
5a	7.19−7.33		4.31	7.55	8.35	*b*	7.75	
6	6.98−7.19		2.91	7.16	8.32	7.23	1.19	17.65
6a	7.20−7.27		4.29	7.55	8.19	7.24	1.20	-
7	6.99		2.87	7.24	8.36	7.29	1.25	17.70
7a	7.16−7.20		4.24	7.55	8.17	7.26	1.21	
8	7.08−7.30		2.82	7.25	8.30	7.29	1.25	17.63
8a	7.35−7.41		4.36	7.63	8.24	7.55	1.25	
9		5.31 (dd), 6.25 (m)	2.97	6.93−7.56	8.97	*c*	7.84	
9a		5.26 (dd), 5.95 (m)	3.91 (d)	7.19−7.32	8.76	7.47 (t)	7.91	18.45
10		1.34 (d), 5.78 (m)	2.94 (d)	7.04−7.26	8.88	7.43 (t)	7.82	18.71

[a] Ligand: s = singlet; m = multiplet; dd = doublet of doublets; t = triplet. [b] Merge with aromatic protons. [c] Merge with dpgH protons.

rocobaloxime is not formed or its amount is reduced when the reaction is carried out in THF or MeCN/$CHCl_3$ (3:1), as the case may be. The reaction in methanol forms only a trace amount of inserted product. The reactions carried out in nonhalogenated solvents also result in loss of some amount of dioxime ligand.

In the gH complex **5**, the reaction forms **5a** and no chlorocobaloxime is formed. The solubility of **5a** is found to be very poor in chloroform, but it is improved when 4-^{t}BuPy is used as the base instead of pyridine. A slight increase in yield is also noticed. Allylcobaloxime (**9**) reacts in a similar fashion and forms the corresponding inserted product **9a** and chlorocobaloxime (**11**). However, the reaction is much more complicated with (3-methylallyl)cobaloxime (**10**). A mixture of products is formed, and the inserted product **10a** is only a small fraction of the total product.

In every reaction, an additional product, insoluble in most organic solvents except methanol, is also formed. It has proved very difficult to characterize this product by ^{1}H NMR. Its crystal structure shows it to be a $Co^{III}-Co^{II}-Co^{III}$ complex (**12**; discussed later).

Chlorocobaloxime (**11**) is formed by the abstraction of a halogen atom from dichloromethane by the intermediate cobaloxime(II) generated during photolysis. This has been confirmed by the reaction of **2** with sulfur dioxide in THF, where no chlorocobaloxime is formed. In a blank reaction, it is found that benzylcobaloxime (**1**) in dichloromethane under identical photolytic conditions but in the absence of SO_2 is stable and does not abstract halogen from dichloromethane.

All the reactions described in this paper are free radical in nature.[9] The radical nature of these reactions is apparent from the characteristics of the reaction: (a) a concentration-dependent induction period; (b) no insertion at 0 °C without irradiation; (c) reactions are inhibited by galvinoxyl, a radical trap. The key step is the homolytic cleavage of the Co−C bond and the stability/reactivity of cobaloxime(II) generated during photolysis. The formation of chlorocobaloxime indicates that the abstraction of halogen from the solvent is more facile in $Co^{II}(dpgH)_2Py$ as compared to $Co^{II}(gH)_2Py$, where no such product is formed. This may seem to be surprising and may contradict the earlier observations of Halpern[19] that the rate of halogen abstraction from alkyl halide by cobaloxime(II) is insensitive to the variation in dioxime unit. However, keeping into account the facts that (a) benzylcobaloxime (**1**) does not abstract halogen from the solvent CH_2Cl_2 under irradiation in the absence of SO_2 and (b) no halogen abstraction by cobaloxime(II) occurs in the oxygen insertion reaction[5] in benzylcobaloxime, the halogen abstraction process must be getting catalyzed in the presence of the substrate sulfur dioxide. This may have some relevance to cobalamins in which the Co−C bond is apparently activated greatly by the coenzyme interaction with apoenzyme, by binding of the resulting holoenzyme to the substrate, or by both of these processes.[20]

The characteristics of the reaction show that the mechanism of the reaction is similar to that reported earlier for $PhCH_2Co(dmgH)_2Py$ with SO_2.[9] However, we have not been able to isolate and characterize the product, $PyCo(dioxime)_2SO_2Co(dioxime)_2Py$, involved in the termination step. However, the side product, the methanol fraction, has been identified and is discussed later. The crystal structures of **3a** and **6a** clearly show a Co−S bond (discussed later).

