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Stereochemistry and Electrophilic Substitution Reactions of Tris(formylacetonato)cobalt(III) and -chromium(III) Chelates

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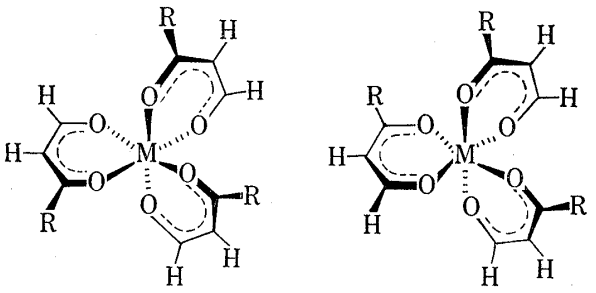
Unsymmetrical β-diketonate metal (III) chelates, tris(formylacetonato)cobalt(III) and -chromium (III) chelates, were synthesized. Fac and mer isomers of these chelates were separated by column chromatography, and the stereochemistry of paramagnetic cobalt(III) chelate is discussed from nuclear magnetic resonance (NMR) spectra.

Electrophilic substitution reactions (chlorination, bromination, iodination, nitration, and thiocyanation) of the fac and mer isomers of these chelates were successful. Infrared, ultraviolet, and NMR spectra were measured for these chelates.

Several papers have been published on the stereochemistry of unsymmetric β-diketonate trivalent metal complexes.[2-6] Paramagnetic tris(formylacetonato)chromium(III)[7] and -vanadium(III)[8] chelates have been reported by Collman, *et al.* and Holm, *et al.*, respectively.



(A) (B)

Fig. 1. Configuration of fac and mer Isomers of Trivalent-metal Chelate of Unsymmetrical Ligand

Two geometrical isomers, facial (fac or *cis*) and meridional (mer or *trans*) forms, are possible for the coordination of three unsymmetrical bidentate ligands (R=CH_3; formylacetone or 1,3-butanedione) to trivalent metal ions as shown in Fig. 1.

The present paper describes the preparation and stereochemistry of diamagnetic tris(formylacetonato)cobalt(III), and the electrophilic substitution reactions of tris(formylacetonato)chromium(III) and -cobalt(III) chelates.

Acetylacetonate metal complexes[9,10] have been known as quasi-aromatic compounds, and many electrophilic substitution reactions have been effected at the central carbon atom of the chelate ring. Malonaldehyde and formylacetone metal complexes are "parent" and "sister" compounds of 1,3-dicarbonyl-metal complexes, respectively. The chemistry of these less-hindered chelates has been reported only in the case of paramagnetic chromium(III) chelates by Collman and Kittleman.[7]

We will now report the preparation and the substitution reactions of fac and mer tris(formylacetonato)cobalt(III) and -chromium(III) chelates, and the stereochemistry of

1) Location: *Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.*
2) R.C. Fay and T.S. Pipper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).
3) R.C. Fay and T.S. Pipper, *J. Am. Chem. Soc.*, **85**, 500 (1963).
4) T. Sasaki, K. Kanematsu, and G. Kinoshita, *J. Chem. Soc.* (*C*), 951 (1969).
5) J.G. Gordon and R.H. Holm, *J. Am. Chem. Soc.*, **92**, 5319 (1970).
6) A.Y. Girgis and R.C. Fay, *J. Am. Chem. Soc.*, **92**, 7061 (1970).
7) *a*) J.P. Collman and E.T. Kittleman, *J. Am. Chem. Soc.*, **83**, 3529 (1961); *b*) J.P. Collman, E.T. Kittleman, W.S. Hurt, and N.A. Moore, *Inorg. Syntheses*, **8**, 144 (1965).
8) F. Rohscheid, R.E. Ernst, and R.H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).
9) J.P. Collman, *Angew. Chem. Intern. Ed.*, **4**, 132 (1965).
10) K. Yamakawa, *Kagaku no Ryoiki*, **16**, 905 (1962).

diamagnetic tris(formylacetonato)cobalt(III) chelate by means of nuclear magnetic resonance (NMR) spectrometry.

