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The Bromination of Tris(3-phenyl-2,4-pentanediono)cobalt(III)*[1]

Yukito MURAKAMI and Katsuyuki NAKAMURA*[2]

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka

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Tris(3-phenyl-2,4-pentanediono)cobalt(III) has been treated with three kinds of bromination reagents; bromine in the presence of pyridine, pyridine perbromide, and *N*-bromosuccinimide. Components of the product species have been detected by means of thin-layer chromatography and fractionated by liquid-chromatography. The characterization of bromination products has been performed by the aid of infrared and nuclear magnetic resonance spectroscopy. The bromination has taken place with the chelate ring remaining intact, and converted methyl groups in the coordinated ligands to bromomethyl. The cleavage of coordinate bonds, which has occurred afterward, has resulted in the formation of a metal-absent brominated ligand. Among various bromination products, the one with lowest bromination degree (monobrominated chelate) has been fully characterized in accordance with the experimental facts: elemental analysis, the appearance of a new infrared band at 1248 cm^{-1} which is attributable to CH_2 wagging vibration of the CH_2Br group, and two doublet NMR peaks at 3.55, 3.69, 3.94 and 4.09 in δ-value which are due to nonequivalent protons of the CH_2Br group. Reaction mechanism has been discussed in terms of electrophilic substitution process.

Much work has been carried out on the halogenation of metal chelate compounds of β-diketones in relation to the quasiaromatic nature of the chelate rings.[1-5] In order to extend the halogenation reaction to the metal complexes formed with 2,4-pentanediones which carry an aromatic substituent at the 3-position, tris(3-phenyl-2,4-pentanediono)-chromium(III)*[3] has been treated in the previous study.[6] In pursuing this type of reaction with the same purpose, tris(3-phenyl-2,4-pentanediono)cobalt(III)*[4] was brominated in this work and the resulting products were characterized by means of infrared and nuclear magnetic resonance spectroscopy. In addition, these results were compared with the reactivity of the chromium chelate.

Experimental

Bromination of Co(PAA)$_3$ with Bromine. (a) $Br_2/Co(PAA)_3=2$. A solution of bromine (0.96 g, 6 mmol) in 10 m*l* of chloroform was added dropwise, with stirring, to a solution of Co(PAA)$_3$ (1.75 g, 3 mmol) and pyridine (0.48 g, 6 mmol) in 150 m*l* of chloroform in 30 min at 25°C, and the stirring was continued for another 15 min. The resulting reaction mixture was evaporated under reduced pressure below 15°C, and extracted with benzene. The extraction residue of blue solid was identified as the pyridine-cobalt(III) complex. The benzene extract was evaporated to remove benzene (A), washed with water, and then dissolved in a small amount of methanol. The methanol solution was allowed to stand overnight in a refrigerator and the resulting green solid (B) was collected. The thin-layer chromatograms with a combination of Wakogel B-O (silica gel with no binder) and chloroform for materials A and B along with other related ones are shown in Fig. 1. The brominated material A was then fractionated into five components by means of liquid-chromatography with a combination of silica gel (60—80 mesh) and benzene. The solid materials recovered from the eluted fractions were recrystallized from chloroform-methanol. These products are (see Fig. 1): i) yellow liquid; ii) green crystals (bromination prod-

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*[1] Contribution No. 148 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

*[2] Present address: Technical Research Laboratories, Asahi Chemical Industries, Ltd., Itabashi-ku, Tokyo.

1) R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

2) J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *ibid.*, **83**, 531 (1961).

3) Y. Nakamura and S. Kawaguchi, This Bulletin, **38**, 954 (1965).

4) Y. Nakamura and S. Kawaguchi, *ibid.*, **40**, 1179 (1967).

5) Y. Nakamura, M. Hirata and S. Kawaguchi, *ibid.* **40**, 2572 (1967).

*[3] Abbreviated as Cr(PAA)$_3$ hereafter.

6) Y. Murakami and T. Wakabayashi, *ibid.*, **38**, 2207 (1965).

