# Bicyclo[3,3,0]octa-2,4-dien-1-yl(cyclo-octa-1,5-diene)cobalt

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Cyclo-octenylcyclo-octa-1,5-dienecobalt $Co(C_8H_{13})(C_8H_{12})$ (I) reacts with cyclo-octa-1,5-diene to give the title complex (II). An intermediate 1—3-η-cyclo-octa-1,5-dienyl(cyclo-octa-1,5-diene)cobalt complex $Co(C_8H_{11})(C_8H_{12})$ (III) has been isolated and characterised. A possible reaction path of the dehydrogenative ring closure of (I) to (II) is discussed.

THERE has been much recent interest in and speculation about the effects which transition metals may have upon symmetry-controlled transformations of organic systems.[1,2] Of particular note is the apparent relaxation by transition metals of symmetry-forbidden ring opening[1] or valence isomerisation[2] of certain strained cyclic systems. However, information is rather scanty on metal-assisted ring-closure reactions. This paper describes an unusually ready ring closure of a C_8 ring system—the formation of a bicyclo[3,3,0]octa-2,4-dien-1-yl derivative of cobalt by dehydrogenative ring closure of cyclo-octa-1,5-diene. Cyclo-octenylcyclo-octa-1,5-dienecobalt, $Co(C_8H_{13})(C_8H_{12})$,[3] reacts with an excess of cyclo-octa-1,5-diene affording cyclo-octene and the bicyclo-octadienyl complex $Co(C_8H_9)(C_8H_{12})$. The stoicheiometry may be expressed by equation (1).

$$Co(C_8H_{13})(C_8H_{12}) + 2C_8H_{12} \longrightarrow Co(C_8H_9)(C_8H_{12}) + 2C_8H_{14} \quad (1)$$
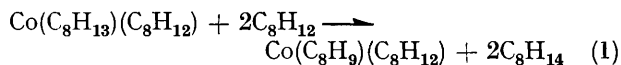
This reaction was found during a study[4,5] of the reaction between $Co(C_8H_{13})(C_8H_{12})$ and cycloheptatriene, which produces a cycloheptadienyl compound $Co(C_7H_9)(C_8H_{12})$ together with isomerised cyclo-octadienes. The princi-

pal reaction may be described by equation (2). The

$$Co(C_8H_{13})(C_8H_{12}) + C_7H_8 \longrightarrow Co(C_7H_9)(C_8H_{12}) + C_8H_{12} \quad (2)$$

mechanistic study[4] showed that a significant amount of cyclo-octene was formed. This prompted us to search for sources of hydrogen and this led to the discovery of the bicyclo-octadienyl compound $Co(C_8H_9)(C_8H_{12})$. During preparation of this manuscript Lehmkuhl and his group have made a brief report[6] on this preparation by the same reaction.

There are a few precedents of metal-assisted ring closure reactions, *e.g.* transformation of a protonated cyclo-octatetraenetricarbonyliron to bicyclo[5,1,0]octa-dienyltricarbonyliron[7] and cyclo-octatrienetricarbonyl-iron to the corresponding bicyclo[4,2,0]octadiene compound.[8,9] Perhaps a more closely related example is the formation of bicyclo[3,3,0]octadienyltricarbonylrhenium from $Re_2(CO)_{10}$ and cyclo-octa-1,5-diene.[10] No mechanistic study has been made of the formation of the bicyclo[3,3,0]system by transition metals, and the mechanism of the dehydrogenative ring closure of cyclo-octa-1,5-diene by cobalt is completely unknown.

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[2] L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.
[3] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1968, 2630.
[4] S. Otsuka and T. Taketomi, *J. Chem. Soc.* (*A*), 1971, 579.
[5] S. Otsuka and T. Taketomi, *J. Chem. Soc.* (*A*), 1971, 583.
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[8] T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6240.
[9] W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1963, 2162.
[10] K. K. Joshi, R. H. B. Mais, F. Nyman, P. G. Owston, and A. M. Wood, *J. Chem. Soc.* (*A*), 1968, 318.