Spectroscopy. UV, IR, NMR, and X-ray crystallography have been the primary means of characterizing the SO_2-inserted products. The Co−C CT band, observed in the parent cobaloxime, disappears in the inserted complex.[9] The ν(Co−SO_2) band in the infrared spectra of the inserted product appears at ν_{sym} (1060−1070 cm^{-1}) and ν_{assym} (1230−1245 cm^{-1}), a range observed for the S-bonded sulfinate group in many similar complexes.[7,9]

^{1}H and ^{13}C NMR Spectra. ^{1}H NMR spectra are easily assigned on the basis of chemical shifts. The signals are assigned according to their relative intensities and are consistent with the related complexes previously described. ^{13}C chemical shifts of similar complexes have not been reported previously. We have therefore assigned these values on the basis of the previously reported ^{13}C NMR values in the cobaloximes.[21] ^{1}H NMR data for compounds **1**−**9** and **1a**−**9a** are given in Table 4, and ^{13}C NMR data for compounds **2**, **6**, **7**, **2a**, **6a**, and **9a** are given in Table 5.

(19) Schneider, P. W.; Phelan, P. F.; Halpern, J. *J. Am. Chem. Soc.* **1968**, *91*, 77.

(20) (a) Toraya, T. *Cell. Mol. Life Sci.* **2000**, *57*, 106. (b) Masuda, J.; Shibata, N.; Morimoto, Y.; Toraya, T.; Yasuoka, N. *Structure (London)* **2000,** *8*, 775. (c) Brown, K. L. *Chem. Rev.* **2005,** *105*, 2075**.**

(21) (a) Gupta, B. D.; Yamuna, R.; Singh, V.; Tiwari, U.; Barclay, T.; Cordes, W. *J. Organomet. Chem.* **2001**, *627*, 80. (b) Gupta, B. D.; Qanungo, K.; *J. Organomet. Chem.* **1997**, *543*, 125.

Table 5. ^{13}C NMR Data for Complexes 2, 6, 7, 2a, 6a, and 7a

		pyridine					
no.	C−N	α	β	γ	aromatic + dpgH	others	CH_2Co
2	151.13	150.14	125.59	138.05	127.74, 128.22, 129.01, 129.56, 129.75, 130.19		32.66
2a	154.29	150.28	126.21	143.43	128.04, 128.33, 129.35, 129.62, 129.80, 132.62, 151.40		63.10
6	137.89	149.25	122.72	162.55	124.83, 126.78, 127.63, 128.05, 128.59, 145.60	30.14, 34.26	34.84
6a	141.34	149.12	123.39	164.25	127.98, 128.10, 129.21, 131.28, 114.87	30.11, 35.11	63.59
7	137.93	149.27	122.81	161.03	121.53, 127.79, 129.73, 130.16	30.18, 32.85	32.85
7a	141.40	149.10	123.42	167.78	127.58, 128.27, 132.56, 149.75	30.11, 35.12	62.46

Sulfur dioxide insertion has affected the chemical shifts of the three groups RCH_2, dioxime, and axial pyridine in the ^{1}H NMR spectra of **1a**−**8a** (Table 4). RCH_2 shifts downfield by 1.0−1.50 ppm in **1a**−**8a** as compared to the case for the parent cobaloxime **1**−**8**; the downfield shift is more in gH complexes as compared to dpgH. Pyridine α-protons are shifted upfield (0.01−0.19 ppm), and the gH protons are shifted downfield by 0.3−0.4 ppm. No comment can be made on the dpgH protons, as these overlap with the benzyl aromatic protons.

