

for 8 min. in a sealed evacuated tube. The contents were dissolved in methylene chloride and chromatographed on alumina.

The methylene chloride eluate gave a fraction (15 mg.) with ultraviolet (λ_{\max} 330; 2-pyridylindole), and the 1% methanol in methylene chloride eluate afforded a sempervirine-like substance (2 mg.), $\lambda_{\max}^{\text{neutral}}$ 385, 340, 286; $\lambda_{\max}^{\text{base}}$ 354, 286.

Emde Reduction of Phenolic O-Methyluntrabrine Chloride.—The crude methyl ether (600 mg.) was dissolved in 80% ethanol (40 ml.), added to prereduced platinum oxide (200 mg.) in alcohol (25 ml.), and stirred in a hydrogen atmosphere for 18 hr. After removal of the catalyst and evaporation, the residue (600 mg.) was shaken with dilute potassium hydroxide and methylene chloride, yielding the crude Emde base (290 mg.) to the organic phase. Chromatography on basic alumina gave from the benzene-ether (2:1) eluate the Emde base (230 mg.) which gave crystals (150 mg.) from ether-hexane, m.p. 107–108°.

Anal. Calcd. for $C_{21}H_{22}N_2O_2$: C, 73.21; H, 9.36; N, 8.13. Found: C, 73.24; H, 9.50; N, 8.06.

Partially Characterized Bases.—All the following bases described contained halide as determined by precipitation with silver nitrate, and the ultraviolet absorption spectra are recorded as λ ($\epsilon_{1\text{cm}}^{1\%}$).

Alkaloid-F.—It was recrystallized from *t*-butyl alcohol-water (20:1), m.p. 242–243°, λ_{\max} 222 (860), 275 (230); λ_{sh} 283 (200), 292 (150); λ_{\min} 246 (75); ν_{\max} 3460, 3410, 1737, 1211 and 750 cm^{-1} .

Anal. Found: C, 64.70; H, 6.81.

Alkaloid-H.—This yellow compound crystallized from ethanol-ethyl acetate, m.p. 300°; $\lambda_{\max}^{\text{EtOH or acid}}$ 312–315 (420), 403

(630); λ_{sh} 245 (341); λ_{\min} 274 (126), 345 (189); $\lambda_{\max}^{\text{base}}$ 227–232 (590), 323 (370), 418–423 (460); λ_{\min} 283 (150), 360 (240); ν_{\max} 3535, 3175, 1640, 1573, 1203, 1062, 853 and 810 cm^{-1} .

Alkaloid-I.—Crystallized from ethanol, it had m.p. 278–280°, λ_{\max} 219 (1200), 273 (240), 279 (250), 289 (210); λ_{\min} 240 (60), 276 (240), 286 (180) with no change in base; ν_{\max} 3300, 3150, 750 cm^{-1} .

Alkaloid-J.—A sample crystallized from ethanol had m.p. 291–293°, λ_{\max} 272 (230), 279 (230), 289 (200); λ_{\min} 240 (51), 276 (220), 286 (160) with no shift in acid or base; ν_{\max} 3437, 3149, 1631, 1245, 1050, 752 cm^{-1} .

Alkaloid-K.—It was obtained crystalline from ethanol, m.p. 207–208°; λ_{\max} 222 (840), 272 (150), 279 (150), 289 (120); λ_{\min} 253 (120), 277 (140), 287 (110).

Alkaloid-N.—It was crystallized from ethanol, m.p. 263–266°, λ_{\max} 266 (210), 270 (220), 277 (210), 280 (160); λ_{sh} 280 (210), 310 (20); λ_{\min} 240 (56), 274 (210), 285 (140), with no shift in acid or base; ν_{\max} 3330, 3140, 1308, 1226, 1110, 1076, 1060, 1048, 903, 758, 740 cm^{-1} .

Acknowledgment.—We wish to express our appreciation to Dr. E. Schlittler for his constant interest and encouragement, to Mr. L. Dorfman and his staff for the analytical and spectral work, and to Dr. M. J. Allen and his staff for the potentiometric microtitrations.

Reactions of Metal Chelates. V.^{1,2} Substitution of Metal Acetylacetonates with Friedel-Crafts Acylating Reagents and Sulfur Electrophiles

JAMES P. COLLMAN, ROGER L. MARSHALL,³ WILLIAM L. YOUNG, III,³ AND CURTIS T. SEARS, JR.

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina

Received October 15, 1962

The inert trisacetylacetonates of chromium(III), cobalt(III), and rhodium(III) have been acylated with acid chlorides in the presence of Lewis acids. Mono-, di-, and triacyl chelates have been characterized. Thiocyanogen, sulfur dichloride, and arenesulfonyl chlorides substitute the chelate rings without catalysis. The reactions of a chelate sulfonyl chloride have been studied.

During a general study of reactions of coordinated ligands we have sought to demonstrate quasi-aromatic chemical properties of metal acetylacetonates.^{1–10} Electrophilic substitution at the central carbon of these chelate rings has been illustrated with a variety of reagents. Through such reactions iodo,⁵ bromo,^{5,11} chloro,⁵ thiocyanato,^{1,12} nitro,⁴ acetyl,⁴ formyl,⁸ chloromethyl,¹³ and aminomethyl¹³ groups have been sub-

stituted directly into the relatively inert trisacetylacetonates of rhodium(III), chromium(III), and cobalt(III).

Since the Friedel and Crafts synthesis of aryl ketones is one of the best-known classical aromatic reactions it was of interest to see if this method could be applied to the acylation of stable metal chelate rings. Furthermore, in certain cases it seemed possible to prepare the anticipated products independently by chelation of triacylamethanes.

The first attempted acylations of chromium(III) acetylacetonate failed, largely because of acid-catalyzed degradation of the chelate ring. Although chromium acetylacetonate is fairly stable in the presence of aluminum chloride, treatment of this chelate with a mixture of aluminum chloride and acetyl chloride led to extensive decomposition. Less powerful acids such as stannic chloride and zinc chloride were not effective in catalyzing this reaction. A mixture of pyridine and acetic anhydride or acetyl chloride also failed to react with this chelate. However, the acetylation was successful when chromium acetylacetonate was allowed to react with acetic anhydride and boron trifluoride etherate in methylene chloride. Under these conditions a complex mixture of acetylated chelates was formed. Careful recrystallization afforded a sample which seemed to be pure triacetylated chelate A.⁴

(1) Previous paper, J. P. Collman, R. P. Blair, R. L. Marshall, and L. Slade, *Inorg. Chem.*, in press.

(2) (a) This research was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society and by the Office of Army Research grant number DA-ORD-[D]-31124-G185. Grateful acknowledgment is made to the donors of these funds. (b) Part of this work was abstracted from the Ph.D. dissertation of R. L. Marshall, University of North Carolina, 1962.

(3) Petroleum Research Fund Fellow.

(4) J. P. Collman, R. A. Moss, S. D. Goldby, and W. S. Trahanovsky, *Chem. Ind. (London)*, 1213 (1960).

(5) J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

(6) J. P. Collman and E. T. Kittleman, *ibid.*, **83**, 3529 (1961).

(7) J. P. Collman, R. P. Blair, A. L. Slade, and R. L. Marshall, *Chem. Ind. (London)*, 141 (1961).

