# Crystal Structures of Multicenter Catalysts. A Comparison of Dichlorobis(2,3,5,6-*tetrahapto*norbornadienedicarbonylcobalt)-tin(IV) and Diphenylbis(2,3,5,6-*tetrahapto*norbornadiene-dicarbonylcobalt)tin(IV)

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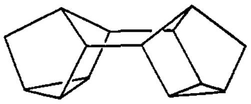
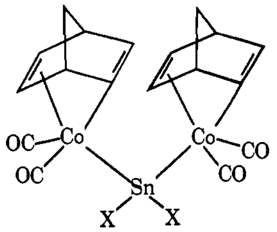
**Abstract**: Single-crystal X-ray diffraction methods have been used to determine the structures of $Cl_2Sn(Co(CO)_2C_7H_8)_2$ (I) and $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ (II); $C_7H_8$ = bicyclo[2.2.1]heptadiene. Both compounds crystallize in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The lattice parameters are: I, $a$ = 18.302 (16), $b$ = 11.838 (13), $c$ = 16.222 (8) Å, $\beta$ = 143.61 (8)°; II, $a$ = 9.310 (11), $b$ = 17.279 (27), $c$ = 20.229 (30) Å, $\beta$ = 123.06 (5°). The intensities of 4728 (I) and 2971 (II) unique reflections were measured on a Picker four-circle goniometer in the $\theta$–$2\theta$ scan mode with Mo K$\alpha$ radiation. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares to $R$ factors of 4.8% (I) and 7.8% (II) for 2977 and 1965 reflections above background, respectively. Hydrogen atoms were not located. Anisotropic temperature factors were assumed for all atoms of I, but only for the Sn and Co atoms of II. Coordination at tin may be described in terms of distorted tetrahedra, with angles Co–Sn–Co = 128.3 (1) and Cl–Sn–Cl = 98.1 (1)° in I and Co–Sn–Co = 118.3 (1) and C–Sn–C = 99.6 (7)° in II. Bond distances to tin are 2.498 (2) and 2.499 (2) Å for Sn–Co and 2.410 (2) and 2.412 (2) Å for Sn–Cl in I, and 2.575 (3) and 2.556 (3) Å for Sn–Co and 2.14 (2) and 2.19 (2) Å for Sn–C in II. The cobalt atoms exhibit distorted trigonal-bipyramidal geometries, where the norbornadiene double bonds chelate one apical and one equatorial site and the carbonyl groups occupy the remaining two equatorial positions. Distances from cobalt atoms to the unsaturated diene carbon atoms range from 2.076 to 2.192 Å. These compounds are active in catalyzing the dimerization of norbornadiene (stereoselectively in the case of I) and their structures are the first to be reported for cobalt–norbornadiene $\pi$ complexes.

One of the underlying reasons for research in organometallic chemistry is the potential application of these compounds to the catalysis and control of organic reactions. Metal–metal bonded compounds are of special interest in this regard, for they afford an opportunity to bring substrates into physical proximity by complex formation on neighboring metal nuclei. A pertinent example is the work of Schrauzer, Bastian, and Fosselius, who showed[1] that norbornadiene can be dimerized stereospecificially to a bisnortricyclene named Binor-S *via* intermediate $\pi$ complexes derived from heterometallic cobalt carbonyl compounds of the type $M(Co(CO)_4)_n$; $n$ = 2, 3; M = Zn, Cd, Hg, Ir. Because Binor-S has not been observed in the product mix when norbornadiene dimerizes in the presence of mononuclear catalysts, its formation is believed to be an indicator for a binuclear reaction mechanism termed[1] a "$\pi$-complex multicenter reaction." Studies[2,3] of the tin derivatives[4,5] $X_2Sn(Co(CO)_4)_2$ have indicated that these also actively catalyze the dimerization of norbornadiene, but in a manner remarkably sensitive to the substituent X. For X = Cl, Br, or I, the reaction is stereospecific for Binor-S, but for X = $CH_3$ or $C_6H_5$ a mixture of dimers other than Binor-S, principally the exo-trans-exo isomer,[6] is obtained.



Binor-S

An important result from the studies[2,3] of the $X_2Sn(Co(CO)_4)_2$ system was the isolation of the crystalline binuclear $\pi$ complexes I and II from the residues of the respective reaction mixtures.[3] These compounds are believed to be intermediates in the $\pi$-complex multicenter reaction and are themselves catalytically active.



I, X = Cl
II, X = $C_6H_5$

Certain properties of these complexes are expected to be governed by the second-order rehybridization effect proposed by Bent.[7,8] According to this theory, p character in the central tin atom should be directed into bonds formed with the more electronegative ligands. Consequently, substitution of chlorine for phenyl at X should produce increased s character in the metal–metal bonds and result in decreased Sn–Co bond distances and an opening of the Co–Sn–Co bond angle. A comparison of the geometric properties of I

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(1) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, **88**, 4890 (1966).

(2) F. P. Boer, J. H. Tsai, and J. J. Flynn, Jr., *ibid.*, **92**, 6092 (1970).

(3) J. H. Tsai, manuscript in preparation.

(4) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

(5) D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967).

(6) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968).

(7) H. A. Bent, *Chem. Rev.*, **61**, 290 (1961).

(8) B. R. Penfold, *Perspect. Struct. Chem.*, **2**, 71 (1968).

**Table I.** Crystal Data

| | | |
|---|---|---|
| Molecular formula | $Cl_2Sn(Co(CO)_2C_7H_8)_2$ | $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ |
| Molecular weight | 603.61 | 687.09 |
| Space group | $P2_1/c$ ($C_{2h}^5$) | $P2_1/c$ ($C_{2h}^5$) |
| Cell constants (25°) *a*, Å | 18.302 (16) | 9.310 (11) |
| *b*, Å | 11.838 (13) | 17.279 (27) |
| *c*, Å | 16.222 (8) | 20.229 (30) |
| $\beta$, deg | 143.61 (8) | 123.06 (5) |
| Volume, Å$^3$ | 2085.0 | 2727.4 |
| Density(calcd), g cm$^{-3}$ | 1.922 ($Z = 4$) | 1.670 ($Z = 4$) |
| Density(measd), g cm$^{-3}$ | 1.95 (1) | 1.665 (1) |
| Crystal dimensions, mm | 0.060 × 0.075 × 0.110 | 0.12 × 0.20 × 0.20 |
| No. of reflections measd | 4728[a] | 2971 |
| No. of reflections above background | 2977 | 1965 |
| Absorption coefficient, $\mu$ (Mo K$\alpha$), cm$^{-1}$ | 30.8 | 21.9 |

[a] A group of 13 additional reflections was measured, but later discarded because of a strong presumption of instrument failure.

and II thus serves as an excellent test for this hypothesis and is especially interesting because it affords an opportunity to correlate these electronic effects with control of catalytic activity. Therefore, the structures of I and II, reported below, were determined by single-crystal X-ray diffraction methods. These are the first X-ray investigations of cobalt–norbornadiene complexes; compounds formed by norbornadiene with Cu, Pd, and Ag have been described by Baenziger and his associates.[9] In related work,[2,10] we have conclusively established the syn ($C_{2v}$) configuration[1,11,12] of Binor-S by determining the crystal structure of its dione derivative.

## Experimental Section

Samples of $Cl_2Sn(Co(CO)_2C_7H_8)_2$ (I) and $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ (II) were supplied by J. H. Tsai. Crystals of I are deep red and vary considerably in habit; the crystal chosen for the present study was mounted externally on a small diameter glass filament with its long dimension, corresponding to the *c* axis, parallel to the central axis of the goniometer head. Crystals of II are also dark red and exhibit a prismatic habit. A suitable specimen was selected, cemented to an interior wall of a 0.3-mm Lindemann glass capillary, and aligned with its *b* axis parallel to the spindle of a Weissenberg goniometer. A larger (Table I) crystal of II was chosen than for I because the phenyl compound was found to be a considerably weaker scatterer and also possessed a lower linear absorption coefficient.

Preliminary surveys of their reciprocal lattices by Weissenberg and precession methods indicated that both compounds exhibited diffraction symmetry $C_{2h}$ with the reflection conditions $h0l$, $l = 2n$, and $0k0$, $k = 2n$, diagnostic of space group $P2_1/c$. The compounds are not, however, isomorphous. The lattice constants were determined by least-squares refinement of 15 (I) and 11 (II) reflections on a Picker four-circle goniometer (Mo K$\bar{\alpha}$ radiation, $\lambda$ 0.71069 Å). The estimated standard deviations calculated from the least-squares analysis were a factor of 5 lower than the errors given in Table I, which reflect our estimate of the reproducibility of our results with different crystals and/or experimental conditions. Experimental densities were measured by the density-gradient technique using aqueous $ZnI_2$ solutions calibrated with $CCl_4$ and $C_2Cl_4$.