*[4] Abbreviated as Co(PAA)$_3$ hereafter. Preparation of this chelate has been mentioned previously (K. Nakamura and Y. Murakami, *Tech. Reports Kyushu Univ.*, **38**, 329 (1965)).

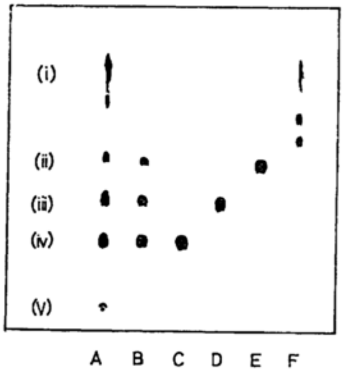

Fig. 1. Thin-layer chromatograms of various bromination products obtained with a combination of Wakogel B-O and chloroform: A, bromination product obtained from the reaction of Co(PAA)$_3$ with bromine at 1:2 molar ratio; B, green solid obtained from A; C, Co(PAA)$_3$; D, BRP-1; E, BRI-2; F, BRP-3.

uct 2*[5]), mp 140—140.5°C (dec.), yield a few mg, R_f 0.30; iii) green crystals (bromination product 1*[5]), mp 161—162.5°C (dec.), yield 100 mg, R_f 0.20; iv) green crystals (unreacted cobalt chelate), mp 183—184°C (dec.), 240 mg, R_f 0.15; v) greenish brown solid (unidentified).

Found for BRP-1: C, 59.83; H, 5.01%. Calcd for $C_{33}H_{32}O_6BrCo$ (monobromochelate): C, 59.74; H, 4.86%.

(b) $Br_2/Co(PAA)_3=6$. A solution of bromine (2.88 g, 18 mmol) in 10 m*l* of carbon tetrachloride was added, with stirring, to a solution of Co(PAA)$_3$ (1.75 g, 3 mmol) and pyridine (2.5 g) in 200 m*l* of carbon tetrachloride in 20 min at 9—11°C. The stirring was continued for another 10 min at 9°C, and the mixture was evaporated under reduced pressure at room temperature. The residue was extracted with benzene, washed with water and then dried over sodium sulfate. The thin-layer chromatogram for this benzene extract is shown in Fig. 1 (bromination product 3*[5]). However, the liquid-chromatographic separation of this extract into components was not successful.

Bromination of Co(PAA)$_3$ with Pyridine Perbromide. A solution of pyridine perbromide (0.72 g, 3 mmol) in 10 m*l* of chloroform was added dropwise, with stirring, to a solution of Co(PAA)$_3$ (1.75 g, 3 mmol) in 150 m*l* of chloroform in 90 min at 1°C, and the stirring of another 60 min was performed at the same temperature. The resulting bluish green solution was evaporated under reduced pressure to remove solvent, and the residue was washed several times with each small portion of water. Into this residue was added a small amount of methanol, and the mixture was allowed to stand overnight in a refrigerator to afford a green precipitate. This solid was then washed with cold methanol and petroleum ether successively; 0.89 g. Repeated liquid-chromatographic separation and purification of this green substance with a combination of silica gel (60—80 mesh) and benzene, followed by recrystallization from benzene, afforded green crystals; mp 161—162°C, yield 10 mg, identified as BRP-1. The unreacted cobalt chelate was also recovered; 0.71 g.

Bromination of Co(PAA)$_3$ with *N*-Bromosuccinimide. A 1.60 g (9 mmol) sample of *N*-bromosuccinimide was added to a solution of Co(PAA)$_3$ (1.75 g, 3 mmol) in 250 m*l* of carbon tetrachloride. Then, the mixture was placed in an oil-bath (85—90°C) and refluxed for 15 min with vigorous stirring. After being cooled down by the use of an ice-water bath, the reaction mixture was filtered off. The filtrate was then concentrated *in vacuo* to recover green solid (1.66 g). Liquid-chromatographic separation of the green material into components with the combination of silica gel (60—80 mesh) and benzene afforded BRP-1 (a few mg), BRP-2 (very small amount), and the unreacted cobalt chelate (1.6 g).

