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Reactions of Metal Chelates. III. Nitration and Formylation of Metal Acetylacetonates[1-4]

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The trisacetylacetonates of chromium(III), cobalt(III), and rhodium(III) have been nitrated by treatment with a mixture of copper(II) nitrate and acetic anhydride. The trinitro chelates were characterized by their infrared and n.m.r. spectra. Formylation of these acetylacetonates was accomplished with $POCl_3$ and dimethylformamide. Both mono- and diformylated cobalt(III) acetylacetonates were isolated and characterized by their n.m.r. spectra. Only the monoformyl chromium(III) and rhodium(III) chelates have been characterized. The structures of these new mixed ligand systems were established by their n.m.r. spectra and by electrophilic substitution of the other rings.

As a part of a general study of the reactions of coördinated ligands we have been investigating the electrophilic substitution of stable metal acetylacetonates. We previously have reported that these complexes exhibit the chemical behavior expected for reactive aromatic systems and are readily substituted at the central carbon of the chelate rings by a variety of electrophiles.[4] Acetylation,[4] iodination,[5] bromination,[5,6] chlorination,[5] and thiocyanogenation[7,8] have been discussed elsewhere.

Herein is described the nitration and formylation of the relatively stable acetylacetonates of chromium(III) (I), cobalt(III) (II), and rhodium(III) (III). In order to study only the reactions of chelated ligands our investigation has been limited to these kinetically stable metal chelates. These acetylacetonates are each optically stable in the solid state[8,9]; however, the chromium chelate (I) racemizes slowly in solution.[10] Although the chromium and cobalt complexes (I and II) are destroyed within 30 min. by mineral acids, they are stable in glacial acetic acid. These chelates do not undergo exchange with radioactive acetylacetone in solution.[6] The rhodium chelate (III) can be recovered unchanged from solution in cold, concentrated sulfuric acid.[9] On the basis of these and other qualitative observations, the kinetic stability of these acetylacetonates seems to be rhodium > cobalt > chromium.

Nyholm[11] obtained bis-(3-nitro-2,4-pentanediono)-copper(II) (VII) by treatment of the usually labile copper(II) acetylacetonate with N_2O_4 in benzene. Our initial attempts to nitrate the more stable chromium(III) acetylacetonate (I) with N_2O_4 in benzene or methylene chloride resulted in the formation of two impure, nonisomeric, nitrogen-containing chelates.[4] These proved intractable in our hands, but subsequent investigation showed that neither of these substances is tris-(3-nitro-2,4-pentanediono)-chromium(III) (IV). The nitro chromium chelate (IV) was isolated from the reaction of $N_2O_4 \cdot BF_3$ with chromium acetylacetonate (I), but the yields were very low. This reagent had been used previously to effect the nitration of reactive benzenoid systems.[12]

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[1] Presented in part before the Division of Inorganic Chemistry, 139th National Meeting of the American Chemical Society, St. Louis, Missouri, March, 1961, p. 4-M.

[2] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

[3] Previous paper, J. P. Collman and E. T. Kittleman, *J. Am. Chem. Soc.*, **83**, 3529 (1961).

[4] A part of this material was reported in a preliminary communication, 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] R. W. Kluiber, *ibid.*, **82**, 4839 (1960).

[7] R. W. Kluiber, *ibid.*, **83**, 3030 (1961).

[8] J. P. Collman and R. P. Blair, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961, p. 5-N.

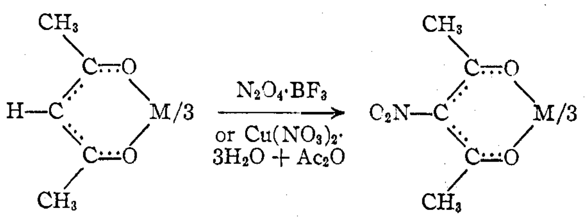
[9] J. P. Collman and R. L. Marshall, unpublished data.

[10] T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 245 (1958).

[11] C. Djoidjeric, J. Lewis, and R. S. Nyholm, *Chem. Ind.* (London), 122 (1959).

[12] G. B. Bachman and J. L. Dever, *J. Am. Chem. Soc.*, **80**, 5871 (1958).

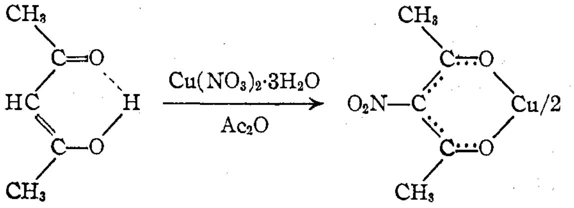
A mixture of copper(II) nitrate trihydrate in acetic anhydride proved very effective in the trinitration of chromium(III), cobalt(III), and rhodium(III) acetylacetonates (I, II, and III). The pure nitro chelates (IV, V, and VI) were isolated in high yield by hydrolysis of the reaction mixtures.