This paper also includes discussion of the possible reaction path on the basis of the isolation of an intermediate $Co(C_8H_{11})(C_8H_{12})$.

EXPERIMENTAL

All preparations and manipulations were carried out under nitrogen on a vacuum line. Cycloheptatriene and cyclo-octa-1,5-diene were commercial products and used after dehydration with molecular sieve 5 Å and distilled.

Preparation of Bicyclo[3,3,0]octadienylcyclo-octa-1,5-dienecobalt.—A homogeneous mixture of $Co(C_8H_{13})(C_8H_{12})$[3] (1·05 g, 3·8 mmol) and cyclo-octa-1,5-diene (5 ml, 37 mmol) in n-heptane (5 ml) was stirred at 65°. The reaction was complete within 10 min as evidenced by the formation of a brownish yellow crystalline precipitate. The cooled slurry was filtered off and recrystallised from n-pentane to give air-stable orange-red *needles* of $Co(C_8H_9)(C_8H_{12})$, m.p. 62—64° (dec. 150—160°) (900 mg, 87%) (Found: C, 70·8; H, 7·5. $CoC_{16}H_{21}$ requires C, 70·6; H, 7·8%); $\nu_{max.}$ (neat) 3120w, 3022s, 3008s, 2985s, 2950s, 2880s, 2840s, 1458s, 1449s, 1434m, 1412w, 1382w, 1368w, 1361w, 1324s, 1307m, 1300w, 1280m, 1236m, 1206s, 1172m, 1150m, 1131m, 1071m, 1042w, 1030s, 993m, 948m, 890m, 883m, 853s, 831w, 812m, 783m, and 697m cm^{-1}.

Isolation of 1—3-η-Cyclo-octa-1,5-dienyl(cyclo-octa-1,5-diene)cobalt, $Co(C_8H_{11})(C_8H_{12})$.—The formation of the cobalt complex $Co(C_8H_{11})(C_8H_{12})$ was observed in the following two cases (a) and (b); we isolated the complex in the case of (a).

(a) *Reaction of $Co(C_8H_{13})(C_8H_{12})$ with cycloheptatriene.* A n-heptane solution of $Co(C_8H_{13})(C_8H_{12})$ (1·82 g, 6·6 mmol) and C_7H_8 (0·3 g, 3·3 mmol) was stirred at 65° for 4 h. A small amount of a fine black precipitate gradually appeared. The black solid was filtered off and shown by its i.r. and ^1H n.m.r. spectra to be composed mainly of the known binuclear compound[4] $[Co(C_7H_8)(C_8H_{12})]_2$, m.p. 150° (dec.) (150 mg). The filtrate was set aside overnight at $-78°$ to allow the starting material $Co(C_8H_{13})(C_8H_{12})$ and the major product $Co(C_7H_9)(C_8H_{12})$[4] to crystallise out (these compounds amounted to about 1·0 g). After filtration, the brown filtrate was concentrated to an oily residue, which was exposed to air (in order to facilitate removal of the starting complex and some undesirable compounds). The residue was then extracted with n-hexane. After being concentrated, the extract was chromatographed on *ca.* 20 g of basic alumina (Woelm, activity grade III). The first portion of the eluant (pale yellow) gave an orange solid which was recrystallised from n-pentane to give *orange needles*, m.p. 118° (dec.) [*ca.* 30 mg, 1·7% based on $Co(C_8H_{13})(C_8H_{12})$].

(b) *Reaction of $Co(C_8H_{13})(C_8H_{12})$ with a limited amount of cyclo-octa-1,5-diene.* A n-heptane solution of $Co(C_8H_{13})$-(C_8H_{12}) (0·48 g, 1·74 mmol) was treated with an equimolar amount of cyclo-octa-1,5-diene at 65° for 2 h. The solvent was removed *in vacuo* and the brown oily residue was exposed to air. Extraction of the residue with n-hexane followed by the same chromatography produced a n-hexane eluant from which an orange-red solid was obtained. The solid was composed of mainly $Co(C_8H_{11})(C_8H_{12})$ and $Co(C_8H_9)(C_8H_{12})$ as detected by its ^1H n.m.r. in C_6D_6.