Preparation of fac and mer Tris(formylacetonato)cobalt(III) and -chromium(III) Chelates

Trivalent metal chelates of unsymmetrical β-diketone have two geometrical isomers as shown in Fig. 1. Formylacetone (1,3-butanedione) is one of the simple unsymmetrical β-diketones. Paramagnetic tris(formylacetonato)chromium(III) chelate was first prepared by Collman and Kittleman[7] and they assumed fac and mer isomers from the chromatographic behavior[2] and formation of the mer isomer predominates.[2]

In the present work, preparation of tris(formylacetonato)chromium(III) was improved by using chromium(III) chloride hexahydrate in place of its anhydrous salt. When the crude fac and mer isomers of the chromium(III) chelate were separated by means of column chromatography, the mer isomer of tris(formylacetonato)chromium(III) was eluted first as violet needles, mp 169.5—170°, and the fac isomer as violet prisms, mp 164.5—166.5°. The amount of mer isomer formed was three times more than that of fac isomers. Preparation of tris(formylacetonato)cobalt(III), according to the modified procedure for tris(acetylacetonato)cobalt(III), was examined. After oxidation of cobalt(II) nitrate with hydrogen peroxide to the cobalt(III) salt, it reacted with sodium formylacetonate to give a mixture of fac and mer tris(formylacetonato)cobalt(III) chelates. Column chromatographic separation of the above cobalt(III) chelate on alumina, eluted with benzene–ethyl acetate (10:1) afforded the mer isomer as green needles, mp 165° (decomp.) before the fac isomer as green prisms, mp 160° (decomp.). Three times more mer isomer was formed than fac isomer. The stereoformulae of the fac and mer isomers of tris(formylacetonato)cobalt(III) were assumed from a similar chromatographic behavior for the corresponding chromium(III) analogs, and were also confirmed by NMR spectrometry which will be described later.

Electrophilic Substitution Reactions

Halogenation (chlorination, bromination, and iodination) of fac and mer tris(formylacetonato)chromium(III) and cobalt(III) chelates with N-halosuccinimide in carbon tetrachloride was carried out by a method similar to that used for quasi-aromatic acetylacetonate-