I, M = Cr
II, M = Co
III, M = Rh

IV, M = Cr
V, M = Co
VI, M = Rh

The copper nitrate–acetic anhydride reagent was effective in nitrating acetylacetone itself. When a mixture of acetylacetone, copper nitrate trihydrate, and acetic anhydride was stirred for 12 hr., a green precipitate formed. This green powder proved to be bis-(3-nitro-2,4-pentanediono)-copper(II) (VII). Evidently insolubility protects the labile copper chelate from the acidic reaction mixture.



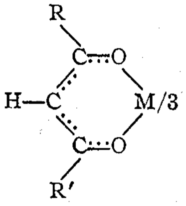
VII

An interesting variation of this scheme was an attempted nitration of acetylacetone with a mixture of chromium(III) nitrate hydrate and acetic anhydride. Chromatography of the crude product on Florisil yielded a small amount of the trinitrated chromium acetylacetonate (IV) as well as two other nitrated chelates—apparently the mono- and dinitrated derivatives.

The nature of the novel copper nitrate–acetic anhydride reagent is unknown. Since the copper nitrate trihydrate forms a deep blue solution in acetic anhydride, it seems likely that the reactive reagent is a copper complex of acetyl nitrate. It seems probable that the use of trifluoroacetic anhydride might increase the reactivity of this nitration mixture. It is interesting that dehydrated, white copper(II) nitrate does not dissolve in acetic anhydride and that this mixture is ineffective as a nitration agent.[13]

Fluoro-substituted metal acetylacetonates fail to react with this nitration mixture. For example the chromium(III) chelate of trifluoroacetylacetone (VIII) failed to form a nitro derivative but was recovered unchanged from the reaction mixture. In a similar manner, the fluoro chelate (VIII) failed to undergo bromination. The corresponding fluoro-rhodium chelate (IX) failed to react with bromine in boiling 1,2-dichloroethane. Evidently the electronegative trifluoromethyl group drastically decreases the reactivity of the chelate ring toward electrophiles. The hexafluoro rhodium chelate (X) also was inert to electrophilic substitution.

The trifluoro rhodium chelate (IX) was separated into its two diastereoisomeric *cis* and *trans* forms by chromatography on alumina. Piper has independently separated and characterized these isomers.[14]



VIII, M = Cr, R = CF_3, R′ = CH_3
IX, M = Rh, R = CF_3, R′ = CH_3
X, M = Rh, R = R′ = CF_3
XI, M = Cr, R = C_6H_5, R′ = CH_3
XII, M = Cr, R = R′ = C_6H_5

Attempted nitration of the chromium(III) chelates of benzoylacetone and dibenzoylmethane (XI and XII) with the copper nitrate–acetic anhydride mixture resulted in destruction of these chelates—probably in the acidic hydrolysis step. Treatment of rhodium acetylacetonate (III) with a cold mixture of nitric and sulfuric acids also resulted in complete decomposition of the chelate.

The previously unknown nitro chelates were characterized by analyses and infrared and nuclear magnetic resonance spectroscopy. The infrared spectra of these nitro acetylacetonates were particularly distinctive. Although substitution of the central carbon of the acetylacetonate rings by groups other than hydrogen usually causes the strong doublet in the 1500–1600-cm.$^{-1}$ region to become a singlet,[3,5,15] the nitro chelates exhibit two strong bands in this region. The lower 1520-cm.$^{-1}$ band apparently is caused by an asymmetric nitro stretching frequency.

There are no absorption peaks at 1200 cm.$^{-1}$ in the spectra of these nitro chelates. A medium band at 1200 cm.$^{-1}$ in the spectra of metal acetylacetonates previously has been assigned to a bend-

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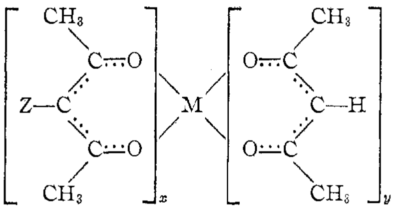
(13) B. Kauffman and M. F. Citro, private communication.

(14) T. S. Piper, private communication.

