Cobalt(III)-tren Complexes of 3-Formylcamphor[1)]

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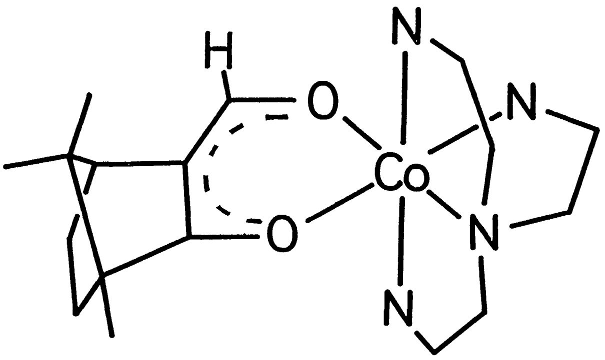
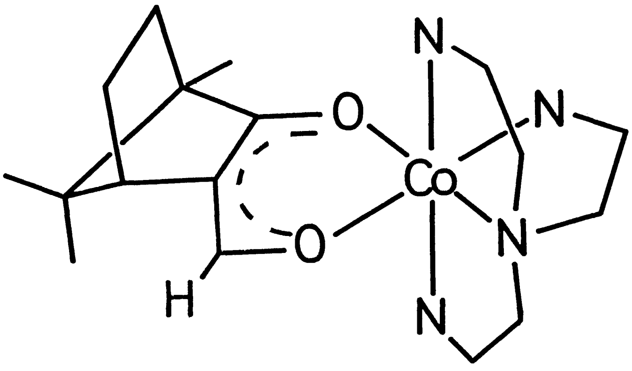
3-Formylcamphor Co(III) complexes of a tripod-like ligand, tren, were prepared and the two possible geometrical isomers were separated successfully. The crystal structure of one of them was determined by X-ray diffraction. A red plate-like crystal was monoclinic, space group $P2_1$, $a=12.401$ (2), $b=9.9400$ (7), $c=10.932$ (1) Å, $\beta=108.44$ (1)°, and $Z=2$. The structure was refined to $R=0.047$ on 2818 reflections. The geometrical isomers were compared sepectroscopically.

There have been few reports on Co(III)-tren complexes compared to those of Co(III)-trien. Until now, the Co(III)-tren complexes containing amino acids, diamines,[3)] and β-diketones[4)] have been reported. The tren complexes are much more suitable for model compounds to study the optical activities of such complexes. Because the trien complexes have two asymmetric centers and, thus, extra isomerisms occur. We have investigated both the crystal structure and optical activity of the Co(III)-tren complexes of unsymmetrical β-diketone type ligands.[4c)] In these complexes a pair of geometrical isomers is possible. If the coordinating atoms are of the same kind as in this case, it is very difficult to differentiate the geometrical structure spectroscopically, due to a lack of fundamental data concerning Co(III)-tren complexes. In the present work, Co(III)-tren complexes of 3-formylcamphorato(fc) were studied. Two geometrical isomers, **I** and **II**, (as shown in Fig. 1) were successfully separated by cation exchange chromatography. Contrary to tris(fc)metal complexes, only little regioselectivity was observed in this case.[5)] We determined the crystal structure of an isomer, **II**, $[Co(fc)(tren)](ClO_4)_2 \cdot H_2O$, eluted slowly on the column of cation-exchanging resin by an X-ray diffraction method, because of the inability to use various forms of spectroscopy.



I



II

Fig. 1. Geometrical isomers of $[Co(fc)(tren)]^{2+}$.

The ^1H NMR and ^{13}C NMR spectra of the two isomers were measured, and almost all of the signals could be assigned. They showed significant differences in the ^1H NMR, ^{13}C NMR, and CD spectra. The geometrical structure of Co(III)-tren complexes can be determined through comparison with the chemical shifts of the carbonyl carbons. The CD spectra can be discussed in terms of both vicinal and quasienantiomeric effects. The vicinal effect is more important than the quasienantiomeric effect in the case of 3-formylcamphor.

