Articles

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Halogenation of Benzyl- and (Heteroaromatic methyl)cobaloximes: Direct Competition between Ring Halogenation and Cobalt-Carbon Bond Cleavage

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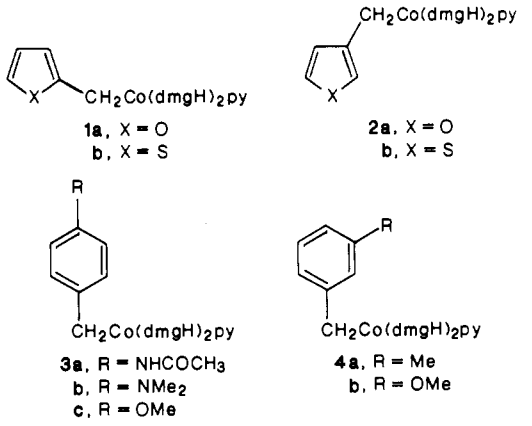
(4-Acetamidobenzyl)- and (4-(dimethylamino)benzyl)cobaloximes react rapidly with low concentrations of chlorine and bromine in acetic acid or chloroform at room temperature under nitrogen. Both ring-halogenated organometallic products and direct Co–C cleavage products are formed. However, (4-methoxybenzyl)cobaloxime forms 4-methoxy-2-halotoluene as the exclusive product. (3-Methylbenzyl)cobaloxime undergoes a substantial proportion of ring substitution by both Br_2 and Cl_2 in competition with the cleavage of the Co–C bond. (3-Methoxybenzyl)cobaloxime forms only the ring-substituted organometallic product. A remarkable difference in reactivity between 2- and 3-isomers of the (thienylmethyl)- and (furylmethyl)cobaloximes is observed; for example, Co–C cleavage is the primary process in furfuryl- and (2-thienylmethyl)cobaloximes whereas ring halogenation occurs much faster in the 3-isomer. The results are discussed in terms of a σ–π delocalization phenomenon by which the electronic effect of a substituent in the benzyl group is effectively transmitted to the Co–C bond reactivity. The substituent effect of the metallomethyl group $-CH_2Co(dmgH)_2py$ is found to be more than that of the methoxy group. The mechanism of the Co–C cleavage is described.

Introduction

In recent years many σ-bonded organometallic complexes of both transition and nontransition metals have been shown to be susceptible to metal–carbon bond cleavage by electrophiles.[1a] Organopentachromium(III) ions, by far, offer the most clean reactions.[1b-d] The most interesting, yet less understood, substrates include the organocobalt(III) and organoiron(II) complexes.[1e] This is because of the seemingly endless variety of reactions they undergo. Organocobalt(III) complexes are, in particular, important in view of their relation to coenzyme B_{12}.[1f] Although many studies with electrophiles such as Hg^{2+} have led to a more rationalized picture about the mode of metal–carbon bond cleavage,[2] considerable complexities arise with halogens,[1a,3a-c] however, due to the attack of the latter at various sites of the complex. Benzylcobaloxime is the most notable example. It has been observed that the metallomethyl group is activating in nature and its magnitude is more than that of the methyl group. However, it is found that it is insufficient on its own to cause any ring substitution by halogens into the benzylcobaloxime.[3d] Substitution by inductively electron-releasing groups also does not enhance ring substitution as compared to the faster Co–C bond cleavage by halogens.[4] Understanding the factors that promote or inhibit the Co–C bond cleavage is of considerable importance in a number of contexts, including the homogeneous catalytic processes as well as the chemistry and biological activity of vitamin B_{12} coenzyme.[5] The comprehensive understanding of these factors remains incomplete because one specific point has never been taken into account in the earlier studies: i.e., in the process of activating or deactivating the benzene ring, it is quite likely that the competitive cleavage of the Co–C bond may also be effected by such substituents.

The present study therefore has been aimed (i) at understanding how the electronic effects of a substituent in the aromatic ring are transmitted to the Co–C bond reactivity toward an electrophile and vice versa, (ii) at synthesizing specific organocobaloximes in which the aromatic ring is activated so that the phenomenon of ring substitution vs Co–C bond cleavage is clearly understood, and (iii) at understanding the Co–C cleavage mechanism.

From a consideration of the points above, the choice of the following systems is made ($dmgH_2$ = dimethylglyoxime; py = pyridine):



Experimental Section

Materials and Instruments. Most of the materials used were imported from Aldrich and were used as such without further purification. Chlorine gas was generated by the reaction of concentrated hydrochloric acid with potassium permanganate and was absorbed into chloroform or acetic acid in the required amount. Iodine chloride was prepared by

(1) (a) Johnson, M. D. In *The Nature and Cleavage of Metal-Carbon Bonds*; Hartley, F. R., Patai, S., Eds.; The Chemistry of the Metal-Carbon Bond 2; Wiley-Interscience: New York, 1985; p 513. (b) Fischer, E. O.; Ofele, K. *Chem. Ber.* **1958**, *91*, 2763. (c) Holmes, J. D.; Jones, D. A. K.; Pettit, R. *J. Organomet. Chem.* **1964**, *4*, 342. (d) Marty, W.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 1246. Espenson, J. H.; Williams, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 1008. Chang, J. C.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1974**, 233. Leslie, J. P.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839. (e) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (f) Brown, K. L. In B_{12}; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, p 245. Halpern, J. *Ibid.*, p 501.

(2) Chrzastowski, J. Z.; Johnson, M. D. *J. Chem. Soc. Dalton Trans.* **1976**, 2456.

(3) (a) Garlatti, R. D.; Tauzher, G.; Costa, G. *J. Organomet. Chem.* **1979**, *182*, 409 and references therein. (b) Daub, G. W. *Prog. Inorg. Chem.* **1977**, *22*, 409. (c) Kemmit, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkenson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 5, p 80. (d) Anderson, S. N.; Ballard, D. H.; Johnson, M. D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 311.

(4) Gupta, B. D.; Kumar, M. *Inorg. Chim. Acta* **1986**, *113*, 9.

(5) Golding, B. T. In B_{12}; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, 543.

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treatment of iodine with dry chlorine at ambient temperature and was distilled before use.

Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Electronic spectra were recorded on a Cary 17D spectrophotometer. ^{1}H NMR spectra were taken on 80-MHz (Bruker WP-80) and 90- and 100-MHz (Varian EM-390 and HA-100) spectrometers. An Iatroscan TH-10 instrument and a Shimadzu chromatograph (GC-9A) were used for obtaining ratios of the organic product mixtures. Elemental analysis was done at the Regional Sophisticated Instrumentation Centre, Lucknow, India, and at IIT, Kanpur, India.

Electrochemical and ESR Measurements. Cyclic voltammetric measurements of $RCo(dmgH)_2py$ (ca. 10^{-4} mol L^{-1}) in dry degassed acetonitrile using tetraethylammonium perchlorate as a supporting electrolyte were recorded on a Bioanalytical Systems CV-27 assembly using a conventional three-electrode unit. The reference electrode was an SCE, and the working electrode was a glassy-carbon rod.

ESR measurements were recorded on a Varian E-109 (X-band) instrument. Organocobaloximes in dichloromethane (ca. 10^{-4} mol L^{-1}) and bromine in dichloromethane (ca. 10^{-4} mol L^{-1}) were mixed together in a 1:1 molar ratio under nitrogen, the solution was immediately cooled down to liquid-nitrogen temperature, and the spectrum was recorded. The spectra were also recorded at variable temperature ranging from liquid-nitrogen to room temperature.