There is a drastic chemical shift in the ^{13}C NMR spectra of **2a**, **6a**, and **7a** (Table 5). For example, CH_2 is shifted downfield by 30 ppm and Py_γ and C═N are shifted by 3−6 ppm with respect to the parent cobaloxime. The chemical shifts of CH_2 in **2a** and **6a** are almost identical, indicating that the nature of dioxime has no effect on the CH_2 shift. In contrast, the ^{13}C signal in the parent cobaloxime **6** appears 2.2 ppm downfield with respect to its value in **2**.

Now, the question arises "Why does dioxime has an effect on CH_2 in the parent cobaloxime but not in the inserted product, and which factors cause such a large shift?"

In general, the chemical shift of CH_2 in benzylcobaloximes depends mainly upon two factors: the ring current[22] of dioxime and the substituent on the CH_2 group. These two factors put together are responsible for cobalt anisotropy.[23] The ring current in the dioxime, in turn, is affected by the substituents on the dioxime and by the ring current of the benzyl group ($\pi-\pi$ interaction with dioxime). This is reflected in the $\delta(^1H)$ CH_2 values of these complexes; for example, it appears downfield in **2** as compared to **6** because of lower ring current and higher cobalt anisotropy in the dpgH complexes[3] ($\Delta\delta_{C-N}$, a measure of the dioxime ring current, supports this view; compare $\Delta\delta_{C-N}$ values in **2a** and **6a**). However, in the case of inserted products **1a**−**8a** the change in chemical shift in CH_2 is due to the substituent SO_2 group only. The effect of the benzyl group on the dioxime ring current is minimized because of its perpendicular orientation; the crystal structure shows that the benzyl group is too far away from the dioxime to have any through-space interaction. Further support that a through-space interaction does not occur comes from ^{13}C NMR spectra. Since it operates mainly through-bond, a 30 ppm downfield shift can arise only due to a direct bond between CH_2 and SO_2 group.

(a) Py_α. Dioxime ring current affects the chemical shift of Py_α. Since gH complexes have a higher ring current than the dpgH complexes, it always appears upfield (0.3−0.7 ppm) in the former (compare **1**−**4** with **5**−**8** and **1a**−**4a** with **5a**−**8a**). However, the difference in chemical shift is not that large (0.01−0.19 ppm upfield shift) when we compare values in **1**−**8** vs those in **1a**−**8a**. This seems justified, since cobalt anisotropy works differently in $XCo(dioxime)_2Py$ and $RCo(dioxime)_2Py$ complexes[3] and $ArCH_2SO_2Co(dioxime)_2Py$ behaves like inorganic cobaloximes.

(b) Py_γ. We have recently proposed that $\delta\Delta Py_\gamma$ can be taken as the measure of the trans effect. The downfield shift in both ^{1}H and ^{13}C NMR in the inserted complexes clearly points to the lower trans effect of the SO_2CH_2Ar group as compared to CH_2Ar.

(c) gH. The downfield shift in **5a**−**8a** as compared to the shifts for **5**−**8** is due to the perpendicular orientation of the benzyl group in the former (see crystal structure details).

Methanol Fraction. ^{1}H NMR could not characterize the methanol fraction obtained from the column separation of the reaction mixture. The NMR spectrum showed the presence of dpgH and pyridine, but surprisingly, the axial benzyl group was missing. Slow evaporation led to the formation of red crystals. The X-ray analysis of these crystals showed the composition as $Co_3S_2N_{10}O_{18}C_{70}H_{70}$. The Diamond diagram of the molecular structure for $[(dpgH)_2PyCo^{III}\text{-}\mu\text{-}SO_3]_2Co^{II}(MeOH)_4$ (**12**) along with a selected numbering scheme is shown in Figure 1. Crystal refinement details are given in Table 2, and selected bond lengths and bond angles are given in Table 6.