The intensity data were gathered using the $\theta$–$2\theta$ scan mode of the diffractometer and Zr-filtered Mo K$\alpha$ radiation. The X-ray tube was set at a 3° takeoff angle and an aperture 6.0-mm square was placed immediately before the scintillation counter at a distance of 30 cm from the crystal. Stray radiation was restricted by the use of 1.5 mm-diameter incident- and exit-beam collimators. Scan angles of 1.5° + $\Delta$, where $\Delta$ is the separation of the K$\alpha$ doublet, were employed; this range was sufficient to allow for the observed mosaic spreads of the crystals. The scan speed was 2°/min. Background counts of 15 sec were taken at each end of the scan by the stationary-crystal–stationary-counter technique. Test reflections were monitored after every 50 measurements and showed fair stability; the maximum deviation from the initial intensity was 3% for II and 5% for I. For I, all unique reflections within the sphere $\sin\theta \leq 0.461$ (equivalent to the Cu K$\alpha$ limit) were recorded, but for II we found it unprofitable to collect data beyond $\sin\theta \leq 0.400$ because of the weakness of the scattering at higher angles. An error $\sigma(I) = [(0.03I)^2 + N_o + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$ in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, in which $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Here $N_o$ is the gross count, $N_b$ is the background count, $k$ is the ratio of scan time to background time, and $F^2$ and $\sigma(F^2)$ refer to the intensities after the Lorentz and polarization corrections. Reflections for which $I < 0$ or $\sigma(I)/I > 0.3$ were denoted absent; only those reflections above background by this definition were used in the structure analysis. No absorption corrections were applied; an examination of selected transmission coefficients indicates that the largest errors in $F$ due to the absence of a correction are of the order of ±2% for I and ±5% for II. Finally, scale and overall temperature factors were computed from intensity statistics by Wilson's method.

## Solution and Refinement of the Structures

**(A) $Cl_2Sn(Co(CO)_2C_7H_8)_2$.** A normal-sharpened three-dimensional Patterson function was calculated.[13] The Sn, Co, and Cl atoms were readily located, and their positions and isotropic temperature factors were refined[14,15a] on a small computer using a subset of 1852 reflections with $\sin\theta \leq 0.35$. After three cycles $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was reduced from 0.333 to 0.206 and $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$ from 0.439 to 0.292. An electron density map[13] from which the heavy atoms were subtracted now revealed the 22 carbon and oxygen atoms. Although the program[14] used at this stage of refinement was of the full-matrix type, storage limitations required us to treat the problem by cycling blocks of 72 variables. After six such cycles, in which the positions and isotropic temperature factors of 27 atoms were refined $R_1$ was 0.064 and $R_2$ 0.084. With the continuation of refinement on a larger computer,[16] the full set of 2977 reflections above background

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[9] (a) N. C. Baenziger, J. R. Doyle, and C. Carpenter, *Acta Crystallogr.*, 14, 303 (1961); (b) N. C. Baenziger, G. F. Richards, and J. R. Doyle, *ibid.*, 18, 924 (1965); (c) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, 3, 1535 (1964); (d) N. C. Baenziger, H. L. Haight, R. A. Alexander, and J. R. Doyle, *ibid.*, 5, 1399 (1966).

[10] F. P. Boer, M. A. Neuman, R. J. Roth, and T. J. Katz, *J. Amer. Chem. Soc.*, 93, 4436 (1971).

[11] T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967).

[12] G. N. Schrauzer, R. K. Y. Ho, and G. Schlesinger, *ibid.*, 543 (1970).

[13] Fourier calculations were performed using program B-149 (Argonne National Laboratory), a version of Shoemaker, Sly, and Van der Hende's ERFR-2 by J. Gvildys.

[14] F. P. Remoortere and F. P. Boer, "A FORTRAN Crystallographic Least-Squares Program (FXLS) for the IBM 1130," Dow Internal Report FL-314.

[15] Atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) p 201; (b) pp 215–216.

[16] Anisotropic least-squares and structure factor calculations were performed using ANL-FLS-14E, J. Gvildy's version of Busing, Martin, and Levy's ORFLS.

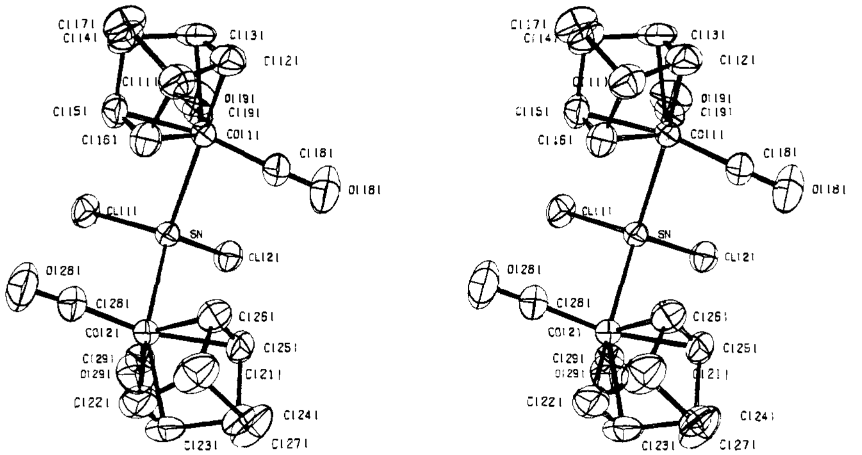

Figure 1. Three-dimensional stereo view of the dichlorobis(2,3,5,6-*tetrahapto*norbornadienedicarbonylcobalt)tin molecule. The ellipsoids represent amplitudes of thermal motion in the crystal at the 50% probability level.

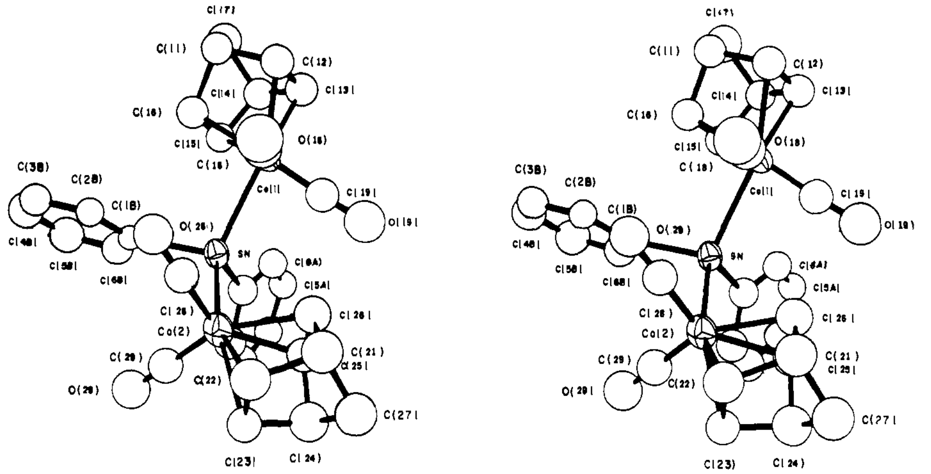

Figure 2. Three-dimensional stereo view of the diphenylbis(2,3,5,6-*tetrahapto*norbornadienedicarbonylcobalt)tin(IV) molecule. The metal atoms are drawn as ellipsoids, and the carbon and oxygen atoms as spheres, of thermal motion at 50% probability.

was introduced, corrections for the real and imaginary parts of the Sn, Co, and Cl anomalous scattering factors[15b] were included, and anisotropic temperature factors for all atoms were assumed. One cycle of full-matrix least-squares refinement (244 variables) reduced $R_1$ from 0.089 to 0.065 and $R_2$ from 0.157 to 0.072. A secondary extinction correction,[17] in the form $I_o^{\text{corr}} = I_o(1 + 2gI_c)$, was now applied to 15 strong low-order reflections. The coefficient $g$ (referred to the scaled intensities) was $2.1 \times 10^{-7}e^{-2}$ and the maximum change in $F_o$ was 27%. After three more cycles, refinement converged at $R_1 = 4.8\%$ and $R_2 = 5.3\%$. In the final cycle, the mean parameter shift was $0.04\sigma$ and no shift exceeded $0.23\sigma$. A difference Fourier[13] showed no peaks above 0.74 e/Å$^3$ and no negative region below $-0.62$ e/Å$^3$. A few of the larger peaks occurred in positions where hydrogen atoms might be expected, but these did not appear to be sufficiently well resolved to justify refinement.

