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The structure of $[\{Co(\eta^4\text{-}C_6H_{10})(CO)_2\}_2SnCl_2]$ in the solid state ($C_6H_{10}\equiv$2,3-dimethylbuta-1,3-diene)

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Abstract

Reaction of $[\{Co(CO)_4\}_2SnX_2]$ (X = Cl, Br or I) with bicyclo [2.2.1] hepta-2,5-diene, C_7H_8, and a variety of 1,3-dienes has allowed the isolation of $[\{Co(\eta^4\text{-}C_7H_8)(CO)_2\}\{Co(CO)_4\}SnX_2]$, $[\{Co(\eta^4\text{-}C_7H_8)(CO)_2\}_2SnX_2]$ and $[\{Co(\eta^4\text{-}C_6H_{10})(CO)_2\}_2SnCl_2]$ only (C_6H_{10} = 2,3-dimethylbuta-1,3-diene). An X-ray diffraction study of $[\{Co(\eta^4\text{-}C_6H_{10})(CO)_2\}_2SnCl_2]$ has shown that in this complex there is distorted tetrahedral coordination about Sn arising from the different electronegativities of its substituents. The coordination about cobalt is most simply described as distorted trigonal bipyramidal (tbp) the first time that this stereochemistry has been found in a five-coordinated d^8 metal complex containing an η^4-(1,3-diene) ligand. The Sn occupies an axial site, and the diene is as near to axial–equatorial as it can be. However, as a consequence of the size and shape of the diene, whereas the midpoint of its C(3)–C(4) bond lies close to the equatorial plane, that of its C(1)–C(2) bond does not lie on the Sn–Co axis. The coordination is distorted from tbp towards square-based pyramidal (sp). It is shown that rotation of the diene about an axis through its centroid and the cobalt atom leads in turn to various tbp and sp structures and distortions thereof. In all these the diene is coordinated axial–equatorial (tbp) or basal–basal (sp), but the other three ligands occupy the other coordination positions in turn.

Key words: Cobalt; Tin; Diolefin; Carbonyl; Crystal structure

1. Introduction

Although $[Fe(\eta^4\text{-diene})(CO)_3]$ complexes of 1,3-dienes and cycloocta-1,5-diene have a square pyramidal (sp) structure [1,2], the complexes of certain substituted bicyclo[2.2.1]hepta-2,5-diene and bicyclo[2.2.2]octa-2,5-dienes are trigonal bipyramidal, (tbp) [3,4], as are the $[Fe(\eta^2\text{-alkene})_2(CO)_3]$ [5]. Following our discovery that the complexes $[Fe(\eta^4\text{-}C_7H_8)(CO)_2(L)]$ (L = CNMe and PPh_3; C_7H_8 = bicyclo[2.2.1]hepta-2,5-diene) have distorted tbp structures [6], it was of interest to find out whether the related $[Co^I(\eta^4\text{-diene})L_3]$ complexes of $Co^{(I)}$ exhibited the same structural dependence on the diene ligand. The only relevant structure that we could find in the literature was that of $[\{Co(\eta^4\text{-}C_7H_8)(CO)_2\}_2SnCl_2]$ [7] which has distorted tbp coordination about the Co atoms. The structures of *trans*-$[Co_2(\eta^4\text{-}C_6H_{10})_2(CO)_2(\mu\text{-}CO)_2]$ [8], and *cis*-$[Co_2(\eta^4\text{-}C_6H_8)_2(CO)_2(\mu\text{-}CO)_2]$ [9] ($C_6H_{10}\equiv$ 2,3-dimethylbuta-1,3-butadiene; C_6H_8 = cyclohexa-1,3-diene) did not seem relevant, but in both there is sp coordination about the Co atoms provided that the Co–Co interactions are ignored. Whilst this work was in progress, the structure of $[Co(\eta^4\text{-}C_6H_{10})(CO)_3][FeCl_3NCMe]$ was reported [10] and the cation shown to be isostructural with the sp $[Fe(\eta^4\text{-1,3-diene})(CO)_3]$ complexes. Thus the five-coordinated $Co^{(I)}$ complexes appeared to exhibit the same structure–diene relationship as related $Fe^{(0)}$ derivatives. However, we had prepared $[\{Co(\eta^4\text{-}C_6H_{10})(CO)_2\}_2SnCl_2]$ and so decided to continue with our investigation. The resulting structure determination was not of high quality but was good enough to show that coordination about Co is distorted tbp.