The crystal structure shows this to be a neutral trinuclear complex having a crystallographic center of inversion occupied by the central Co(2) atom. Similar such structures have recently been reported.[24] All three Co centers are in distorted-octahedral coordination environments. The central Co(2) is in the +2 oxidation state, and the terminal Co atoms are in the +3 state. In the terminal Co atoms the dpgH ligand occupies four equatorial positions and the two axial positions are occupied by sulfur of the bridging SO_3^{2-} anion and a nitrogen of pyridine. Six oxygen atoms—two from the bridging sulfinato-*O* and four from methanol—surround the central Co(2) atom. The EPR spectrum recorded at room temperature and at 120 K in the solid state and in solution (CH_2Cl_2 + MeCN) gives only broad signals and no hyperfine splitting (Supporting Information). This is in accordance with the recent finding in similar trinuclear complexes, where the EPR signals were shown to disappear above 30 K due to fast spin−lattice relaxation of the high-spin Co(II) complex.[24a] The crystal structure is also supported by FAB mass and elemental analysis (Anal. Calcd for $Co_3S_2N_{10}O_{18}C_{70}H_{70}$: C, 53.20; H, 4.43; N, 8.86; S, 4.05. Found: C, 51.23; H, 3.86; N, 8.74; S, 3.92). In the FAB mass spectrum we have not been able to see the molecular ion peak but the major peaks at *m*/*z* 616, 538, and 835 correspond to $[M1]^+$ ($(dpgH)_2Co$ pyridine), $[M1 - pyridine]^+$, and $[M - M1 - 4MeOH]^+$ respectively.

We are unable to offer any explanation for the formation of the trinuclear complex, but efforts are underway to develop a general procedure for its synthesis.

(22) (a) López, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1986**, *111*, L19. (b) López, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chem.* **1986**, *25*, 2962. (c) Gilaberte, J. M.; López, C.; Alvarez, S.; Font-Altaba, M.; Solans, X. *New J. Chem.* **1993**, *17*, 193.

(23) (a) Charland, J. P.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. Marzilli, L. G. *Inorg. Chem.* **1993**, *32*, 4256. (b) Moore, S. J.; Marzilli, L. G. *Inorg. Chem.* **1998**, *37*, 5329.

(24) (a) Rat, M.; de Sousa, R. A.; Tomas, A.; Frapart, Y.; Tuchagues, J.-P.; Artaud, I. *Eur. J. Inorg. Chem.* **2003**, 759. (b) Fukuhara, C.; Asato, E.; Shimoji, T.; Katsura, M.; Matsumoto, K.; Ooi, S. *J. Chem. Soc., Dalton Trans.* **1987**, 1305. (c) House, D. A.; McKee, V.; Steel, P. *Inorg. Chem.* **1986**, *25*, 4884. (d) Golobic, A.; Stefane, B.; Polanc, S. *Polyhedron* **1999**, *18*, 3661.

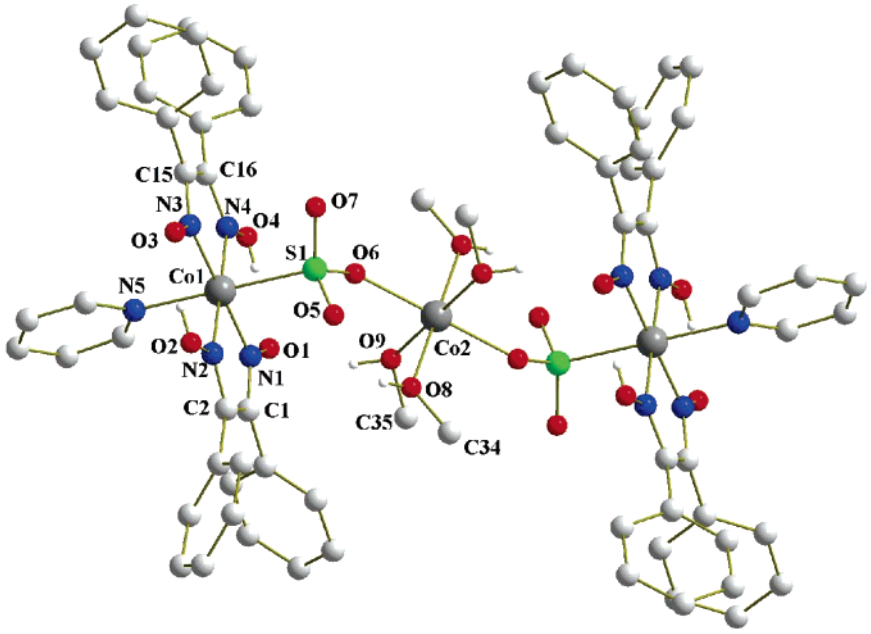

Figure 1. Structure of $[(dpgH)_2PyCo^{III}\text{-}\mu\text{-}SO_3]_2Co^{II}(MeOH)_4$ (**12**).