Experimental

Materials. a) Preparation of Ligands. Hfc was prepared by the Claisen Reaction of camphor with pentyl formate.[6)] The resulting white powder was confirmed through a measurement of the ^1H NMR. The starting complex, $[Co(CO_3)(tren)]^+$, was prepared as before.[4)]

b) Preparation of the Isomers, I and II. An isomeric mixture of fc complexes was prepared (as described previously) and separated by cation-exchanging chromatography using a 0.5 M (1 M=1 mol dm^{-3}) sodium chloride solution.[4)] A solution of the mixture (3 mmol in each column) was poured into an SP-Sephadex (C-25, 3×150 cm) column. The isomers were eluted by a 0.25 M sodium sulfate solution and completely separated into two bands, which were named **I** and **II** in the order of elution. After excess sodium sulfate was removed by adding ethanol to each eluted solution, six equivalents of sodium perchlorate were added. The resulting perchlorate crystals of each isomer, **I** or **II**, were filtered. The two isomers were recrystallized from a 5% aqueous solution of sodium perchlorate. IR (KBr) 3100—

3300 cm^{-1} broad peak (N–H stretching), 1610 cm^{-1} (carbonyl stretching). Yield: 19% from the beginning of preparation of complex mixtures. Relative ratio of **I**:**II**=45:55. Found for **I**: C, 33.87; H, 5.85; N, 9.30%. Found for **II**: C, 33.73; H, 5.80; N, 9.19%. Calcd for [Co(fc)(tren)]$(ClO_4)_2 \cdot H_2O$=$C_{17}H_{33}N_4O_{10}Cl_2Co \cdot H_2O$: C, 33.84; H, 5.85; N, 9.29%.

Physical Measurement. The absorption spectra were recorded on a Hitachi 200-10 spectrophotometer and the CD spectra on a JASCO J-500A spectropolarimeter. All measurements were carried out in aqueous solution at room temperature. The ^{1}H and ^{13}C NMR spectra were recorded in deuterium oxide on a Hitachi R-20, JEOL JNM-FX90, and GX-400 NMR spectrometer at room temperature. The internal reference used was dioxane (methylene protons and carbons were assumed as 3.71 and 67.40 ppm, respectively). Calculations for structure analyses were carried out on a HITAC M-680 computer at the University of Tokyo.

Table 1. Atomic Parameters[a)]

Atom	x	y	z	B_{eq}
Co	30704(4)	50000	23261(5)	209(1)
Cl(1)	62749(14)	98600(19)	26900(15)	447(4)
Cl(2)	20410(12)	96688(15)	25786(14)	383(4)
O(1)	1530(3)	5502(4)	1976(4)	31(1)
O(2)	3154(3)	3728(4)	3652(3)	28(1)
O(3) m1	6697(9)	8601(12)	2625(10)	59(3)
O(4) m1	5747(12)	10341(13)	1462(7)	83(4)
O(5) m1	5435(12)	9501(19)	3249(11)	87(5)
O(6) m1	6927(9)	10790(11)	3596(11)	61(3)
O(7) m2	2176(20)	10924(13)	2314(19)	122(9)
O(8) m2	967(11)	9554(43)	2452(21)	199(17)
O(9) m2	2101(21)	8790(16)	1613(14)	141(9)
O(10) m2	2516(13)	9011(14)	3773(9)	79(4)
O(11)	1453(5)	4584(6)	−1318(5)	58(2)
O(12) m3	6398(32)	10662(35)	3674(13)	213(17)
O(13) m3	7131(13)	8752(19)	2862(13)	71(5)
O(14) m3	6425(36)	10682(29)	1690(24)	168(17)
O(15) m3	5124(18)	9721(29)	2486(57)	258(26)
O(16) m4	2600(13)	8880(19)	2017(15)	74(5)
O(17) m4	896(15)	9896(46)	2005(18)	170(15)
O(18) m4	2759(25)	10875(25)	2835(36)	167(17)
O(19) m4	2261(21)	9772(56)	3987(19)	163(15)
N(1)	4660(3)	4702(4)	2496(4)	26(1)
N(2)	2706(4)	3461(5)	1142(4)	30(1)
N(3)	3044(4)	6269(5)	978(4)	28(1)
N(4)	3621(4)	6323(5)	3733(4)	33(1)
C(1)	4743(4)	3240(6)	2162(6)	33(1)
C(2)	3767(5)	2926(6)	959(5)	34(1)
C(3)	5018(5)	5596(7)	1583(5)	34(1)
C(4)	4201(5)	6767(6)	1147(6)	36(1)
C(5)	5313(4)	4993(8)	3868(4)	35(1)
C(6)	4901(5)	6325(7)	4221(5)	37(1)
C(7)	2304(5)	3463(6)	4051(5)	31(1)
C(8)	1250(5)	4029(7)	3574(6)	35(1)
C(9)	941(3)	4984(6)	2604(4)	25(1)
C(10)	−275(4)	5399(6)	2414(5)	32(1)
C(11)	−169(6)	6234(10)	3623(8)	53(2)
C(12)	113(7)	5257(17)	4733(8)	76(4)
C(13)	211(6)	3873(11)	4031(8)	63(3)
C(14)	−753(5)	4022(9)	2653(9)	56(2)
C(15)	−770(8)	2964(10)	1694(13)	81(4)
C(16)	−1953(7)	4113(17)	2777(15)	104(5)
C(17)	−858(5)	6113(9)	1155(7)	49(2)