(8) J. P. Collman, R. L. Marshall, W. L. Young, III, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).

(9) J. P. Collman and E. T. Kittleman, *ibid.*, **1**, 499 (1962).

(10) J. P. Collman, R. L. Marshall, and W. L. Young, III, *Chem. Ind. (London)*, 1380 (1962).

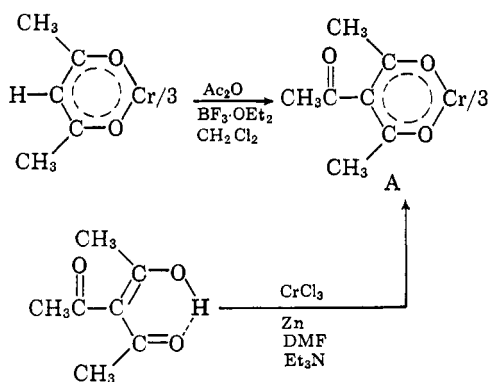
(11) R. W. Klüber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

(12) R. W. Klüber, *ibid.*, **83**, 3030 (1961).

(13) J. P. Collman, R. L. Marshall, and R. H. Barker, unpublished results.

Later experiments showed that this sample was contaminated with mono- and diacetylated chromium chelates.

Another apparently pure triacetylated chromium chelate was prepared by treating chromium(III) acetate hydrate with pure triacetylmethane in hot dimethylacetamide. This chelate and the purified Friedel-Crafts product had nearly identical infrared spectra and melting points. However, it was later found that hydrolysis of the ligand during the chelation reaction gave rise to an impure product. Later, when a completely nonaqueous chelation technique had been developed,^{6,9} an authentic sample of the pure triacetylated chelate A was prepared from anhydrous chromium(III) chloride, zinc dust, dimethylformamide, and triethylamine. The pure triacetylated chelate A had a slightly different infrared spectrum than the Friedel-Crafts product. Careful chromatography of the Friedel-Crafts product then demonstrated that it was contaminated with partially acetylated chelates. Attempts to purify further the acetylation product and to isolate mono- and diacetylated chromium chelates were successful. Chromatography of this mixture under a variety of conditions did not effect a clean separation.



Dryden¹⁴ had reported earlier that infrared spectra of unsubstituted metal acetylacetonates exhibit a doublet at 1580 and 1520 cm^{-1} whereas 3-substituted acetylacetonates show only a singlet in this region (about 1560 cm^{-1}). A second band in the 1500–1600- cm^{-1} region in the spectrum of our Friedel-Crafts product was at first⁴ thought to be a violation of Dryden's rule, but the lower frequency band (1520 cm^{-1}) is now known to come from the mono- and diacetylated impurities. We have since found Dryden's rule to be valid for a large number of substituted metal acetylacetonates, and at this date are aware of no exception to this rule. Additional studies of the infrared spectra of mixed-ring metal acetylacetonates show that the vibrations of the three rings are independent of each other above 700 cm^{-1} .¹³

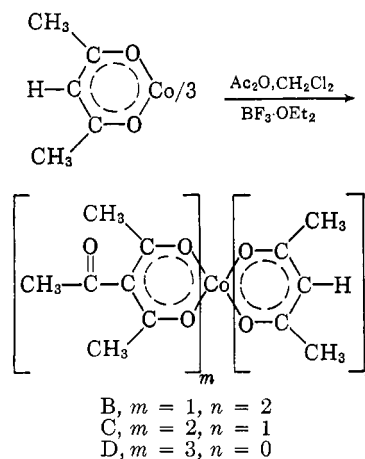
Another infrared band characteristic of unsubstituted acetylacetonate chelate rings is the weak (–H) in-plane bending mode at 1195 cm^{-1} . The absence of this band is good evidence of complete substitution of all chelate rings.^{15,16}

(14) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

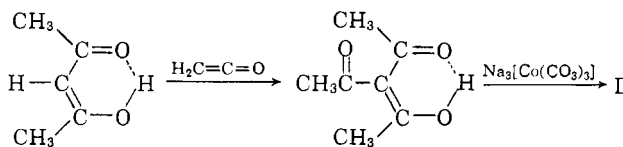
(15) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

(16) C. Djoidjevic, J. Lewis, and R. S. Nyholm, *Chem. Ind. (London)*, 122 (1959).

The Friedel-Crafts acetylation of cobalt(III) acetylacetonate gave more clear-cut results. Under the same conditions used for the chromium chelate, the cobalt compound yielded a mixture of four chelates which were readily separated by chromatography or alumina. Cobalt acetylacetonate and the mono-, di-, and triacetylated cobalt acetylacetonates (B, C, and D) were eluted from the column in that order.



The structures of the acetylated chelates were assigned on the basis of their infrared spectra, proton magnetic resonance spectra, and elemental analyses. Furthermore, the triacetylated chelate D was prepared independently by reaction of triacetylmethane with $\text{Na}_3[\text{Co}(\text{CO}_3)_3]$.



Comparison of the infrared spectra of the mono- and diacetylated cobalt chelates, B and C, showed only the anticipated differences in peak intensities. Each spectrum exhibited an uncoordinated ketone band at 1680 cm^{-1} , two strong peaks from 1500–1600 cm^{-1} , and a small band at 1195 cm^{-1} . By contrast, the spectrum of the pure triacetylated cobalt chelate D showed in addition to a strong band at 1680 cm^{-1} only a single peak in the 1500–1600- cm^{-1} region (1555 cm^{-1}) and no absorption near 1195 cm^{-1} . This spectrum was identical with that of the pure triacetylated chromium chelate A, prepared from the pure ligand under anhydrous conditions.

The nuclear magnetic resonance spectra of the diamagnetic mono-, di-, and triacetylated cobalt(III) chelates (B, C, and D) provided additional evidence for the assigned structures. A benzene solution of monoacetylated chelate, B, exhibited signals at 4.65, 7.91, 8.02, and 8.07 (doublet) τ with relative intensities of 2:6:3:12. Comparison with the parent acetylacetonate which has peaks at 8.10 and 4.65 τ in the ratio 6:1 showed that the 8.02 peak is caused by the uncoordinated acetyl group, whereas the doublet at 8.07 τ must be due to the methyl groups on the two unsubstituted chelate rings. The doublet is caused by the different chemical environment of the methyl groups on each of these rings arising from differential anisotropy of the neighboring rings.¹⁰ The peak at 7.91 is then

assigned to the methyl groups on the single acetylated chelate ring.

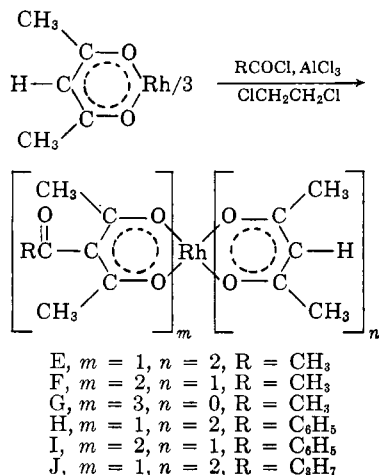
The spectrum of the diacetylated chelate, C, exhibited peaks at 4.40, 7.93 (doublet), 8.03, and 8.09 τ with intensities of 1:12:6:6, respectively. This is exactly the spectrum anticipated by comparison with the monoacetyl spectrum.