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

Table I

Proton Spin Resonance Spectra of Chelates



Z	M	x	y	N.m.r. signals in $\tau^{a,b}$			
...	Co	0	3		4.43 (1)		7.81 (6)^d
...	Rh	0	3		4.65 (1)		7.89 (6)^c
O_2N	Co	3	0				7.43^d
O_2N	Rh	3	0				7.59^d
HCO	Co	1	2	−0.21 (1)	4.36 (2)	7.39 (6)	7.83 (12)^d
HCO	Co	2	1	−0.28 (2)	4.44 (1)	7.37 (12)	7.80 (6)^d
HCO	Rh	1	2	−0.03 (1)	4.51 (2)	7.42 (6)	7.89 (12)^c

[a] Spectra were measured at 60 Mc. with tetramethylsilane as an internal standard, τ = 10.00 p.p.m. [b] Integrated intensities are in parentheses. [c] Spectrum determined in CCl_4. [d] Spectrum determined in C_6H_6.

ing mode of the hydrogen at the central carbon atom.[11,16] We have found that the absence of this peak is an excellent measure of complete substitution of metal acetylacetonates. Another particularly striking feature of these spectra is a very narrow, strong band at 825 cm.$^{-1}$, which is probably a nitrogen–oxygen mode.

The proton spin resonance spectra[17] summarized in Table I provide conclusive proof of the structures assigned to the diamagnetic nitro cobalt and rhodium chelates. The nitro chelates (V and VI) exhibit only one signal at 7.4 τ, whereas the unsubstituted acetylacetonates give signals at 7.8 and 4.4 τ with integrated intensities of 6:1. The higher field signal (7.8 τ) thus is assigned to the methyl protons and the lower signal to the ring hydrogen. The lower value (7.4 τ) of the methyl protons in the nitro chelates probably is caused by the electronegative nitro groups.

The nitro chelates (IV, V, VI, and VII) represent a class of complexes which are not available through direct chelation since the parent ligand, 3-nitro-2,4-pentanedione, is unknown. Preliminary attempts to isolate this nitro diketone by acid hydrolysis of the nitro copper chelate (VII) resulted in an intractable oil. However, it seems as if these nitro chelates could act as intermediates for heterocyclic syntheses involving 3-nitro-2,4-pentanedione. Schemes involving reactions on chelated substrates may become useful in organic syntheses.

Functional groups substituted on metal chelate rings often show unusual chemical properties which probably are associated with the novel steric and electronic environment around these groups. For example, the halogen atoms substituted on metal acetylacetonate rings are surprisingly inert to nucleophiles and to lithium and magnesium.[5] The nitro groups on the nitro chromium and rhodium chelates (IV and VI) are resistant to chemical and catalytic reduction. Since rhodium complexes are much more stable to acids and bases, the nitro rhodium chelate (VI) can be subjected to more strenuous reducing conditions without destroying the chelate rings. Treatment of the nitro rhodium chelate (VI) with zinc dust in hot acetic acid, and with stannous chloride and dry HCl in acetic acid, resulted only in the recovery of starting material. Attempted catalytic hydrogenation of the nitro chromium and rhodium chelates (IV and VI) in acetic acid with PtO_2 at 60 p.s.i. also afforded only starting material.[18]

Attempted catalytic or chemical reduction of the nitro cobalt chelate (V) resulted in the immediate formation of cobalt(II) and decomposition of the complex. Evidently this involves reduction of cobalt(III) to cobalt(II) through the unsaturated bonds of the ligand. The optical stability[8] of the nitro cobalt chelate (V), even under conditions of mild acidity, would seem to preclude direct reduction of the highly shielded cobalt(III) ion by means of a prior dissociation mechanism.

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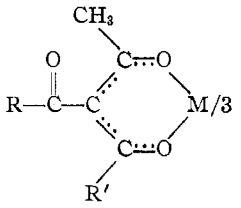
(16) K. Nakamoto, H. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961); K. Nakamoto, H. J. McCarthy, and A. E. Martell, *ibid.*, **83**, 1272 (1961).

(17) We are indebted to American Cyanamid Company, E. I. du Pont Savannah River Laboratory, Chemstrand Corporation, and Varian Associates for determinations of n.m.r. spectra.

(18) A report appeared recently mentioning the reduction of the nitro chromium chelate but neither experimental details nor analytical data were presented: E. Bayer, *Angew. Chem.*, **73**, 533 (1961).