**(B) $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$.** The three metal atoms were located in a normal-sharpened three-dimensional Patterson function.[13] Phases based on these atoms were used to construct an electron density difference map[8] which revealed the positions of the 34 C and O atoms. The coordinates and isotropic temperature factors of these atoms were refined by least squares on the small computer in blocks of 72 variables as before.[14] After 11 cycles, the isotropic refinement had converged completely at $R_1 = 0.096$ and $R_2 = 0.099$. The ratio of observations to atoms did not seem to justify complete anisotropic refinement; therefore, anisotropic temperature factors were assigned only to the metal atoms. The real and imaginary parts of the metal anomalous scattering factors[15b] were also introduced at this time. Three cycles of full-matrix refinement of 164 variables on a larger computer[16] gave final values of $R_1 = 0.078$ and $R_2 = 0.079$ for the 1965 reflections above background. In the final cycle, the mean parameter shift was $0.01\sigma$, with a maximum shift of only $0.05\sigma$. The largest peaks in the final difference map were in the vicinity of the tin atom and had amplitudes up to 1.37 e/Å$^3$. The amplitudes of most of the remaining peaks were less than 0.8 e/Å$^3$.

**(C) Results.** Final position and thermal parameters for I and II, with their standard errors as calculated[16] in the final least-squares cycles, are given in Tables II and III, respectively. Also given are the root-mean-square amplitudes of thermal motion. The directions of these components may be inferred from the three-dimensional stereoscopic molecular drawings[18]

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[17] G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 411.

[18] C. K. Johnson, "ORTEP: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.

**Table II.** Positional and Thermal Parameters for $Cl_2Sn(Co(CO)_2C_7H_8)_2$

(A) Coordinates and Anisotropic Temperature Factors[a,b]

| Atom | $x$ | $y$ | $z$ | $10^4\beta_{11}$ | $10^4\beta_{22}$ | $10^4\beta_{33}$ | $10^4\beta_{12}$ | $10^4\beta_{13}$ | $10^4\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Sn | 0.23805 (5) | 0.07366 (4) | 0.00515 (5) | 57 (1) | 46 (1) | 70 (1) | 0 (0) | 48 (1) | 0 (0) |
| Co(1) | 0.30753 (9) | 0.25711 (8) | 0.12847 (10) | 59 (1) | 47 (1) | 74 (1) | −4 (1) | 51 (1) | −4 (1) |
| Co(2) | 0.18885 (9) | −0.10653 (8) | 0.03394 (11) | 59 (1) | 46 (1) | 97 (1) | 0 (1) | 58 (1) | 1 (1) |
| Cl(1) | 0.0629 (2) | 0.1202 (2) | −0.2386 (2) | 80 (2) | 94 (2) | 68 (2) | 11 (2) | 50 (2) | 2 (2) |
| Cl(2) | 0.3810 (2) | 0.0280 (2) | 0.0261 (2) | 86 (2) | 82 (2) | 139 (3) | 7 (2) | 92 (2) | 2 (2) |
| C(11) | 0.2417 (8) | 0.3256 (7) | 0.2268 (9) | 96 (9) | 70 (7) | 98 (10) | 5 (7) | 78 (9) | −1 (7) |
| C(12) | 0.3440 (8) | 0.3722 (8) | 0.2647 (9) | 104 (10) | 65 (7) | 113 (11) | 1 (7) | 84 (10) | 14 (8) |
| C(13) | 0.2888 (9) | 0.4301 (7) | 0.1500 (11) | 138 (11) | 35 (6) | 194 (15) | −6 (7) | 140 (12) | −17 (8) |
| C(14) | 0.1491 (9) | 0.4218 (7) | 0.0371 (9) | 104 (9) | 67 (7) | 120 (11) | 28 (7) | 85 (10) | 30 (8) |
| C(15) | 0.1282 (7) | 0.2944 (7) | 0.0008 (9) | 53 (7) | 83 (7) | 99 (10) | 3 (6) | 54 (8) | −15 (7) |
| C(16) | 0.1855 (8) | 0.2363 (7) | 0.1168 (9) | 77 (8) | 74 (7) | 131 (12) | 2 (6) | 87 (9) | −2 (8) |
| C(17) | 0.1451 (9) | 0.4231 (8) | 0.1306 (10) | 129 (1) | 76 (8) | 145 (13) | 21 (8) | 116 (11) | 13 (9) |
| C(21) | 0.2723 (10) | −0.1566 (9) | 0.2684 (12) | 141 (13) | 101 (10) | 186 (16) | 28 (9) | 141 (14) | 47 (11) |
| C(22) | 0.1685 (10) | −0.2132 (8) | 0.1234 (13) | 110 (11) | 76 (9) | 234 (20) | 15 (8) | 136 (14) | 51 (11) |
| C(23) | 0.2226 (10) | −0.2737 (8) | 0.1091 (11) | 131 (12) | 48 (7) | 160 (16) | −2 (8) | 104 (13) | 22 (9) |
| C(24) | 0.3649 (8) | −0.2561 (7) | 0.2492 (10) | 87 (9) | 66 (7) | 126 (12) | 25 (7) | 77 (10) | 34 (8) |
| C(25) | 0.3736 (7) | −0.1301 (8) | 0.2312 (8) | 66 (8) | 75 (8) | 82 (10) | 8 (6) | 50 (8) | 24 (7) |
| C(26) | 0.3157 (8) | −0.0681 (8) | 0.2427 (9) | 93 (9) | 73 (7) | 100 (11) | 4 (7) | 73 (9) | 21 (8) |
| C(27) | 0.3745 (9) | −0.2457 (9) | 0.3540 (11) | 127 (12) | 109 (10) | 156 (15) | 55 (9) | 117 (12) | 69 (10) |
| C(18) | 0.4520 (8) | 0.1922 (7) | 0.2804 (9) | 62 (8) | 73 (7) | 95 (11) | 3 (6) | 55 (8) | −3 (7) |
| O(18) | 0.5468 (6) | 0.1538 (7) | 0.3767 (7) | 76 (7) | 158 (9) | 125 (10) | 22 (6) | 62 (7) | 14 (8) |
| C(19) | 0.3081 (8) | 0.3112 (7) | 0.0269 (9) | 87 (9) | 67 (7) | 110 (11) | −17 (6) | 79 (9) | −18 (7) |
| O(19) | 0.3081 (7) | 0.3479 (6) | −0.0383 (8) | 187 (10) | 104 (7) | 193 (11) | −15 (7) | 172 (10) | 7 (7) |
| C(28) | 0.0421 (8) | −0.0503 (8) | −0.0748 (10) | 71 (8) | 82 (9) | 130 (12) | 5 (7) | 74 (9) | 8 (8) |
| O(28) | 0.5462 (6) | −0.0184 (7) | −0.1469 (8) | 81 (7) | 159 (9) | 193 (12) | 34 (6) | 94 (8) | 42 (9) |
| C(29) | 0.1787 (8) | −0.1684 (8) | −0.0760 (10) | 83 (9) | 68 (8) | 131 (13) | −5 (7) | 79 (10) | −9 (8) |
| O(29) | 0.1704 (7) | −0.2081 (6) | −0.1473 (8) | 149 (9) | 118 (8) | 190 (12) | −19 (7) | 135 (10) | −64 (8) |

(B) Root-Mean-Square Thermal Displacements (Å) along Principal Axes[c]

| Atom | Axis 1 | Axis 2 | Axis 3 | Atom | Axis 1 | Axis 2 | Axis 3 |
|---|---|---|---|---|---|---|---|
| Sn | 0.180 (1) | 0.182 (1) | 0.205 (1) | C(23) | 0.165 (15) | 0.272 (13) | 0.343 (14) |
| Co(1) | 0.177 (1) | 0.191 (1) | 0.205 (1) | C(24) | 0.176 (13) | 0.254 (12) | 0.286 (13) |
| Co(2) | 0.180 (2) | 0.185 (2) | 0.234 (2) | C(25) | 0.174 (13) | 0.224 (12) | 0.273 (12) |
| Cl(1) | 0.179 (3) | 0.244 (3) | 0.286 (3) | C(26) | 0.186 (13) | 0.239 (12) | 0.271 (13) |
| Cl(2) | 0.198 (3) | 0.245 (3) | 0.258 (3) | C(27) | 0.189 (14) | 0.256 (13) | 0.341 (14) |
| C(11) | 0.202 (12) | 0.221 (12) | 0.254 (12) | C(18) | 0.192 (12) | 0.221 (12) | 0.252 (12) |
| C(12) | 0.190 (13) | 0.239 (12) | 0.274 (13) | O(18) | 0.205 (10) | 0.312 (10) | 0.344 (10) |
| C(13) | 0.149 (13) | 0.251 (12) | 0.304 (12) | C(19) | 0.196 (12) | 0.226 (13) | 0.248 (12) |
| C(14) | 0.181 (13) | 0.259 (13) | 0.277 (12) | O(19) | 0.188 (11) | 0.288 (9) | 0.338 (9) |
| C(15) | 0.173 (12) | 0.211 (12) | 0.277 (12) | C(28) | 0.200 (12) | 0.240 (13) | 0.276 (12) |
| C(16) | 0.178 (12) | 0.230 (12) | 0.250 (12) | O(28) | 0.199 (10) | 0.324 (10) | 0.369 (10) |
| C(17) | 0.209 (13) | 0.237 (13) | 0.289 (12) | C(29) | 0.213 (13) | 0.225 (12) | 0.274 (13) |
| C(21) | 0.210 (14) | 0.253 (13) | 0.329 (14) | O(29) | 0.199 (10) | 0.299 (9) | 0.367 (10) |
| C(22) | 0.184 (14) | 0.229 (13) | 0.372 (15) | | | | |

[a] Standard errors are given in parentheses. [b] The anisotropic temperature factors are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] Ordered on increasing magnitude.