It is noteworthy that in chloroform these two spectra are the same except that the peak caused by the uncoordinated acetyl groups is the lowest field methyl signal. This might arise from some type of unsymmetrical solvation in one of the two solvents.

A solution of triacetylated chelate D in benzene exhibited two single peaks at 7.98 and 8.04 τ in the ratio of 2:1. These signals are easily assigned to the methyl groups on the chelate ring and the uncoordinated acetyl methyls.

Since Friedel-Crafts acylation of chromium and cobalt acetylacetonates under the same conditions affords mostly a triacetylated chromium chelate and little or no starting material, but very little triacetylated cobalt chelate and a relatively large amount of starting material, it would seem that chromium acetylacetonate is more reactive than cobalt acetylacetonate. Extensive degradation during the work-up and chromatography steps introduces some uncertainty into this argument. However, the acylation of rhodium acetylacetonate illustrates a clear-cut decrease in reactivity of this chelate ring.

Acetylation of rhodium(III) acetylacetonate proved to be much more difficult than that of the chromium(III) and cobalt(III) chelates. Under the same conditions which had been successful with the other metals (boron trifluoride-acetic anhydride for thirty-minute reaction at room temperature), rhodium(III) acetylacetonate failed to react. Treatment of the rhodium chelate with a large excess of this acetylating agent at 40° for five hours afforded a 19% yield of monoacetylated chelate E and 50% recovered starting material. Fortunately, this loss in reactivity of rhodium complexes parallels in increased resistance to acid degradation of these chelate rings. It was, therefore, possible to employ acid chlorides and aluminum chloride to acylate rhodium acetylacetonate. Under such conditions the mono- and diacetylated rhodium chelates, E and F, were obtained along with substantial quantities of recovered starting material. The mixtures were separated by chromatography and the diamagnetic mono-



and diacetylated chelates, E and F, identified by their n.m.r. spectra. Except for changes in chemical shift values the n.m.r. spectra of E and F exactly paralleled those of the analogous cobalt chelates B and C. The infrared spectra were also very similar.

The symmetrical triacetylated rhodium chelate A was not obtained from this reaction even under more vigorous conditions.

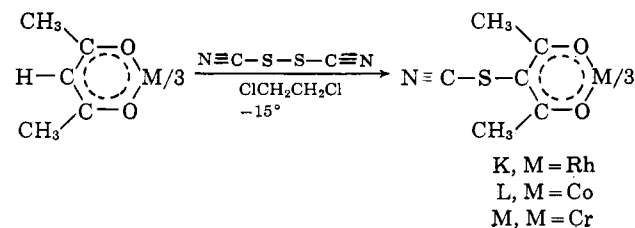
Attempted acetylation of rhodium acetylacetonate with acetic anhydride and polyphosphoric acid at room temperature was unsuccessful and reaction at 60° led to extensive decomposition of the chelate. It was noted that rhodium acetylacetonate is almost completely insoluble in polyphosphoric acid in contrast to cold concentrated sulfuric acid, in which the chelate can be dissolved without decomposition.

Treatment of chromium and cobalt acetylacetonates with other acylation reagents such as propionyl chloride, propionic anhydride, butyryl chloride, butyric anhydride, benzoyl chloride, and *p*-nitrobenzoyl chloride in the presence of aluminum chloride or boron trifluoride etherate resulted in extensive chelate degradation. Small amounts of acylated chelates isolated from these reactions were not tractable in our hands. It seems likely that increased bulk in the acylating agent sterically inhibits the Friedel-Crafts reaction so that competing ring degradation dominates. However, benzoyl chloride and butyryl chloride were used successfully to substitute rhodium(III) acetylacetonate in the same manner as the acylation of the rhodium chelate. Monobenzoylated, dibenzoylated, and monobutyrylated rhodium chelates, H, I, and J, were prepared in this way.

Friedel-Crafts reactions of rhodium acetylacetonate with diphenylcarbonyl chloride or ethyl chlorocarbonate in the presence of aluminum chloride were not successful. Attempted alkylations of rhodium acetylacetonate with benzyl chloride using boron trifluoride or aluminum chloride were also unsuccessful. Attempts to introduce allyl groups into chromium acetylacetonate failed.

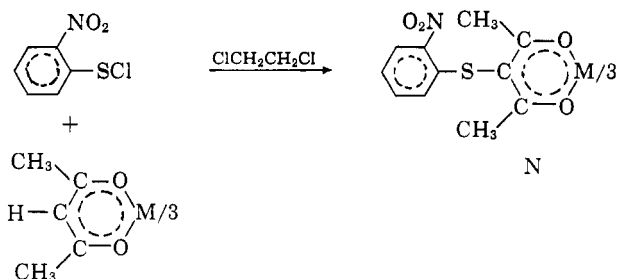
Kluiber¹² had reported earlier that sulfur electrophiles can be conveniently introduced into metal acetylacetonate rings. He described the preparation of the trissulfenyl chlorides and thiocyanates of cobalt(III) and chromium(III) acetylacetonates and the conversion of the chromium trissulfenyl chloride into the trithiocyanate derivative. The trifunctionality of the chromium sulfenyl chloride made a study of its reactions difficult.

We have also studied the introduction of sulfur electrophiles into metal acetylacetonate chelate rings. Thus treatments of rhodium(III), cobalt(III), and chromium(III) acetylacetonates with thiocyanogen gives high yields of the trithiocyanato chelates, K, L, and M. The diamagnetic rhodium and cobalt chelates show only one signal in their proton resonance spectra.

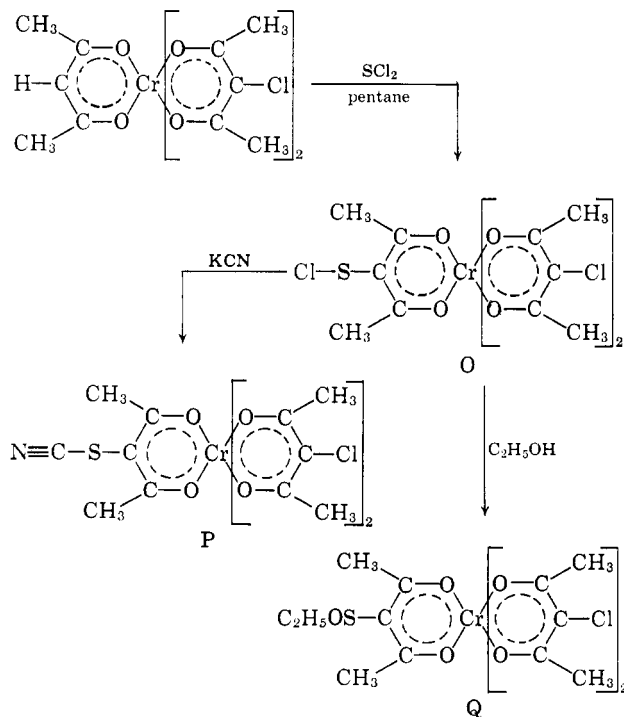


The infrared spectra of these chelates exhibit the anticipated nitrile peak at 2150 cm.^{-1} , a single peak in the $1500\text{--}1600\text{ cm.}^{-1}$ region (1555 cm.^{-1}) and no absorption at 1195 cm.^{-1} .