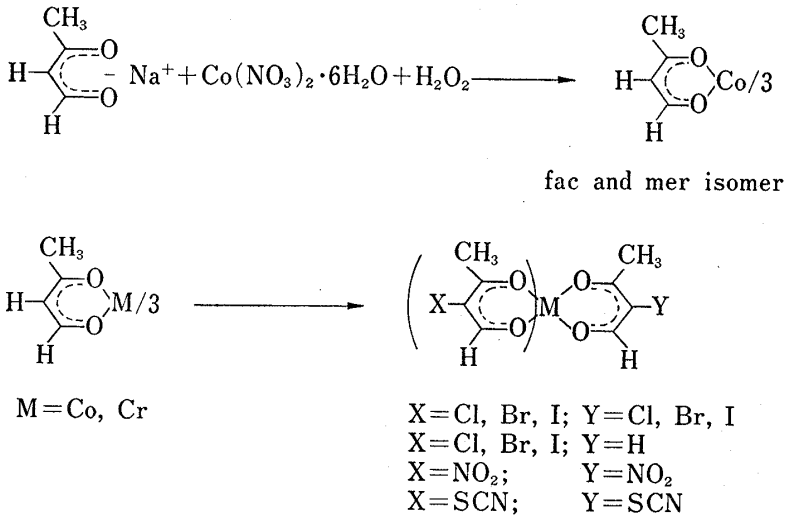


Chart 1

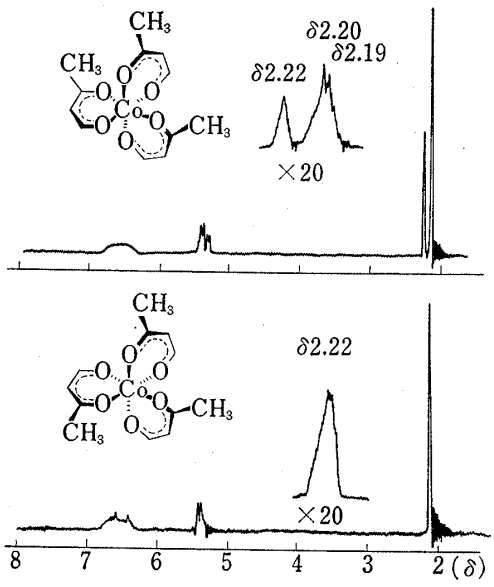


Fig. 2. NMR Spectra of mer and fac Tris(1,3-butanedionato)cobalt(III) Chelates

metal chelates.[11] A halogen atom was introduced into the central atom in the ring. These halogenated derivatives are listed in the experimental section.

Collman, *et al.*[12] have previously reported the thiocyanation of chromium(III) acetylacetonate. Thiocyanation of fac and mer tris(formylacetonato)chromium(III) and -cobalt(III) chelates with thiocyanogen in dichloroethane solution gave trithiocyanate derivatives.

NMR Spectra of fac and mer Tris(formylacetonato)cobalt(III)

NMR spectra of the diamagnetic fac and mer tris(formylacetonato)cobalt(III) are shown in Fig. 2. In the spectrum of the mer isomer (A), which has no symmetrical element, the methyl proton resonance lines appeared at δ 2.20 and 2.22, but the fac isomer (B) has C-3 symmetry, and only one resonance line appeared at δ 2.15 for methyl protons. The signal at δ 5.50 was assigned to C-2 H because its chemical shift is similar to the chemical shift of C-3 H of the acetylacetonate metal chelates. These signals disappear in many electrophilic substitution reactions. In the mer isomer, double doublet signals were observed around at δ 5.5, whereas in the fac isomer doublet signals appeared at δ 5.5, and in both isomers a broad signal were observed around at δ 6.50. The broadness and the lower field chemical shift are evidence for the assignment of this signal to C-1 H resonance line. This broad line at around δ 6.50 does not disappear by many substitution reactions. Electrophilic attack of acetylacetonate and other 1,3-disubstituted β-diketonate metal chelates can only take place at the central C-3 carbon atom, but formylacetonate metal chelates have two types of C–H group, and the central C-2 H is only substituted by electrophilic reactions. Halogenation causes linear correlation between a magnitude of the chemical shift and the masses of hydrogen atom as shown in Fig. 3. The chemical shifts of fac and mer tris(formylacetonato)cobalt(III) and their substituted derivatives are listed in Table I.

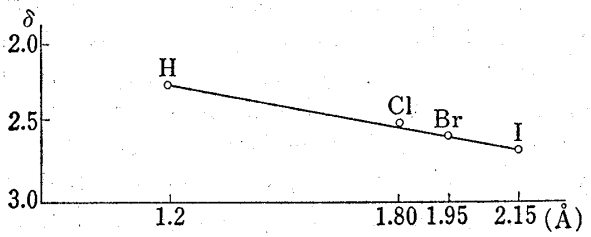


Fig. 3. Correlation of Methyl Proton Chemical Shift and Van der Waals Radii of Substituent

TABLE I. Chemical Shift of mer and fac Isomers of $Co(X\text{-foac})_3$ (in $CDCl_3$, ppm, TMS as Internal Reference)

X	compound	CH_3	C_2-H	C_1-H
H	mer	2.20 2.22	5.45(q)	6.55(b)
H	fac	2.22	5.42(d)	6.50(b)
Cl	mer	2.45 2.47	—	6.87(b)
Cl	fac	2.48	—	6.91(b)
Br	mer	2.52 2.53	—	7.00(b)
Br	fac	2.54	—	6.92(b)
I	mer	2.63 2.64	—	7.12(b)
I	fac	2.64	—	7.13(b)
NO_2	mer	2.80 2.92	—	8.20(b)
NO_2	fac	2.91	—	8.33(b)
SCN	mer	2.72 2.74	—	7.30(b)
SCN	fac	2.74	—	7.40(b)

(d) doublet, (q) quartet, (b) broad

Infrared (IR) Spectra

No difference was found between fac and mer isomers in their IR spectra in the range of 4000—650 cm^{-1}, nor was there any difference in their substituted derivatives. In this region,