(Figures 1 and 2) where thermal motion is represented by ellipsoids of 50% probability. The observed and calculated structure factors are available on request.[19] Table IV compares bond distances in the two structures, while interatomic angles are summarized in Table V. The standard errors given in Tables IV and V were calculated[20] from the variance–covariance matrices generated in the final least-squares cycles.

The numbering system used is derived from the conventional one for norbornadiene, with the first digit indicating with which cobalt (1 or 2) the atom is associated. Because the structure of I showed approximate $C_2$ symmetry (Figure 1) the numbering system of the atoms was chosen to make atoms with the same second digit symmetry equivalent. The atoms of II can be made equivalent to those of I by simple rotations about the Sn–Co bonds.

## Discussion

The results show that both molecular structures are based on the expected tetrahedral arrangement at the tin atom and on a distorted trigonal-bipyramidal configuration at the cobalt atoms, where tin is axial, the carbonyls are equatorial, and the norbornadiene molecule chelates one axial and one equatorial site. (Here the diene double bonds, labeled 23 and 56 at the axial and equatorial positions, respectively, are considered as single ligands.)

The geometries of the tin atoms provide convincing evidence that the second-order hybridization effect[7,8] plays an important role in these compounds. The Co–Sn–Co angles, 118.3 ± 0.1° in II and 128.3 ± 0.1° in I, show major deviations from the ideal tetrahedral angle of 109.5° in a direction consistent with the relative

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(19) A table of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(20) J. Gvildys, "ANL-FFE, A FORTRAN Crystallographic Function and Error Program," Program Library B115, Argonne National Laboratory, Argonne, Ill. The program is based on ORFFE by Busing, Martin, and Levy.

**Table III.** Position and Thermal Parameters for $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$[a,b]

| Atom | $x$ | $y$ | $z$ | $10^4\beta_{11}$ | $10^4\beta_{22}$ | $10^4\beta_{33}$ | $10^4\beta_{12}$ | $10^4\beta_{13}$ | $10^4\beta_{23}$ | Rms amplitudes of thermal motion, Å Axis 1 | Axis 2 | Axis 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sn | 0.0802 (2) | 0.2143 (1) | 0.2925 (1) | 127 (2) | 35 (1) | 28 (1) | −9 (1) | 38 (1) | −1 (1) | 0.176 | 0.204 | 0.237 |
| Co(1) | 0.3731 (3) | 0.1470 (2) | 0.3548 (2) | 118 (5) | 48 (2) | 31 (1) | 1 (2) | 35 (2) | 4 (1) | 0.186 | 0.211 | 0.272 |
| Co(2) | −0.0099 (4) | 0.2638 (2) | 0.3843 (2) | 167 (6) | 41 (1) | 37 (1) | 11 (2) | 58 (2) | 3 (1) | 0.175 | 0.233 | 0.261 |

| Atom | $x$ | $y$ | $z$ | $B$[c] | Rms ampl, Å | Atom | $x$ | $y$ | $z$ | $B$[c] | Rms ampl, Å |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C(11) | 0.4393 (25) | −0.0019 (12) | 0.3257 (12) | 4.5 (0.5) | 0.240 | O(19) | 0.5010 (21) | 0.3039 (10) | 0.3841 (10) | 7.6 (0.4) | 0.310 |
| C(12) | 0.5629 (26) | 0.0571 (12) | 0.3819 (12) | 4.8 (0.5) | 0.248 | C(28) | 0.0086 (25) | 0.1718 (13) | 0.4189 (12) | 4.6 (0.5) | 0.240 |
| C(13) | 0.5806 (26) | 0.1151 (13) | 0.3415 (13) | 5.0 (0.5) | 0.251 | O(28) | 0.0193 (18) | 0.1068 (9) | 0.4381 (9) | 5.8 (0.4) | 0.272 |
| C(14) | 0.4659 (26) | 0.0944 (13) | 0.2528 (13) | 4.8 (0.5) | 0.246 | C(29) | −0.2115 (28) | 0.2754 (13) | 0.2963 (13) | 5.1 (0.5) | 0.255 |
| C(15) | 0.2843 (25) | 0.1076 (11) | 0.2402 (12) | 4.1 (0.5) | 0.229 | O(29) | −0.3486 (20) | 0.2811 (10) | 0.2407 (9) | 6.6 (0.4) | 0.289 |
| C(16) | 0.2677 (25) | 0.0475 (12) | 0.2843 (12) | 4.5 (0.5) | 0.240 | C(1A) | 0.0602 (25) | 0.3017 (12) | 0.2129 (11) | 4.5 (0.5) | 0.240 |
| C(17) | 0.4705 (30) | 0.0033 (14) | 0.2562 (14) | 6.3 (0.6) | 0.284 | C(2A) | −0.0752 (27) | 0.3547 (14) | 0.1809 (13) | 5.3 (0.5) | 0.260 |
| C(21) | 0.2086 (29) | 0.3262 (13) | 0.5356 (13) | 5.7 (0.6) | 0.269 | C(3A) | −0.1023 (29) | 0.4085 (14) | 0.1218 (14) | 6.1 (0.6) | 0.278 |
| C(22) | 0.0166 (28) | 0.3013 (13) | 0.4935 (13) | 5.5 (0.5) | 0.264 | C(4A) | 0.0173 (27) | 0.4136 (13) | 0.0998 (12) | 5.0 (0.5) | 0.252 |
| C(23) | −0.0837 (25) | 0.3576 (12) | 0.4335 (12) | 4.4 (0.5) | 0.236 | C(5A) | 0.1579 (26) | 0.3646 (12) | 0.1324 (12) | 4.5 (0.5) | 0.239 |
| C(24) | 0.0519 (30) | 0.4164 (14) | 0.4376 (13) | 5.8 (0.6) | 0.271 | C(6A) | 0.1786 (26) | 0.3113 (12) | 0.1900 (12) | 4.6 (0.5) | 0.243 |
| C(25) | 0.1373 (27) | 0.3628 (13) | 0.4057 (13) | 4.8 (0.5) | 0.247 | C(1B) | −0.1152 (21) | 0.1335 (10) | 0.2077 (10) | 2.8 (0.4) | 0.187 |
| C(26) | 0.2329 (27) | 0.3114 (12) | 0.4652 (13) | 5.2 (0.5) | 0.256 | C(2B) | −0.1483 (23) | 0.0661 (11) | 0.2353 (11) | 3.6 (0.4) | 0.212 |
| C(27) | 0.1829 (29) | 0.4158 (14) | 0.5271 (14) | 6.1 (0.6) | 0.277 | C(3B) | −0.2665 (27) | 0.0121 (13) | 0.1813 (13) | 4.7 (0.5) | 0.245 |
| C(18) | 0.3814 (29) | 0.1195 (14) | 0.4386 (14) | 6.2 (0.6) | 0.279 | C(4B) | −0.3433 (31) | 0.0225 (15) | 0.1025 (15) | 6.4 (0.6) | 0.286 |
| O(18) | 0.3928 (22) | 0.0968 (10) | 0.4963 (11) | 8.1 (0.5) | 0.321 | C(5B) | −0.3092 (31) | 0.0914 (15) | 0.0731 (14) | 6.4 (0.6) | 0.287 |
| C(19) | 0.4440 (27) | 0.2379 (13) | 0.3706 (13) | 5.1 (0.5) | 0.255 | C(6B) | −0.1927 (27) | 0.1476 (13) | 0.1274 (13) | 5.2 (0.5) | 0.256 |

[a] Errors given in parentheses. [b] The anisotropic temperature factors are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. [c] Isotropic temperature factor, Å.