a) Positional parameters are multiplied by 10^5 for Co, Cl, 10^4 for O, N, C. $B_{eq}=4/3 \cdot \boldsymbol{a}(\text{beta}) \cdot \boldsymbol{a}$ are multiplied by 10^2 for Co, Cl, 10^1 for O, N, C. m_j indicate multiplicities of each atom. m1=0.56, m2=0.54, m3=0.44, m4=0.46.

X-Ray Data Collection. The unit cell-parameters and reflection data using a single crystal (ca. 0.42×0.37×0.47 mm) were measured on a Rigaku four-circle diffractometer (AFC-3) with graphite-monochromatized Mo $K\alpha$ rediation at The Institute for Solid State Physics. The cell dimensions were determined by least-squares calculations based on 40 reflections ($15.2 < \theta < 24.9$). Systematic absences of 0, k, 0 ($k=2n+1$) led to the space group $P2_1$.

Crystal data: $C_{17}H_{35}N_4O_{11}Cl_2Co$, M.W.=603.33, space group $P2_1$, a=12.401(2), b=9.9396(7), c=10.932(1) Å, β=108.44(1)°, V=1278.3(2) Å^3, Z=2, D_x=1.568, D_m=1.562 g cm^{-3} (by the floatation), (Mo $K\alpha$)=9.710 cm^{-1}, $F(000)$=628. The intensity data were collected by the θ–2θ scan technique up to $2\theta=55°$ with a scan rate of 2° min^{-1} in θ. The intensity data were converted to F_o data in the usual manner. A total of 2818 independent reflections with $|F_o| > 2.5\sigma\ |F_o|$ of the measured 3347 reflections were considered, as observed, and used for the structure analysis. Absorption was not corrected.

Determination of the Crystal Structure of the Isomer II. The structure was solved by a heavy-atom method using the UNICS III program system. All of the non-hydrogen atoms were refined by block-diagonal least squares with anisotropic thermal parameters. Hydrogen atoms were located using difference Fourier maps, except for the hydrogens of water, which were included in a refinement with isotropic thermal parameters. At a later stage of the refinement, the oxygen atoms of two perchlorate ions were found to have disordered dispositions. The final positional parameter shifts of almost all atoms, except for the oxygen atoms of the perchlorate, were less than the standard deviations. The final residual values were R=0.047 and R_w=0.066, where the weights are $w=1/(1.0+0.011|F_o|^2)$ for $|F_o|<15.0$ and $w=1/(\sigma^2/|F_o|+0.011|F_o|^2)$ for $F_o>15.0$. The final defference Fourier map showed a peak of 0.6 e Å^{-3}. The map showed several peaks less than 0.3 e Å^{-3}. The configuration was assigned on the basis of the known configuration of d-camphor. The y-coordinate of the cobalt

Table 2. Interatomic Distances and Bond Angles for [Co(fc)(tren)]$(ClO_4)_2 \cdot H_2O$

