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Crystal and Molecular Structure of the β Modification of 2-Biphenylyltellurium Triiodide, $C_{12}H_9TeI_3$

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The structure of the β crystal form of 2-biphenylyltellurium triiodide, $C_{12}H_9TeI_3$, has been determined by use of data obtained on an automated diffractometer with monochromatized Mo Kα radiation. The red crystals are monoclinic; the space group is $P2_1/c$, with $a = 11.788$ (3) Å, $b = 13.858$ (6) Å, $c = 9.792$ Å, $\beta = 97.36$ (2)°, $V = 1586.4$ (9) Å^3, and $Z = 4$. The observed and calculated densities are 2.75 (5) g cm^{-3} and 2.770 (2) g cm^{-3}, respectively. The structure was determined by heavy-atom methods and refined by use of full-matrix least-squares procedures to a conventional R index of 4.3% based on 1725 independent relections. The configuration about tellurium is trigonal bipyramidal with two iodine atoms in axial positions at 2.828 (1) and 3.028 (1) Å and an I–Te–I angle of 176.02 (5)°. Two equatorial positions are occupied by an iodine atom at 2.748 (1) Å and a carbon atom at 2.15 (1) Å with an I–Te–C bond angle of 98.1 (3)°. The configuration about tellurium may alternatively be considered octahedral if one includes an intermolecularly bonded iodine atom at 3.703 (1) Å and a carbon atom, C(12), which makes a very short intramolecular contact of 3.18 (1) Å with tellurium. The molecular structure in the β crystal is very similar to that in the α modification. The principal differences in the crystal structures of the α and β forms are in the intermolecular bonding arrangements of the heavy atoms.

Introduction

Structural studies of 2-biphenylyltellurium triiodide and 2-biphenylyltellurium tribromide have been reported.[1,2] In both structures, the configuration about tellurium was found to be essentially trigonal bipyramidal with two halogen atoms in axial positions and with the third halogen atom plus a carbon atom and a pair of electrons in the equatorial positions. Intermolecular or secondary bonding is of considerable importance in the triiodide but is almost absent in the tribromide. In both molecules very close Te–C(12) intramolecular contacts (2.945 Å in the tribromide and 3.317 Å in the triiodide) were observed and were considered to be related to the ease with which a five-membered heterocyclic ring is closed to form the corresponding dibenzotellurophene dihalide.

In the preparation of the triiodide previously described,[1] two crops of crystals were obtained. One consisted of fine, dark red crystals and the other of small, well-formed, black polyhedra. The first structural study was performed on the latter crystals which will henceforth be referred to as the black or α form. The present investigation was carried out to determine the crystal and molecular structure of the red or β form.

Experimental Section

Crystals suitable for the present study were selected from the crop of red crystals mentioned in ref 1. A preliminary examination of several specimens by means of precession photographs showed them to have monoclinic symmetry but with a unit cell definitely different from that of the black crystals. The specimen selected for data collection (with the faces and dimensions given in Table I) was mounted on a Syntex $P\bar{1}$ autodiffractometer equipped with a scintillation counter and a graphite monochromator. The automatic centering, indexing and least-squares programs of the instrument were applied to 15 selected reflections in the 2θ range from 15 to 25° to obtain the lattice parameters given with other crystallographic data in Table I.

Intensity measurements were made with Mo Kα radiation with a scan rate of 2.0°/min from 1.25° below 2θ for $K\alpha_1$ to 1.25° above 2θ for $K\alpha_2$. The background was counted for half the scan time at each end of the scan range. Three strong reflections, (222), (404), and (600), were checked after each 97 intensity measurements and these showed only random variations consistent with their respective $\sigma(I)$ values. Measurements of 2791 unique reflections not excluded by the space group were made in the range out to $2\theta = 50°$. Among these, 1725 reflections for which $I > 3\sigma(I)$ were used in the structure determination and refinement. All measured reflections were corrected for Lorentz and polarization effects and processed to give $|F_o|$ values as previously reported.[3] Because of the crystal dimensions, absorption corrections were not considered necessary. The calculated maximum and minimum transmission factors given in Table I indicate that absorption effects could have caused errors of no more than ~1% in the values of $|F_o|$.