**Table IV.** Bond Distances (Å)[a]

| $Cl_2Sn(Co(CO)_2C_7H_8)_2$ | | $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ | |
|---|---|---|---|
| | Bonds to Tin | | |
| Sn–Cl(1) | 2.410 (2) | Sn–Co(1) | 2.575 (3) |
| Sn–Cl(2) | 2.412 (2) | Sn–Co(2) | 2.566 (3) |
| Sn–Co(1) | 2.498 (1) | Sn–C(1A) | 2.139 (20) |
| Sn–Co(2) | 2.499 (1) | Sn–C(1B) | 2.190 (17) |
| | Bonds to Cobalt | | |
| Co(1)–C(12) | 2.192 (9) | Co(1)–C(12) | 2.187 (21) |
| Co(1)–C(13) | 2.149 (9) | Co(1)–C(13) | 2.162 (21) |
| Co(1)–C(15) | 2.076 (9) | Co(1)–C(15) | 2.104 (20) |
| Co(1)–C(16) | 2.099 (8) | Co(1)–C(16) | 2.104 (20) |
| Co(1)–C(18) | 1.779 (9) | Co(1)–C(18) | 1.723 (24) |
| Co(1)–C(19) | 1.775 (9) | Co(1)–C(19) | 1.665 (23) |
| Co(2)–C(22) | 2.172 (10) | Co(2)–C(22) | 2.182 (22) |
| Co(2)–C(23) | 2.141 (9) | Co(2)–C(23) | 2.198 (21) |
| Co(2)–C(25) | 2.081 (8) | Co(2)–C(12) | 2.085 (21) |
| Co(2)–C(26) | 2.098 (9) | Co(2)–C(26) | 2.105 (21) |
| Co(2)–C(28) | 1.771 (9) | Co(2)–C(28) | 1.707 (23) |
| Co(2)–C(29) | 1.796 (11) | Co(2)–C(29) | 1.757 (22) |
| | Carbon–Oxygen Distances | | |
| C(18)–O(18) | 1.137 (9) | C(18)–O(18) | 1.180 (24) |
| C(19)–O(19) | 1.144 (10) | C(19)–O(19) | 1.225 (23) |
| C(28)–O(28) | 1.145 (10) | C(28)–O(28) | 1.175 (22) |
| C(29)–O(29) | 1.140 (10) | C(29)–O(29) | 1.157 (21) |
| | Carbon–Carbon Distances | | |
| C(11)–C(12) | 1.529 (13) | C(11)–C(12) | 1.493 (25) |
| C(12)–C(13) | 1.388 (13) | C(12)–C(13) | 1.359 (26) |
| C(13)–C(14) | 1.537 (13) | C(13)–C(14) | 1.548 (27) |
| C(14)–C(15) | 1.551 (12) | C(14)–C(15) | 1.582 (26) |
| C(15)–C(16) | 1.392 (12) | C(15)–C(16) | 1.431 (25) |
| C(16)–C(11) | 1.551 (11) | C(16)–C(11) | 1.588 (26) |
| C(11)–C(17) | 1.565 (12) | C(11)–C(17) | 1.586 (28) |
| C(14)–C(17) | 1.575 (13) | C(14)–C(17) | 1.575 (29) |
| C(21)–C(22) | 1.548 (15) | C(21)–C(22) | 1.563 (27) |
| C(22)–C(23) | 1.385 (15) | C(22)–C(23) | 1.434 (27) |
| C(23)–C(24) | 1.569 (13) | C(23)–C(24) | 1.586 (28) |
| C(24)–C(25) | 1.552 (12) | C(24)–C(25) | 1.570 (28) |
| C(25)–C(26) | 1.418 (13) | C(25)–C(26) | 1.365 (25) |
| C(26)–C(21) | 1.561 (12) | C(26)–C(21) | 1.580 (29) |
| C(21)–C(27) | 1.534 (13) | C(21)–C(27) | 1.561 (30) |
| C(24)–C(27) | 1.566 (14) | C(24)–C(27) | 1.535 (29) |
| | | C(1A)–C(2A) | 1.399 (26) |
| | | C(2A)–C(3A) | 1.424 (28) |
| | | C(3A)–C(4A) | 1.408 (26) |
| | | C(4A)–C(5A) | 1.388 (26) |
| | | C(5A)–C(6A) | 1.413 (26) |
| | | C(6A)–C(1A) | 1.420 (26) |
| | | C(1B)–C(2B) | 1.397 (23) |
| | | C(2B)–C(3B) | 1.401 (25) |
| | | C(3B)–C(4B) | 1.357 (27) |
| | | C(4B)–C(5B) | 1.441 (30) |
| | | C(5B)–C(6B) | 1.422 (28) |
| | | C(6B)–C(1B) | 1.392 (24) |

[a] Standard errors in parentheses.

electronegativities. (Pauling's electronegativity scale[21] gives Sn, 1.8; Co, 1.8; C, 2.5; and Cl, 3.0.) We note that the opening of the Co–Sn–Co angles with increasingly electronegative X substituents had been predicted[5] in the parent carbonyl compounds $X_2Sn(Co(CO)_4)_2$, X = Cl, $C_6H_5$, from changes in the absorbances of the $A_1$ and $B_1$ carbonyl stretching bands; however, our present results show that the method of calculation[5] leads to exaggeration of the angles.[3] The X–Sn–X angles (C–Sn–C, 99.6 (7)°, and Cl–Sn–Cl, 98.1 (1)°) are significantly less than the tetrahedral angle and indicative of increased p character in the Sn–X bonds. Steric repulsion does not appear to be a factor in opening Co–Sn–Co angles, as no unusually short intramo-

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(21) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 93.