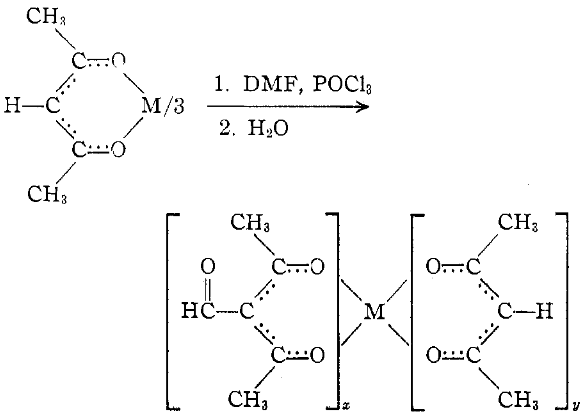
Our unsuccessful attempts to reduce the nitro chelates to the corresponding amino chelates have been disappointing because of the possibility of converting such amino chelates into stable diazonium salts. Further attempts to prepare the amino chelates are being studied.

An interest in obtaining metal chelates substituted with reactive functional groups prompted our initial attempts to formylate these acetylacetonates. Furthermore it seemed that such a reaction might lead to one (XIII) of a pair of isomeric chelates that differed by coördination of a formyl or an acetyl group. Isomers of this type derived from tricarbonyl compounds have not been studied, but it seems likely that coördination of 3-formyl-2,4-pentanedione would lead to the other isomer (XIV)—with an uncoördinated acetyl group.



XIII, R = H, R′ = CH_3
XIV, R = CH_3, R′ = H

N-methylformanilide and phosphorus oxychloride proved ineffective in the formylation of chromium(III) acetylacetonate, although small amounts of an impure chelate aldehyde were detected. The acetylacetonates of chromium, cobalt, and rhodium were readily formylated by phosphorus oxychloride and dimethylformamide. Probably because of the other electrophilic reagent involved, the formylation reaction seems slower than many of the other electrophilic substitutions of these metal acetylacetonates. Treatment of cobalt acetylacetonate under one set of conditions afforded mostly the monoformyl chelate (XVIa); whereas under more vigorous conditions the diformyl chelate (XVIb) was formed. Attempted formylation of the dialdehyde chelate (XVIb) yielded mostly the starting material (XVIb) and a small amount of a new compound—apparently the trialdehyde (XVIc), but this material was not fully characterized. Unlike the mono- and diacetyl cobalt chelates the mono- and dialdehydes were difficult to separate by chromatography. Because of this we were in error when we reported earlier that only the monoaldehyde (XVIa) was formed in this reaction. Only the monoformylated chromium and rhodium chelates (XV and XVII) have been characterized.

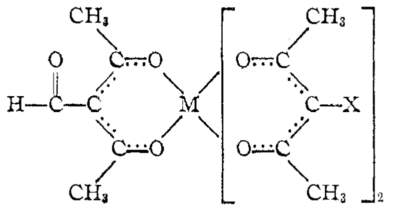


XV, M = Cr, x = 1, y = 2
XVIa, M = Cr, x = 1, y = 2
XVIb, M = Co, x = 2, y = 1
XVIc, M = Co, x = 3, y = 0
XVII, M = Rh, x = 1, y = 2

The structures of the aldehyde chelates (XVIa, XVIb, and XVII) were confirmed by their nuclear magnetic resonance spectra—see Table I. For example, the monocobalt aldehyde (XVIa) exhibited proton signals at 7.80, 7.35, 4.42, and −0.06 τ with relative intensities of 12:6:2:1. These signals are assigned to the methyl groups on the two unsubstituted rings, the methyl groups on the formylated ring, the hydrogen on the unsubstituted chelate rings, and the formyl hydrogen, respectively. The diformyl chelate (XVIb) exhibited a similar spectrum, but with intensity ratios of 6:12:1:2.

The infrared spectra of the chelate aldehydes added further support to the assigned structures. The uncoördinated formyl groups gave rise to a carbonyl band at about 1670 cm.$^{-1}$, whereas a band at 1200 cm.$^{-1}$ indicated at least one unsubstituted chelate ring. A doublet at 1565 and 1530 cm.$^{-1}$ also indicated that not all acetylacetonate rings were substituted at the central carbon.

The monoaldehyde structures were further confirmed by substitution of the other two rings by electrophiles. These rings were brominated, chlorinated, and nitrated, giving rise to a series of hitherto unknown mixed ligand chelates. Such inert mixed ligand chelates of 1,3-dicarbonyl compounds would be difficult to prepare by disproportionation or direct chelation reactions. Chelates of this type may be key monomers from which non-crosslinked coördination polymers can be prepared, since either mono- or difunctionality can now be built into inert trisbidentate chelates by this procedure. Furthermore, such mixed ligand chelates are potential substrates for the measurement of interannular electronic effects and unsymmetrical ligand field effects.