Upon heating the C_6D_6 solution at 60° the characteristic triplet at δ 5·00 p.p.m. (J 7·5 Hz) and a complex triplet at δ 4·65 p.p.m. (J 6·5 Hz) of $Co(C_8H_{11})(C_8H_{12})$ disappeared leaving only resonances due to the bicyclic complex $Co(C_8H_9)(C_8H_{12})$. No attempt was made to isolate the intermediate because of the small yield.

RESULTS AND DISCUSSION

Preparation and Characterisation.—Complexes containing the penta-*hapto*-bicyclo[3,3,0]octa-2,4-dien-1-yl (C_8H_9, tetrahydropentalenyl) or penta-*hapto*-bicyclo-[3,3,0]octa-2,4,7-trien-1-yl (C_8H_7, dihydropentalenyl) ligand have been synthesised with many metals including manganese,[11-14] rhenium,[10] iron,[15] rhodium,[16] and platinum[16] by a variety of preparative routes.

C_8H_9 C_8H_7
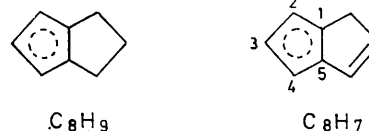
The preparations of iron, rhodium, and platinum complexes use a hydrocarbon having the bicyclic skeleton. The dihydropentalenylmanganese complex $Mn(C_8H_7)$-$(CO)_3$ was obtained by an interesting method employing acetylene[11,12] or cyclo-octatetraene.[12] The latter preparative reaction apparently involves intramolecular cyclisation of the C_8 polyene ring, although the mechanism has not been studied.

The smooth dehydrogenative ring closure of cyclo-octa-1,5-diene by the low-valent cobalt complex $Co(C_8H_{13})(C_8H_{12})$ (I) is noteworthy. Thus, cyclo-octa-1,5-diene reacts rapidly with $Co(C_8H_{13})(C_8H_{12})$ at 60—65° affording the reasonably air-stable, diamagnetic, orange-red complex $Co(C_8H_9)(C_8H_{12})$ (II). The yield is quantitative provided the diene is present in large excess. With less than equimolar amounts of 1,5-diene, the yield decreases considerably ($<20\%$). The amount of cyclo-octene produced supports the stoicheiometry [equation (1)] which shows that the excess diene merely acts as a hydrogen acceptor. Indeed an olefin such as cyclo-heptatriene acting as a hydrogen acceptor reacts with $Co(C_8H_{13})(C_8H_{12})$ to produce a small amount of the bicyclo-octadienyl compound (II). Cyclo-octetraene, maleic anhydride, or dimethyl maleate failed to give an appreciable amount of (II). When $Co(C_8H_{13})(C_8H_{12})$ alone was heated in n-heptane at 60—65° for 5 h a very small amount of (II) ($3·5\%$) was obtained, most of the starting complex (I) being recovered unchanged. In this case irradiation with light does not improve the yield.

The new compound (II) was identified by its analysis and mass and ^1H n.m.r. spectra. The i.r. spectrum (neat) shows absorptions at 3120, 1412, 1131, 1030, and

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[12] U.S.P. 3,100,211—3,100,214/1963 (*Chem. Abs.*, 1964, **60**, 549).

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[15] T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.*, 1963, **85**, 2030.

[16] T. J. Katz and J. J. Mrowca, *J. Amer. Chem. Soc.*, 1967, **89**, 1105.

853 cm^{-1}, which may be ascribable [17] to a substituted cyclopentadienyl group, and at 2985, 2950, 2880, 2840, 1434, and 1280 cm^{-1} assignable to the methylene groups. In the ^{1}H n.m.r. spectrum two low-field signals at δ (from Me$_4$Si) 4·10 (doublet, 2H) and 4·24 p.p.m. (triplet, 1H) can readily be assigned to the two types of protons of the cyclopentadienyl group on the basis of their chemical shifts and small coupling constants (2 Hz).[18] The olefinic protons of the cyclo-octadiene ligand give rise to one signal at δ 3·16 p.p.m. (complex, half height-width of 10 Hz, 4H) indicating the four protons to be magnetically equivalent. If the stereochemistry is rigid, the olefinic protons of the cyclo-octadiene would be expected to show inequivalence.[3,5] The absence of such an anisotropic effect due to 1,2-disubstituted cyclopentadienyl ligand implies that the molecule is fluxional like the analogous cycloheptadienylcyclo-octa-1,5-diene-cobalt.[5]