**Table V.** Bond Angles (deg)[a]

| $Cl_2Sn(Co(CO)_2C_7H_8)_2$ | | | | $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ | | | |
|---|---|---|---|---|---|---|---|
| Vertex | Atom 1 | Atom 2 | Angle | Vertex | Atom 1 | Atom 2 | Angle |
| C(11) | C(16) | C(12) | 99.8 (0.7) | C(11) | C(16) | C(12) | 99.8 (1.6) |
| C(12) | C(11) | C(13) | 107.7 (0.8) | C(12) | C(11) | C(13) | 110.0 (1.8) |
| C(13) | C(12) | C(14) | 106.4 (0.8) | C(13) | C(12) | C(14) | 106.9 (1.8) |
| C(14) | C(13) | C(15) | 100.3 (0.6) | C(14) | C(13) | C(15) | 98.9 (1.6) |
| C(15) | C(14) | C(16) | 106.2 (0.7) | C(15) | C(14) | C(16) | 105.3 (1.7) |
| C(16) | C(15) | C(11) | 107.4 (0.8) | C(16) | C(15) | C(11) | 107.4 (1.7) |
| C(17) | C(14) | C(11) | 93.6 (0.6) | C(17) | C(14) | C(11) | 94.7 (1.7) |
| C(14) | C(13) | C(17) | 100.1 (0.8) | C(14) | C(13) | C(17) | 101.3 (1.7) |
| C(14) | C(15) | C(17) | 100.8 (0.7) | C(14) | C(15) | C(17) | 98.8 (1.7) |
| C(11) | C(12) | C(17) | 99.8 (0.7) | C(11) | C(12) | C(17) | 101.4 (0.7) |
| C(11) | C(16) | C(17) | 100.6 (0.7) | C(11) | C(16) | C(17) | 96.8 (1.6) |
| C(21) | C(26) | C(22) | 98.7 (0.8) | C(21) | C(26) | C(22) | 98.5 (1.7) |
| C(22) | C(21) | C(23) | 108.0 (0.9) | C(22) | C(21) | C(23) | 107.3 (1.8) |
| C(23) | C(22) | C(24) | 105.4 (0.9) | C(23) | C(22) | C(24) | 104.9 (1.7) |
| C(24) | C(23) | C(25) | 99.0 (0.6) | C(24) | C(23) | C(25) | 99.6 (1.7) |
| C(25) | C(24) | C(26) | 105.8 (0.8) | C(25) | C(24) | C(26) | 104.7 (1.8) |
| C(26) | C(25) | C(21) | 106.4 (0.8) | C(26) | C(25) | C(21) | 110.2 (1.9) |
| C(27) | C(24) | C(21) | 94.7 (0.7) | C(27) | C(24) | C(21) | 96.4 (1.9) |
| C(24) | C(23) | C(27) | 100.8 (0.8) | C(24) | C(23) | C(27) | 98.9 (1.7) |
| C(24) | C(25) | C(27) | 100.9 (0.8) | C(24) | C(25) | C(27) | 103.1 (1.8) |
| C(21) | C(22) | C(27) | 100.9 (0.9) | C(21) | C(22) | C(27) | 98.7 (1.8) |
| C(21) | C(26) | C(27) | 101.0 (0.8) | C(21) | C(26) | C(27) | 98.6 (1.8) |
| Sn | Cl(1) | Cl(2) | 98.1 (0.1) | Sn | C(1A) | C(1B) | 99.6 (0.7) |
| Sn | Cl(1) | Co(1) | 105.2 (0.1) | Sn | C(1A) | Co(1) | 108.7 (0.5) |
| Sn | Cl(1) | Co(2) | 107.4 (0.1) | Sn | C(1A) | Co(2) | 112.4 (0.6) |
| Sn | Cl(2) | Co(1) | 106.7 (0.1) | Sn | C(1B) | Co(1) | 107.5 (0.4) |
| Sn | Cl(2) | Co(2) | 107.2 (0.1) | Sn | C(1B) | Co(2) | 108.6 (0.4) |
| Sn | Co(1) | Co(2) | 128.3 (0.1) | Sn | Co(1) | Co(2) | 118.3 (0.1) |
| Co(1) | Sn | C(18) | 88.0 (0.3) | Co(1) | Sn | C(18) | 94.2 (0.7) |
| Co(1) | Sn | C(19) | 87.1 (0.3) | Co(1) | Sn | C(19) | 82.6 (0.7) |
| Co(1) | Sn | C(12) | 153.2 (0.2) | Co(1) | Sn | C(12) | 159.9 (0.6) |
| Co(1) | Sn | C(13) | 155.9 (0.3) | Co(1) | Sn | C(13) | 146.5 (0.6) |
| Co(1) | Sn | C(15) | 90.5 (0.2) | Co(1) | Sn | C(15) | 86.1 (0.5) |
| Co(1) | Sn | C(16) | 90.4 (0.2) | Co(1) | Sn | C(16) | 93.4 (0.6) |
| Co(1) | C(18) | C(19) | 109.2 (0.4) | Co(1) | C(18) | C(19) | 105.7 (1.1) |
| Co(1) | C(18) | C(12) | 87.9 (0.4) | Co(1) | C(18) | C(12) | 87.8 (1.0) |
| Co(1) | C(18) | C(13) | 116.1 (0.4) | Co(1) | C(18) | C(13) | 119.3 (1.0) |
| Co(1) | C(18) | C(15) | 150.1 (0.4) | Co(1) | C(18) | C(15) | 140.7 (1.0) |
| Co(1) | C(18) | C(16) | 111.2 (0.4) | Co(1) | C(18) | C(16) | 101.3 (1.0) |
| Co(1) | C(19) | C(12) | 119.1 (0.4) | Co(1) | C(19) | C(12) | 116.1 (0.9) |
| Co(1) | C(19) | C(13) | 85.8 (0.4) | Co(1) | C(19) | C(13) | 88.7 (0.9) |
| Co(1) | C(19) | C(15) | 100.5 (0.4) | Co(1) | C(19) | C(15) | 113.2 (0.9) |
| Co(1) | C(19) | C(16) | 137.4 (0.4) | Co(1) | C(19) | C(16) | 152.9 (1.0) |
| Co(1) | C(12) | C(13) | 37.3 (0.3) | Co(1) | C(12) | C(13) | 36.4 (0.7) |
| Co(1) | C(12) | C(15) | 80.1 (0.3) | Co(1) | C(12) | C(15) | 79.9 (0.8) |
| Co(1) | C(12) | C(16) | 66.6 (0.3) | Co(1) | C(12) | C(16) | 66.6 (0.8) |
| Co(1) | C(13) | C(15) | 68.2 (0.4) | Co(1) | C(13) | C(15) | 67.7 (0.8) |
| Co(1) | C(13) | C(16) | 80.2 (0.3) | Co(1) | C(13) | C(16) | 79.9 (0.8) |
| Co(1) | C(15) | C(16) | 38.9 (0.3) | Co(1) | C(15) | C(16) | 39.8 (0.7) |
| Co(2) | Sn | C(28) | 88.6 (0.3) | Co(2) | Sn | C(28) | 89.2 (0.7) |
| Co(2) | Sn | C(29) | 85.8 (0.3) | Co(2) | Sn | C(29) | 83.9 (0.7) |
| Co(2) | Sn | C(22) | 154.5 (0.3) | Co(2) | Sn | C(22) | 158.5 (0.6) |
| Co(2) | Sn | C(23) | 156.0 (0.3) | Co(2) | Sn | C(23) | 151.5 (0.6) |
| Co(2) | Sn | C(25) | 91.1 (0.2) | Co(2) | Sn | C(25) | 89.2 (0.6) |
| Co(2) | Sn | C(26) | 91.2 (0.2) | Co(2) | Sn | C(26) | 93.2 (0.6) |
| Co(2) | C(28) | C(29) | 107.7 (0.4) | Co(2) | C(28) | C(29) | 109.6 (1.0) |
| Co(2) | C(28) | C(22) | 86.8 (0.4) | Co(2) | C(28) | C(22) | 86.1 (0.9) |
| Co(2) | C(28) | C(23) | 115.1 (0.4) | Co(2) | C(28) | C(23) | 119.2 (0.9) |
| Co(2) | C(28) | C(25) | 150.0 (0.4) | Co(2) | C(28) | C(25) | 140.5 (0.9) |
| Co(2) | C(28) | C(26) | 110.3 (0.4) | Co(2) | C(28) | C(26) | 102.7 (0.9) |
| Co(2) | C(29) | C(22) | 119.3 (0.4) | Co(2) | C(29) | C(22) | 117.4 (0.9) |
| Co(2) | C(29) | C(23) | 86.5 (0.4) | Co(2) | C(29) | C(23) | 87.1 (0.9) |
| Co(2) | C(29) | C(25) | 102.3 (0.4) | Co(2) | C(29) | C(25) | 109.5 (0.9) |
| Co(2) | C(29) | C(26) | 141.8 (0.4) | Co(2) | C(29) | C(26) | 147.5 (0.9) |
| Co(2) | C(22) | C(23) | 37.4 (0.4) | Co(2) | C(22) | C(23) | 38.2 (0.7) |
| Co(2) | C(22) | C(25) | 80.4 (0.4) | Co(2) | C(22) | C(25) | 81.2 (0.8) |
| Co(2) | C(22) | C(26) | 67.0 (0.4) | Co(2) | C(22) | C(26) | 67.5 (0.8) |
| Co(2) | C(23) | C(25) | 68.4 (0.4) | Co(2) | C(23) | C(25) | 68.5 (0.8) |
| Co(2) | C(23) | C(26) | 81.0 (0.4) | Co(2) | C(23) | C(26) | 80.1 (0.8) |
| Co(2) | C(25) | C(26) | 39.7 (0.3) | Co(2) | C(25) | C(26) | 38.0 (0.7) |
| C(18) | Co(1) | O(18) | 176.8 (0.9) | C(18) | Co(1) | O(18) | 175.9 (2.2) |
| C(19) | Co(1) | O(19) | 178.8 (0.8) | C(19) | Co(1) | O(19) | 178.1 (2.0) |
| C(28) | Co(2) | O(28) | 177.2 (0.9) | C(28) | Co(2) | O(28) | 175.7 (2.0) |
| C(29) | Co(2) | O(29) | 178.9 (0.9) | C(29) | Co(2) | O(29) | 175.8 (1.9) |

**Table V** (*Continued*)

| $Cl_2Sn(Co(CO)_2C_7H_8)_2$ |  |  |  | $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ |  |  |  |
|---|---|---|---|---|---|---|---|
| Vertex | Atom 1 | Atom 2 | Angle | Vertex | Atom 1 | Atom 2 | Angle |
|  |  |  |  | C(2A) | C(1A) | C(3A) | 121.3 (2.0) |
|  |  |  |  | C(3A) | C(2A) | C(4A) | 119.8 (2.2) |
|  |  |  |  | C(4A) | C(3A) | C(5A) | 120.9 (2.1) |
|  |  |  |  | C(5A) | C(4A) | C(6A) | 117.4 (1.9) |
|  |  |  |  | C(6A) | C(5A) | C(1A) | 124.3 (2.0) |
|  |  |  |  | C(1A) | C(6A) | C(2A) | 115.8 (2.0) |
|  |  |  |  | C(1A) | C(6A) | Sn | 124.3 (2.0) |
|  |  |  |  | C(1A) | C(2A) | Sn | 119.9 (2.0) |
|  |  |  |  | C(2B) | C(1B) | C(3B) | 119.7 (1.8) |
|  |  |  |  | C(3B) | C(2B) | C(4B) | 120.9 (2.1) |
|  |  |  |  | C(4B) | C(3B) | C(5B) | 120.0 (2.3) |
|  |  |  |  | C(5B) | C(4B) | C(6B) | 119.4 (2.2) |
|  |  |  |  | C(6B) | C(5B) | C(1B) | 118.3 (2.0) |
|  |  |  |  | C(1B) | C(6B) | C(2B) | 121.6 (1.8) |
|  |  |  |  | C(1B) | C(6B) | Sn | 118.9 (2.0) |
|  |  |  |  | C(1B) | C(2B) | Sn | 119.3 (2.0) |

[a] Standard errors computed from the variance–covariance matrix are given in parentheses.

lecular contacts between the cobalt ligands are found (*vide infra*), but steric factors will, of course, tend to limit the decrease in the X–Sn–X angles.