Synthesis of Organic Precursors. 3- and 4-methoxybenzyl bromide,[6a,e] 4-acetamidobenzyl chloride,[6b] 3-methylbenzyl chloride,[6d] and 2- and 3-thienyl bromide[6f,g] were prepared by the literature methods. 4-(Dimethylamino)benzyl alcohol was tosylated in the presence of sodium hydride at −40 °C.[6c] Furfuryl alcohol was brominated with PBr_3 in ether according to the method by Zanetti.[6h] Since pure furfuryl bromide is unstable, its ethereal solution was used in the cobaloxime preparation. 3-Furyl bromide was prepared from propargyl alcohol as outlined by Tada et al.[6i]

Synthesis of Organocobaloximes. All the organocobaloximes were synthesized by following the literature procedure[7] from bis(dimethylglyoximato)(pyridine)cobalt(I) and organic halides or tosylates. Cobaloxime(I) was generated in situ by anaerobic disproportionation of cobaloxime(II) in highly alkaline conditions or by $NaBH_4$ reduction of chlorocobaloxime. The aquocobaloximes were prepared by the method of Abley et al.[8] All cobaloximes give satisfactory spectral characteristics.

Reaction of Organocobaloximes with Halogens in Acetic Acid and Chloroform. The following examples illustrate the procedure.

(a) Addition of Bromine. A solution of bromine (1 or 2 mmol in 10 mL of acetic acid) was added dropwise over a period of 20 min into (4-methoxybenzyl)cobaloxime (1 mmol, 0.49 g, in 20 mL of acetic acid) at room temperature under nitrogen in the dark. The reaction mixture was stirred for a further 10 min, and the green solid was filtered off. The filtrate was poured into water (50 mL), and the organic product was extracted with solvent ether (50 mL).[30] The extract was washed with sodium bicarbonate (5% solution), sodium metabisulfite (5% solution), and water. The ether layer was dried over anhydrous $MgSO_4$. On removal of ether, the product was shown to be pure 4-methoxy-2-bromotoluene by ^{1}H NMR.

(b) Addition of Chlorine. A solution of chlorine (1 mmol in 10 mL of acetic acid) was added dropwise over a period of 20 min into a stirred solution of (3-thienylmethyl)cobaloxime (1 mmol, 0.47 g, in 20 mL of acetic acid) under nitrogen at room temperature in the dark. The mixture was stirred for a further 20 min. The filtrate was poured into water containing 5% pyridine.[31,32] The orange precipitate was filtered off, washed with ether, and dried under vacuum. The ^{1}H NMR spectrum indicated this to be ((5-chloro-3-thienyl)methyl)cobaloxime. The primary aqueous layer was extracted with solvent ether and worked up as above.

(c) Salt Formation of 2-Thienylmethyl Halides with Hexamethylenetetramine (HMTA). In a typical experiment, the organic product obtained after the reaction of (2-thienylmethyl)cobaloxime with halogen was dissolved in chloroform (5 mL) and solid HMTA (0.3 g, 2 mmol) was added portionwise to the solution. The mixture was heated at 50–55 °C for 0.5 h. The precipitated solid was filtered off and recrystallized further from alcohol.

(d) Formation of Benzyl Ethers of Furfuryl Halides. In a typical experiment, an excess of benzyl alcohol (3 mol equiv) and solid KOH (2 mol equiv) were added to 20 mL of an ethereal solution containing organic product from the reaction of furfurylcobaloxime with halogens. The mixture was heated to reflux for 0.5 h, after which ether was distilled off. The residue was dissolved into water, extracted with ether, and dried over anhydrous $MgSO_4$. Solvent evaporation and distillation gave benzyl furfuryl ether.

(e) Formation of 4-(Dimethylamino)benzyl Phenyl Sulfide. After the reaction of bromine with (4-(dimethylamino)benzyl)cobaloxime was over, thiophenol and triethylamine were added. The stirring was continued for an additional 20 min, after which the green solid was filtered off. The filtrate was concentrated and poured directly into solvent ether. The ethereal solution was washed with 1 M sodium hydroxide solution followed by dilute sodium metabisulfite solution and water. The ether layer was dried over anhydrous magnesium sulfate, and the product was characterized by ^{1}H NMR and elemental analysis.

(f) Competitive Bromination. A solution of bromine (1 mmol, 0.18 g in 10 mL of chloroform) was added dropwise to a stirred solution of 3-methylthiophene (1 mmol, 0.098 g) and (3-thienylmethyl)cobaloxime (**2b**) (1 mmol, 0.47 g) in 20 mL of chloroform at room temperature under nitrogen in the dark. The solution was stirred for 0.5 h and was then worked up as described under (b). ((5-Bromo-3-thienyl)methyl)cobaloxime was the only product isolated, and 3-methylthiophene was recovered.

(g) Reaction of (4-Methoxybenzyl)cobaloxime (3c) with Hydrogen Bromide. HBr generated by an equimolar reaction of tetralin with dry Br_2 was dissolved in dry chloroform. The HBr solution (2 mmol in 10 mL of chloroform) was added dropwise to a solution of (4-methoxybenzyl)cobaloxime (**3c**) (0.49 g, 1 mmol, in 15 mL of chloroform) under nitrogen in the dark. Workup of the reaction mixture was similar to that described in (a).

Results

Furfurylcobaloxime (**1a**) reacts rapidly with 1 or 2 molar equiv of Cl_2, Br_2, or I_2 in chloroform or acetic acid and under a nitrogen atmosphere. The reactions are done under conditions where the concentration of halogen is kept as low as possible so that the reactions of higher order in halogen are negligible. Furfuryl halide (**5a–c**, respectively) is the exclusive organic product formed in each case, the inorganic product being the halocobaloxime $XCo^{III}(dmgH)_2py$ (X = Cl, Br, I). Similar reactions of (2-thienylmethyl)cobaloxime (**1b**) with halogens (Cl_2, Br_2, I_2) under identical conditions lead to the exclusive formation of 2-thienylmethyl halides (**5d–f**) along with the halocobaloxime. The reaction of **1a** with ICl gives furfuryl iodide (**5c**) and chlorocobaloxime as the organic and inorganic products, respectively. The halides **5a–f** are unstable and are isolated and characterized as their adducts with hexamethylenetetramine (for **5d** and **5e**) and as furfuryl ethers (for **5a–c**). On the other hand, the reactions of (3-furylmethyl)- and (3-thienylmethyl)cobaloxime (**2a** and **2b**, respectively) with a 1:1 molar ratios of Cl_2, Br_2, I_2, and ICl give the corresponding 5-halo-substituted organometallic compounds **7a–7f**. However, the reactions of **2a** and **2b** with 2 mol equiv of halogens give **6a–6f** as the organic products. The latter compounds **6a–6f** are also formed from the reactions of organometallic products **7a,b,d,e** with 1 mol equiv of halogen (Cl_2 or Br_2). When a mixture of (3-thienylmethyl)cobaloxime and (4-methylbenzyl)cobaloxime (1 mmol each) is reacted with bromine (1 mmol), ((5-bromo-3-thienyl)methyl)cobaloxime (**7e**) is the exclusive product isolated. The details of the product formation and their physical and other characteristics are given in Tables I and II.