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2. Experimental details

The complexes [{Co(CO)$_4$}$_2$SnX$_2$] were prepared by published methods [11]. Other chemicals were purchased.

All reactions were carried out under nitrogen in solvents that had been dried and deoxygenated by refluxing over calcium hydride. They were monitored by IR spectroscopy.

2.1. *The reaction of [{Co(CO)$_4$}$_2$SnX$_2$] with dienes*

A solution of [{Co(CO)$_4$}$_2$SnX$_2$] (0.9 mmol) and bicyclo[2.2.1]hepta-2,5-diene (5 cm^3) in *n*-hexane (100 cm^3) was refluxed for 40 min, filtered when hot and cooled to −30°C. The red crystals that precipitated and were filtered off, dried and shown to be of [{Co(η^4-C$_7$H$_8$)(CO)$_2$}{Co(CO)$_4$}SnX$_2$] complexes which were obtained in about 80% yields. When the reactions were carried out in refluxing *n*-heptane, the complexes [{Co(η^4-C$_7$H$_8$)(CO)$_2$}$_2$SnX$_2$] were isolated in the same way but required purification by recrystallization from benzene–hexane mixtures. The reactions of isoprene, cyclohexa-1,3-diene and 2,3-dimethylbuta-1,3-diene were carried out similarly, but the only isolable product from them was [{Co(η^4-C$_6$H$_{10}$)(CO)$_2$}$_2$SnCl$_2$].

Elemental analysis (Table 1) were carried out by the Analytical Laboratory of University College, Dublin. IR spectra (Table 1) were recorded on Perkin–Elmer 1710 and 1720 Fourier transform spectrometers.

2.2. *Crystal structure determination*

Crystal data are given in Table 2. The structures were solved by direct methods, SHELX86 [12] and refined by the full-matrix least-squares method using SHELX76 [13]. The crystal did not diffract strongly and the data were not of optimum quality but were more than sufficient to establish the structure. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The Sn, Co, Cl and O atoms were refined anisotropically. Carbon atoms were refined isotropically. The atomic scattering factors for non-hydrogen and hydrogen atoms, and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [14–16]. Calculations were carried out on a VAX 6610 computer. The ORTEP program was used to obtain the drawings [17]. Fractional atomic coordinates are given in Table 3, and selected bond angles and bond lengths in Table 4. The following tables have been deposited: complete lists of bond lengths and angles, and table of

TABLE 1. Melting points, analyses and IR spectra of the [{Co(η^4-diene)(CO)$_2$}{Co(CO)$_4$}SnX$_2$] and [{Co(η^4-diene)(CO)$_2$}$_2$SnX$_2$] complexes described in the text

Diene [a]	X	M.p. [b]	Analyses, found (calculated)			IR spectra [c] (cm^{-1})		
			C (%)	H (%)	X (%)			
[{Co(η^4-diene)(CO)$_2$}{Co(CO)$_4$}SnX$_2$]								
C$_7$H$_8$	Cl	93–95	27.0	1.5	13.4	1995(4.5)	2009(8.1)	2021(8.8)
			(27.5)	(1.4)	(12.5)	2035(9.5)	2041(7.8)	2096(10)
C$_7$H$_8$	Br	102–103	24.3	1.4	24.4	1996(4.1)	2010(7.0)	2020(7.7)
			(23.9)	(1.2)	(24.4)	2034(8.3)	2040(7.0)	2095(10)
C$_7$H$_8$	I	105–106	19.8	1.1	32.9	1995(5.7)	2006(8.9)	2018(9.6)
			(20.8)	(1.1)	(33.9)	2032(9.9)	2040(8.5)	2092(10)
[{Co(η^4-diene)(CO)$_2$}$_2$SnX$_2$]								
C$_7$H$_8$ [d]	Cl	123, dec.	35.5	2.4	11.1	1971(6.9)	1985(9.3)	
			(35.8)	(2.7)	(11.8)	2007(9.1)	2031(10)	
C$_7$H$_8$ [d]	Br	130, dec.	31.2	2.4	22.9	1971(7.1)	1984(10)	
			(31.2)	(2.3)	(23.1)	2006(8.4)	2030(10)	
C$_7$H$_8$ [d]	I	145, dec.	27.5	2.0	31.9	1970(6.1)	1983(9.4)	
			(27.5)	(2.0)	(32.3)	2005(7.3)	2028(10)	
C$_6$H$_{10}$	Cl	120, dec.	31.4	3.5	12.0	1996(5.1)	2006(10)	
			(32.9)	(3.4)	(12.2)	2029(6.4)	2050(8.7)	