11) *a*) J.P. Collman, R.A. Moss, H. Maltz, and C.X. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961); *b*) R.W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).
12) J.P. Collman, R.L. Marshall, W.L. Young, III, and C.T. Sears, Jr., *J. Org. Chem.*, **28**, 1449 (1963).

the difference between chromium(III) and cobalt(III) chelates was only 2—3 cm^{-1}. Two absorption bands of strong intensity were observed in the 1600—1500 cm^{-1} region, these two bands were similar to those in the acetylacetonate metal chelates, and they have been identified as C=C and C=O complex bands.[13] Two strong bands at 1410 and 1330 cm^{-1}, and medium band at 1224 cm^{-1} were observed. The band at 1190 cm^{-1}, which had been assigned for C–H stretching band in acetylacetonate metal chelates,[11] was absent, and in its stead a weak band appeared at 1123 cm^{-1}. In the IR spectra of substituted derivatives, two absorption bands of strong intensity in 1600—1500 cm^{-1} region become one absorption band which appeared near the higher frequencies band of unsubstituted chelate. The absorption bands at 1224 and 1123 cm^{-1} disappeared, and a new medium band appeared near 1190 cm^{-1}.

In the far IR region in 650—200 cm^{-1} of the fac and mer isomers, absorption bands were somewhat at variance by the central metal ion. In tris(formylacetonato)chromium(III) chelate, the band at 472 cm^{-1} band was more intense than that at 457 cm^{-1} for the mer isomer, and two medium bands were observed at 397 and 361 cm^{-1}, but a medium band appeared at 373 cm^{-1} only for the mer isomer.

In substituted derivatives, there was a band at around 500 cm^{-1} and it appeared at a higher frequency for the mer isomer than for the fac isomer.

Tris(formylacetonato)cobalt(III) chelate showed a similar IR absorption spectrum as that of chromium(III) chelate. There was an absorption band of strong intensity at 492 cm^{-1} in the mer isomer, but at 476 cm^{-1} band in the fac isomer. There were no absorption bands in the 400—350 cm^{-1} region, but a broad weak band was observed at 403 cm^{-1}, both in the mer and fac isomers. Main IR bands are listed in Table II.

Table II. Infrared Spectral Data of mer and facTris(1,3-butanedionato)cobalt(III) and -chromium (III) Chelate and Their C_2 Substituted Derivatives

Metal	Substituent	Compound	ν cm^{-1} (intensity)			
Co	H	mer	1580(s), 1502(s), 1405(s),	1330(s), 1224(m),	1123(w),	492(m)
Co	H	fac	1580(s), 1502(s), 1407(s),	1330(s), 1224(m),	1123(w),	476(m)
Co	Cl	mer	1580(s)	1324(s)	1201(w)	486(m)
Co	Cl	fac	1580(s)	1324(s)	1201(w)	484(m)
Co	Br	mer	1565(s)	1323(s)	1192(w)	502(s)
Co	Br	fac	1565(s)	1325(s)	1193(w)	482(s)
Co	I	mer	1560(s)	1330(s)	1190(w)	508(s)
Co	I	fac	1555(s)	1320(s)	1190(w)	485(s)
Co	NO_2	mer	1583(s), 1512(s)	1316(s)	1195(s)	512(m)
Co	NO_2	fac	1583(s), 1518(s)	1316(s)	1195(m)	495(m)
Co	SCN	mer	2336(m), 1572(s)		1190(w)	502(m)
Co	SCN	fac	2336(m), 1572(s)		1190(w)	483(m)
Cr	H	mer	1580(s), 1499(s)	1340(s), 1228(m),	1125(w),	478(s)
Cr	H	fac	1580(s), 1498(s)	1340(s), 1228(m),	1124(w),	461(s)
Cr	Cl	mer	1583(s)	1315(s)	1200(w)	466(s)
Cr	Cl	fac	1580(s)	1315(s)	1200(w)	456(s)
Cr	Br	mer	1573(s)	1323(s)	1197(w)	478(m)
Cr	Br	fac	1570(s)	1318(s)	1195(w)	462(m)
Cr	I	mer	1560(s)	1321(s)	1190(w)	485(m)
Cr	I	fac	1559(s)	1322(s)	1190(w)	462(m)
Cr	NO_2	mer	1590(s), 1525(s)	1320(s)	1195(w)	492(m)
Cr	NO_2	fac	1590(s), 1525(s)	1320(s)	1194(w)	478(m)
Cr	NCS	mer	2338(m), 1575(s)	1337(s)	1190(vw)	485(m)
Cr	NCS	fac	2338(m), 1575(s)	1337(s)	1190(vw)	467(m)