Bond distances/Å			
Co–O(1)	1.893(4)	Co–O(2)	1.901(4)
Co–N(1)	1.943(4)	Co–N(2)	1.962(5)
Co–N(3)	1.933(5)	Co–N(4)	1.974(6)
O(1)–C(9)	1.260(7)	O(2)–C(7)	1.289(7)
C(8)–C(9)	1.384(9)	C(7)–C(8)	1.366(8)
C(9)–C(10)	1.513(8)	C(8)–C(13)	1.530(13)
C(7)–H(C-7)	1.07(10)		
Bond angles/degree			
O(1)–Co–O(2)	97.9(2)	O(1)–Co–N(1)	171.1(2)
O(2)–Co–N(1)	91.0(2)	O(2)–Co–N(3)	177.7(2)
N(1)–Co–N(2)	87.7(2)	N(1)–Co–N(3)	86.8(2)
N(1)–Co–N(4)	86.3(2)	Co–O(1)–C(9)	120.3(4)
N(2)–Co–N(4)	169.8(2)	O(1)–C(9)–C(8)	129.1(6)
C(7)–C(8)–C(9)	125.1(6)	O(2)–C(7)–C(8)	124.9(6)
Co–O(2)–C(7)	122.8(4)	O(1)–C(9)–C(10)	122.6(5)
C(7)–C(8)–C(13)	129.5(7)		
O(2)–C(7)–H(C-7)	118(5)	C(8)–C(7)–H(C-7)	117(5)

atom was fixed at 0.5. The final positional paprameters of non-hydrogen atoms and selected bond distances and angles are listed in Tables 1 and 2. The positional parameters of hydrogen atoms (Table a), the thermal parameters of all the atoms (Table b), structure factors (Table c), and nonessential interatomic distances and angles (Table d) are being kept as Document No. 9103 at the Office of the Editor of Bull. Chem. Soc.

Results and Discussion

The Crystal Structure of Complex II. Two rod-like complex cations lie along the *a*-axis on different levels along the *b*-axis by y=0.5, and the remaining space is filled with two water molecules and four perchlorate ions. As is often observed in other perchlorate salts, the perchlorate ions have disordered positions; furthermore, several interatomic distances and angles of the perchlorate ions deviate from the normal values and the thermal parameters of several oxygen atoms are unreasonably large.

A perspective drawing of the complex cation is shown in Fig. 2. The cobalt atom is octahedrally surrounded by two oxygen and four nitrogen atoms. Since the three primary nitrogen atoms are constrained to approach the tertiary nitrogen (N(1)) to form three five-membered chelate rings (denoted as A, B, and C as shown in Fig. 2), the angles subtended at the cobalt atom by the chelate rings are compressed to an average angle of 87.0°, and the interatomic distance of Co–N(3) is significantly short compared with those of Co–N(2) and Co–N(4). The two chelate rings, B and C, have an almost symmetrical conformation. These features are very similar to those of other tren complexes. Although the six-membered chelate ring adopts an almost planar conformation, the atoms with large thermal parameters within fc group are rather flexible perpendicularly to the ring as a whole, as is obseved in the ellipsoid of each atoms. This flexibility might be responsible for the relatively large standard deviation of several interatomic distances and angles (C(12), C(13), C(15), and C(16)).

Characterization of I and II. Though the infrared spectra of the two isomers showed only general features of β-diketonatocobalt(III) complexes, no notable difference was observed between them. Several significant differences were observed in the ^{1}H NMR, ^{13}C NMR, CD spectra. Upon assigning the NMR spectra, we had to refer to the assignment of $[Co(acac)(tren)]^{2+}$ and camphor. Twelve protons and six carbons of the tren part in $[Co(acac)(tren)]^{2+}$ were assigned based on the H–H and C–H cosy spectra; the results are shown in Table 3. The same names were used as those used in the crystal structure for the non-hydrogen atoms, and all of the protons were indicated with the names of non-hydrogen atoms to which the protons were attached. We assumed that the four protons of the four methylene group of the B and C ring facing the acac ring shifted by more than the opposite four protons. Refering to the tren and camphor parts, the essential peaks of the two isomers could be assigned as shown in Table 4. Within the chelate ring of 3-formylcamphor in **I** and **II**, the carbon atoms in the trans side to the tertiary nitrogen

Table 3. NMR Spectra of $[Co(acac)(tren)]^{2+a)}$

Carbon number	^{1}H	^{13}C
C(1) or C(5)	2.742, 3.581	61.749
C(2) or C(6)	3.076, 3.396	45.400
C(3)	3.244 (triplet)	61.292
C(4)	2.910	43.827

a) Chemical shifts were given in ppm.