[a] C$_7$H$_8$ ≡ bicyclo[2.2.1]hepta-2,5-diene; C$_6$H$_{10}$ ≡ 2,3-dimethylbuta-1,3-diene.

[b] Determined in sealed tubes: dec., decomposed without melting.

[c] Absorption bands due to υ(CO) vibrations only. Peak positions with relative peak heights in parentheses. Spectra run in hexane solution unless it is stated otherwise.

[d] IR spectra run in carbon disulphide solution.

TABLE 2. Crystal data for [{Co(η^4-C_6H_{10})(CO)$_2$}$_2$SnCl$_2$] (1)

Crystal size (mm)	0.5 × 0.4 × 0.2
Formula	$C_{16}H_{20}Cl_2Co_2O_4Sn$
M (amu)	583.794
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.417(1)
b (Å)	14.760(3)
c (Å)	14.461(2)
β (°)	102.77(2)
U (Å^3)	2168(5)
Z	4
D_c (g cm^{-3})	1.79
μ (cm^{-1})	27.6
F(000)	1144
Radiation	Mo Kα
Graphite monochromator	$\lambda = 0.71069$ Å
Diffractometer	Enraf-Nonius CAD4F
Orienting Reflections; range	25; $13 < \theta < 20°$
Temperature (°C)	22
Scan method	$\omega - 2\theta$
Data collection range	$4 < 2\theta < 34°$
Number of unique data	6291
Total $I > 4\sigma I$	3967
Number of Parameters fitted	147
R [a], unit weights (%)	10.53
Quality-of-fit indicator [b]	5.3
Largest Shift/estimated standard deviation, final cycle	< 0.001
Largest positive peak (electrons Å^3)	1.6
Largest negative peak (electrons Å^3)	−1.98

[a] $R_w = [[\Sigma_w(|F_0 - F_c|)^2]/[\Sigma_w(|F_0|)^2]]^{1/2}$.

[b] Quality of fit $= [\Sigma_w(|F_0| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

atomic coordinates for hydrogen atoms, and of thermal parameters.

3. Results and discussion

The thermal reaction of [{Co(CO)$_4$}$_2$SnX$_2$] (X = Cl, Br or I) with bicyclo[2.2.1]hepta-2,5-diene gives in turn [{Co(η^4-C_7H_8)(CO)$_2$}{Co(CO)$_4$}SnX$_2$] and [{Co(η^4-C_7H_8)(CO)$_2$}$_2$SnX$_2$] as red crystalline solids that are stable in air (*cf.* ref. 7). The corresponding reactions of 1,3-dienes were much less amenable to investigation. They took place under thermal or photochemical conditions, but the products were unstable, and the only one which we were able to isolate was [{Co(η^4-C_6H_{10})(CO)$_2$}$_2$SnCl$_2$] (**1**) (C_6H_{10} = 2,3-dimethylbuta-1,3-diene). All the complexes are red crystalline solids. Their IR spectra (Table 1) are consistent with their structures, and their υ(CO) frequencies suggest that the 1,3-diene is a better acceptor ligand than bicyclo[2.2.1]hepta-2,5-diene with its two non-conjugated double bonds.

A crystal of [{Co(η^4-C_6H_{10})(CO)$_2$}$_2$SnCl$_2$] (**1**) was subject to an X-ray diffraction study. The structure and atom labelling of the molecule is shown in Fig. 1. In many respects the structure is similar to that of its bicyclo[2.2.1]hepta-2,5-diene counterpart, [{Co(η^4-C_7H_8)(CO)$_2$}$_2$SnCl$_2$] (**2**) [7], structural features which are common to both have similar dimensions.