In a similar manner, arenesulfonyl chlorides were also found to substitute these chelate rings. No catalysis was required for these reactions. The aryl sulfide chelates N formed very stable 1:1 solvates with benzene, a common phenomenon in acetylacetonate chemistry.^{11,12,17} These sulfides were surprisingly resistant to oxidation and failed to react with 30% hydrogen peroxide. Attempts to prepare a chelate sulfone by treatment of rhodium(III) acetylacetonate with benzenesulfonyl chloride and aluminum chloride failed.



In order to avoid the complications attending the reactions of trissulfonyl chlorides it seemed desirable to prepare a mono-functional chelate sulfenyl chloride. This was done by treating dichlorinated chromium acetylacetonate with sulfur dichloride. The dichloro chlorosulfonyl chelate, O, was then allowed to react with cyanide ion to form the dichloro thiocyanato chelate P. In a similar way, reaction of the sulfenyl chloride with dry ethanol afforded ethyl sulfenate Q.



Use of partially halogenated metal acetylacetonates to introduce only one reactive functional group into chelate rings and, therefore, avoid the complications of

(17) J. F. Steinbeck and J. H. Burns, *J. Am. Chem. Soc.*, **80**, 1839 (1958).

trifunctionality deserves more comment. Although such a scheme is often necessary when one wishes to study the reactions of functional groups on chelate rings, unexpected complications may arise. The chloro groups in dichlorinated chromium acetylacetonate are subject to electrophilic cleavage from the chelate rings.¹⁸ Thus the mixed-ring chelates may be contaminated and require tedious purification. Use of blocking groups such as nitro which cannot be cleaved by electrophiles results in strong deactivation of the remaining unsubstituted ring.¹³ These problems currently are being studied in attempts to prepare linear polymers with a chelate ring backbone.

Experimental

All melting points were taken on a Kofler hot stage apparatus fitted with a polarizing microscope and are not corrected. Infrared spectra were recorded on a Perkin-Elmer Infracord fitted with sodium chloride optics and with a Perkin-Elmer Model 421 double grating spectrophotometer. Nuclear magnetic resonance spectra were measured with a Varian A-60 spectrometer at 60 Mc. using tetramethylsilane as an internal standard. Chemical shifts are reported in τ values and relative intensities are given in parentheses.

Acetylation of Tris(2,4-pentanedionato)rhodium(III) Using Acetic Anhydride and Boron Trifluoride.—To a stirred solution of rhodium(III) acetylacetonate¹⁹ (500 mg., 1.25 mmoles) in 100 ml. of pure methylene chloride was added 770 mg. (7.5 mmoles, 0.71 ml.) of freshly distilled acetic anhydride and 1.06 g. (7.5 mmoles, 0.91 ml.) of freshly distilled boron trifluoride etherate. The reaction mixture was heated at reflux under nitrogen for 5 hr.

The reaction mixture was poured into 250 ml. of water and ice containing enough sodium carbonate to neutralize the acidic by-products and stirred rapidly. The separated methylene chloride phase was extracted twice more with small portions of pure water, dried with calcium chloride, and evaporated to yield a light yellow, amorphous powder.

The crude mixture of chelates was dissolved in benzene and purified by chromatography using a 12×1 in. column of Merck alumina and benzene as an eluent. Three bands were collected over a long period. The first band, which was recovered from the solvent by flash evaporation on a rotating Rinco evaporator and then recrystallized from benzene-heptane, weighed 250 mg., m.p. $260\text{--}263^\circ$. An infrared spectrum and a mixture melting point showed this band to be recovered rhodium acetylacetonate, m.p. $260\text{--}261^\circ$; infrared (KBr), 1565, 1515, 1380, 1268, 1200, 1020, 935 cm.^{-1} ; ultraviolet (ethanol), λ_{max} 258 $\text{m}\mu$ (ϵ 9040), 317 (10,700); n.m.r. (CCl_4), 7.89 (6), 4.65 τ (1).

The second band afforded 105 mg. (19%) of pure (3-acetyl-2,4-pentanedionato)-bis(2,4-pentanedionato)rhodium(III), m.p. $252\text{--}253^\circ$; infrared (KBr), 1675, 1550, 1360, 1265, 1240, 1200, 1060, 1025, 935 cm.^{-1} ; ultraviolet (ethanol), λ_{max} 258 $\text{m}\mu$ (ϵ 12,750), 317 (10,200). The n.m.r. spectrum of this acetylated chelate was consistent with the assigned structure: (CHCl_3), 7.85 (6), 7.84 (6), 7.82 (6), 7.55 (3), 4.46 (2) τ ; (CCl_4), 7.89, 7.87, 7.85, 7.62, 4.63 τ .

Anal. Calcd. for $\text{C}_{17}\text{H}_{23}\text{O}_7\text{Rh}$: C, 46.17; H, 5.24. Found: C, 46.32; H, 5.32.

The third band afforded 12 mg. of an intractable chelate. An infrared spectrum of this substance indicated a more intense uncoordinated carbonyl absorption than possessed by the mono-acetylated product.

An acetylation reaction attempted at the boiling point of 1,2-dichloroethane (83°) for 1 hr. resulted in major decomposition of the chelate system and less than 10% recovery of starting material. No acetylated products were detected.

Acetylation of Tris(2,4-pentanedionato)rhodium(III) using Acetyl Chloride and Aluminum Chloride.—To a stirred suspension of 2.0 g. (15 mmoles) of sublimed, anhydrous aluminum chloride in 50 ml. of pure 1,2-dichloroethane under a nitrogen atmosphere was added 1.18 g. (15 mmoles, 1.07 ml.) of freshly distilled acetyl

(18) J. P. Collman, W. L. Young, III, R. H. Barker, and M. Yamada, 142nd National Meeting of American Chemical Society, Organic Division, Atlantic City, N. J., September, 1962; Abstract of papers, p. 40-Q.

(19) F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).

chloride. The resulting solution was cooled to -20° with a methanol-ice bath. To this mixture was added over a 10-min. period a solution of 1.00 g. (2.5 mmoles) of rhodium(III) acetylacetonate in 20 ml. of 1,2-dichloroethane. The solution was stirred for an additional 20 min. during which time the temperature rose to -15° . The reaction mixture was poured into 200 ml. of ice and water containing 15 ml. of concentrated hydrochloric acid and stirred vigorously. The aqueous layer became slightly yellow indicating some decomposition of the chelate system. The organic phase was extracted once more with water, dried over potassium carbonate, and filtered. The crude mixture of chelates was recovered by solvent evaporation.

Chromatographic purification of the crude product in the usual way afforded three chelates. The first band afforded 300 mg. of recovered rhodium acetylacetonate. The second band yielded 350 mg. of (3-acetyl-2,4-pentanediono)bis(2,4-pentanediono)rhodium(III), m.p. 252–254°. The identity of this monoacetylation product was confirmed by comparing its infrared spectrum and nuclear magnetic resonance spectrum with those of a sample of the material obtained previously.