The mass spectrum shows characteristic fragments in support of the structure. The intense peaks are recorded in the Table. The parent ion Co(C$_8$H$_9$)(C$_8$H$_{12}$)$^+$ (m/e

Part of the mass spectra ^{a} of Co(C$_8$H$_9$)(C$_8$H$_{12}$) and Co(C$_8$H$_{11}$)(C$_8$H$_{12}$)

	Co(C$_8$H$_9$)(C$_8$H$_{12}$) ^{b}			Co(C$_8$H$_{11}$)(C$_8$H$_{12}$) ^{c}	
m/e	R.A.^{d}	Ion	m/e	R.A.^{d}	Ion
272	79·3		274	100	
270	30·5		272	29·0	
255	9·8	Co(C$_7$H$_7$)(C$_8$H$_9$)$^+$	270	12·6	
243	31·7	Co(C$_6$H$_7$)(C$_8$H$_9$)$^+$	260	5·6	Co(C$_7$H$_9$)(C$_8$H$_{12}$)$^+$
242	100	Co(C$_6$H$_6$)(C$_8$H$_9$)$^+$	243	9·8	Co(C$_6$H$_7$)(C$_8$H$_9$)$^+$
241	19·5		242	25·7	Co(C$_6$H$_6$)(C$_8$H$_9$)$^+$
229	17·1	Co(C$_5$H$_5$)(C$_8$H$_9$)$^+$	229	4·2	Co(C$_5$H$_5$)(C$_8$H$_9$)$^+$
218	11·0	Co(C$_4$H$_6$)(C$_8$H$_9$)$^+$	218	2·8	Co(C$_4$H$_6$)(C$_8$H$_9$)$^+$
165	17·1		168	13·1	
164	62·2	CoC$_8$H$_9$$^+$	166	41·1	CoC$_8$H$_{11}$$^+$
163	67·1		165	30·8	
162	80·5	CoC$_8$H$_7$$^+$	164	50·0	CoC$_8$H$_9$$^+$
161	18·3	CoC$_8$H$_6$$^+$	162	30·8	CoC$_8$H$_7$$^+$
138	35·4	CH$_3$C$_5$H$_4$Co$^+$	151	7·5	
137	53·7	CoC$_6$H$_6$	150	8·9	CoC$_7$H$_7$$^+$
124	30·5	CoC$_5$H$_5$	138	47·7	CH$_3$C$_5$H$_4$Co$^+$
105	15·9	C$_8$H$_9$$^+$	137	49·1	CoC$_6$H$_6$$^+$
103	31·7	C$_8$H$_7$$^+$	124	47·7	CoC$_5$H$_5$
102	9·8		105	10·3	C$_8$H$_9$$^+$
59	29·3	Co$^+$	102	14·0	
			91	17·8	
			79	36·9	
			67	41·6	
			59	6·1	Co$^+$

^{a} 75 eV. ^{b} Chamber temperature 150, 160°. ^{c} Chamber temperature 125, 150°. ^{d} R.A. = Relative area.

272) is abundant, and this loses a molecule of hydrogen yielding Co(C$_8$H$_9$)(C$_8$H$_{10}$)$^+$ (270). The next most intense peak is at m/e 255 and assignable to an unusual species Co(C$_7$H$_7$)(C$_8$H$_9$)$^+$ in which the cobalt atom presumably acquires an inert-gas configuration (the C$_7$H$_7$ ligand is regarded as being co-ordinated as a penta-*hapto*-tropylium ion). The most intense peak at m/e 242 is due to Co(C$_6$H$_6$)(C$_8$H$_9$)$^+$. A related complex, dihydropentalenylcyclo-octa-1,5-dienerhodium Rh(C$_8$H$_7$)-(C$_8$H$_{12}$) [16] also shows abundantly an analogous ion Rh(C$_6$H$_6$)(C$_8$H$_7$)$^+$ owing to the same fragmentation of the cyclo-octadiene ligand.