Unlike the above cases, the reactions of benzylcobaloximes (**3** and **4**) with halogens form entirely different products; for example, the reaction of (4-acetamidobenzyl)cobaloxime (**3a**) with Br_2 in a 1:1 molar ratio forms both the organic (**8a**) and organometallic products (**8c**) in a 44:56 ratio. The same reaction with 1 mol excess of bromine forms the additional product **8b**, which results due to the cleavage of the Co–C bond in **8c**. Similarly, the reaction of **3a** with chlorine forms both organic (**8d** and **8e**) and organometallic products (**8f**). The reaction of (4-dimethylamino)-benzyl)cobaloxime (**3b**) with Br_2 (1 or 2 equiv) forms only the

(6) (a) Grice, R.; Owens, L. N. *J. Chem. Soc.* **1963**, 1947. (b) Nystrom, R. F.; Brown, W. C. *J. Am. Chem. Soc.* **1948**, *70*, 3738. (c) Klamann, D.; Weherstahl, P.; Dujomerites, H. *Justus Liebigs Ann. Chem.* **1968**, *76*, 714. (d) Carpenter, M. S.; Easter, W. M. *J. Org. Chem.* **1954**, *19*, 87. (e) Beard, W. O., Jr.; Wanenam, D. N.; Hauser, C. R. *J. Org. Chem.* **1961**, *26*, 2310. (f) Wilberg, K. B.; McShane, H. F. In *Organic Synthesis*, 3rd ed.; Gilman, H., Ed.; Wiley: New York, 1963; Collect. Vol. 3, p 197. (g) Campagne, E.; Fuller, B. F. In *Organic Synthesis*, 3rd ed.; Gilman, H., Ed.; Wiley: New York, 1963; Collect. Vol. 4, p 921. (h) Zanetti, J. E. *J. Am. Chem. Soc.* **1927**, *49*, 1065. (i) Okabe, M.; Tamaguva, H.; Tada, M. *Synth. Commun.* **1963**, *13*, 373.
(7) Schrauzher, G. N. *Inorg. Synth.* **1968**, *11*, 61.
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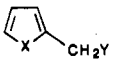
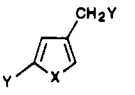
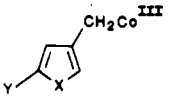
Table I. Products of the Reactions of Halogen with Organocobaloximes in Acetic Acid or Chloroform in the Dark under a Nitrogen Atmosphere

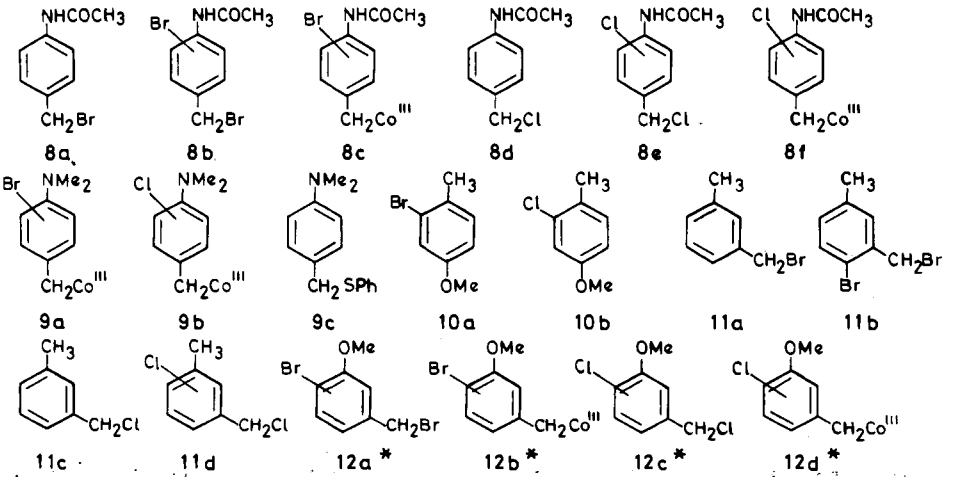
(a) Organocobaloximes 1 and 2

		org product[a,b]		organomet product[a]
				
organocobaloxime	halogen (amt, mol)	5	6	7
1a	Cl_2 (1 or 2)	**a**: X = O; Y = Cl	none	none
	Br_2 (1 or 2)	**b**: X = O; Y = Br	none	none
	I_2 (1 or 2)	**c**: X = O; Y = I	none	none
	ICl (1 or 2)	**c**: X = O; Y = I	none	none
1b	Cl_2 (1 or 2)	**d**: X = S; Y = Cl	none	none
	Br_2 (1 or 2)	**e**: X = S; Y = Br	none	none
	I_2 (1 or 2)	**f**: X = S; Y = I	none	none
	ICl (1 or 2)	**f**: X = S; Y = I	none	none
2a	Cl_2 (1)	none	none	**a**: X = O; Y = Cl
	Cl_2 (2)	none	**a**: X = O; Y = Cl[c]	none
	Br_2 (1)	none	none	**b**: X = O; Y = Br
	Br_2 (2)	none	**b**: X = O; Y = Br[c]	none
	I_2 (1)	none	none	**c**: X = O; Y = I
	ICl (1)	none	none	**c**: X = O; Y = I
2b	Cl_2 (1)	none	none	**d**: X = S; Y = Cl
	Cl_2 (2)	none	**d**: X = S; Y = Cl	none
	Br_2 (1)	none	none	**e**: X = S; Y = Br
	Br_2 (2)	none	**e**: X = S; Y = Br	none
	I_2 (1)	none	none	**f**: X = S; Y = I
	ICl (1)	none	none	**f**: X = S; Y = I
7a	Cl_2 (1)	none	**a**: X = O; Y = Cl	
7b	Br_2 (1)	none	**b**: X = O; Y = Br	
7d	Cl_2 (1)	none	**d**: X = S; Y = Cl	
7e	Br_2 (1)	none	**e**: X = S; Y = Br	

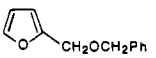
(b) Organocobaloximes 3 and 4

organocobaloxime	halogen (amt, mol)	products[d]	percentage ratio[e]	organocobaloxime	halogen (amt, mol)	products[d]	percentage ratio[e]
3a	Br_2 (1)	**8a,c**	44:56	**4a**	Br_2 (2)	**11a,b**	50:50
	Br_2 (2)	**8a,b,c**	48:17:35		Cl_2 (2)	**11e,d**	75:25
	Cl_2 (1)	**8d,e,f**	55:15:30	**4b**	Br_2 (1)	**12a,b**	42:56
	Cl_2 (2)	**8d,e,f**	57:18:25		Br_2 (2)	**12a,b**	60:40
3b	Br_2 (1 or 2)	**9a**	100		Cl_2 (1)	**12c,d**	46:51
	Cl_2 (1)	**9b,c**	67:37		Cl_2 (2)	**12c,d**	49:35
	Cl_2 (2)	**9b,c**	60:40				
3c	Br_2 (1 or 2)	**10a**	100				
	Cl_2 (1 or 2)	**10b**	100				

(c) Product Numbers with Structures[f]



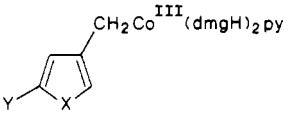
[a] Isolated yield 90%. [b] (i) Compound **5f** is highly unstable and is partially characterized. (ii) The melting point of the hexamethylenetetramine salt of **5d** is 120–125 °C, and that of **5e** is 160–161 °C. (iii) The same furfuryl ether



is obtained from **5a**, **5b**, or **5c**: bp 120 °C (2 mm) (lit. bp 118–120 °C (2 mm)); ^{1}H NMR (δ, $CDCl_3$): 4.44 (s, 2 H), 4.52 (s, 2 H), 6.28 (br, s, 1 H), 6.30 (br s, 1 H), 7.30 (br s, 5 H), 7.37 (m, 1 H). [c] ^{1}H NMR (δ, $CDCl_3$): **6a**, 4.21 (s, 2 H), 6.95 (d, 1 H), 7.65 (d, 1 H); **6b**, 4.17 (s, 2 H), 6.90 (d, 1 H), 7.58 (d, 1 H); **6e**, 4.37 (s, 2 H), 6.90 (d, 1 H), 7.17 (d, 1 H). [d] See page 32 for product numbers. [e] Product ratio based on isolated yield (isolation >90% in all cases). [f] An asterisk by the structure number indicates a mixture of two positional isomers.