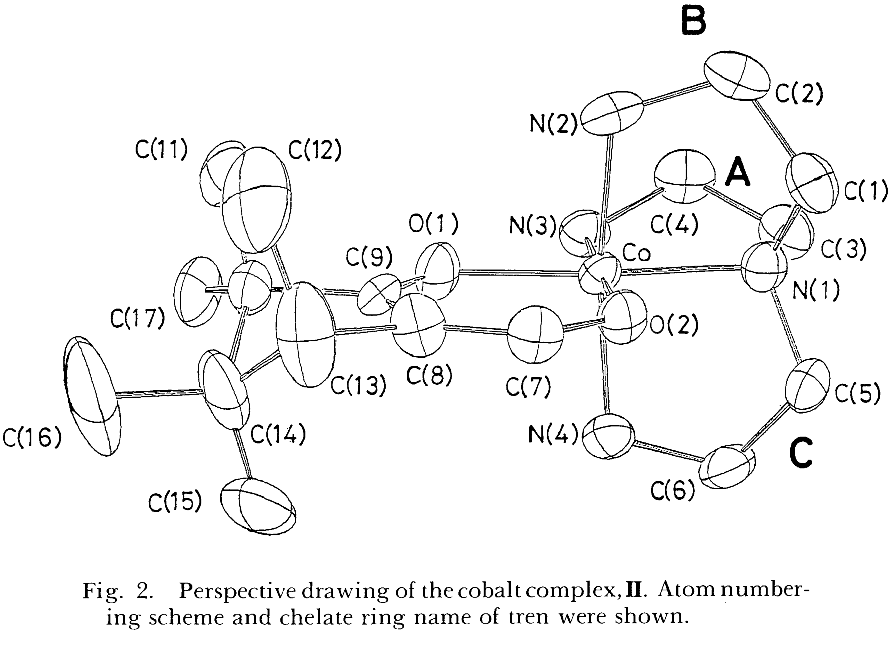


Fig. 2. Perspective drawing of the cobalt complex, **II**. Atom numbering scheme and chelate ring name of tren were shown.

Table 4. Comparison of Two Isomers, **I** and **II** in ^{1}H and ^{13}C NMR

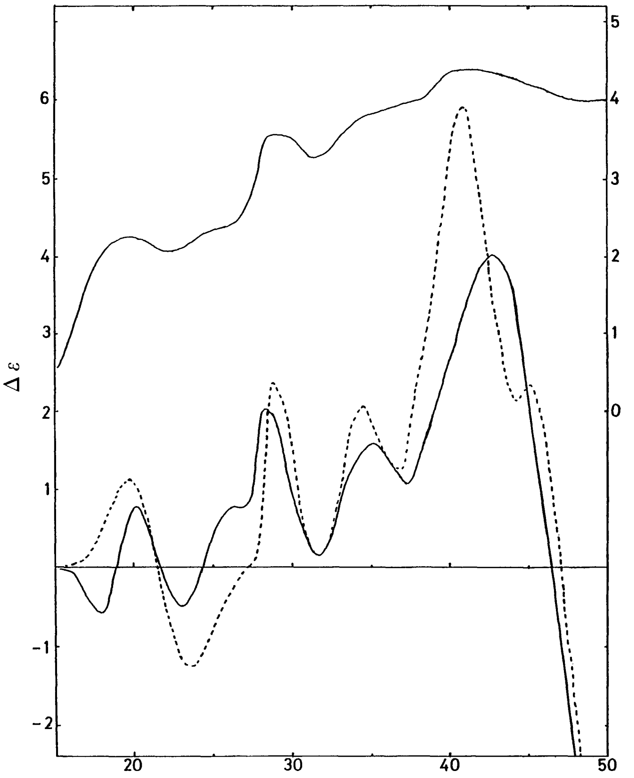
Carbon number	Isomer, **I**		Isomer, **II**	
	^{1}H	^{13}C	^{1}H	^{13}C
C(1) or C(5)	2.807	61.877	2.703	61.882
	3.573		3.519	
C(2) or C(6)	3.207	45.601	3.068	45.707
	3.444	45.765	3.409	45.817
C(3)	3.287	61.822	3.257	61.708
C(4)	2.921	43.863	2.941	44.046
C(7)	6.980	173.123	6.831	170.238
C(8)		117.436		117.001
C(9)		205.145		207.158
C(10)		60.231		60.174
C(11)	1.281	31.171	1.110	31.239
	1.765		1.691	
C(12)	1.281	28.099	1.293	28.203
	2.042		2.018	
C(17)	1.073	9.098	0.957	9.103

a) Chemical shifts were given in ppm.

atom of tren were deshielded more than those in the cis side.