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) in 12

Co1−S1	2.2373(12)	Co2−O9	2.076(3)
Co1−N5	2.044(4)	S1−O5	1.471(3)
Co2−O6	2.054(3)	S1−O6	1.496(3)
Co2−O8	2.091(3)	S1−O7	1.461(3)
O5−S1−Co1	109.43(15)	O6−Co2−O8	89.47(13)
O6−S1−Co1	106.14(13)	O9−Co2−O8	89.93(14)
O7−S1−Co1	108.89(14)		
d (Å)	0.0086(1)	*τ* (twist) (deg)	72.15
α (deg)	7.69		

X-ray Crystal Structure. A slow evaporation of solvent from the solution of **3a** and **6a** (dichloromethane, benzene, and hexane) in the refrigerator resulted in the formation of orange crystals. The X-ray analysis of these crystals showed the composition as $[4\text{-}CNC_6H_4CH_2(SO_2)Co(dpgH)_2Py]\cdot 2C_6H_6$ (**3a**) and $[C_6H_5CH_2(SO_2)Co(gH)_2(4\text{-}^tBuPy)]_2\cdot 2CH_2Cl_2\cdot C_6H_6\cdot H_2O$ (**6a**). The crystal structure of **6a** shows two molecules in the *asymmetric unit* of the unit cell. Since there is a structural variation in these molecules, these are numbered as **6a-I** and **6a-II** and the crystal data are given separately.

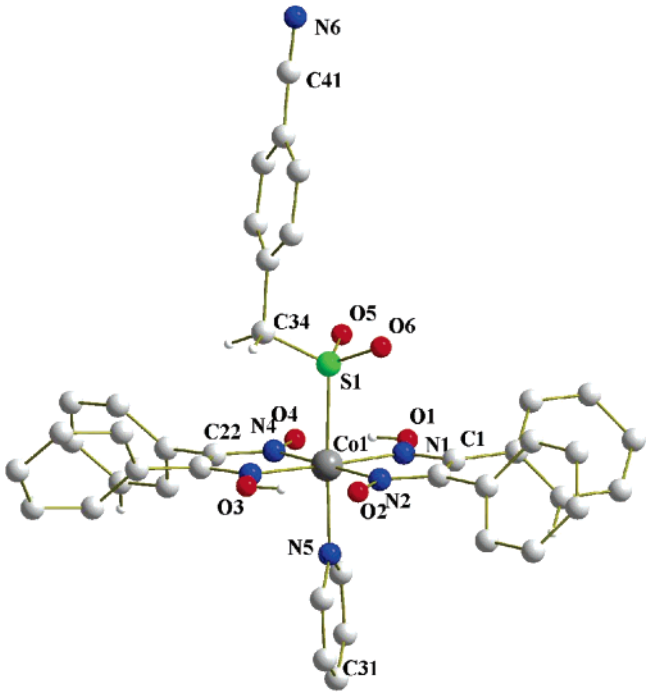

Figure 2. Structure of 4-CN-$C_6H_4CH_2SO_2Co(dpgH)_2Py$ (**3a**).