Of the two ligands in (II) cyclo-octa-1,5-diene frag-

ments more readily as manifested by the abundant ions such as Co(C$_5$H$_5$)(C$_8$H$_9$)$^+$ (m/e 229) and Co(C$_8$H$_9$)$^+$ (m/e 164). The fragmentation may be expressed as follows:

SCHEME 1

Intermediate Co(C$_8$H$_{11}$)(C$_8$H$_{12}$) *and the Reaction Path.*— The reaction between Co(C$_8$H$_{13}$)(C$_8$H$_{12}$) (I) and an excess of cyclo-octa-1,5-diene is rapid and only the formation of (II) can be observed. With a limited amount of the diene another species Co(C$_8$H$_{11}$)(C$_8$H$_{12}$) (III) is formed. Thus, the reaction between cyclo-octa-1,5-diene and (I) (1 : 1) produced a mixture of (II) and the new complex (III), which has been isolated from the reaction of (I) with cycloheptatriene. The complex (III) is an orange-red, diamagnetic crystalline compound, m.p. 118° (dec.). The compound in the solid state is fairly stable both to air and heat; in solution however it decomposes slowly even at room temperature. The compound is identified by its ^{1}H n.m.r. and mass spectrum.

The ^{1}H n.m.r. spectrum shows two low-field signals of equal intensity (1H); a triplet at δ 5·00 p.p.m. (J 7·5 Hz) and a complex triplet at δ 4·65 p.p.m. (J 6·5 Hz). The coupling scheme as well as the chemical shifts suggest the presence of an allylic group, but the intensity ratio indicates lack of symmetry of the π-allyl co-ordination site. There are complex signals due to the olefinic protons ranging from δ 4·1 to 3·5 p.p.m. (7H), showing absence of unco-ordinated olefinic bonds, and more complex signals due to seven methylene groups ranging from δ 3·2 to δ 0·9 p.p.m. (14H). The mass spectrum (*vide infra*) excludes a bicyclic structure for the C$_8$H$_{11}$ ligand. Thus the above spectral features can best be accommodated by structure (III) (see Scheme 2).

The mass spectrum (Table 1) furnishes further support for the structure (III). The parent ion (m/e 274) and the ion CoC$_{16}$H$_{21}$$^+$ (m/e 272) are abundant. The fragmentation differs markedly from that of (II). For example, a peak at m/e 260 ascribable to Co(C$_7$H$_9$)-(C$_8$H$_{12}$)$^+$ indicates a fragmentation of the C$_8$H$_{11}$ ligand retaining the cyclo-octadiene ligand intact. This contrasts with the case of (II) which shows reluctance to

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[18] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

cleavage of the bicyclo[3,3,0]octadienyl system compared to the cyclo-octa-1,5-diene ligand. Further, the spectrum contains a fairly strong peak at m/e 166 ($CoC_8H_{11}^+$) which is weak in the spectrum of (II). These features exclude the bicyclo[3,3,0]octenyl structures (below) for the C_8H_{11} ligand and hence bicyclo[3,3,0]octadienyl compounds, e.g. $H_2Co(C_8H_9)(C_8H_{12})$.