s: strong; m: medium; w: weak; vw: very weak

13) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).

Ultraviolet Absorption Spectra

Ultraviolet (UV) absorption spectral data are listed in Table III. fac and mer isomers of tris(formylacetonato)cobalt(III) and -chromium(III) gave nearly identical spectra in the 220—360 nm region. Halogenated, nitrated, and thiocyanated derivatives showed maximum shifts to a longer wave length region. UV spectra of tris(formylacetonato)chromium(III) and cobalt(III) chelates were measured in methanol solution, and those of other substituted derivatives, which were less soluble in ethanol, were measured in chloroform solution.

Table III. Ultraviolet Absorption Data of mer and fac Tris(1,3-butanedionato)cobalt(III) and -chromium(III) Chelate and Their G-2 Substituted Derivatives

Metal	Substituent	Compound	λ_{max} nm (ε)
Co(III)	H	mer	228(56500), 257(48600), 336(10200)
Co(III)	H	fac	229(51600), 257(46800), 336(11600)
Co(III)	Cl	mer	259(27000), 354(6100)
Co(III)	Cl	fac	258(31600), 353(7640)
Co(III)	Br	mer	257(30800), 356(7000)
Co(III)	Br	fac	257(32600), 356(7700)
Co(III)	I	mer	256(36200), 360(6740)
Co(III)	I	fac	256(34700), 360(6710)
Co(III)	NO_2	mer	281(39800)
Co(III)	NO_2	fac	281(36700)
Co(III)	SCN	mer	306(shoulder)
Co(III)	SCN	fac	306(shoulder)
Cr(III)	H	mer	261(10000), 275(9400), 304(7850), 338(12800)
Cr(III)	H	fac	261(9800), 275(9200), 304(7600), 338(12700)
Cr(III)	Br	mer	280(8350), 326(shoulder)
Cr(III)	Br	fac	279(8650), 326(shoulder)
Cr(III)	NO_2	mer	284(30000), 324(16300)
Cr(III)	NO_2	fac	283(30500), 323(16700)
Cr(III)	SCN	mer	336(12200)
Cr(III)	SCN	fac	336(9740)

Experimental

All melting points were determined on Yamato Melting Point Apparatus and are uncorrected. NMR spectra were measured with a Jeol JNM-4H-100 spectrometer at 100 MHz, using tetramethylsilane as internal reference. IR spectra were measure with a Hitachi Perkin-Elmer 225 grating spectophotometer and UV spectra were measured with a Hitachi EPU-2 spectrophotometer.

Sodium Salt of Formylacetone——It was synthesized by the Claisen condensation reaction according to the procedure reported by Collman and Kittleman.[7] A mixture of ethyl formate (55.5 g) acetone (21 g) and ether (200 ml) was added dropwised with vigorous stirring to an ether suspension of NaH (8.2 g) at 0°. After stirring for 6 hr at 5°, it was allowed to stand for 12 hr at room temperature. The yellow precipitate formed was collected, washed with ether, and then dried in vacuum at room temperature. The Na salt of formylacetone was obtained (35 g; 93% yield).