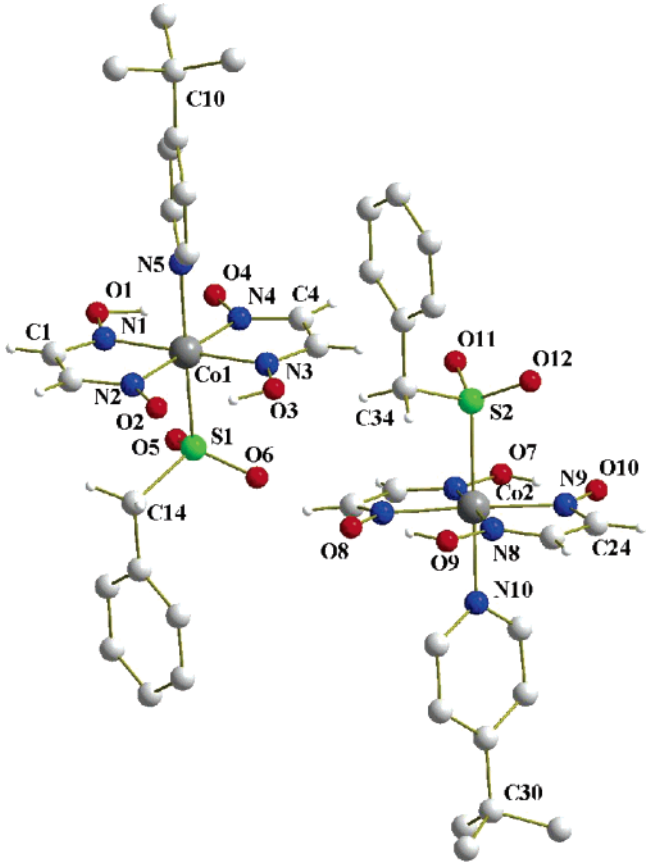

Figure 3. Structure of $[C_6H_5CH_2SO_2Co(gH)_2(4\text{-}^tBuPy)]_2$ (**6a**).

Diamond diagrams of the molecular structures for **3a** and for **6a-I** and **6a-II** along with selected numbering schemes are shown in Figures 2 and 3, respectively. Selected bond lengths

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) and Structural Data for 3a and 6a

	3a	6a-I	6a-II
Co−S1	2.2258(18)	2.2406(11)	2.2416(11)
S1−O5	1.546(8)	1.470(3)	1.467(3)
S1−O6	1.482(8)	1.462(3)	1.460(3)
S−CH_2	1.656(12)	1.811(4)	1.821(4)
Co−N5	1.975(5)	2.011(3)	2.013(3)
Co−S1−CH_2(ax)	116.7(4)	108.93(13)	107.59(13)
S−CH_2−C	111.99(85)	111.78(26)	112.37(28)
Co−N−C(ax)	178.49(31)	178.85(19)	175.58(19)
O1−O4	2.485(5)	2.496(4)	2.523(4)
O2−O3	2.463(6)	2.489(5)	2.507(4)
d (Å)	0.0147(2)	−0.0091(5)	0.0353(5)
α (deg)	1.50	−3.88	11.10
τ (twist) (deg)	88.51	83.67	79.57

and bond angles are given in Table 7. These are the first crystal structures of SO_2-inserted cobaloxime complexes.

All of the crystal structures clearly show a cobalt−sulfur bond with sulfur in a tetrahedral geometry. The geometry around each cobalt atom is distorted octahedral, with four nitrogen atoms of the dioxime (dpgH, gH) in the equatorial plane and pyridine/^{t}BuPy and SO_2CH_2R groups in axial positions. The CH_2R group is perpendicular to the equatorial N_4 plane.

The deviation of the cobalt atom from the mean equatorial N_4 plane (*d*) is 0.0147(2) for **3a**, −0.0091(5) for **6a-I**, and 0.0353(5) for **6a-II** with dihedral angles[25] of 1.50, 3.88, and 11.10°, respectively. The opposite sign of *d* suggests that the deviation is toward the base in **3a** and **6a-II** and toward the RCH_2SO_2 group in **6a-I**. The pyridine plane is almost parallel to the C−C bond of the dioxime, as expected, with twist angles[26] (τ) of 88.51, 83.67, and 79.57°, respectively. The Co−S/Co−N bond lengths are 2.2258(18)/1.975(5), 2.2406(11)/2.011(3), and 2.2416(11)/2.013(3) Å in **3a**, **6a-I**, and **6a-II**. S−CH_2 bond lengths are 1.656(12), 1.810(7), and 1.820(6) Å. The Co−S−C bond angles are 116.7(4)° for **3a**, 108.93(13)° for **6a-I** and 107.59(13)° for **6a-II**.