Bromination of Cr(PAA)$_3$ with Bromine. A solution of bromine (5.75 g, 36 mmol) in 30 m*l* of carbon tetrachloride was added dropwide, with stirring, to a solution of Cr(PAA)$_3$ (3.45 g, 6 mmol) and pyridine (2.85 g, 36 mmol) in 500 m*l* of carbon tetrachloride in 35 min at 15°C, and the stirring was continued for another 20 min. Then, the mixture was filtered off, and the filtrate was concentrated *in vacuo* and then extracted with benzene. The thin-layer chromatogram with a combination of Wakogel B-O and benzene for the benzene extract is shown in Fig. 2. The product was then fractionated into components by means of liquid-chromatography with a combination of silica gel (60—80 mesh) and benzene: i) yellow oily liquid, 530 mg; ii) green solid, 150 mg; iii) and iv) dark yellow solid, 220 mg; v) brownish violet solid, 430 mg; and vi) unreacted chromium chelate, 560 mg.

Spectral Measurements. The infrared spectra were obtained on a Koken Model DS-301 spectrophotometer equipped with sodium chloride optics.*[6]

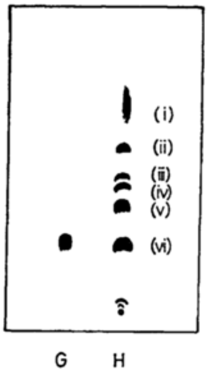

Fig. 2. Thin-layer chromatograms of Cr(PAA)$_3$ (G) and its bromination product (H) obtained with a combination of Wakogel B-O and benzene.

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*[5] Bromination products 1, 2 and 3 are designated as BRP-1, BRP-2, and BRP-3, respectively, throughout this paper.

*[6] Measurements were carried out by Miss Y. Tomita of this Department.

The NMR spectra were recorded on a Varian A-60 spectrophotometer*7 operating at 60 Mc. Chemical shifts are reported in ppm from internal tetramethylsilane (TMS) and data are good to 0.5 cps. The spectra were calibrated by the use of chloroform signal (436 cps from TMS) as the secondary reference. Chloroform used as solvent was purified by the standard method and was free from alcohol. Fractional distillation of this solvent was carried out just before use.

Characterization of Bromination Products

As described in the preceding section, the brominated material obtained from $Co(PAA)_3$ consists of various species of different bromination-degree. Among these reaction products, however, BRP-1 was obtained in the highest yield, relative to others, under mild conditions. BRP-1 was isolated in the form of green crystals and eluted from a chromatographic column before the unreacted chelate $Co(PAA)_3$. First of all in characterizing this material, elemental analysis confirms this undoubtedly to be a monobrominated chelate. Infrared spectra, which are illustrated in Fig. 3, provide the second information. Among various alteration of absorption peaks in the brominated product with reference to the starting chelate $Co(PAA)_3$, the appearance of a new peak at 1248 cm^{-1}, which can be assigned to CH_2 wagging vibration of the CH_2Br group,[6,7] is most significant and provides the decisive evidence for the characterization of the bromination product. In addition, the following changes in absorption bands are observed: absorption peaks due to asymmetric and symmetric deformation of CH_3 group in $Co(PAA)_3$, which appear at 1423 and 1349 cm^{-1} respectively, diminish their intensity in the bromination product. On the other hand, in the brominated material the 1433 cm^{-1} band assigned to CH_2 deformation is detected and the 1300—1400 cm^{-1} region, where the CH_3 symmetric deformations demonstrate their peaks, becomes more crowded by the appearance of other peaks at 1387 and 1368 cm^{-1}. Moreover, the CH_3 rocking vibration absorb-

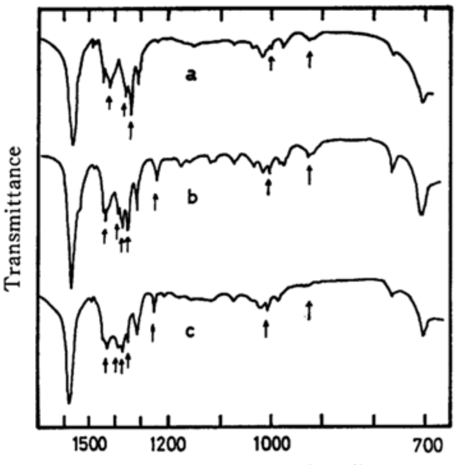

Fig. 3. IR spectra of cobalt(III) chelates (KBr disk method): a, $Co(TAA)_3$; b, BRP-1; c, BRP-2.