All of the complexes of [Co(3-X-acac)(tren)]$^{2+}$(X=H, naphthyl, 2,4-dinitro-1-naphthyl, etc.) previously prepared showed two peaks for the methyl groups in ^{1}H NMR and ^{13}C NMR, and for the carbonyl carbons in ^{13}C NMR.[4)] This is probably due to an electronic deformation of the coordination sphere produced by the three five-membered chelate rings of tren. Thus, the remaining coordination site in the Co(tren) system became unbalanced, resulting in a magnetically different field. If these observations are also true for other Co(III)-tren complexes, and the assignments of carbonyl carbons can be established, the geometrical structure can be determined in terms of the chemical shifts of the carbonyl carbons. Limitations of this assumption, however, have to be ascertained. Since we could not find any papers in the literature that describes any clearly assigned ^{13}C peaks of the carbon atoms (carbonyl or thiocyanato group) of the tren and trien complexes in a similar environment, the problems remained unsolved.

Absorption and Circular Dichroism Spectra of the Isomers. Both of the spectra are shown in Fig. 3. Since the absorption spectra of the isomers **I** and **II** were superimposable to each other, only that of isomer **I** is shown. Though they resembled that of [Co(acac)-(tren)]$^{2+}$, but all of the transition peaks shifted slightly to a lower-wave number region. Especially, the charge-transfer band shifted to 29.4×10^3 cm^{-1}, probably because the chelate ring of fc was strained and the antibonding π-orbitals levels decreased. The CD spectra of **I** and **II** were compared with that of [{Co(tren)}^{2}(tae)]$^{4+}$.[4d)] Two electronic transitions regions, at 17—21×10^3 cm^{-1} and 23—27×10^3 cm^{-1}, were assigned to the d-d* transitions of the first and the second absorption bands, respectively. The CD spectra showed that the electronic transitions of present complexes shifted to a lower wave-number region compared with the corresponding transition of [{Co(tren)}$_2$(tae)]$^{4+}$. The origin of every transitions became obscure at region higher than 40×10^3 cm^{-1}, due to the overlap of various transition.



Wave number/10^3 cm^{-1}

Fig. 3. Absorption and CD spectra.

Akamatsu et al. reported that vicinal and quasi-enantiomeric effects can contribute to the CD spectra in the case of Co(III)-tren complexes containing optically active amino acids and diamines.[3b)] They claimed that the latter effect is dominant. If the quasi-enantiomeric effect is also dominant in the present complex, almost all of the corresponding CD peaks would show opposite signs to each other. The CD spectra of the isomeric complexes, **I** and **II**, resembled each other as a whole, and showed peaks of the same sign. This fact indicates that the vicinal effect is dominant, in contrast to the case of amino acids and diamines. In the present fc complexes, bulky alkyl groups which cause chirality are incorporated directly into the chelate ring. The vicinal effect may be more important in this case.

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References

1) Following abreviations were used in this report; trien for triethylenetetramine, tren for tris(2-aminoethyl)amine, Hfc for 3-formylcamphor, and fc for 3-formylcamphorate, Hacac for acetylacetone, H_2tae for tetraacetylethane.

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3) a) Y. Mitsui, Y. Iitaka, Y. Kushi, and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **1976**, 2095. b) K. Akamatsu, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 3000 (1981).

4) a) Y. Nakano and S. Sato, *Inorg. Chem.*, **19**, 3391 (1980); b) Y. Nakano and S. Sato, *Inorg. Chem.*, **21**, 1315 (1982); c) Y. Nakano and S. Sato, *Bull. Chem. Soc. Jpn.*, **55**, 1683 (1982); d) Y. Nakano, Y. Yoshikawa, and H. Kondo, *J. Am. Chem. Soc.*, **108**, 7630 (1986); e) Y. Nakano, Y. Yoshikawa, J. Hasegawa, T. Asano, Y. Igarashi, and S. Masuhara, *J. Chem. Soc., Chem. Commun.*, **1987**, 1481.

5) Y. T. Chen and G. W. Everett, *J. Am. Chem. Soc.*, **90**, 6660 (1968).

6) A. W. Bishop, L. Claisen, and W. Sinclair, *Justus Liebigs Ann. Chem.*, **281**, 314 (1894).

7) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," John Wiley and Sons, New York (1972), p. 397.