A comparison of crystal structure details in **3a**, **6a-I**, and **6a-II** show some interesting differences. The shorter Co−S and Co−N(axial) bond distances in **3a** as compared to the values in **6a-I** and **6a-II** might be due to the lower ring current in the dioxime in **3a.** The bond angle of 116.7(4)° supports this argument and may further suggest a higher sp^2 character of the Co−S bond in **3a**. The shortening of the Co−N(py) bond in **3a** is in line with the reported data in $CH_3Co(dpgH)_2Py$ (2.052 Å),[11c] $CH_3Co(gH)_2Py$ (2.064 Å),[27a] and $ClCo(dpgH)_2Py$ (1.965 Å).[27b] $PhCH_2SO_2Co(dpgH)_2Py$ behaves like an inorganic cobaloxime.

The structure of **6a-II** differs from those of **3a** and **6a-I**. The major difference lies in the orientation of the benzyl group. The benzyl group is perpendicular to the dioxime plane in all three cases. In **3a** and **6a-I** the planes of the benzyl group and pyridine/^{t}BuPy ring are at angles of 29.61 and 31.04°, but in **6a-II** the angle is 75.33°, which places it over toward the O−H···O plane.[28] This is very unusual in cobaloxime chemistry, since the axial ligands are usually perpendicular to the O−H···O plane. This may have resulted because of a large deviation in the pyridine twist angle and high α value (11°) in **6a-II** as compared to those in **3a** and **6a-I.**

The insertion of sulfur dioxide seems to affect the orientation of the benzyl group; for example, a comparison of the molecular structure of **6a** with that of the parent complex $BnCo(gH)_2(4\text{-}^t BuPy)$ (**6**)[29] shows that the orientation of the benzyl group in **6** is on the dioxime plane, as found in other benzylcobaloxime structures also,[21a] whereas it is almost perpendicular to the dioxime plane in **6a**. This has greatly affected the ^{1}H NMR shifts in the molecule, as discussed earlier. A similar comparison with **3a** cannot be made, since there is no crystal structure known for any benzyl dpgH complex.

Conclusions

The insertion of sulfur dioxide into the Co−C bond in $ArCH_2Co(dioxime)_2B$ is facile, but abstraction of halogen from the solvent is a competing reaction. In addition, a neutral trinuclear complex is also formed. X-ray crystallography has structurally characterized the inserted product and the trinuclear complex for the first time. The insertion of sulfur dioxide affects the orientation of the benzyl group.

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Supporting Information Available: Figures giving ^{1}H and ^{13}C NMR spectra for **2a** and **6a**, FAB mass spectrum for **12** and CIF files giving crystal data for **3a**, **6a**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files have also been deposited with the Cambridge Crystallographic Data Centre. CCDC numbers for **3a**, **6a**, and **12** are 278661, 278659, and 278660, respectively. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EX, U.K. (fax, +44-1223-336033; web, http://www.ccdc.cam.ac.uk/).

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(25) The dihedral angle, α (butterfly bending angle), is the angle between two dioxime planes.

(26) τ (known as the twist angle) is the angle between two virtual planes. One plane is formed by considering the middle point of the C−C bond of two oxime units that pass through cobalt and the pyridine/^{t}BuPy nitrogen and the other containing the pyridine nitrogen and the four carbons of pyridine.

(27) (a) Bresciani-Pahor, N.; Randaccio, L.; Zangrando, E.; Toscano, P. J. *Inorg. Chim. Acta* **1985**, *96*, 193. (b) López, C.; Alvarez, S.; Anguiló, M.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1987**, *127*, 153.

(28) These are the angles between the plane containing the $S(SO_2)$−$C(CH_2)$ and the six carbons of the phenyl with respect to the plane formed by the pyridine nitrogen and the four carbons of pyridine. If we consider the planes containing Co−N(Py)−C(para carbon of Py) and Co−$S(SO_2)$−$C(CH_2)$−C(C1 of phenyl)−C(C4 of phenyl), then the angles have the values 6.77, 6.20, and 82.35° for **3a**, **6a-I** and **6a-II.**

(29) Gupta, B. D.; Chadha, P. Unpublished data.