3.1. Coordination about Sn

The tin atom in **1** is four coordinated. The two Cl and two Co atoms lie at the apices of a grossly distorted tetrahedron with the Cl–Sn–Cl angle equal to 96.6(3)° and the Co–Sn–Co angle equal to 129.6(1)°. These distortions are similar to those found in **2** [7] and may be ascribed to the same cause, namely the increased p character of the bonds to the more electronegative Cl ligand than of those to Co [18]. Another consequence of this is the short Sn–Co bonds (2.518(3) and 2.521(3) Å) and long Sn–Cl bonds (2.434(5) and 2.419(6) Å; *cf.* Sn–Cl bond of 2.31(1) Å in SnCl$_4$ [19]).

3.2. Coordination about Co

The coordination about the two Co atoms in **1** is similar to that found in **2** [7] and is best described as

TABLE 3. Fractional atomic coordinates for [{Co(η^4-C_6H_{10})(CO)$_2$}$_2$SnCl$_2$] (1) with estimated standard deviations in parentheses

Atom	x	y	z
Sn(1)	0.28521(13)	0.07029(8)	0.73802(8)
Co(1)	0.5162(3)	0.1096(2)	0.8234(2)
Co(2)	0.1288(2)	0.1557(1)	0.6097(1)
Cl(1)	0.2864(7)	−0.0809(3)	0.6711(5)
Cl(2)	0.1743(7)	0.0298(6)	0.8625(4)
O(1)	0.5182(15)	−0.0698(10)	0.9071(11)
O(2)	0.4339(24)	0.2366(13)	0.9531(12)
O(3)	−0.0470(15)	0.0073(10)	0.6143(11)
O(4)	0.2799(14)	0.1091(10)	0.4685(9)
C(1)	0.7092(23)	0.1509(16)	0.8739(16)
C(2)	0.7035(20)	0.0893(14)	0.7976(14)
C(3)	0.6091(21)	0.1138(14)	0.7130(15)
C(4)	0.5385(21)	0.1962(15)	0.7109(15)
C(5)	0.7825(28)	0.0041(19)	0.8051(20)
C(6)	0.5860(23)	0.0550(16)	0.6250(16)
C(7)	0.5218(19)	0.0022(14)	0.8729(14)
C(8)	0.4721(22)	0.1869(16)	0.9019(16)
C(9)	0.0092(20)	0.2436(14)	0.5121(14)
C(10)	−0.0207(17)	0.2541(12)	0.6044(12)
C(11)	0.0919(20)	0.2710(14)	0.6785(14)
C(12)	0.2187(20)	0.2794(14)	0.6584(14)
C(13)	−0.1473(24)	0.2395(18)	0.6157(18)
C(14)	0.0705(20)	0.2761(15)	0.7799(14)
C(15)	0.0197(18)	0.0655(13)	0.6138(12)
C(16)	0.2248(18)	0.1247(12)	0.5247(13)

TABLE 4. Selected bond lengths (Å) and bond angles (°) for $[\{Co(\eta^4\text{-}C_6H_{10})(CO)_2\}_2SnCl_2]$ (**1**) with estimated standard deviations in parentheses