Fac and mer Isomers of Tris(formylacetonato)cobalt(III)——A solution of $Co(NO_2)_2 \cdot 6H_2O$ (20 g) and 30% H_2O_2 (12 ml) in EtOH (50 ml) was added dropwise to a slurry of anhyd. sodium formylacetonate (22 g), synthesized as above and used without purification, in EtOH (100 ml) at 0° for 30 min. After stirring 1 hr at 0°, it was stirred for an additional 8 hr at room temperature. H_2O (300 ml) was added to the reaction mixture and it was then extracted with benzene. The benzene layer was washed with H_2O and dried. Evaporation of the solvent afforded a crude mixture of fac and mer isomer, which were purified by dry column chromatography on Al_2O_3. Mixture of benzene–ethyl acetate (10: 1) was used as the eluting solvent. Mer isomer was eluted before fac isomer. Recrystallization of mer isomer from EtOH gave green needles (2.78 g; 13% yield), mp 165° (decomp.). *Anal.* Calcd. for $C_{12}H_{15}O_6Co$: C, 46.85; H, 4.77. Found: C, 46.29; H, 4.96.

Recrystallization of fac isomer from EtOH gave green prisms (0.86 g; 4% yield), mp 160° (decomp.). *Anal.* Calcd. for $C_{12}H_{15}O_6Co$: C, 46.85; H, 4.77. Found: C, 46.37; H, 5.03.

fac and mer Isomers of Tris(formylacetonato)chromium(III)——According to the modified procedure described by Collman, *et al.*,[7b] a mixture of $CrCl_3 \cdot 6H_2O$ (0.5 g) and Zn dust (0.5 g) in dimethylformamide (DMF) (5 ml) was stirred at room temperature. After stirring for 15 min, DMF (15 ml) was added and the mixture was cooled to 0°. A mixture of $CrCl_3 \cdot 6H_2O$ (8.3 g), Zn dust (0.5 g), and anhyd. sodium formylacetonate (10.9 g) was added to the above mixture, and stirred vigoroursly for 1.5 hr. The reaction mixture was poured into H_2O (100 ml), and extracted with benzene. The organic layer was dried and evaporated. A crude mixture of fac and mer isomers of tris (formylacetonato)chromium(III) was obtained (4.85 g; 57% yield).

Separation of the isomeric mixture of the chromium(III) chelates by column chromatography by elution with benzene–EtOAc (10: 1) gave the mer isomer before the fac isomer. Recrystallization of the mer isomer from EtOH gave violet needles (2.8 g; 37% yield), mp 169.5—170° (reported,[7b] mp 169—169.5°). Recrystallization of the fac isomer from EtOH gave violet prisms (1.2 g; 12% yield), mp 164.5—165.5° (reported,[7b] mp 165—166°).

Chlorination of fac and mer Tris(formylacetonato)cobalt(III) and -chromium(III) Chelates——General Procedure: Metal(III) formylacetonate (0.6 mmol) and N-chlorosuccinimide (4 mmol) were stirred in a mixture of CCl_4 (6 ml) and AcOH (6 ml) at room temperature. After 1 hr it was extracted with 10% Na_2CO_3 solution. The organic layer was washed with H_2O and dried. The crude product was chromatographed on silica gel using benzene–hexane mixture as an eluting solvent. Three bands were observed. Fraction 1 was the predominant part which gave trichlorinated chelate. Fraction 2 gave the dichlorinated compound, and a small amount of the third band gave the monochlorinated compound. Recrystallizations of these chlorinated compounds were performed by using CH_2Cl_2–hexane mixture as a solvent. The chlorinated tris(formylacetonato)cobalt(III) [Co(Cl-foac)$_x$] and -chromium(III) [Cr(Cl-foac)$_x$] chelates obtained are listed below. mer Co(Cl-foac)$_3$: Green needles, mp 143° (decomp.), 30% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Cl_3Co$: C, 34.49; H, 2.87. Found: C, 34.25; H, 2.93. fac Co(Cl-foac)$_3$: Green prisms, mp 135° (decomp.), 14.5% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Cl_3Co$: 34.49; H, 2.87. Found: C, 34.39; H, 2.60. mer Co(Cl-foac)$_2$ (foac): Green plates, mp 139° (decomp.), 12% yield. *Anal.* Calcd. for $C_{12}H_{13}O_6Cl_2Co$: C, 37.60; H, 3.39. Found: C, 37.54; H, 3.62. fac Co(Cl-foac)$_2$ (foac): Green prisms, mp 127.5—129°, 17% yield. *Anal.* Calcd. for $C_{12}H_{13}O_6Cl_2Co$: C, 37.60; H, 3.39. Found: C, 37.81; H, 3.67. mer Cr(Cl-foac)$_3$: Purple needles, mp 198—199°, 46% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Cl_3Cr$: C, 35.08; H, 2.92. Found: C, 35.30; H, 2.73. fac Cr(Cl-(foac)$_3$: Purple plates, mp 174—175°, 32% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Cl_3Cr$: C, 35.08; H, 2.92. Found: C, 34.79; H, 3.03.