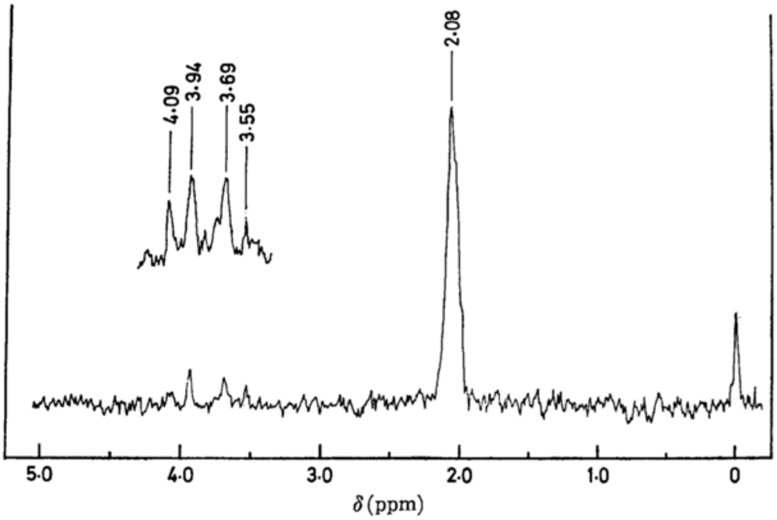

Fig. 4. NMR spectrum of the brominated cobalt(III) chelate (BRP-1) in chloroform (73 mg/0.8 ml); TMS as an internal reference.

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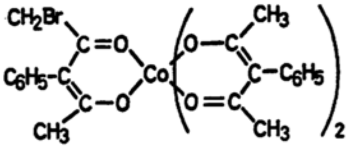
*7 Measurements were carried out by Mr. Y. Nakayama and Mr. M. Fukumitsu of this Department.

7) N. B. Colthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York (1964), p. 317.

ing at the 1000 cm^{-1} region increases its band-intensity as Co(PAA)$_3$ is converted to the brominated substance. The NMR spectrum is to be investigated in the third place. Figure 4 shows the NMR spectrum for the bromination product in part, where proton signals characteristic of CH$_3$ and CH$_2$X group can be observed. A NMR signal at δ 2.08 is attributed to CH$_3$ protons, while four signals at 3.55, 3.69, 3.94 and 4.09 in δ-value are due to protons of the CH$_2$Br group. Judging from the steric interaction of the CH$_2$Br group with the phenyl in the brominated chelate, it is reasonable to consider that the former is somehow fixed in space relative to the latter. This may provide a small chemical shift difference between two protons of the CH$_2$Br group (CH$_a$H$_b$ type) and then produces two doublets as a result. In conformity with the above experimental evidence, structure I is now assigned to BRP-1, where only one methyl is brominated to bromomethyl (CH$_2$Br) among six methyl groups in the chelate.



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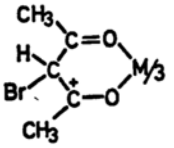

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BRP-2 was isolated as green crystals and eluted from chromatographic column faster than BRP-1. All the significant changes in infrared spectrum noticed for BRP-1 become more apparent in BRP-2, and in addition the 929 cm^{-1} band in the unbrominated chelate attributable to the coupling stretching vibration of C–CH$_3$ and CO[8] reduces its intensity