Bond lengths			
Sn(1)-Co(1)	2.518(3)	Sn(1)-Co(2)	2.521(3)
Sn(1)-Cl(1)	2.434(5)	Sn(1)-Cl(2)	2.419(6)
Co(1)-C(1)	2.07(2)	Co(1)-C(2)	2.09(2)
Co(1)-C(3)	2.04(2)	Co(1)-C(4)	2.12(2)
Co(1)-C(7)	1.74(2)	Co(1)-C(8)	1.74(2)
Co(2)-C(9)	2.11(2)	Co(2)-C(10)	2.12(2)
Co(2)-C(11)	2.05(2)	Co(2)-C(12)	2.10(2)
Co(2)-C(15)	1.76(2)	Co(2)-C(16)	1.81(2)
O(1)-C(7)	1.18(2)	O(2)-C(8)	1.17(2)
O(3)-C(15)	1.11(2)	O(4)-C(16)	1.12(2)
C(1)-C(2)	1.42(3)	C(2)-C(3)	1.44(3)
C(2)-C(5)	1.49(3)	C(3)-C(4)	1.42(3)
C(3)-C(6)	1.51(3)	C(9)-C(10)	1.45(2)
C(10)-C(11)	1.42(2)	C(10)-C(13)	1.38(3)
C(11)-C(12)	1.42(3)	C(11)-C(14)	1.53(3)
Bond angles			
Co(2)-Sn(1)-Co(1)	129.6(1)	Cl(1)-Sn(1)-Co(1)	108.6(2)
Cl(1)-Sn(1)-Co(2)	103.0(2)	Cl(2)-Sn(1)-Co(1)	104.7(2)
Cl(2)-Sn(1)-Co(2)	109.5(2)	Cl(2)-Sn(1)-Cl(1)	96.6(3)
C(7)-Co(1)-Sn(1)	86.1(7)	C(8)-Co(1)-Sn(1)	96.3(8)
C(16)-Co(2)-Sn(1)	90.5(6)	C(15)-Co(2)-Sn(1)	85.1(6)
C(8)-Co(1)-C(7)	109.(1)	C(16)-Co(2)-C(15)	106.8(8)
O(1)-C(7)-Co(1)	176.(2)	O(2)-C(8)-Co(1)	175.(2)
O(3)-C(15)-Co(2)	178.(2)	O(4)-C(16)-Co(2)	176.(2)
C(3)-C(2)-C(1)	114.(2)	C(11)-C(10)-C(9)	114.(2)
C(4)-C(3)-C(2)	119.(2)	C(12)-C(11)-C(10)	121.(2)
C(5)-C(2)-C(1)	124.(2)	C(13)-C(10)-C(9)	120.(2)
C(5)-C(2)-C(3)	122.(2)	C(13)-C(10)-C(11)	126.(2)
C(6)-C(3)-C(2)	121.(2)	C(14)-C(11)-C(10)	117.(2)
C(6)-C(3)-C(4)	119.(2)	C(14)-C(11)-C(12)	122.(2)

tbp, distorted from the ideal. * Axial sites are occupied by Sn(1) and C(1)-C(2) of the C_6H_{10} ligand, whilst C(3)-C(4) and the two CO ligands occupy the equatorial positions. Because of the nature of the diene ligand and its restricted bite, the midpoint M(14) of C(3)-C(4), lies close to but not in the Co(1), C(7), C(8) plane and the bond itself is tilted so that there is an angle of 22.6° between the Co(1), C(7), C(8) and Co(1), C(3), C(4) planes, even though the predictions by Hoffmann and coworkers [20] suggest that coplanarity would be preferred. The midpoint M(12) of the C(1)-C(2) bond, does not lie on the Sn(1)-Co(1) axis, the M(12)-Co(1)-Sn(1) angle equals 154.5°, and this axis is markedly tilted with respect to the Co(1), C(7), C(8) plane, but it should be noted that C(1)-Co(1)-Sn(1) is close to linear (171.1(6)°). In contrast, the coordination about Co in **2** [7] is more symmetrical, with the C=C lying very close to the equatorial plane of the tbp and the Sn-Co axis very close to perpendicular to this plane, but in both compounds the linkage Sn-Co-M(axial) deviates greatly from 180° (about 163° in **2**), the M(equatorial)-Co-CO angles are not equal (119.0 and 131.6° in **1**; about 121 and 130° in **2**), and the CO-Co-CO angles differ from 120° (109.0(1) in **1** and about 109° in **2**).

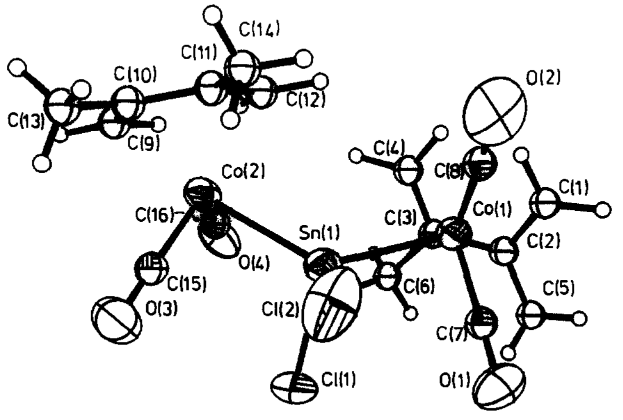

Fig. 1. The structure of $[\{Co(\eta^4\text{-}C_6H_{10})(CO)_2\}_2SnCl_2]$, with atom numbering.

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* As the coordination about Co(1) and Co(2) are superimposable, only Co(1) is considered in this discussion.