Table II

(a) UV and ^{1}H NMR Spectra (100 MHz) of Organocobaloximes[a] **2** and **7**

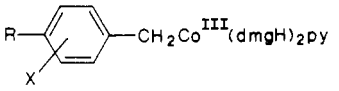


compd no.	X	Y	^{1}H NMR chem shift δ, ppm: arom	CH_2	dmgH	py	UV λ_{max}, nm (CH_3OH)
2a	O	H	6.00, 7.12	2.55	2.00, 2.10	7.15, 7.75, 8.42	238, 286, 348
2b	S	H	6.75, 7.20	2.85	2.00, 2.10	7.30, 7.70, 8.50	239, 277, 359
7a	O	Cl	6.40, 6.74	2.44	2.37[b]	7.2–8.2	245, 362, 475
7b	O	Br	6.42, 6.78	2.41	2.30[b]	7.24, 7.61, 8.10–8.50	225, 362, 450
7c	O	I	6.36, 6.75	2.35	2.35	7.2–8.3	215, 280, 365
7c	S	Cl	6.68, 7.19	2.65	2.30, 2.38	7.58, 8.15, 8.42	235, 282, 475
7e	S	Br	6.58, 6.90	2.66	2.38[b]	7.22, 7.61, 8.14–8.45	235, 282, 364
7f	S	I	6.52, 6.85	2.56	2.33, 2.42	7.20, 7.64, 8.25	215, 260, 450

(b) Spectral and Analytical Characteristics of the Organic Products from the Reaction of Halogens with Benzylcobaloximes **3** and **4**

compd no.[d]	mp [bp], °C	^{1}H NMR chem shift δ, ppm ($CDCl_3$): arom	CH_2	other	UV λ_{max}, nm (CH_3OH)
8a	186	7.00–7.44 (m)	4.34 (s)	2.05 (s) [Me]	285, 239
8b	210	8.06–8.30 (m)	4.47 (s)	2.23 (s) [Me]	284, 234
8d	151–153	7.18–7.56 (m)	4.53 (s)	2.16 (s) [Me]	289, 227
8e	182–183	7.96–8.20 (m)	4.40 (s)	2.12 (s) [Me]	286, 238
9c	57	7.00–7.80 (m)	3.80 (s)	2.88 (s) [Me]	313, 302, 256
10a	[110–113 (8 mm)]	6.75–7.40 (m)		2.26 [Me], 3.80 [OMe]	216, 245, 287, 310 sh
10b	[88 (5 mm)]	6.80–7.50 (m)		2.34 [Me], 3.91 [OMe]	216, 249, 282, 310 sh
11a	[74 (10 mm)]	7.08 (m)	4.38 (s)	2.24 [Me]	270, 235
11b	[81 (5 mm)]	7.10 (m)	4.45 (s)	2.29 [Me]	274, 235
11c	[83 (10 mm)]	7.14 (m)	4.44 (s)	2.36 [Me]	268, 232
11d	[94 (5 mm)]	7.14 (m)	4.47 (m)	2.36 [Me]	268, 231
12a[c]	91–98	6.60–7.58 (m)	4.50 (s), 4.55 (s)	3.90, 3.80 [OMe]	213, 239, 293, 304 sh
12c[c]	39–45	6.53–7.42 (m)	4.40, 4.46	3.86, 3.80 [OMe]	212, 229, 287, 279, 309 sh

(c) Spectral and Analytical Characteristics of



compd no.	R	X	^{1}H NMR chem shift δ, ppm ($CDCl_3$): dmgH	arom	CH_2	py: β	py: α	py: γ	other	anal. found (calcd), %: C	H	N	X	UV-vis λ_{max}, nm (CH_3OH)
8c	4-NHCOMe	Br	2.05	7.23–7.90	3.09	7.60	7.76	8.43	2.30[e]	44.2 (44.3)	4.87 (4.7)	14.6 (14.1)	13.4 (13.4)	456, 361, 280, 235
8f	4-NHCOMe	Cl	2.15	7.00–7.50	2.99	7.54	7.74	8.60	2.23[e]	47.5 (47.9)	4.82 (5.0)	15.0 (15.2)	6.3 (6.4)	460, 362, 282, 235
9a	4-N(Me)$_2$	Br	2.10	7.00–7.55	2.78	7.70	7.78	8.50	2.88[f]	45.6 (45.3)	5.3 (5.1)	14.5 (14.4)	13.9 (13.7)	435, 347
9b	4-N(Me)$_2$	Cl	2.06	7.00–7.36	2.77	7.40	7.60	8.44	2.84[f]	49.3 (49.1)	5.7 (5.5)	15.8 (15.8)	6.6 (6.6)	437, 345, 320, 245
12b[c]	3-OMe	Br	2.02	6.34–7.40	2.88	7.30	7.70	8.54	3.88[g]	44.6	4.87	12.3	14.2	469, 359, 277, 232
			1.98	6.34–7.40	2.75	7.30	7.70	8.84	3.77[g]	(44.3)	(4.7)	(12.8)	(14.0)	
12d[c]	3-OMe	Cl	2.10	6.28–6.90	2.80	7.40	7.77	8.48	3.92[g]	48.0	5.28	13.4	6.8	466, 357, 279, 232
			2.00	6.28–6.90	2.72	7.40	7.77	8.48	3.86[g]	(48.1)	(5.1)	(13.7)	(6.7)	

[a] All compounds give satisfactory elemental analyses. [b] Broad singlet. [c] Having positional isomers. [d] See Table Ic for product number structures. [e] –NHCOMe. [f] –NMe_2. [g] –OMe.

ring-substituted organometallic products (**9a**) whereas the reaction with chlorine forms organometallic and organic products (**9b** and **9c**, respectively). The organic product 4-(dimethylamino)benzyl chloride so formed is highly unstable and is, therefore, isolated and characterized as 4-(dimethylamino)benzyl phenyl sulfide (**9c**). The halogenation of (4-methoxybenzyl)cobaloxime (**3c**) with Br_2 and Cl_2 forms exclusively the ring-halogenated toluene 4-methoxy-2-halotoluene (**10a** and **10b**) in quantitative yield. The reaction of (3-methylbenzyl)cobaloxime (**4a**) with Br_2 under similar conditions forms 3-methylbenzyl bromide (**11a**) and 3-methyl-6-bromobenzyl bromide (**11b**) in a 50:50 ratio whereas chlorination forms 3-methylbenzyl chloride (**11c**) and 3-methyl-*X*-chlorobenzyl chloride (**11d**) in a 75:25 ratio. The assignment of the position of chlorine in the ring in **11d** is not clear due to the compact nature of the aromatic proton resonances. However, the ^{1}H NMR spectrum indicates it to be a mixture of two positional isomers.

On the other hand, the reaction of (3-methoxybenzyl)cobaloxime (**4b**) with Br_2 or Cl_2 (1 or 2 equiv) forms both organic (**12a** or **12c**) and organometallic products (**12b** or **12d**) in varying proportion. Each of these products is a mixture of two positional isomers as shown by ^{1}H NMR. All the spectral and analytical characteristics of products **8–12** are given in parts b and c of Table II.