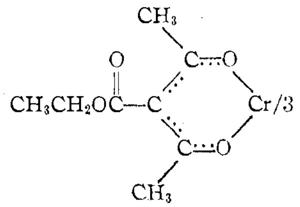


X = Br, NO_2
M = Co, Cr

XVIII

The aldehyde groups on the chelates XV, XVI, and XVII were surprisingly unreactive. Attempts to convert the formyl groups into oxime derivatives failed—even under rather strenuous conditions. Sodium borohydride in tetrahydrofuran had no effect on the chromium aldehyde (XVa). The aldehyde chelates gave positive Fehlings and Tollens tests, but preparative oxidation of the aldehyde groups has not yet proven successful. The lack of reactivity by the uncoordinated aldehyde group probably is best explained by the steric crowding of the two flanking methyl groups and by the high electron density on the central carbon of the chelate ring.

Further attempts to convert the aldehyde chelates to chelate carboxylic acids are being investigated. Attempts to saponify the ester, tris-(3-carbethoxy-2,4-pentanediono)-chromium (III) (XIX)[4] have led to decomposition of the complex.



XIX

Experimental[19-21]

Nitration of Tris-(2,4-pentanediono)-chromium(III). (A) By the Copper Nitrate–Acetic Anhydride Method.—A slurry of finely divided copper(II) nitrate trihydrate (10.75 g., 0.04 mole) in 200 ml. of acetic anhydride was stirred for 15 min. at 0°. At the end of this time a portion of the copper nitrate had dissolved to form a deep blue solution. To this slurry was added chromium(III) acetylacetonate (5.0 g., 0.014 mole), and the resulting slurry was stirred for 2 hr. at 0°. The cooling bath was removed and the mixture was stirred for another hour. The slurry was decomposed by stirring with a mixture of 600 ml. of water, 600 g. of ice, and 15 g. of sodium acetate. The resulting deep red precipitate was collected on a filter and washed first with water and then with ethanol. Red-violet needles were formed by recrystallizing the crude product (IV) from ethanol–chloroform; yield 4.9 g. (70%), m.p. 256–257°.

Anal. Calcd. for $C_{15}H_{18}N_3O_{12}Cr$: C, 37.20; H, 3.75; N, 8.68. Found: C, 36.91; H, 3.87; N, 8.77.

(B) Through Treatment with $N_2O_4 \cdot BF_3$.—To a cold slurry of $N_2O_4 \cdot BF_3$ (12.78 g., 0.1 mole) in 200 ml. of dry methylene chloride was added a solution of chromium acetylacetonate (4.0 g., 0.027 mole) in 25 ml. of methylene chloride. The mixture was stirred for 10 min. at 0° and then decomposed by shaking with a cold aqueous solution of urea and sodium bicarbonate. The green organic layer was removed and dried. The solvent was removed and the brown oil was crystallized from ethanol. The red-brown needles, m.p. 254–255°, weighed 0.32 g.

Tris-(3-nitro-2,4-pentanediono)-cobalt(III) (V).—This nitro chelate was prepared by the copper nitrate–acetic anhydride method; green crystals, m.p. 198° dec., 71% yield.

Anal. Calcd. for $C_{15}H_{18}N_3O_{12}Co$: C, 36.67; H, 3.69; N, 8.68. Found: C, 36.42; H, 3.82; N, 8.63.

Tris-(3-nitro-2,4-pentanediono)-rhodium(III) (VI).—This nitro chelate was prepared by the copper nitrate–acetic anhydride method; yellow crystals, m.p. 290–300° dec., 79% yield.

Anal. Calcd. for $C_{15}H_{18}N_3O_{12}Rh$: C, 33.66; H, 3.39; N, 7.85. Found: C, 34.06; H, 3.43; N, 7.83.

Bis-(3-nitro-2,4-pentanediono)-copper(II) (VII).—To a solution of acetylacetone (10 ml., 9.76 g., 0.09 mole) in 50 ml. of acetic anhydride was added in three portions copper(II) nitrate trihydrate (7.89 g., 0.033 mole) while the solution was stirred and maintained at 0°. The mixture was stirred at 0° for 2 hr. and then at room temperature for 18 hr. The green mixture was decomposed with a sodium acetate–ice-water mixture. The green crystals were collected, washed three times with cold water, and then recrystallized from ethanol-chloroform, m.p. 230–234° dec., 4.81 g. (42%).

Anal. Calcd. for $C_{10}H_{12}O_8N_2Cu$: C, 34.13; H, 3.41; N, 7.97. Found: C, 34.47; H, 3.60; N, 7.51.

An attempt to nitrate copper acetylacetonate by this method destroyed the chelate.