C₈H₁₁   C₈H₁₁
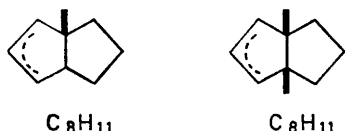
Accepting the proposed structure for (III), one can visualise the following reaction path leading to the final product (II). The mechanistic details of the step (I) to (III) have not been studied. However, in view of the similar hydride-transfer observed in the reaction between
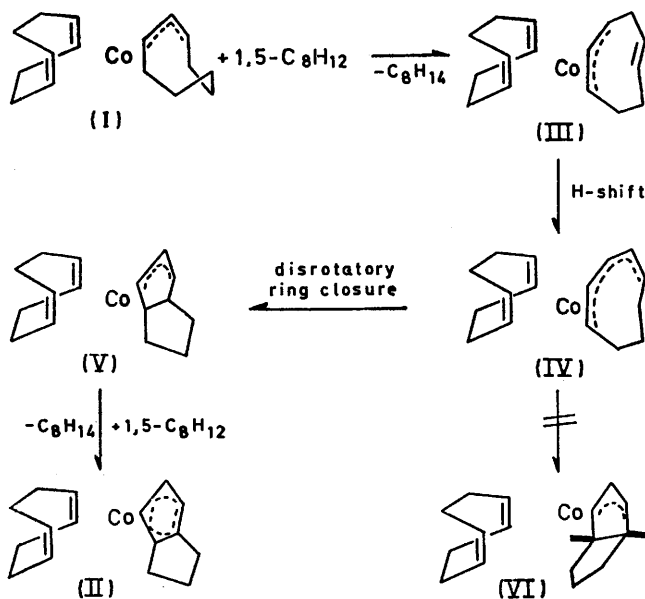
SCHEME 2

(I) and cycloheptatriene,[4] it is likely that the cyclo-octene molecule liberated in this step is derived from the cyclo-octenyl ligand in (I). The transformation of (I) to (III) might be a multi-step reaction. The next step would require either a 1,3- or 1,4-hydride shift forming a delocalised 5π-system since the separated 2π–3π system

in (III) is obviously unfavourable for the ring closure to a five-membered ring system (vide infra). In order to account for the formation of (II) from (IV) a ring closure with a dehydrogenation process must be postulated. An intermediate (V) seems most likely; this is derived from an allowed disrotatory ring-closure and provides a geometrical alignment of the two hydrogen atoms attached to the bridgehead atoms of the C_8H_{11} ligand susceptible to abstraction by the metal. An alternative (VI) is unlikely to be involved because of the steric repulsion between the two ligands and the unfavourable geometrical position of the hydrogen atoms to be removed.

The conversion of cyclo-octa-2,4-dien-1-yl anion in good yield to cyclo[3,3,0]oct-3-en-2-yl anion with a cis-ring junction [19] is in accord with the orbital symmetry conservation rules.[20] The conversion of cyclo-octa-2,4-dien-1-yl carbonium ion is expected to proceed in a conrotatory manner. However, Moon and Ganz [21] found that the cyclo-octadienyl carbonium ion was converted in the presence of Ag^+ ion into cyclo[3,3,0]oct-3-en-2-yl cation with a cis-ring junction. It has been demonstrated [1,2,22,23] that transition-metal ions may reduce the potential barrier of a symmetry-forbidden process dramatically. Also a transition-metal ion can produce a stereochemical reaction path entirely different from that of a thermal reaction.[24] Thus the functions of transition metals in electrocyclic reactions may be quite specific depending upon the identity of metal ion and the non-reacting ligand. Reaction of cyclo-octatriene with $Co(C_5H_5)(CO)_2$ or $Fe_3(CO)_{12}$ at 100—120° produces a bicyclo[4,2,0]octadiene system.[9] The moiety $Co(C_5H_5)$ or $Fe(CO)_3$ apparently prefers to be co-ordinated with a
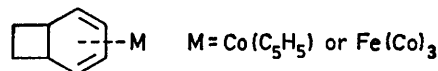
diene thus causing the cyclisation different from the present system Co(1,5-diene). These facts suggest that the transannular cyclisation of a medium ring polyene could be controlled by proper choice of a metal moiety.

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[20] R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry,' Verlag Chemie, 1970.
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[22] H. Hogeveen, H. C. Volger, J. Amer. Chem. Soc., 1967, 89, 2486; Rec. Trav. Chim., 1967, 86, 830; H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeck, J. Amer. Chem. Soc., 1969, 91, 218; ibid., 2137.
[23] F. D. Mango and J. H. Schachtschneider, J. Amer. Chem. Soc., 1971, 93, 1123.
[24] For example, M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, J. Amer. Chem. Soc., 1971, 93, 1043.