The distortion of the coordination about Co in **1** is away from tbp towards sp with a basal C_6H_{10} ligand C(8)O as the apical group, and *trans* basal angles of 154.5° for Sn(1)–Co(1)–M(12) and 131.6° for C(7)–Co(1)–M(34). The extent of the deformation may be gauged from the effect of rotating the diene about an axis through the Co atom which passes midway between M(12) and M(34). A rotation of 12° gives a more symmetrical tbp with two equal M(34)–Co(1)–CO angles of 125.4°, but the axial Sn moiety has to be moved by about 5° to bring it onto the plane which bisects the C(7)–Co(1)–C(8) angle. A rotation of −25.5° leads to the sp structure mentioned above, with C(8) apical and the two *trans* basal angles equal at 143°. The basal plane is very distorted from a square and the apical ligand is markedly off centre. If rotation is through 104°, the sp coordination obtained is much more symmetrical, with *trans* basal angles of 144.5° for C(8)–Co(1)–M(34) and C(7)–Co(1)–M(12), a reasonably symmetrical basal square, the M(12)–Co(1)–C(8) angle is 88.1° and the M(34)–Co(1)–C(7) is 86.8° and an apical Sn atom which is only about 5° from the plane which bisects the M(12)–Co(1)–M(34) or C(7)–Co(1)–C(8) angles. In both of the sp species mentioned above, the 1,3-diene is coordinated the "right way up" as it is in the $[Co(\eta^4\text{-}C_6H_{10})(CO)_3]^+$ cation [10] but, during its rotation, sp structures appear in which the diene is "upside down". Various tbp species also appear. In all of them the diene coordinates axial–equatorial. The sp species which is closest to the observed structure of **1**, has a basal Sn(1)–Co(1)–C(8) angle of 86.1(7)°, compared with 92.85(24)° in $[Co(\eta^4\text{-}C_6H_{10})(CO)_3][FeCl_3\text{-}NCMe]$, whilst the apical–Co(1)–basal angles are 96.3(8) and 109.0(10)°, compared with 101.27(25) and 104.20(24)°.

Because of the relatively poor quality of the structure determination, the errors in bond lengths and angles are relatively large, especially for the light atoms, and fine details of the bonding within the $C_6H_{10}Co$ moiety are not available. However, it is clear that the parameters are similar to those found in comparable complexes in which conjugate dienes are coordinated to Co, such as $[Co(\eta^4\text{-}C_6H_{10})(CO)_3][FeCl_3NCMe]$ [10], *trans*-$[Co_2(\eta^4\text{-}C_6H_{10})_2(CO)_2(\mu\text{-}CO)_2]$ [8], and *cis*-$[Co_2(\eta^4\text{-}C_6H_8)_2(CO)_2(\mu\text{-}CO)_2]$ [9]. It should be remembered that in all these complexes there is a sp configuration in the $Co(\eta^4\text{-diene})(C)_3$ moiety (the metal–metal bonds are ignored in the last two).

4. Conclusions

(1) It is not valid to assume that five-coordinated complexes of 1,3-dienes with d^8 first-row transition metals such as $Fe^{(0)}$ and $Co^{(I)}$ adopt the sp structure whilst only those of bicyclo[2.2.1]hepta-2,5-diene and related dienes with short bite and parallel double bonds prefer a tbp structure. In the $Co^{(I)}$ series at least, tbp coordination is observable in the presence of conjugate dienes.

(2) The rotation of the C_6H_{10} diene about its centroid–Co axis brings about a continuous change in the coordination polyhedron about the Co atom, passing alternately through tbp and sp structures variously distorted from the ideal. In the former the diene always coordinates axial–equatorial but not on the pseudo-threefold axis; in the latter the diene always coordinates basal–basal but may be the right way up or upside down. The degree of distortion of the coordination polyhedron from either tbp or sp may be related to an angle of rotation to a first approximation.

(3) The above diene rotation is a special case of the turnstile rotation mechanism for site exchange in five-coordinated complexes. In this case, at least, it can bring about isomer interchange of sp with tbp species, albeit distorted ones. However, the distorted tbp coordination found in **1** suggests that the Berry pseudo-rotation mechanism ought also to be considered in any discussion of site and isomer interchange in **1** and related species.

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