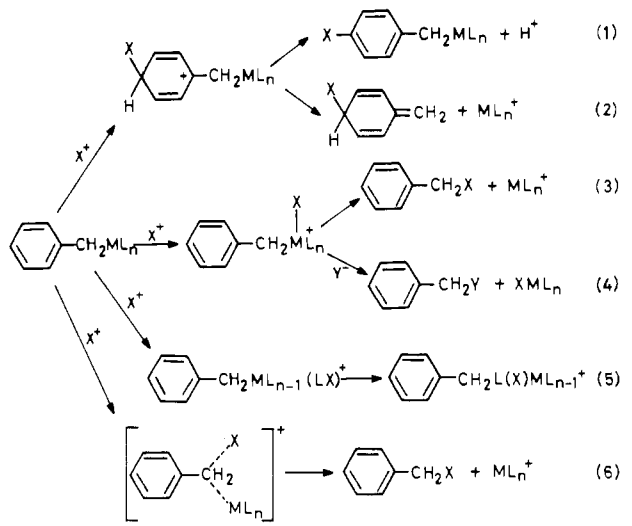
Furthermore, many independent experiments give the following information.

1. (4-Methoxybenzyl)cobaloxime (**3c**) does not show any sign of reaction with pure HBr in chloroform under nitrogen even after 72 h. The original cobaloxime is recovered.

2. The reaction of (4-methoxybenzyl)cobaloxime (**3c**) with halogen in the presence/absence of K_2CO_3 forms the same product, 4-methoxy-2-halotoluene.

3. In the reaction of (3-methoxybenzyl)cobaloxime (**4b**) with

Scheme I



bromine, a careful monitoring of the reaction indicates that the organic product is formed simultaneously with the organometallic product right from the beginning.

4. When a mixture of (3-thienylmethyl)cobaloxime (**2b**) and 3-methylthiophene (1:1 molar ratio) is brominated (1 mol equiv), ((5-bromo-3-thienyl)methyl)cobaloxime (**7e**) is the exclusive organometallic product formed and 3-methylthiophene is recovered.

5. All efforts to separate the product mixtures **8a,b** and **8d,e** by chromatography fail (many solvent systems were tried), and hence, the position of halogen in the ring cannot be accurately assigned. Similarly, the position of halogen in the organometallic products **8c**, **8f**, **9a**, and **9b** cannot be accurately assigned because of the complexities in the aromatic region and also because part of the aromatic region is obscured by pyridine resonances.

6. In general, the reactivity of halogen follows the order $Cl_2 > Br_2 > I_2$.

7. No appreciable change in reaction time is noted when the solvent is changed from chloroform to acetic acid. The same products are formed in both cases; however, the yields are slightly better (~10%) in chloroform solution.

Discussion

In principle an electrophile may attack a benzylmetal complex ($PhCH_2ML_n$) at a variety of sites[9] (Scheme I). Attack may take place at the benzene ring leading to substitution[10] (eq 1) and/or to metal–carbon bond cleavage[11] (eq 2), attack may take place at the metal[12] center, leading to a variety of products, including those from a reductive-elimination process (eq 3) and from nucleophilic displacement at the α-carbon (eq 4), attack may take place at the ligand L, leading to a variety of products, including those from an insertion process[13] (ligand migration, eq 5), and attack may also take place directly at the α-carbon[14] (on the carbon–metal bond orbital, eq 6). Reactions of all six types are known, and the path followed is clearly a function of the particular electrophile, its interaction with the HOMO of the complex, and the nature of the reaction medium. In all cases a certain degree of electron transfer occurs.[15] In general, chlorine is more reactive than bromine, and iodine is relatively unreactive. Thus, while most aromatic compounds may be halogenated by molecular chlorine

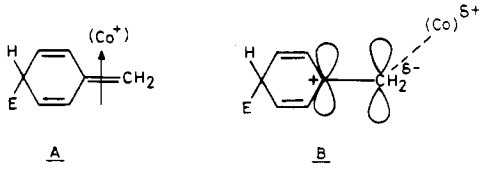


Figure 1.

and bromine, there is no clear-cut case of iodination by molecular iodine. Much of the information about the mechanism of these reactions has come from broad comparisons of reactivity and from product studies,[16] despite the fact that the order of reaction with respect to halogen is frequently greater than 1, particularly in the case of the reaction of bromine in acetic acid. Only at low bromine concentrations in acetic acid are these substitutions first order in the halogen. Therefore, all the reactions described in the present work are carried out by the very slow addition of the dilute bromine/chlorine solutions to the benzylcobaloxime solution in order to keep the halogen concentration as low as possible. Under such conditions, reactions of higher order in halogen should be negligible and the comparison between substitution and cobalt–carbon bond cleavage should be more meaningful. However, if the reactions are carried out with higher concentrations of halogen than are used here, other products may well be obtained.

Halogenation of benzylcobaloxime with Cl_2, Br_2, I_2, and ICl results in a rapid cleavage of the Co–C bond, leading to the corresponding benzyl halides.[3,33] (Para-substituted benzyl)cobaloximes, $4\text{-}RC_6H_4CH_2Co(dmgH)_2py$ (R = Me, $CHMe_2$, CMe_3), behave similarly, and corresponding benzyl halides are the exclusive organic products formed.[4] However, in the present case, the formation of substantial ring-halogenated organometallic and/or organic products in the reaction of Br_2 and Cl_2 with $4\text{-}NHCOCH_3C_6H_4CH_2$, $4\text{-}NMe_2C_6H_4CH_2$, $4\text{-}OMeC_6H_4CH_2$, $3\text{-}MeC_6H_4CH_2$, and $3\text{-}OMeC_6H_4CH_2$ cobaloximes (**3** and **4**) points to a more activated aromatic nucleus in such systems[17] as compared to that in the parent benzylcobaloxime and its 4-alkyl derivatives. It is to be noted, however, that although ring activation is achieved by introducing such groups into the benzylcobaloxime, Co–C cleavage is still a facile process in all these reactions. This is justified in view of the experimental observations. It seems, therefore, that these systems represent a unique class of cobaloximes where both the aromatic and Co–C bonds are simultaneously activated toward attack by halogen. In order to rationalize such a fact further, one needs to understand various electronic factors that promote such activation, for example (a) the inherent reactivity of the $Co–CH_2$ bond toward halogen, (b) the reactivity of the aromatic ring toward the halogen, and (c) the effect of the substituents in the benzyl group on factors a and b.

Since the electron-donating influence of the metallomethyl group to the aromatic ring has been suggested to be conugative in nature by NMR[18] and chemical studies, two possibilities can be visualized for such an electron donation. In A (Figure 1), the formation of a π-complex takes place where the metal occupies different positions relative to the benzene nucleus in the initial and the transition states. Formation of such a complex is less likely with cobalt in +3 oxidation state. In B, a vertical stabilization is achieved, following a σ–π overlap, the cobalt atom with its appendant ligands remaining essentially in the same position relative to the benzyl group in both the initial and the transition state. For reactions in the present study that attain or approach the encounter rate, the activation energy must be very low and hence the transition state more closely resemble the initial state. Under such conditions the conjugative electron-donating effect of the $-CH_2Co^{III}(dmgH)_2py$ group is expected to operate via

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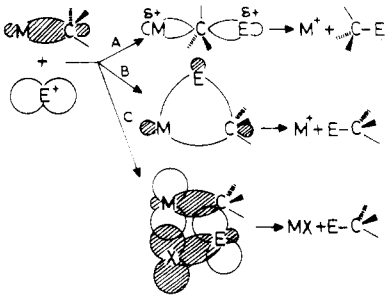


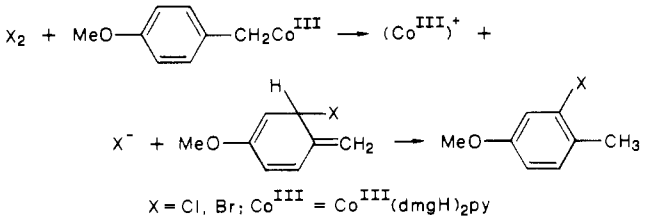
Figure 2.

transition state B rather than A.