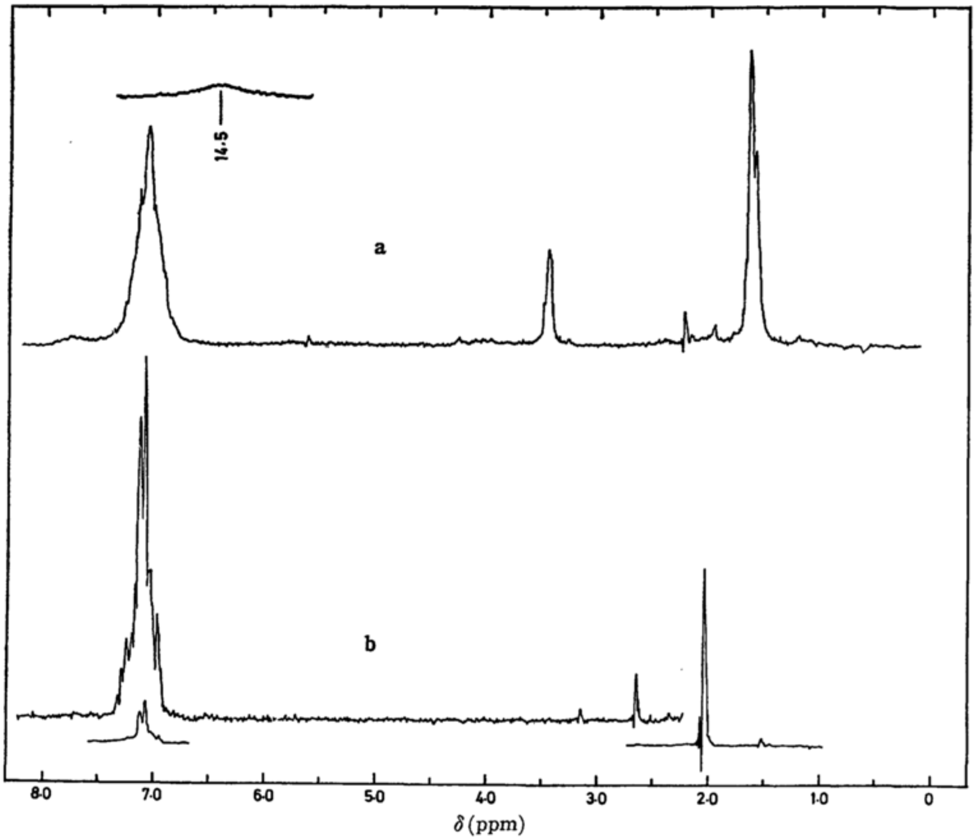

Fig. 5. NMR spectra of 2,4-pentanediones: a, yellow liquid (the metal-free bromination product of Co(PAA)$_3$); b, 3-bromo-3-phenyl-2,4-pentanedione.

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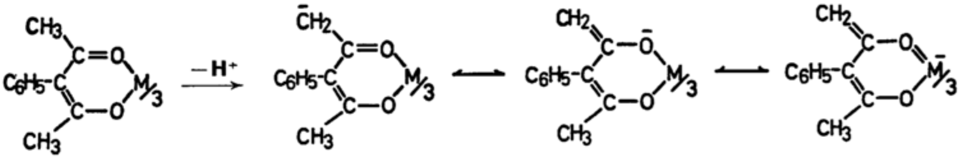
[8] K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).



II III IV V

in this product. The above experimental facts suggest that the material is of higher bromination-degree with more bromomethyl groups relative to BRP-1.

It is evident that BRP-3 contains two kinds of cobalt complexes as thin-layer chromatogram indicates (Fig. 1). But characterization of these species was not performed since these cobalt complexes were not made completely free from yellow oily liquid. Nevertheless, investigation and comparison of chromatographic behavior and infrared spectra of bromination products of Cr(PAA)$_3$ with those of Co(PAA)$_3$ suggest that above brominated cobalt complexes contain more bromomethyl groups than BRP-2 does.