Increased s character in the metal–metal bonds is also reflected in the shortening of the Sn–Co bond lengths of the chloro derivative (2.488 (1) and 2.489 (1) Å) with respect to those of the phenyl derivative (2.566 (3) and 2.575 (3) Å). Incidentally, although there are a fair number of X-ray studies of Sn–Mn and Sn–Fe systems,[8] we are aware of only one prior structure report[22] containing a tin–cobalt bond (in diphenyl(tetracarbonylcobalt)(pentacarbonylmanganese)tin, Sn–Co = 2.66 Å). We note also that the Sn–Cl bond distances (2.410 (2) and 2.412 (2) Å) are elongated considerably with respect to the value[23] of 2.31 (1) Å found in $SnCl_4$, where ideal tetrahedral symmetry obtains.

The trigonal-bipyramidal configuration found in the -$(Co(CO)_2C_7H_8)$ fragments has not been observed previously in norbornadiene complexes. In fact, in only one of the three reported structures,[9] the complex with $PdCl_2$ where the geometry is square planar,[9a] was norbornadiene found to chelate a single metal atom. Table VI summarizes the bond angles at cobalt calculated for trigonal bipyramids where two of the vertices are assumed to be the midpoints of the C=C bonds. The principal reason for distortion from an ideal trigonal-bipyramidal geometry appears to be the limited angle that can be spanned by two norbornadiene double bonds within the constraint that the Co–‖ bonds be approximately orthogonal to the nodal planes of the unsaturated carbon atoms. As in the dichloropalladium complex, this condition is obeyed quite closely: the norbornadiene molecules of I and II are oriented so that lines joining the cobalt atoms with the midpoints of the double bonds are all within 3° of a right angle with respect to planes formed by the unsaturated carbon atoms and the bridgehead carbon atoms. The resulting ‖–Co–‖ angles (23–Co–56, Table VI) vary between 71.3 and 72.8° in the two structures, substantially below the right angle between axial and equatorial substituents in an ideal trigonal bypyramid. Since the Sn–Co–56 angles are in fact very close to 90°, the distortion of the coordination polyhedron may be considered to originate at the apex opposite to Sn, where the 23 double bonds form angles from 158.5 to 163.5° with the Sn atoms, as compared to an ideal value of 180°. A second type of distortion also occurs in both structures and is somewhat surprising: the two angles formed by the equatorial carbonyls with the equatorial 56 double bond are always unequal, with one value being approximately 120 and the other 130° (Table VI). Table VI also shows that bond angles in I obey the pseudo-twofold axis very closely, whereas some crystallographically significant differences occur between related angles on the two cobalt entities of II.

**Table VI.** Angles (deg) at Cobalt Atoms Based on a Trigonal Bipyramid[a]

|  |  | $Cl_2Sn(Co(CO)_2C_7H_8)_2$ |  | $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$ |  |
|---|---|---|---|---|---|
| Angle | Type | Co(1) | Co(2) | Co(1) | Co(2) |
| Sn–Co–23 | aa | 162.3 | 163.5 | 158.5 | 163.0 |
| 8–Co–9 | ee | 109.2 | 107.7 | 105.7 | 111.4 |
| 8–Co–56 | ee | 130.6 | 130.1 | 120.8 | 119.7 |
| 9–Co–56 | ee | 120.1 | 122.2 | 133.2 | 128.4 |
| Sn–Co–56 | ae | 90.5 | 91.2 | 89.6 | 90.9 |
| Sn–Co–8 | ae | 88.0 | 88.9 | 94.3 | 88.3 |
| Sn–Co–9 | ae | 87.1 | 85.9 | 81.8 | 83.7 |
| 23–Co–56 | ae | 71.9 | 72.3 | 71.3 | 72.8 |
| 23–Co–8 | ae | 102.2 | 101.2 | 103.7 | 103.6 |
| 23–Cl–9 | ae | 102.8 | 103.2 | 103.9 | 102.7 |

[a] a = axial, e = equatorial; 8 and 9 represent the respective carbonyls, 23 and 56 the midpoints of the respective double bonds.

The structures also show that the inductive effect of the halogen substituent weakens the π bonds between cobalt and its ligands. By depleting electron density in the tin orbitals, the 3d → 5d π interaction between the metals should be increased, resulting in reduced availability of cobalt 3d electrons for back-donation to vacant π* orbitals in the cobalt and olefin ligands.[5] The carbonyl groups are particularly sensitive to this effect: the average Co–C bond length is 1.780 Å in I compared to 1.714 Å in II. As a consequence of the decreased electron availability to the π* orbitals, C≡O bonds in the chloro derivative are also some-

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(23) R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, 30, 339 (1959).

**Table VII.** Distances and Angles in Norbornadiene Compounds Averaged According to $C_{2v}$ Symmetry

| | I | II | NBD | NBD·CuCl | NBD·PdCl$_2$ |
|---|---|---|---|---|---|
| Bond, Å | | | | | |
| C(1)–C(2) | 1.550 | 1.564 | 1.522 | 1.539 | 1.553 |
| C(1)–C(17) | 1.560 | 1.564 | 1.588 | 1.530 | 1.547 |
| C(2)–C(3) | 1.396 | 1.406 | 1.333 | 1.345 | 1.366 |
| Angle, deg | | | | | |
| C(1)–C(2)–C(13) | 106.7 | 107.1 | 109.1 | 106.9 | 107.0 |
| C(2)–C(1)–C(7) | 100.6 | 99.7 | 96.4 | 99.4 | 100.0 |
| C(2)–C(1)–C(6) | 99.5 | 99.2 | 102.2 | 103.4 | 100.3 |
| C(1)–C(7)–C(4) | 94.2 | 95.6 | | | |
| Ref | This work | This work | 26 | 9c | 9b |

what stronger than those of the phenyl compound, as evidenced by shorter $C{\equiv}O$ distances (average 1.142 Å in I *vs.* 1.184 Å in II) and a corresponding shift to higher $C{\equiv}O$ stretching frequencies in the infrared (2034 (s), 2005 (m), 1984 (s), 1970 (sh) in I *vs.* 2011 (s), 1991 (s), 1960 (s), 1951 (sh) in II). A similar shift has been reported for the parent carbonyls $Cl_2Sn(Co(CO)_4)_2$[4] and $(C_6H_5)_2Sn(Co(CO)_4)_2$.[5] An important exception from this pattern occurs for the bond distances from cobalt to the sp$^2$ carbons of the dienes, which are approximately equal in the two structures (perhaps because the Co–C(sp)$^2$ distances can be altered only at the expense of the orthogonality of the Co–|| bonds to the diene nodal planes). However, the Co–C(sp$^2$) bond lengths do show a significant difference between axial and equatorial positions: the average equatorial Co–C bond length is 2.089 Å in I and 2.100 Å in II, while the average axial distance is 2.161 Å in I and 2.182 Å in II. The longer axial distances are in accord with Gillespie's rule.[24] A range of distances from 1.96 to 2.15 Å has been reported in other complexes formed by cobalt with unsaturated hydrocarbons.[25]

Bond distances and angles in the norbornadiene fragments of I and II are compared to those of free norbornadiene[26] and to the values found in the norbornadiene complexes with cuprous chloride and palladium(II) chloride in Table VII. All values are averages, assuming $C_{2v}$ symmetry for the fragment. The most interesting differences are the increased length of the double bonds, from 1.333 in norbornadiene[26] to 1.396 in I and 1.406 in II and the sharper C(2)–C(1)–C(6) bond angle (99.5° in I and 99.2° in II *vs.* 102.2° in norbornadiene itself). The former effect is, of course, due to the participation of the $\pi$ electrons in bonding to the metal, while the latter change facilitates a closer approach of the molecule to the metal nucleus. The carbonyl ligands show small deviations from linearity (up to 4.3°; see Table V), which may well be real.