Bromination of fac and mer Tris(formylacetonato)cobalt(III) and -chromium(III) Chelate——General Procedure: A solution of metal (III) formylacetonate (1.5 mmol) and N-bromosuccinimide (4.8 mmol) in $CHCl_3$ (20 ml) was refluxed for 5 min. The reaction mixture was washed with 10% Na_2CO_3 and H_2O. The $CHCl_3$ layer was dried, and concentrated to 7 ml. EtOH (3 ml) was added to the $CHCl_3$ solution and the tribrominated complexes crystallized. These compounds were recrystallized from CH_2Cl_2 and EtOH mixture. The brominated tris(formylacetonato)cobalt(III) [Co(Br-foac)$_x$] and -chromium(III) [Cr(Br-foac)$_x$] obtained are listed below. mer Co(Br-foac)$_3$: Green needles, mp 140.5° (decomp.), 82% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Br_3Co$: C, 26.13; H, 2.18. Found: C, 26.42; H, 2.25. fac Co(Br-foac)$_3$: Green prisms, mp 137° (decomp.), 83% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Br_3Co$: C, 26.13; H, 2.18. Found: C, 26.24; H, 2.07. mer Cr(Br-foac)$_3$: Brown needles, mp 179—181°, 75% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Br_3Cr$: C, 26.47; H, 2.21. Found: C, 26.70; H, 2.16. fac Cr(Br-foac)$_3$: Brown prisms, mp 167—168°, 79% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6Br_3Cr$: C, 26.47; H, 2.21. Found: C, 26.75; H, 2.15.

Iodination of fac and mer Tris(formylacetonato)cobalt(III) and -chromium(III) Chelate——General Procedure: A solution of metal (III) formylacetonate (0.13 mmol) and N-iodosuccinimide (1 mmol) in $CHCl_3$ were stirred at room temperature. After 30 min, the $CHCl_3$ layer was washed with 10% Na_2CO_3 and H_2O, the solvent was evaporated under a reduced pressure, and the residue was chromatographed on silica gel. Triiodinated compounds were obtained and recrystallized from a mixture of CH_2Cl_2 and EtOH. The iodinated tris(formylacetonato)cobalt(III) [Co(I-foac)$_x$] and -chromium(III) [Cr(I-foac)$_x$] chelates obtained are listed below. mer Co(I-foac)$_3$: Dark green prisms, mp 149° (decomp.), 51% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6I_3Co$: C, 20.81; H, 1.73. Found: C, 20.93; H, 1.68. fac Co(I-foac)$_3$: Dark green plates, mp 155° (decomp.), 50% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6I_3C_0$: C, 20.81; H, 1.73. Found: C, 21.08; H, 1.75. mer Cr(I-foac)$_3$: Brown needles, mp 168—169°, 40% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6I_3Cr$: C, 21.02; H, 1.75. Found: C, 20.91; H, 2.08. fac Cr(I-foac)$_3$: Brown needles, mp 173—174°, 35% yield. *Anal.* Calcd. for $C_{12}H_{12}O_6I_3Cr$: C, 21.02; H, 1.75. Found: C, 21.64; H, 1.77.