The third band afforded 110 mg. of yellow crystals, m.p. 259–261 dec. The infrared spectrum, nuclear magnetic resonance spectrum, and elemental analysis indicate that this compound is (2,4-pentanediono)bis(3-acetyl-2,4-pentanediono)rhodium(III), the diacetylated chelate: infrared (KBr), 1700, 1685, 1560, 1520, 1420, 1350, 1275, 1240, 1200, 1055, 1020, 950, 925 cm^{-1} ; ultraviolet (ethanol), λ_{max} 259 $\text{m}\mu$ (ϵ 12,050), 317 (7360); n.m.r. (CHCl_3), 7.84 (6), 7.82 (6), 7.80 (6), 7.55 (6), 4.46 (1) τ ; (CCl_4), 7.86, 7.85, 7.80, 7.61, 4.63 τ .

Anal. Calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_8\text{Rh}$: C, 47.12; H, 5.20. Found: C, 47.33; H, 5.23.

This reaction afforded a 33% recovery of starting material, a 32% yield of monoacetylated product, and a 13% yield of diacetylated product. Repetition of this experiment using acetyl chloride in place of 1,2-dichloroethane as solvent yielded 40% starting material, 18% monoacetyl, and 10% diacetyl chelate.

Butyrylation of Tris(2,4-pentanediono)rhodium(III).—Treatment of 1.0 g. of rhodium acetylacetonate with 2.0 g. of aluminum chloride and 1.6 g. of *n*-butyryl chloride in 75 ml. of 1,2-dichloroethane under the same conditions described before yielded 67% recovered starting material and 100 mg. (8.5%) of (3-butyl-2,4-pentanediono)bis(2,4-pentanediono)rhodium(III); m.p. 185–187; infrared (KBr), 1680, 1560, 1520, 1370, 1270, 1205, 1020, and 930 cm^{-1} ; ultraviolet (ethanol), λ_{max} 260 $\text{m}\mu$ (ϵ 8020), 317 (6980); n.m.r. (CHCl_3), 9.05 triplet (3), multiplet 8.70–8.15 (2), 7.88 (6), 7.87 (6), 7.85 (6), 7.36 triplet (2), 4.47 (2) τ .

Anal. Calcd. for $\text{C}_{19}\text{H}_{27}\text{O}_7\text{Rh}$: C, 48.52; H, 5.79. Found: C, 48.43; H, 5.93.

An additional 10 mg. of an impure acylated chelate was obtained from the third band, but attempts to purify this crude product failed.

Benzoylation of Tris(2,4-pentanediono)rhodium(III).—Treatment of 1.0 g. of rhodium acetylacetonate with 2.00 g. of aluminum chloride and 4.22 g. (30 mmoles, 3.5 ml.) of freshly distilled benzoyl chloride in 80 ml. of 1,2-dichloroethane under the same conditions for 1 hr. afforded 330 mg. (33%) of starting material, 120 mg. of monobenzoylated chelate and 40 mg. of dibenzoylated chelate.

The monobenzoyl compound, (3-benzoyl-2,4-pentanediono)bis(2,4-pentanediono)rhodium(III), 150 mg. (11%), m.p. 231–232°, was the second band eluted from the column with benzene. The spectral characteristics and elemental analysis of this compound confirm the assigned structure: infrared (KBr), 1660, 1560, 1515, 1370, 1282, 1267, 1245, 1195, 1133, 892 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 316 $\text{m}\mu$ (ϵ 8550); n.m.r., 7.97 (6), 7.82 (6), 7.75 (6), 4.43 (2), 1.65–2.5 (5) τ .

Anal. Calcd. for $\text{C}_{25}\text{H}_{25}\text{O}_7\text{Rh}$: C, 52.39; H, 5.00. Found: C, 52.78; H, 5.00.

The dibenzoylated chelate, (2,4-pentanediono)bis(3-benzoyl-2,4-pentanediono)rhodium(III), 40 mg. (4%), m.p. 205–208°, was removed from the column by extruding the third band and extracting with boiling benzene-methanol. The spectral characteristics and analyses of this chelate confirm the assigned structure: infrared (KBr), 1660, 1555, 1515, 1360, 1280, 1245, 1133, and 890 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 311 $\text{m}\mu$ (ϵ 5620); n.m.r. (CHCl_3), 7.94 (6), 7.86 (6), 7.72 (6), 4.50–4.40 (1), 1.65–3.65 (10) τ .

Anal. Calcd. for $\text{C}_{29}\text{H}_{29}\text{O}_8\text{Rh}$: C, 57.24; H, 4.80. Found: C, 57.60; H, 4.95.

Preparation of Triacetylmethane.—Ketene was generated from reagent acetone in a cracking apparatus²⁰ and was passed for 3 hr. into 200 g. of acetylacetone. The orange liquid was evaporated at 70° to an orange oil by a rotatory evaporator, then vacuum distilled at 27 mm. The third fraction (b.p. 108–112°) was redistilled at 30 mm. to give 105.9 g. (28.5%) of a faintly yellow oil (b.p. 111–113°) which was shown to be pure by vapor phase chromatography and identified as triacetylmethane by its physical properties, infrared spectrum, and chelation with copper(II) acetate.

Preparation of Bis(3-acetyl-2,4-pentanediono)copper(II).—To 2 ml. of triacetylmethane in 1 ml. of ethanol was added 4 ml. of saturated copper(II) acetate solution. The solution turned immediately dark blue. After stirring at room temperature for 25 min., small crystals of blue bis(3-acetyl-2,4-pentanediono)copper(II) were obtained. Yield: 0.35 g., m.p. 207–207.5°; infrared (KBr), 1685, 1582, 1450, 1400, 1350, 1239, 1055 cm^{-1} .

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_6\text{Cu}$: C, 48.66; H, 5.25. Found: C, 48.44; H, 5.55.

Preparation of Tris(3-acetyl-2,4-pentanediono)chromium(III) from Triacetylmethane. A.—An intimate mixture of 0.5 g. of anhydrous chromium trichloride and 0.5 g. of zinc dust was added to 5 ml. of dimethylformamide. An exothermic reaction ensued and a green solution was formed. To this solution was added 8 ml. (8.6 g., 60 mmoles) of triacetylmethane, 3.16 g. (20 mmoles) of anhydrous chromium(III) chloride, and 0.3 g. of zinc dust. To the green mixture was added dropwise 8.3 ml. (6.0 g., 60 mmoles) of triethylamine. The exothermic reaction was kept at about 60° by stirring the mixture through an external water bath. The purple mixture was stirred for an additional 1.5 hr. and then poured into 300 ml. of water. The purple precipitate was collected on a filter, washed with water, sucked dry, and then dissolved in methylene chloride and filtered. The organic phase was dried over magnesium sulfate and evaporated to a purple solid. Recrystallization from benzene-heptane afforded purple crystals, m.p. 195–197°, 5.87 g. The mother liquor afforded an additional 0.47 g.; total yield 6.34 g. (66.7%). Another recrystallization afforded an analytical sample, m.p. 197–198°. A test chromatographic column showed only a single chelate. The infrared spectrum and elemental analyses indicated that the product was pure tris(3-acetyl-2,4-pentanediono)chromium(III); infrared (KBr), 1687, 1560, 1450, 1420, 1360, 1242, 1055 cm^{-1} .

Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{O}_9\text{Cr}$: C, 53.05; H, 5.69. Found: C, 53.28; H, 5.88.

B.—To a stirred suspension of 0.83 g. of chromium(III) acetate hydrate in 10 ml. of dimethylacetamide was added 1.42 g. of triacetylmethane. The mixture was heated to 80° or 16 hr. and then combined with 50 ml. of water. The resulting solution was extracted with two 50-ml. portions of chloroform. The chloroform extracts were combined, washed with two 100-ml. portions of water, and then dried over calcium sulfate. The solvent was removed and the purple oil was crystallized from ethanol. Two recrystallizations from ethanol yielded 0.14 g. (8.6%) of the triacetylated chromium(III) chelate as a purple powder, m.p. 197–199°. The infrared spectrum of this chelate indicated the presence of a small amount of unsubstituted chelate rings.

C.—To a solution of 0.37 g. of tris(tetrahydrofuran)trichlorochromium(III) and 0.43 g. of triacetylmethane in 25 ml. of 1:1 acetone-water was added 0.3 g. of triethylamine. The mixture was stirred for an hour and the resulting purple solution was then extracted with 20 ml. of methylene chloride. The solution was dried, the solvent removed, and the purple residue crystallized from benzene-heptane. The resulting powder was further purified by chromatography on alumina. The yield of triacetylated chromium(III) acetylacetonate was 0.19 g. (25%), m.p. 196–198°. The infrared spectrum of this product indicated the presence of a small amount of unsubstituted chelate rings.

Acetylation of Chromium(III) Acetylacetonate.—To a solution of 10 g. of chromium acetylacetonate and 10.5 g. of freshly distilled acetic anhydride in 50 ml. of anhydrous methylene chloride under nitrogen was added 10 ml. of pure borontrifluoride etherate. The deep purple solution was stirred at room temperature for 30 min. and then shaken vigorously with cold aqueous potassium acetate. The organic phase was dried, filtered, and the solvent removed. The purple oil was poured into ethanol, and the resulting violet crystals were collected and then recrystallized from ethanol. The crude purple powder, 5.7 g. (52%), melted at

192–194°. Two more recrystallizations from ethanol afforded an analytical sample of tris(3-acetyl-2,4-pentanedion)chromium(III), m.p. 198–200°. The infrared spectrum of this sample indicated a small amount of partially acetylated chelate was present.

Anal. Calcd. for $C_{21}H_{27}O_9Cr$: C, 53.05; H, 5.69. Found: C, 53.03; H, 6.10.

Acetylation of Cobalt(III) Acetylacetonate.—To a solution of 10 g. of cobalt(III) acetylacetonate and 10.5 g. of acetic anhydride in 50 ml. of anhydrous methylene chloride was added 10 ml. of freshly distilled boron trifluoride etherate. The deep green solution was stirred for 30 min. and then decomposed with cold potassium acetate solution. The organic phase was separated, dried, and evaporated to dryness. The crude green powder was taken up in benzene and purified by chromatography on a 52 × 6 cm. column of alumina. Elution was begun with benzene and completed with methylene chloride–benzene. Four green bands were collected and each crystalline product was recrystallized from ethanol.

The first band afforded 0.15 g. of cobalt(III) acetylacetonate, identified by mixture melting point with an authentic sample and its infrared spectrum.

The second band yielded 0.57 g. of (3-acetyl-2,4-pentanedion)bis(2,4-pentanedion)cobalt(III), m.p. 185–186°; infrared (KBr), 1675, 1565, 1517, 1370, 1279, 1245, 1191, and 1057 cm^{-1} . The proton magnetic resonance spectrum of the monoacetylated chelate showed signals at 8.08 (6), 8.06 (6), 8.02 (3), 7.91 (6), and 4.20 (2) τ in benzene.

Anal. Calcd. for $C_{17}H_{23}O_7Co$: C, 51.27; H, 5.78. Found: C, 51.26; H, 5.83.

The third band afforded 0.68 g. of (2,4-pentanedion)bis(3-acetyl-2,4-pentanedion)cobalt(III), m.p. 184–185°. A mixture melting point with the monoacetylated chelate was 180–182°. The infrared and n.m.r. spectra and elemental analysis confirmed the structure of the diacetylated chelate: infrared (KBr), 1678, 1560, 1518, 1390, 1360, 1241, 1191, and 1057 cm^{-1} ; n.m.r., 8.09 (6), 8.03 (6), 7.94 (6), 7.92 (6), and 4.70 (1) τ in benzene.

Anal. Calcd. for $C_{19}H_{25}O_8Co$: C, 51.83; H, 5.68. Found: C, 51.44; H, 5.75.

The fourth band yielded only an oily green solid. This chelate was further purified by chromatography on Florisil, using methylene chloride–2-propanol as an eluent. Recrystallization from ethanol gave 0.08 g. of tris(3-acetyl-2,4-pentanedion)cobalt(III) as green needles, m.p. 169–170°; infrared (KBr), 1689, 1561, 1311, 1246, and 1059 cm^{-1} , no 1191- cm^{-1} band; n.m.r., 8.04 (1) and 7.98 (2) τ in benzene.

Anal. Calcd. for $C_{21}H_{27}O_9Co$: C, 52.28; H, 5.64. Found: C, 52.27; H, 5.92.

Preparation of Tris(3-acetyl-2,4-pentanedion)cobalt(III) by Chelation of Triacetylmethane: A. With Cobaltous Carbonate and Hydrogen Peroxide.—To a suspension of 0.50 g. of cobaltous carbonate in 3.58 g. of triacetylmethane was added slowly with vigorous stirring 12 ml. of 10% hydrogen peroxide. After stirring 20 min. at 50°, the green solution was diluted with 100 ml. of water and extracted with three 35-ml. portions of chloroform. The extracts were combined and dried over anhydrous magnesium sulfate. Upon removal of the solvent, a green oil resulted which was purified by chromatography on alumina. Three green bands were separated, collected, and crystallized from benzene–heptane. The first band (0.245 g.) was identical in melting point and infrared spectrum to (3-acetyl-2,4-pentanedion)bis(2,4-pentanedion)cobalt(III). The infrared spectrum and melting point identified the solid from the second band (0.265 g.) as (2,4-pentanedion)bis(3-acetyl-2,4-pentanedion)cobalt(III). The third band gave a modest yield (0.165 g.) of a compound identical in melting point to tris(3-acetyl-2,4-pentanedion)cobalt(III). The infrared spectrum of this compound, however, revealed the presence of a slight impurity of the diacetylated chelate. Further purification of this band by alumina chromatography gave pure tris(3-acetyl-2,4-pentanedion)cobalt(III), m.p. 169–170°.