The molecular conformations of I and II differ considerably with respect to rotations about the Sn–Co bonds. We define a torsion angle as the dihedral angle between (1) the plane defined by a cobalt atom and the midpoints of its two associated double bonds, and (2) the central plane formed by the tin and the two cobalt atoms. If 0° is taken as the angle at which the Co–56 and the Sn–Co′ bonds are eclipsed, the conformations at Co(1) and Co(2) are given by clockwise rotations (viewed from Co to Sn) of 59.0 and 49.6°, respectively, for I and 134.5 and 63.9°, respectively, for II. (If $C_2$ symmetry were obeyed exactly in I, the two torsion angles would have been equal.) These conformations avoid any unusually short intramolecular contacts. The interatomic distances between the four ligands of the tin atom in I are all well above respective sums of atomic van der Waals radii. The shortest of these contacts are C(28)···Cl(1), 3.594; O(29)···Cl(2), 3.620; C(18)···C(26), 3.691; C(29)···Cl(1), 3.756; O(19)···Cl(1), 3.804; O(18)···C(26), 3.833; O(18)···C(25), 3.853; O(19)···Cl(2), 3.867; and C(16)···C(26); 3.870 Å. The last contact is the shortest between diene molecules. In II, there are a few contacts between carbonyl groups that are moderately close as can be seen toward the front of Figure 2. These include O(18)···O(28), 3.029; O(18)-···C(28), 3.271; C(18)···C(28), 3,371; and C(18)···O(28), 3.399 Å. Other contacts that are fairly short are, in order of increasing distance, C(19)···C(6A), 3.338; C(16)···C(1B), 3.349; C(19)···C(1A), 3.386; C(15)···C(1B), 3.413; C(19)···C(2A), 3.456; C(29)···C(1B), 3.457; and C(16)···C(2B), 3.464 Å. The conformation of II avoids any intramolecular interactions between norbornadienes. These conformational differences may well apply only to the solid state and result from packing forces, since the nmr spectra[27] indicate that there is little hindrance to rotation about the Sn–Co bonds in solution.

The phenyl groups of II are also oriented in different ways: phenyl A is twisted approximately perpendicular to the plane formed by Sn, C(1A), and C(1B), while phenyl B lies approximately in this plane (Figure 2). Bond distances and angles in the phenyl group are all within three standard deviations of the respective average values of 1.407 Å and 120°.

Neither crystal structure contains any unusually short intermolecular interactions. In I (Figure 3),[18] the shortest C···O (3.377 Å) and O···O (3.403 Å) contacts occur through the inversion center at the origin, while the short C···Cl interaction, 3.489 Å, arises through a contact between chlorine and norbornadiene generated by the *c* glide. The shortest intermolecular C···C distance is 3.590 Å. Molecules of II lie in sheets perpendicular to *y* (Figure 4),[18] with one norbornadiene ligand filling the hollow between two phenyls and a

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(26) C. F. Wilcox, S. Winstein, and W. H. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960).

(27) J. P. Heeschen, private communication. Spectra were run at 60 MHz in $CD_2Cl_2$ containing tetramethylsilane as internal chemical shift reference.

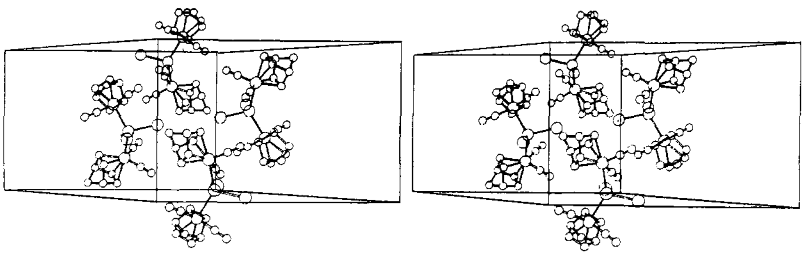

Figure 3. Three-dimensional stereo drawing of a unit cell of $Cl_2Sn(Co(CO)_2C_7H_8)_2$. The view is perpendicular to the *xy* plane with *y* vertical.

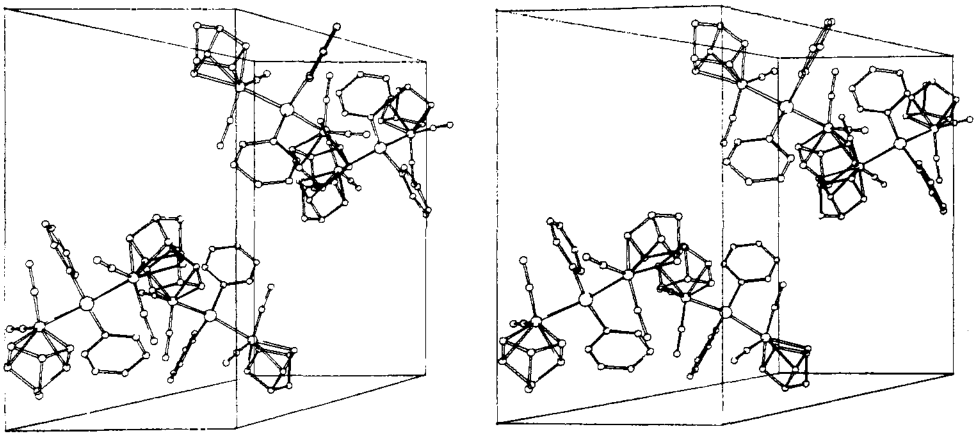

Figure 4. Three-dimensional stereo drawing of a unit cell of $(C_6H_5)_2Sn(Co(CO)_2C_7H_8)_2$. The view is again perpendicular to the *xy* plane with *y* vertical.

cobalt entity of a second molecule related by the *c* glide. The shortest C···O contact is 3.318 Å and the shortest C···C distance is 3.440 Å.

The amplitudes and anisotropy of thermal motion in I (Table II and Figure 1) generally appear to increase with distance from the central Sn atom and are largest at the carbonyl oxygens. The heavy atoms of II (Table III and Figure 2) exhibit a considerable amount of anisotropy.

Correlation of the molecular structures with the nmr spectra[27] of I and II permits some useful observations. At room temperature only one signal from the olefinic protons is observed at $\tau$ 5.82 for I and $\tau$ 6.16 for II. Upon cooling, the singlet splits into two equal intensity peaks at −95° for I and −30° for II. No further splitting is observed above −120°. Free rotation about the Sn–Co bonds would, of course, make all equatorial, and similarly all axial, protons equivalent. Exchange of equatorial and axial positions, resulting in coalescence to a singlet, can be achieved formally by applying twice the transformations of pseudorotation[28] on a trigonal bipyramid, using the C=C bonds in turn as the pivots. The resulting transformation is equivalent to sliding the norbornadiene over the apex opposite to tin while the equatorial carbonyls flip to the other side.

The difference in coalescence temperatures is consistent with our metric data, indicating that $\pi$ bonds to tin are weaker for X = Cl and supports the hypothesis that electronegative X substituents will promote the lability of the ligands at cobalt. These results may have a bearing on the changes in catalytic selectivity induced by varying the X substituent,[2,3] for molecular models show[2] that the trigonal-bipyramidal geometries found at cobalt in these studies are not suitable for constructing a transition state for formation of Binor-S, even when free rotation about the Sn–Co bonds is assumed. A rearrangement of the ligands at cobalt must first take place, and the contribution of this process to the total energy of the transition state would be expected to be less for the electronegative X substituents.

We note that formation of Binor-S while maintaining $C_{2v}$ symmetry violates the noncrossing rule: the highest filled $\pi$ molecular orbital for the dienes in the transition state is antisymmetric with respect to both mirror planes and correlates with a $\sigma^*$ orbital in Binor-S, whereas the highest filled $\sigma$ MO in Binor-S, symmetric with respect to both symmetry planes, correlates with the lowest $\pi^*$ orbital of the dienes. Mango[29] has suggested that a d orbital of appropriate symmetry from the metal catalyst can facilitate forbidden reactions by accepting electrons from a filled $\pi$ MO, while back-donation from a second d orbital, again of appropriate symmetry, supplies electrons to the $\pi^*$ orbital used in $\sigma$-bond formation. It is, therefore, interesting to observe that, if the efficacy of the catalyst were proportional to the strength of the interaction between metal d orbitals and the olefin, we would expect the phenyl derivative to be the desired catalyst. This expectation contravenes the observed result and implies that a simple orbital symmetry argument, based on this assumption, does not predict reactivity in this case. Accordingly, additional experiments and interpretation directed to the question of whether weak or strong d$\pi$ complexes will in general provide a more effective means of promoting symmetry-forbidden concerted reactions will be of considerable interest.

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