Since we know now that the activating influence of $-CH_2Co^{III}(dmgH)_2py$ by itself or in conjunction with inductively electron-donating groups at the para position of the aromatic ring is insufficient to cause ring substitution, it seems certain that the electrophile substitution into the aromatic ring in the present systems $RC_6H_4CH_2Co^{III}$ must be due to the combined effect of substituent R and $-CH_2Co^{III}(dmgH)_2py$ group and such an effect is conjugative in nature.[34] This means that the electronic effect of the substituents in the para position is effectively transmitted to the Co–C bond and hence the Co–C bond reactivity is enhanced toward an electrophile. This is supported by earlier observations of Johnson,[3,18] Brown,[18] and their co-workers, who have suggested that the effect of any substituent in the para position of the benzene ring is effectively transmitted to cobalt through the methylene group but such an effect is not transmitted through σ bonds.[35] It implies that the effective transmission of π-electron density of the substituent R will be most facile in transition state B.[36]

As Co–C bond cleavage in **3a,b** and **4a,b** is directly competing with enhanced electron density in the aromatic ring by the extended $\sigma-\pi$ conjugation, it is very difficult to quantify the relative extent of activation of the aromatic ring and the α-carbon by such a process. However, as a point of interest it is found that only one halogen enters into the benzene ring to give the organometallic product. All attempts to put a second halogen into the ring fail and result in the cleavage of the Co–C bond. This may be due to the fact that halogen deactivates the ring toward further halogenation and hence cleavage of the Co–C bond occurs.

The halogenation of (4-methoxybenzyl)cobaloxime (**3c**) forms exclusively the ring-halogenated toluene **10a** or **10b**, a product observed for the first time in such studies:[37]

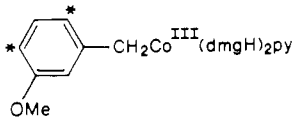


The exclusive formation of this isomer alone and the complete absence of other isomers where the halogen is ortho to the methoxy group points to the more activating effect of the $-CH_2Co^{III}(dmgH)_2py$ group than the methoxy group. The products **10b** probably arise by the attack of halogen on the ring with a concerted cleavage of the Co–C bond.

The possibility that bromination occurs without cleavage and then the HBr present cleaves the Co–benzyl bond is ruled out since the reaction of **3c** with pure HBr in chloroform under identical conditions is very slow and does not form any 4-methoxytoluene, though the Co–C bond cleavage takes place on prolonged standing (4 days). Furthermore, the same product (**10a**) is formed even when the reaction of **3c** is carried out with Br_2 in the presence of K_2CO_3. A similar observation is made in the reaction of **3a** and **3b**, where the HBr produced in the reaction does not effect the Co–C bond cleavage within the reaction time.

It is clear from the above discussion that conjugatively electron-donating groups like NMe_2, $NHCOCH_3$, and OMe contribute to a large degree toward the ring halogenation. Furthermore, the effect of such a group when it is present at the para position is also transmitted to the metallomethyl group through extended $\sigma-\pi$ delocalization and hence favors the competitive Co–C bond cleavage as well.

If the above viewpoint is correct, then meta substitution into the benzene ring will completely inhibit such extended $\sigma-\pi$ delocalization and should not enhance the Co–C bond reactivity. However, the corresponding ring substitution should become more facile. The results indicate that meta substitution seems to be more effective in causing ring substitution; for example, in the bromination of (3-methylbenzyl)cobaloxime (**4a**), both 3-methylbenzyl bromide (**11a**) and 6-bromo-3-methylbenzyl bromide (**11b**) are formed in equal proportion. The product distribution indicates that 50% of the reaction involves an initial attack of Br_2 on the ring followed by Co–C cleavage and 50% of the reaction involves direct Co–C cleavage prior to ring substitution. 3-Methylbenzyl bromide is inert to bromination under these reaction conditions. (3-Methoxybenzyl)cobaloxime (**4b**), on the other hand, forms only the ring-substituted organic and organometallic products[38] (**12a,c** and **12b,d**, respectively). Each of these products is a mixture of two positional isomers as indicated by ^1H NMR spectra, and all efforts to separate them have failed. A complete absence of 3-methoxybenzyl halide points out that no direct Co–C cleavage of the parent cobaloxime (**4b**) takes place (such a product, if it forms at all, is inert to further halogenation). It is certain from the product distribution that the initial attack of halogen is in the ring followed by Co–C bond cleavage. The formation of two positional isomers is not really surprising if one takes into account the electron densities in **4b**. For example, both positions



4b

marked with asterisks in the structure have large electron density. The marginal difference between these two positions depends upon the overall activating effect of $-CH_2Co(dmgH)_2py$ vs that of OMe. In view of our results, where the $-CH_2Co^{III}(dmgH)_2py$ group is found to be more activating than OMe, we believe that the isomer formed in higher proportion (65%) will have the halogen ortho to the $-CH_2Co(dmgH)_2py$ group.

Further direct proof for the extended $\sigma-\pi$ delocalization phenomenon comes from the study of **1** and **2**, where a remarkable difference in reactivity of these two systems is observed;[23] for example, Co–C cleavage is the primary process in furfuryl- and (2-thienylmethyl)cobaloximes (**1a** and **1b**), forming the corresponding organic halides (**5a–5f**), whereas ring halogenation occurs much faster in the 3-isomer and leads to the formation of new organometallic products (**7a–7f**) in which the 5-position of the heterocyclic ring is substituted.[39] The exclusive formation of 5-substituted organometallic product and the complete absence of 2-substituted product points to the increased steric crowding by the bulkier $-CH_2Co^{III}(dmgH)_2py$ group at the 3-position. However, the difference in reactivity of **1** and **2** can be rationalized as follows. The effect of the heteroatom bond pair in **1** is effectively transmitted to the Co–C bond by extended $\sigma-\pi$ delocalization, making it more susceptible to attack by halogen, whereas the same cannot occur in **2**. Hence, the formation of observed products is justified. The competitive bromination of (3-thienylmethyl)cobaloxime (**2b**) in the presence of an equivalent amount of 3-methylthiophene leads exclusively to the brominated (3-thienylmethyl)cobaloxime (**5e**), indicating once again that $-CH_2Co(dmgH)_2py$ is much more activating than the methyl group.