Yellow liquid which came off first from a chromatographic column was not stable in the air at room temperature, and turned brown by evolution of white acidic fumes upon overnight standing. Since this yellow substance freshly obtained from a chromatographic column reacted with copper acetate to yield the corresponding metal chelate species, it is evident that this yellow substance still hold the β-diketone moiety. The NMR spectrum for the yellow substance obtained when 2 mol of bromine reacted with 1 mol of Co(PAA)$_3$ is shown in Fig. 5. The NMR signals located at 1.64, 3.48, 7.13 and 14.5, which can be assigned to protons of CH_3, CH_2Br, C_6H_5, and OH respectively, demonstrate their intensity ratio to be approximately 4:1:5:1. Thus, the NMR evidence suggests that this yellow liquid consists of 3-phenyl-2,4-pentanedione and 1-bromo-3-phenyl-2,4-pentanedione at approximately equal ratio. Moreover, it is clear that no bromine has been introduced at the 3-position of 3-phenyl-2,4-pentanedione, as understood by comparison of the NMR spectrum for 3-bromo-3-phenyl-2,4-pentanedione with the above one (Fig. 5 a, b).

The comparison of the bromination products for Cr(PAA)$_3$ with those obtained previously in this laboratory[6] by means of spectroscopic and other physical and chemical methods confirms the bromination product ii stated in the preceding section to be the highly brominated chelate (with hexa or pentabromomethyl groups) in agreement with the previous results, while the later fractions from a chromatographic column (iii—v) were identified as less-brominated compounds.

Discussion

3-Phenyl-2,4-pentanedione undergoes substitution with bromine at the 3-position to yield 3-bromo-3-phenyl-2,4-pentanedione, while the metal-absent material (yellow liquid) obtained by the bromination of Co(PAA)$_3$ and Cr(PAA)$_3$ carries only a bromomethyl group. Thus, the bromination takes place undoubtedly with the chelate ring remaining intact, and the cleavage of coordinate bonds occurs afterward. In the halogenation reaction of metal complexes formed with the unsubstituted 2,4-pentanedione, the reagents employed for that purpose were considered to be electrophilic.[9] If the same situation can be applied to the present reaction, an activated complex, which is formed through deprotonation of methyl groups, may be represented by resonance structures III—V. In accordance with our previous spectroscopic studies on the metal complexes of 3-phenyl-2,4-pentanedione,[10,11] it became evident that the phenyl ring interacts electronically with the chelate ring and the π-electron delocalization in the chelate ring increases as a result relative to the corresponding metal complexes of the unsubstituted 2,4-pentanedione. This effect may help to stabilize the above-mentioned activated state and thus facilitate the reaction. Moreover, the effect of metal species on the reactivity was also noticed in this work. At 2:1 molar ratio of bromine to Cr(PAA)$_3$, no bromination product was detected, while various bromination products were obtained in the reaction of Co(PAA)$_3$ under comparable experimental conditions. Judging from this result, the cobalt chelate is more reactive than the corresponding chromium chelate. This may be ascribed to the greater π-electron delocalization in the chelate rings of Co(PAA)$_3$ than in those of Cr(PAA)$_3$ as became evident by spectroscopic studies.[10,11]

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[9] J. P. Collman, *Angew. Chem., Internat. Edit.*, **4**, 132 (1965).

[10] Y. Murakami and K. Nakamura, This Bulletin, **39**, 901 (1966).

Meanwhile, Kluiber[1] has put forward an activated complex shown by VI for the bromination of 2,4-pentanedione complexes, where the chelate ring remains intact throughout the transformation. In the bromination of either $Co(PAA)_3$ or $Cr(PAA)_3$, however, a great steric hindrance of the phenyl group seems to be exerted against a bromine approaching to the 3-position, and this interaction prohibits the formation of an activated complex similar to VI. As a result, this effect fails to give any kind of the 3-brominated compounds.

In summary, the bromination of both $Co(PAA)_3$ and $Cr(PAA)_3$ proceeds with retention of coordinate bonds. The reactivity of 3-phenyl-2,4-pentanedione complexes suffers metal-dependency and $Co(PAA)_3$ is more reactive than $Cr(PAA)_3$. On the other hand, a bromomethyl group seems to destabilize the coordinate bonds in the brominated complexes and the metal-free brominated ligand was also produced as a result.

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11) Y. Murakami, K. Nakamura, H. Uchida and Y. Kanaoka, *Inorg. Chim. Acta*, June (1968).