Nitration of Acetylacetone with Chromium Nitrate and Acetic Anhydride.—To a solution of acetylacetone (3.07 g., 0.031 mole) in 30 ml. of acetic anhydride and 3 ml. of ethanol was added slowly with stirring at 0°, chromium-(III) nitrate 9-hydrate (4.02 g., 0.010 mole). The purple solution was stirred for 2 hr. at 0–5° and then stirred at room temperature for 22 hr. The solution was decomposed by stirring for 3 hr. with a mixture of 250 ml. of H_2O, 250 g. of ice, and 3.0 g. of sodium acetate. The violet precipitate was collected and washed with water; yield, 2.58 g. of crude product. Chromatography on Florisil with benzene as the eluent afforded three products: band I was tris-(3-nitro-2,4-pentanediono)-chromium(III) (IV); band II, m.p. 241.5–242°, infrared maxima 1565, 1570, 1370, 1330, 1270, 1190, 960 cm.$^{-1}$; band III, m.p. 169.5–172°, infrared maxima 1565, 1510, 1370, 1330, 1270, 1190, 910 cm.$^{-1}$. The last two bands exhibit spectra very similar to the other nitro chelates and may be mono- and dinitro derivatives.

Tris-(1,1,1-trifluoro-2,4-pentanediono)-chromium(III) (XIII).—A mixture of 1,1,1-trifluoro-2,4-pentanedione

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[19] Melting points were determined on a Kofler micro hot stage apparatus using polarized light, but these are not corrected.

[20] Infrared spectra were determined on a Perkin-Elmer "Infracord" Model 137.

[21] We are indebted to T. D. Epley and G. Everett, Jr., for syntheses of several of our intermediates.

(10.0 g., 0.065 mole), 20 g. of urea, chromium trichloride hexahydrate (4.00 g., 0.067 mole), and 105 ml. of water was heated on a steam bath for 16 hr. The red-violet crystals were collected and recrystallized from chloroform–ethanol; yield 3.48 g. (31.5%), m.p. 150–151.5°. Chromatography on alumina failed to separate the fluoro chelate into diastereoisomeric *cis* and *trans* forms.

Anal. Calcd. for $C_{15}H_{12}O_6F_9Cr$: C, 35.25; H, 2.30; F, 33.40. Found: C, 35.26; H, 2.66; F, 32.52.

Monoformylation of Tris-(2,4-pentanediono)-cobalt(III).—To a solution of cobalt(III) acetylacetonate (10.68 g., 0.03 mole) in 80 ml. of freshly distilled, dry dimethylformamide was added dropwise phosphorus oxychloride (5.53 ml., 9.25 g., 0.06 mole). The solution was stirred magnetically and maintained at 0–5° during the addition, at 0° for 30 min., and then at room temperature for an additional 30 min. The green solution then was combined with a mixture of 1500 ml. of 1:1 ice–water and 10.0 g. of sodium carbonate monohydrate, and this slurry was stirred for 3 hr. The dull green crude crystalline product was collected on a filter, washed with three 10-ml. portions of water, sucked dry, and then recrystallized two times from ethanol–methylene chloride. The yield of pure (3-formyl-2,4-pentanediono)-bis-(2,4-pentanediono)-cobalt(III) (XVIa) was 6.37 g. (55%), m.p. 171.5–173.5 dec. The purity of the product was tested by chromatography of a small portion on Florisil using chloroform as an eluent. Under the same conditions a synthetic mixture of mono- and dialdehydes gave rise to two bands. The infrared spectrum of the pure monoaldehyde exhibits principal bands at 1604, 1560, 1517, 1421, 1371, 1275, 1208, and 1189 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{21}O_7Co$: C, 50.01; H, 5.47. Found: C, 49.33; H, 5.28.

Diformylation of Tris-(2,4-pentanediono)-cobalt(III).—To a solution of cobalt(III) acetylacetonate (10.68 g., 0.03 mole) in 125 ml. of freshly distilled, dry dimethylformamide was added dropwise phosphorus oxychloride (16.66 ml., 27.8 g., 0.18 mole). The solution was stirred magnetically and maintained at 0–5° during the addition and then at room temperature for 2.5 hr. The green solution then was combined with a mixture of 3000 ml. of 1:1 ice–water and 30 g. of sodium carbonate monohydrate, and this slurry was stirred for 15 hr. Deep green crystals of the crude product (9.0 g.) were collected on a filter, washed with two 50-ml. portions of water, sucked dry, and then recrystallized two times from ethanol–methylene chloride. The recrystallization step removes any monoformyl product which may be present. The yield of pure (2,4-pentanediono)-bis-(3-formyl-2,4-pentanediono-cobalt(III) (XVIb) was 7.52 g. (63%), m.p. 155–157° dec. The purity of the product was tested by chromatography and confirmed by an n.m.r. spectrum. The infrared spectrum of the dialdehyde exhibited all the peaks found in the monoaldehyde, but the anticipated changes in relative intensities of the peaks were observed.