Mechanistic Aspects. Halogenation has been shown to occur in organocobaloximes by a free-radical mechanism,[24a] a direct

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Table III. EPR and Cyclic Voltammetric Parameters for $RCo^{III}(dmgH)_2py$ Complexes

compd no.	R	g(iso) (±0.0003)	$10^3A(iso)^{Co}$, cm^{-1} (±0.5)	CV $E_{1/2}$, V vs SCE
1a	furfuryl			0.980[a]
1b	2-thienylmethyl	2.0054	18.9	0.950[a]
2a	3-furylmethyl			0.931[a]
2b	3-thienylmethyl	2.0048	19.7	0.973[a]
3a	4-acetamidobenzyl	2.0021	19.4	0.851
3b	4-(dimethylamino)benzyl	2.0134	18.2	1.036
3c	4-methoxybenzyl	2.0043	18.7	
4a	3-methylbenzyl	2.0023	18.8	0.869
4b	3-methoxybenzyl	2.0068	18.7	0.847

[a] Irreversible oxidation.

electrophilic mechanism,[24b] an oxidative dealkylation mechanism[24c] consisting of an oxidation to organocobalt(IV) species followed by a carbocation transfer to a nucleophilic acceptor, and by a single-electron-transfer mechanism.[19] Support for each mechanism has been accrued in the literature,[25] but no conclusive mechanism has been accepted so far. This is probably because the nature of the end product(s) is the same irrespective of the mechanism, and it becomes very difficult to establish the relative contribution of each mechanism to the overall process.

Mechanistic studies on the halogenation of benzylcobaloximes are rather few. Earlier studies by Johnson et al.[3] and by us[4,17,23] have shown that halogenation of benzyl- and (para-substituted benzyl)cobaloximes, $4\text{-}RC_6H_4CH_2Co^{III}(dmgH)_2py$ (R = NO_2, CHO, COOH, Cl, Br, CN), leads to the formation of a mixture of products including the benzyl halides and benzyl ethers of dimethylglyoxime, the latter being the characteristic decomposition product of organocobalt(IV) species.[26] The formation of this byproduct is suggested to arise as a result of an oxidative dealkylation mechanism.[27] However, it is to be noted that though the formation of dimethylglyoxime ether products points to the intermediate formation of organocobalt(IV) species, the absence of such a product does not rule out its intermediate formation in solution because it may be quite likely that its lifetime in solution under the reaction conditions may be quite short. (Of course, this statement is true only for those cobaloximes that are within the limits of the oxidation potential of the halogen.) Recently, Tauzher et al.[24b] have preferred the electrophilic mechanism in the halogenation studies of benzylcobaloxime with ICl and ICl_2^- and have made further generalizations that other benzylcobaloxime derivatives will also react via a similar mechanism although they studied only benzylcobaloxime.

In the present study the exclusive formation of the halogenated organometallic and/or organic products and the complete absence of dmg ether products may lead to an initial consideration that a predominantly electrophilic mechanism is operative in these cases; however, it seems less probable in view of the preliminary ESR and cyclic voltammetric study of these reactions (Table III). When a solution of organocobaloxime (e.g., $4\text{-}NHCOCH_3C_6H_4CH_2Co^{III}$ 10^{-4} M solution in CH_2Cl_2) and Br_2 (1:1 molar ratio) in CH_2Cl_2 under N_2 is brought to liquid-N_2 temperature, a well-defined EPR spectrum consisting of eight relatively broad (~20 G) but well-resolved lines (Figure 3) is exhibited corresponding to one unpaired electron on cobalt(IV) with a ^{59}Co nuclear spin ($I = {}^7/_2$, g_{iso} = 2.002 06). Although a slight anisotropy is evident, the resolution is insufficient to permit evaluation of both the parallel and perpendicular components and only a single g value (relative to DPPH) of $M = {}^7/_2$ and $M = -{}^7/_2$ hyperfine component lines and a single A value are determined.

An additional short-lived signal at g (g_{iso} = 2.000 55) is also observed, which is expected to represent $Br_2/Br_2^{\bullet-}$.[28] When the frozen solution is brought to room temperature, the eight-line Co^{IV} signal disappears instantaneously, which is due to decomposition of the Co^{IV} species. Similar observations are made with (4-(dimethylamino)benzyl)cobaloxime as well.

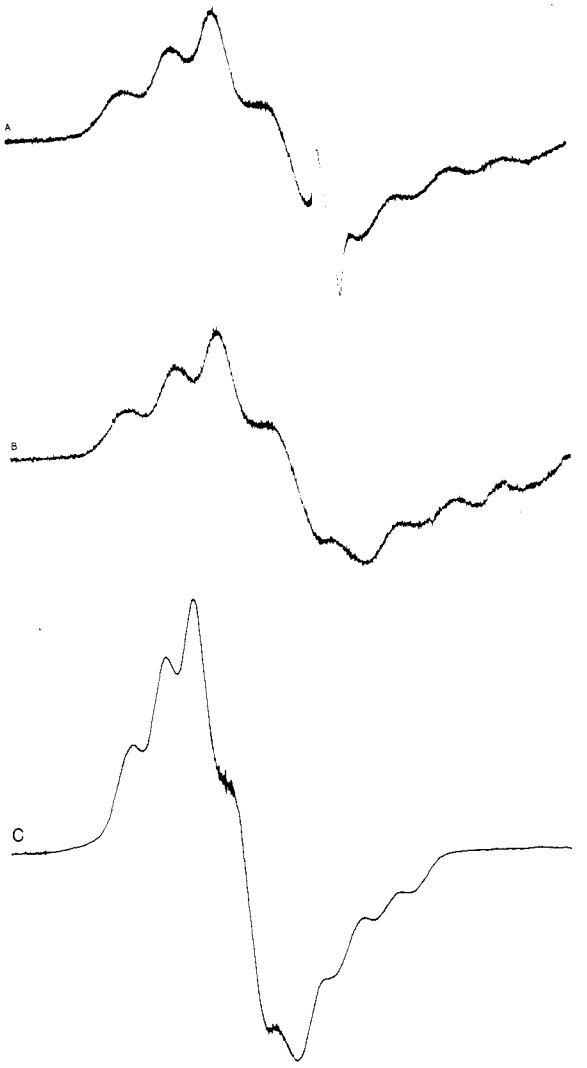

Figure 3. (a) First-derivative EPR spectrum of $[4\text{-}NHCOCH_3C_6H_4CH_2Co^{IV}(dmgH)_2py]^+$ in frozen CH_2Cl_2 at liquid-nitrogen temperature. The spectrum was taken just after mixing the Br_2 solution and organocobaloxime solution, showing the formation of $Br_2^{\bullet-}$ in the initial stage, which slowly disappears on standing. The microwave frequency was 9.289 GHz, and the power was 2 mW. (b) First-derivative EPR spectrum of $[4\text{-}NHCOCH_3C_6H_4CH_2Co(dmgH)_2py]^+$ in frozen CH_2Cl_2 at liquid-nitrogen temperature. The microwave frequency was 9.289 GHz, the field was set at 3300 G with a scan range of 200 G, and the microwave power used was 2 mW. (c) First-derivative EPR spectrum of $[4\text{-}NHCOCH_3C_6H_4CH_2Co^{III}(dmgH)_2py]^+$ in frozen CH_2Cl_2 at liquid-nitrogen temperature. The microwave frequency was 9.289 GHz, the field was set at 3330 G with a scan range of 500 G, and the microwave power was 2 mW.