B. With Sodium Tricarbonatocobalt(III) 3-Hydrate.—To a suspension of 0.89 g. of sodium tricarbonatocobalt(III) trihydrate in 10 ml. of 1:1 acetone–water was added with stirring at 50° 1.56 g. of triacetylmethane. After 45 min., the black-green suspension was extracted with two 25-ml. portions of chloroform. The green extract was washed with 50 ml. of water, dried over anhydrous magnesium sulfate, and evaporated to a bright green oil. The oil upon crystallization from benzene–heptane gave 0.18 g. (11.4%) of crude tris(3-acetyl-2,4-pentanedion)cobalt(III). Purification of this material by Florisil

chromatography afforded 0.10 g. of pure tris(3-acetyl-2,4-pentanedion)cobalt(III) identical in melting point and infrared spectrum to an authentic sample obtained from the Friedel–Crafts acetylation. The chromatography also revealed traces of mono- and diacetylated cobalt(III) acetylacetonates.

Treatment of Chromium(III) and Cobalt(III) Acetylacetonates with Ketene. Into a solution of 5.0 g. of chromium acetylacetonate in a solution of 50 ml. of xylene, 25 ml. of toluene, and 25 ml. of benzene was bubbled through a vigorous stream of gaseous ketene for 2 hr. The chelate was recovered by evaporation of the solvent and chromatography in the usual manner. A mixture melting point of this product with an authentic sample of chromium(III) acetylacetonate was not depressed. Only the starting material was detected in the work-up. A similar experiment using cobalt(III) acetylacetonate also yielded only the starting material.

Treatment of Rhodium(III) Acetylacetonate with Diphenylcarbamyl Chloride.—To a stirred suspension of 533 mg. (4 mmoles) of anhydrous aluminum chloride in 35 ml. of dichloroethane was added 928 mg. of diphenylcarbamyl chloride. The resulting suspension was cooled to 0°. To this mixture was added dropwise 400 mg. of rhodium acetylacetonate in 15 ml. of dichloroethane. The reaction was allowed to stir for 1 hr. at room temperature. The usual work-up afforded 365 mg. of recovered rhodium acetylacetonate.

A similar experiment with ethyl chlorocarbonate gave the same results.

Treatment of Tris(3-phenylthio-2,4-pentanedion)rhodium(III) with Hydrogen Peroxide.—A solution of 100 mg. of the sulfide chelate, 20 ml. of acetic acid, and 10 ml. of 30% hydrogen peroxide was stirred at room temperature for 30 min. The usual work-up afforded only the starting material. A repetition of this experiment at a higher reaction temperature resulted in nearly total decomposition of the chelate system; however, the recovered chelate had not been oxidized.

Treatment of Rhodium(III) Acetylacetonate with Benzyl Chloride under Friedel–Crafts Conditions.—To a stirred mixture of 800 mg. (6 mmoles) of anhydrous aluminum chloride and 400 mg. (1 mmole) of rhodium acetylacetonate in 50 ml. of 1,2-dichloroethane was added dropwise 840 mg. (6 mmoles) of freshly distilled benzyl chloride in 10 ml. of 1,2-dichloroethane. The mixture was stirred under nitrogen for 30 min. and then decomposed with dilute hydrochloric acid and worked up in the usual manner. The starting material was recovered in high yield. Little decomposition was noticed and no other chelates were detected—even by chromatography.

Similar experiments with boron trifluoride etherate and varying conditions gave the same result.

Tris(3-thiocyanato-2,4-pentanedion)chromium(III).—Lead thiocyanate was prepared by dropwise addition of an aqueous solution of sodium thiocyanate to a rapidly stirred solution of lead nitrate. The insoluble salt was collected by suction filtration and washed several times with ice–water and finally with anhydrous ether. The salt was stored in a vacuum desiccator over phosphorus pentoxide in the dark.

Thiocyanogen was prepared by dropwise addition of a solution of 10.5 g. (0.066 mole, 3.37 ml.) of bromine in 20 ml. of 1,2-dichloroethane to a vigorously stirred suspension of 21.4 g. (0.066 mole) of anhydrous lead thiocyanate in 80 ml. of 1,2-dichloroethane cooled to -15° . The red bromine color was allowed to disappear before each successive addition of bromine. The mixture of thiocyanogen and lead bromide was stirred for 5 min. after the bromine addition was completed.

The solid lead bromide was allowed to settle and the colorless thiocyanogen solution was filtered into a stirred solution of 7.0 g. (0.02 mole) of chromium(III) acetylacetonate in 50 ml. of 1,2-dichloroethane cooled to -15° . The mixture was stirred for 2 hr. at -15° and then allowed to come to room temperature and react for an additional hour. The reaction mixture was extracted two times with water. The organic phase was dried with calcium chloride, filtered, and evaporated to dryness. The red powder was recrystallized from 95% ethanol to yield 7.85 g. of pure tris(3-thiocyanato-2,4-pentanedion)chromium(III), m.p. 191–192°; a second crop of 2.10 g., m.p. 190–192°, was obtained by concentration of the mother liquor. The total yield was 9.95 g. (95.6%); infrared (KBr), 2150, 1555, 1405, 1360, 1330, 1175, 1060, and 1025 cm^{-1} .

Anal. Calcd. for $C_{15}H_{15}O_5N_3S_3Cr$: C, 41.53; H, 3.49; N, 8.07; S, 18.48. Found: C, 41.56; H, 3.56; N, 7.78; S, 17.81.

Tris(3-thiocyanato-2,4-pentanediono)cobalt(III).—Under the same conditions used for the analogous chromium complex the green crystalline tris(3-thiocyanato-2,4-pentanediono)cobalt(III) was formed in 76% yield, m.p. 166–167° dec.; infrared (KBr), same as chromium complex; ultraviolet (CHCl_3), λ_{max} 300 $\text{m}\mu$ (ϵ 13,750); n.m.r. (CCl_4), 7.30 τ .

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_3\text{S}_3\text{Co}$: C, 40.98; H, 3.44; N, 7.97; S, 18.24. Found: C, 40.34; H, 3.92; N, 7.98; S, 18.43.

Tris(3-thiocyanato-2,4-pentanediono)rhodium(III).—Under the same conditions used for the analogous chromium complex the yellow crystalline trithiocyanatorrhodium chelate was prepared in 98% yield, m.p. 214–215°; infrared (KBr), 2150, 1550, 1365, 1331, 1055, 1025, 918 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 310 $\text{m}\mu$ (ϵ 65,500); n.m.r. (CHCl_3), 7.30 τ .

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_3\text{S}_3\text{Rh}$: C, 37.90; H, 3.18; N, 7.35. Found: C, 37.74; H, 3.42; N, 7.83, 7.06.

Tris(3-phenylthio-2,4-pentanediono)chromium(III).—To a stirred solution of 3.40 g. (0.01 mole) of chromium(III) acetylacetonate in 50 ml. of 1,2-dichloroethane was added dropwise a solution of 5.8 g. (0.04 mole) of freshly prepared benzenesulfonyl chloride in 25 ml. of 1,2-dichloroethane. The temperature quickly rose to 40° and local boiling was observed. The reaction was stirred at room temperature for 30 min. The mixture was extracted with dilute aqueous sodium carbonate. The green aqueous layer indicated some decomposition had taken place. The organic layer was separated, dried over potassium carbonate, filtered, and evaporated to dryness. The grey-purple, amorphous residue was recrystallized from 80% ethanol to yield 2.0 g. (32.7%) of crystalline tris(3-phenylthio-2,4-pentanediono)chromium(III), m.p. 90–100°. An analytical sample was prepared by two more recrystallizations from ethanol–water, m.p. 104–105°; infrared (KBr), 1550, 1470, 1410, 1360, 1330, 1070, 1025, 920 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 326 $\text{m}\mu$ (ϵ 14,400).