Anal. Calcd. for $C_{17}H_{21}O_8Co$: C, 49.51; H, 5.14. Found: C, 49.15; H, 5.21.

Formylation of Tris-(2,4-pentanediono)-chromium(III).—The monoformyl chelate (XV) was prepared in the same way as the cobalt aldehyde (XVI). The violet crystalline aldehyde (XV) was obtained in 49% yield, m.p. 162–163° dec.

Anal. Calcd. for $C_{16}H_{21}O_7Cr$: C, 50.93; H, 5.57. Found: C, 50.97; H, 5.51.

The infrared spectrum of the chromium and cobalt aldehydes (XV and XVI) were very similar.

Formylation of Tris-(2,4-pentanediono)-rhodium(III).—To a solution of rhodium acetylacetonate (0.40 g., 0.001 mole) in 40 ml. of freshly distilled, dry dimethylformamide (DMF) was added phosphorus oxychloride (0.85 ml., 1.38 g., 0.009 mole) in 1 portion. The solution was stirred at room temperature for 105 min. The mixture was decomposed as described above. The aqueous DMF solution was back extracted with methylene chloride. The yellow crystalline product and the extract were combined and dried, and the solvent was removed. Chromatography on alumina and elution with benzene afforded 0.38 g. of pure rhodium acetylacetonate, m.p. 260–261°. Elution of 1:1 benzene–methylene chloride afforded 0.030 g. of the rhodium monoaldehyde (XVII) (7% yield). The crude aldehyde, m.p. 230–234°, was purified by chromatography on alumina and recrystallization from benzene–heptane, m.p. 233–235°.

Anal. Calcd. for $C_{16}H_{21}O_7Rh$: C, 44.87; H, 4.91. Found: C, 44.92; H, 4.90.

Tris-(1,1,1,5,5,5-hexafluoro-2,4-pentanediono)-rhodium(III) (X).—A solution of rhodium nitrate containing 0.088 g. of Rh^{+3} in 23 ml. was treated with a 10% aqueous sodium carbonate solution until rhodium hydroxide just began to precipitate. This solution was combined with 3 ml. of hexafluoroacetylacetone in a 50-ml. flask fitted with a Dry Ice condenser. The solution was heated at reflux for 30 min. and then treated again with aqueous sodium carbonate until rhodium hydroxide began to precipitate. The mixture then was heated at reflux for another 30 min. The cold finger was removed and allowed to warm to room temperature. The yellow crystalline product was washed from the cold finger with acetone and the crystals were collected and dried, m.p. 114.5–115°. The infrared spectrum of this chelate exhibits intense bands at 1610, 1560, 1535, 1450, 1435, 1350, 1260, 1210, 1150, 1100, 820, 810, 750, 715, and 705 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_3O_6F_{18}Rh$: C, 24.88; H, 0.42. Found: C, 25.64; H, 0.75.

Nitration of the Formyl Chromium Chelate (XVa).—To 15 ml. of acetic anhydride was added powdered copper(II) nitrate trihydrate (0.77 g., 0.0032 mole), and the slurry was stirred at 0° for 30 min. To the resulting deep blue mixture was added the aldehyde chelate (XV) (0.30 g., 0.0008 mole). The blue-violet solution was stirred for 2 hr. at 0–5° and then 3 more hr. at room temperature. The solution was decomposed by stirring for 2 hr. with 500 ml. of 1:1 ice–water which was buffered with 2.0 g. of sodium acetate. The fine purple precipitate was collected and recrystallized from ethanol–methylene chloride; yield 0.20 g. (54%), m.p. 217.5–218° dec. The infrared spectrum of bis-(3-nitro-2,4-pentanediono)-3-formyl-2,4-pentanediono)-chromium(III) exhibits all of the peaks found in the aldehyde and nitro chelates (XV and IV) except that there is no peak at 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{19}O_{16}N_2Cr$: C, 41.12; H, 4.10; N, 6.00. Found: C, 40.74; H, 3.98; N, 6.13.

Nitration of the Formyl Cobalt Chelate (XVI).—The green crystalline bis-(3-nitro-2,4-pentanediono)-3-formyl-2,4-pentanediono)-cobalt(III) was prepared by the same method used for the chromium analog; yield 32%, m.p. 183.4–184° dec.

Anal. Calcd. for $C_{16}H_{19}O_{11}N_2Co$: C, 40.52; H, 4.04; N, 5.91. Found: C, 41.11; H, 4.08; N, 5.63.