Figure 4 depicts the cyclic voltammogram for the oxidation of (4-acetamidobenzyl)cobaloxime in acetonitrile at 25 °C. The voltammogram is characteristic of a reversible one-electron-oxidation process at low scan rates (20 mV s^{-1}) according to the equation

$$[4\text{-}NHCOCH_3C_6H_4CH_2Co(dmgH)_2py] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [4\text{-}NHCOCH_3C_6H_4CH_2Co(dmgH)_2py]^+$$

($E_c - E_a$ = 60 ± 10 mV, n = 1.0). Similar observations are made

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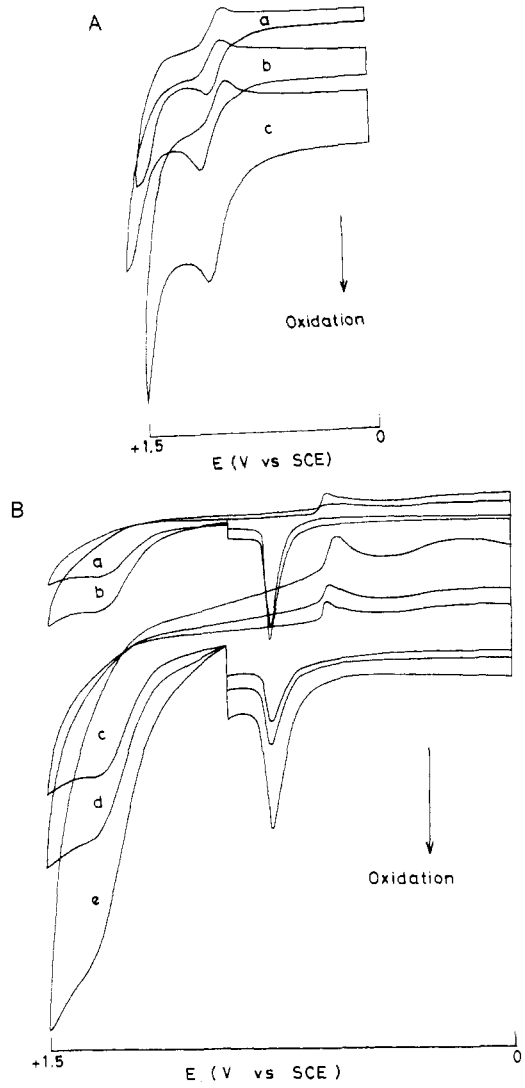

Figure 4. (A) Cyclic voltammograms of acetonitrile solutions of [4-$NHCOCH_3C_6H_4CH_2Co^{III}(dmgH)_2py$] (ca. 10^{-4} mol/L) containing tetraethylammonium perchlorate supporting electrolyte. Scan rates: (a) 20 mV/s; (b) 50 mV/s; (c) 100 mV/s. (B) Cyclic voltammograms of acetonitrile solutions of 2-furylcobaloxime (ca. 10^{-4} mol/L) containing tetraethylammonium perchlorate supporting electrolyte. Scan rates (mV/s): (a) 20 mV/s; (b) 50 mV/s; (c) 100 mV/s; (d) 200 mV/s; (e) 500 mV/s.

for compounds **3b**, **4a**, and **4b** (Table III). The trend of $E_{1/2}$ values is in the expected direction of increasing ease of oxidation of organocobalt(III) with increasing donor strength of the substituent in the aromatic ring[29] and provides further support to the results obtained in the halogenation of these cobaloximes. However, in the case of **1a**, **1b**, **2a**, and **2b** cyclic voltammograms characteristic of irreversible one-electron-oxidation processes even at scan rates as high as 500 mV s^{-1} are obtained (Table III, Figure 4).

The EPR observations (Figure 3, Table III) clearly suggest that halogenation reactions in the present system do involve RCo^{IV} formation. The lifetime of the latter is assumed to be very short, which prevents its decomposition to the dmg ether.

The participation of a direct free-radical mechanism involving a unimolecular homolysis of the Co–C bond seems less likely since the reactions are done in the dark and under a nitrogen atmosphere. The relative extent of direct electrophilic and oxidative dealkylation mechanisms is difficult to predict at this stage, and work in this direction is under way.

Unlike the above cases the exclusive formation of iodo compounds in the reaction of ICl with **1a,b** and **2a,b** shows that halogenation is occurring by a direct electrophilic mechanism. However, extrapolation of this result to the reactions of Br_2 and Cl_2 is unworthy since these are stronger oxidants than ICl.

Registry No. **1a**, 92785-12-1; **1b**, 92785-13-2; **2a**, 92785-14-3; **2b**, 92785-15-4; **3a**, 113149-80-7; **3b**, 113149-79-4; **3c**, 42194-65-0; **4a**, 36583-13-8; **4b**, 113149-81-8; **5a**, 617-88-9; **5b**, 4437-18-7; **5c**, 117680-17-8; **5d**, 765-50-4; **5d** (hexamethylenetetramine salt), 6296-08-8; **5e**, 45438-73-1; **5e** (hexamethylenetetramine salt), 117680-16-7; **5f**, 58703-22-3; **6a**, 92753-14-5; **6b**, 92753-15-6; **6d**, 73919-91-2; **6e**, 73919-93-4; **7a**, 92785-08-5; **7b**, 92785-09-6; **7c**, 117686-98-3; **7d**, 92785-10-9; **7e**, 92785-11-0; **7f**, 117686-99-4; **8a**, 66047-05-0; **8b**, 117680-18-9; **8c**, 113173-09-4; **8d**, 54777-65-0; **8e**, 117680-19-0; **8f**, 113173-11-8; **9a**, 113173-10-7; **9b**, 113173-12-9; **9c**, 956-71-8; **10a**, 36942-56-0; **10b**, 54788-38-4; **11a**, 620-13-3; **11b**, 27561-50-8; **11c**, 620-19-9; **11d**, 35655-52-8; **12a**, 113172-87-5; **12b**, 113173-08-3; **12c**, 117680-20-3; **12d**, 117687-00-0.

(29) Halpern, J.; Chan, M. S.; Roche, T. S.; Tom, G. M. *Acta Chem. Scand.* **1979**, *A33*, 141.
(30) In the case of reactions in chloroform, the filtrate was concentrated and poured directly into solvent ether.
(31) In the case of reactions in chloroform, the filtrate was concentrated and poured directly into solvent ether.
(32) In the case of reactions with ICl and I_2, the solution was washed initially with aqueous sodium thiosulfate and water before further workup.
(33) The formation of dmgH ether product in chlorination is an artifact of the electrochemical influences of the reactants.
(34) This may be an excellent example of true hyperconjugation in which the attenutation of the inductive effect of the cobalt center by interposition of a methylene group between the Co atom and the aryl group makes the metallomethyl group more electron-donating in nature.[18] This is further justified and supported by X-ray evidence, which suggests a near-sp^2 hybridization of the methylene carbon,[21] which would be ideal for such hyperconjugative interaction.
(35) In general, the influence of the conjugatively electron-releasing groups on the ring substitution is markedly greater than their influence on the side-chain reaction as shown by the much greater values of the Brown σ^+ constants and the Hammett σ^+ constants for such substituents and by the generally larger values of σ for such substitution reactions.[1a]
(36) One must also consider Pratt's view that any increase in the electron density at the α-carbon weakens the Co–C bond strength by Coulombic forces.[20]
(37) (a) It is to be noted that **3c** forms 4-methoxybenzyl iodide with I_2 at 40 °C in the dark.[22] This arises partly from the inert character of I_2 toward electrophilic substitution of the aromatic ring and the high electron affinity of iodine. (b) The synthesis of **10a** and **10b** in quantitative yield by this procedure may become valuable since other methods of preparations are lengthy and low-yielding (e.g.: Carpenter, M. S.; Ester, W. H. *J. Org. Chem.* **1955**, *20*, 401).
(38) Since the reaction is almost instantaneous and probably approaches the encounter rate, the ratio of the organic and organometallic products depends upon the concentrations and the rate of addition of halogen.
(39) This is the first example where iodine has been shown to substitute into the aromatic ring in such organocobaloximes.