Anal. Calcd. for $\text{C}_{33}\text{H}_{33}\text{O}_6\text{S}_3\text{Cr}$: C, 58.82; H, 4.94; S, 14.27. Found: C, 58.57; H, 5.21; S, 13.14.

Tris(3-*o*-nitrophenylthio-2,4-pentanediono)cobalt(III).—To a stirred solution of 3.51 g. (0.01 mole) of cobalt acetylacetonate in 50 ml. of 1,2-dichloroethane cooled to 0° was added dropwise a solution of 7.55 g. (0.04 mole) of *o*-nitrobenzenesulfonyl chloride in 50 ml. of 1,2-dichloroethane at such a rate that the temperature did not rise above 5°. The mixture was stirred for an additional 30 min. at 0–5°.

The organic phase was extracted four times with water. The fourth aqueous wash was neutral to litmus. The organic phase was dried over potassium carbonate, filtered, and evaporated to a dark, viscous oil. The oil was taken up in hot benzene, treated with activated charcoal, filtered, and then diluted with an equal volume of hot heptane. Slow cooling of this solution afforded brown crystals which were collected and air dried. The first crop weighed 6.20 g., m.p. 211–212° dec., and a second crop of 1.0 g. was obtained by concentrating the mother liquor (total yield 80.7% calculated for benzene solvate); infrared (KBr), 1590, 1565, 1550, 1515, 1410, 1360, 1335, 1300, 1100, 1072, 1038, 845 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 370 $\text{m}\mu$ (ϵ 23,700); n.m.r. (CCl_4), 7.46 (18), 2.71 (18) τ (broad). The infrared n.m.r. and elemental analysis of this substance indicate that it is a monobenzene solvate. It is remarkable that treatment at 100° and 0.1 mm. for 24 hr. failed to remove the benzene.

Anal. Calcd. for $\text{C}_{33}\text{H}_{30}\text{O}_{12}\text{N}_3\text{S}_3\text{Co}\cdot\text{C}_6\text{H}_6$: C, 52.50; H, 4.06; N, 4.70. Found: C, 51.71; H, 4.06; N, 4.85.

Tris(3-*o*-nitrophenylthio-2,4-pentanediono)chromium(III).—Under the same conditions as the cobalt analog this chromium chelate was prepared in 80% yield, m.p. 251–252°. Again the spectral properties and elemental analysis indicate a monobenzene solvate; infrared (KBr), 1583, 1565, 1550, 1512, 1410, 1360, 1445, 1300, 1240, 1070, 1035, 1015, 915, 845 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 367 $\text{m}\mu$ (ϵ 21,300).

Anal. Calcd. for $\text{C}_{33}\text{H}_{30}\text{O}_{12}\text{N}_3\text{S}_3\text{Cr}\cdot\text{C}_6\text{H}_6$: C, 52.81; H, 4.09; N, 4.74; S, 10.84. Found: C, 51.92, 52.73; H, 4.10, 4.17; N, 4.74, 5.09; S, 10.29.

Tris(3-*o*-nitrophenylthio-2,4-pentanediono)rhodium(III).—In a manner similar to that described before the rhodium thioether was prepared in 70% yield, m.p. 261–263°; infrared (KBr), 1588, 1565, 1540, 1515, 1450, 1410, 1360, 1335, 1300, 1245, 1100, 1065, 1035, 915, 845 cm^{-1} ; ultraviolet (CHCl_3), λ_{max} 268 $\text{m}\mu$ (ϵ 16,500), 369 (14,300); n.m.r. (CCl_4), 7.46, 2.71 τ (broad). Again the thioether was a very stable monobenzene solvate.

Anal. Calcd. for $\text{C}_{33}\text{H}_{30}\text{O}_{12}\text{N}_3\text{S}_3\text{Rh}\cdot\text{C}_6\text{H}_6$: C, 49.95; H, 3.87; N, 4.48. Found: C, 50.39; H, 4.02; N, 4.55.

Reaction of Sulfur Dichloride with Dichlorinated Chromium(III) Acetylacetonate.—To a suspension of 6.0 g. (14.3 mmoles) of (2,4-pentanediono)bis(3-chloro-2,4-pentanediono)chromium(III) in 50 ml. of pure pentane was added 3.2 ml. (49 mmoles) of freshly distilled sulfur dichloride. The mixture was stirred for 12 hr., and then the solid product was collected and washed several times with pure pentane. Recrystallization from benzene–heptane afforded 4.5 g. of (3-chlorothio-2,4-pentanediono)bis(3-chloro-2,4-pentanediono)chromium(III), tan crystals, m.p. 153, 153.5°; infrared (KBr), 1550, 1450, 1410, 1360, 1335, 1290, 1040, 1020, 980, 920, and 705 cm^{-1} .

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{O}_6\text{S}_2\text{Cr}$: C, 37.20; H, 3.72; S, 6.62; Cl, 22.00. Found: C, 37.74; H, 3.75; S, 6.29; Cl, 21.72.

Treatment of Chelate Sulfonyl Chloride with Cyanide.—To a solution of 1.00 g. (2 mmoles) of (3-chlorothio-2,4-pentanediono)bis(3-chloro-2,4-pentanediono)chromium(III) in 20 ml. of benzene was added 0.26 g. (4 mmoles) of potassium cyanide and the mixture was stirred for 1 hr. The mixture was filtered and the filtrate was evaporated. The brown powder was taken up in benzene and purified by chromatography on Florisil (deactivated by addition of 10% water). The first band was collected, the solvent evaporated, and the product recrystallized from benzene–heptane, 405 mg., tan needles, m.p. 198–199°. The infrared spectrum was almost identical with that of the starting material.

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{Cl}_2\text{O}_6\text{NSCr}$: C, 40.43; H, 3.81; N, 2.94; S, 6.74; Cl, 14.91. Found: C, 40.21; H, 3.99; N, 2.69; S, 6.46; Cl, 14.60.

Reaction of Chelate Sulfonyl Chloride with Ethanol.—To a solution of 1.00 g. (2 mmoles) of (3-chlorothio-2,4-pentanediono)bis(3-chloro-2,4-pentanediono)chromium(III) in 20 ml. of benzene was added 0.184 g. (4 mmoles) of absolute ethanol and 0.216 g. (2 mmoles) of triethylamine. The solution was stirred for 1.5 hr., filtered, and the solvent was removed. The residue was purified by chromatography on Florisil (deactivated by 10% water) using benzene as the eluent. The first band afforded (3-ethoxysulfonyl-2,4-pentanediono)bis(3-chloro-2,4-pentanediono)chromium(III) after recrystallization from benzene–heptane, m.p. 245–246°, 56 mg.; infrared (KBr), 1550, 1480, 1440, 1375, 1355, 1320, 1160, 1075, 1050, 1025, 925, 690 cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{23}\text{Cl}_2\text{O}_7\text{SCr}$: C, 41.30; H, 4.69; S, 6.48; Cl, 14.34. Found: C, 41.26; H, 4.19; S, 6.49; Cl, 15.11