Bromination of the Formyl Cobalt Chelate (XVIa).—To a solution of the monoformyl cobalt chelate (1.0 g., 0.0026 mole) in 20 ml. of chloroform was added N-bromosuccinimide (1.01 g., 0.0057 mole). The green solution was stirred at room temperature for 90 min., after which it was extracted with 25 ml. of aqueous 5% $NaHSO_3$ solution and then with 25 ml. of water. The organic layer was separated and dried, and the solvent was removed. The green residue was purified by chromatography on Florisil using 1:1 benzene–methylene chloride as an eluent. The second band was collected and recrystallized from benzene–ethanol. The bis-(3-bromo-2,4-pentanediono)-(3-formyl-2,4-pentanediono)-cobalt(III) was isolated as green crystals, m.p. 162–165° dec., yield 0.234 g. The infrared spectrum of this chelate exhibits the same bands as the tribromo and the monoformyl cobalt chelates except that there is no band at 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{19}O_7BrCo$: C, 35.45; H, 3.53; Br, 29.48. Found: C, 35.34; H, 3.47; Br, 30.36.

Attempted Catalytic Hydrogenation of Tris-(3-nitro-2,4-pentanediono)-chromium(III) (IV).—A solution of 0.20 g. of the nitro chelate (IV) in 25 ml. of glacial acetic acid was treated with 60 p.s.i. of hydrogen over 0.025 g. of PtO_2 for 2 hr. at room temperature. The solution was filtered and decomposed with 10 ml. of ice water. The red-brown precipitate was collected and found to be the pure nitro chelate (IV). Attempted reduction of the rhodium nitro chelate (VI) gave the same results.

Attempted Catalytic Hydrogenation of Tris-(3-nitro-2,4-pentanediono)-cobalt(III) (V).—When the nitro cobalt chelate was treated in the above manner, the acetic acid solution became pink and no product could be isolated from the reaction mixture.

Attempted Chemical Reductions of Tris-(3-nitro-2,4-pentanediono)-rhodium(III) (VI).—(A) Gaseous hydrogen chloride was bubbled into a suspension of 5.0 g. of stannous chloride dihydrate in 100 ml. of glacial acetic acid until the mixture became a homogeneous solution. The solution was chilled in an ice bath to the point where it was semi-solid and 0.40 g. of the nitro rhodium chelate (VI) was added while the solution was stirred vigorously. The ice bath was removed and the mixture was stirred for 45 min. The solution was decomposed with 500 g. of ice-water. The yellow precipitate was collected and dried; yield 0.21 g. An infrared spectrum of this product showed that it was the nitro rhodium chelate (VI).

The acidic filtrate was neutralized with 6 *N* sodium hydroxide and then extracted three times with methylene chloride. The extracts were colorless and left no residue upon evaporation of the solvent.

(B) A mixture of 0.10 g. of the rhodium nitro chelate (VI), 1.0 g. of zinc dust, and 100 ml. of glacial acetic acid was heated quickly to the boiling point and then allowed to cool to room temperature. The total reaction time was 30 min. The usual workup afforded a small amount of the nitro chelate (VI). The majority of the starting material seemed to have been destroyed during the reaction.

Notes

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Borazine Derivatives. II. A Carbon-Bridged Bisborazine Compound[1]

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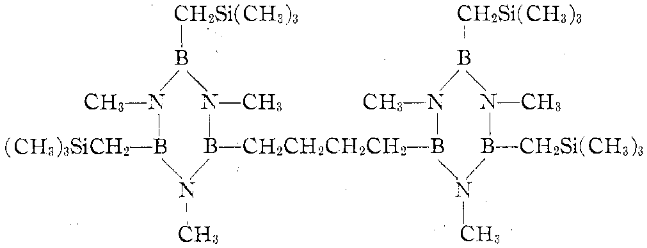
In a previous paper[1] we described the preparation of B-tris-(trimethylsilylmethyl)-N-trimethylborazine and related compounds by the Grignard procedure. These compounds exhibited high thermal stability and were stable toward basic hydrolysis and oxidation. For some possible applications it was desirable to have similar compounds, but of higher molecular weight. One approach to this goal examined by us involved the linking of borazine rings through difunctional organic groups. We report here the synthesis of B-chloro-B-bis-(trimethylsilylmethyl)-N-trimethylborazine and its reaction with the di-Grignard reagent of 1,4-dichlorobutane to give the carbon-bridged borazine I. This compound was not



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[1] Part I. D. Seyferth and H. P. Kögler, *J. Inorg. Nucl. Chem.*, **15**, 99 (1960).