Nitration of fac and mer Tris(formylacetonato)cobalt(III) and -chromium(III) Chelate——General Procedure: A powder of $Cu(NO_3)_2$ (10 mmol) was added, with stirring, to AcOH at 0°, and a blue slurry was formed. To this slurry metal (III) formylacetonate (1 mmol) was added and the mixture was stirred for 40 min at 0°. This cold reaction mixture was poured into H_2O (100 ml) which contained KOAc (10 g). The mixture was stirred for 3 hr and extracted with benzene. The benzene layer was washed with 10% Na_2CO_3 and H_2O, and dried. Removal of the solvent left crude nitrated compounds. Recrystallization of the crude nitrated compound from CH_2Cl_2–EtOH mixture gave the trinitrated compound. The nitrated tris(formylacetonato)cobalt (III) [Co(NO_2-foac)$_x$] and -chromium(III) [Cr(NO_2-foac)$_x$] chelates obtained are listed below. mer Co(NO_2-foac)$_3$: Dark green prisms, mp 177° (decomp.), 42% yield, *Anal.* Calcd. for $C_{12}H_{12}O_{12}N_3Co$: C, 32.07; H, 2.67; N, 9.35. Found: C, 32.26; H, 2.84; N, 9.11. fac Co(NO_2-foac)$_3$: Dark green needles, mp 166° (decomp.), 31%

yield. *Anal.* Calcd. for $C_{12}H_{12}O_{12}N_3Co$: 32.07; H, 2.67; N, 9.35. Found: C, 32.31; H, 2.83; N, 9.12. mer $Cr(NO_2\text{-foac})_3$: Purple needles, mp 204° (decomp.), 45% yield. *Anal.* Calcd. for $C_{12}H_{12}O_{12}N_3Cr$: C, 32.58; H, 2.71; N, 9.50. Found: C, 32.33; H, 2.96; N, 9.66. fac $Cr(NO_2\text{-foac})_3$: Purple plates, mp 185° (decomp.), 40% yield. *Anal.* Calcd. for $C_{12}H_{12}O_{12}N_3Cr$: C, 32.58; H, 2.71; N, 9.50. Found: C, 32.68; H, 2.95; N, 9.75.

Thiocyanation of fac and mer Tris(formylacetonato)cobalt(III) and -chromium(III) Chelate——General Procedure: $Pb(SCN)_2$ (1.85 mmol) and Br_2 (1.87 mmol) are allowed to react in $(CH_2Cl)_2$ (20 ml) at −15°, by the method of Collman, *et al.*[13] The resulting $(SCN)_2$ solution of $(CH_2Cl)_2$ was used for the thiocyanation reaction. To $(CH_2Cl)_2$ (20 ml) solution of metal (III) formylacetonate (0.65 mmol), $(CH_2Cl)_2$ solution of $(SCN)_2$, was added dropwise with stirring. The mixture was stirred at room temperature. The reaction mixture was washed with 10% Na_2CO_3 and H_2O, $(CH_2Cl)_2$ layer was dried, concentrated to 10 ml under a reduced pressure, and EtOH (5 ml) was added. The thiocyanated compound crystallized from its solutions and then was recrystallized from benzene. The thiocyanated tris(formylacetonato)cobalt(III) [$Co(SCN)_x$] and -chromium(III) [$Cr(SCN\text{-foac})_x$] chelates are listed blow. mer $Co(SCN\text{-foac})_3$: Green needles, mp 155° (decomp.), 76% yield. *Anal.* Calcd. for $C_{15}H_{12}O_6N_3S_3Co$: C, 37.11; H, 2.47. Found: C, 37.10; H, 2.47. fac $Co(SCN\text{-foac})_3$: Green plates, mp 144° (decomp.), 74% yield. *Anal.* Calcd. for $C_{15}H_{12}O_6N_3S_3Co$: C, 37.11; H, 2.47. Found: C, 37.14; H, 2.44. mer $Cr(SCN\text{-foac})_3$: Purple needles, mp 208° (decomp.), 60% yield. *Anal.* Calcd. for $C_{15}H_{12}O_6N_3S_3Cr$: C, 37.66; H, 2.51. Found: C, 37.60; H, 2.61. fac $Cr(SCN\text{-foac})_3$: Purple plates, mp 199° (decomp.), 89% yield. *Anal.* Calcd. for $C_{15}H_{12}O_6N_3S_3Cr$: C, 37.66; H, 2.51. Found: C, 37.38; H, 2.34.

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