Table I. Crystallographic Data for β-$C_{12}H_9TeI_3$[a]

Cell dimensions at 22 °C (λ(Mo Kα) 0.710 69 Å)
$a = 11.788$ (3) Å
$b = 13.858$ (6) Å
$c = 9.792$ (2) Å
$\beta = 97.36$ (2)°
$V = 1586.4$ (9) Å^3

Density
Obsd, by flotation, 2.75 (5) g cm^{-3}
Calcd, for $Z = 4$, 2.770 (2) g cm^{-3}

Systematic absences
$0k0$ with $k = 2n + 1$
$h0l$ with $l = 2n + 1$

Space group $P2_1/c$ (No. 14)

Equivalent positions
A = x, y, z
B = $1 - x, 1 - y, 1 - z$
C = $1 - x, {}^1/_2 + y, {}^1/_2 - z$
D = $x, {}^1/_2 - y, {}^1/_2 + z$

Crystal dimensions
(100)-$(\bar{1}00)$: 0.11 mm
(011)-$(0\bar{1}\bar{1})$: 0.10 mm
$(0\bar{1}1)$-$(01\bar{1})$: 0.10 mm

Absorption data
μ(Mo Kα) = 78.1 cm^{-1}
T(min) = 0.560
T(max) = 0.567

[a] Estimated standard deviations in the least significant digits are given in parentheses in this and in following tables.

Determination and Refinement of the Structure

The structure determination and refinement followed the same steps and used the same programs employed in the investigation of the α triiodide.[1] The only significant difference was the apparent absence of secondary extinction effects in the present study. The final value of $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.043 and that of $R_w = [\sum w||F_o| - |F_o||^2/\sum w|F_o|^2]^{1/2}$ was 0.047. The weights, w, assigned to the $|F_o|$ values were given by the expression $w = [1/\sigma(F_o)]^2$. In the final least-squares cycle, the largest shift in any iodine or tellurium atom parameter was 0.01σ while the maximum shift in a C atom parameter was 0.03σ. The "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ was 1.34. In this expression, $N_o = 1725$, the number of observed reflections used in the refinement, and $N_v = 145$, the number of parameters, varied. A final difference Fourier map showed no maxima above 0.5 e Å^{-3} except in the vicinity of the iodine and tellurium atoms where maxima up to 1.2 e Å^{-3} were observed.

Table II. Atomic Positional Parameters in β-$C_{12}H_9TeI_3$[a]

Atom	*x*	*y*	*z*
I(1)	0.35138 (10)	0.48916 (9)	0.35133 (11)
I(2)	0.11360 (9)	0.70471 (8)	0.37352 (10)
I(3)	0.01658 (9)	0.59108 (8)	0.72003 (10)
Te	0.18904 (8)	0.54512 (7)	0.52527 (9)
C(1)	0.3201 (11)	0.6144 (9)	0.6649 (11)
C(2)	0.3643 (12)	0.6995 (11)	0.6286 (14)
C(3)	0.4500 (14)	0.7431 (11)	0.7244 (16)
C(4)	0.4832 (13)	0.7019 (12)	0.8507 (15)
C(5)	0.4367 (12)	0.6162 (11)	0.8829 (13)
C(6)	0.3535 (11)	0.5692 (10)	0.7929 (13)
C(7)	0.3030 (12)	0.4769 (11)	0.8322 (14)
C(8)	0.2513 (14)	0.4708 (12)	0.9524 (14)
C(9)	0.2006 (16)	0.3853 (14)	0.9870 (16)
C(10)	0.2023 (17)	0.3066 (13)	0.9031 (20)
C(11)	0.2509 (16)	0.3084 (12)	0.7864 (18)
C(12)	0.3028 (12)	0.3950 (11)	0.7482 (14)

[a] The idealized (calculated) positional parameters of the hydrogen atoms are given in Table IV which is available as part of the supplementary material.

Table III. Atomic Thermal Parameters in β-$C_{12}H_9TeI_3$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	82 (1)	82 (1)	88 (1)	8 (1)	9 (1)	−23 (1)
1(2)	77 (1)	58 (1)	88 (1)	6 (1)	−14 (1)	17 (1)
I(3)	61 (1)	59 (1)	99 (1)	−6 (1)	4 (1)	−19 (1)
Te	55 (1)	38 (1)	61 (1)	1 (1)	−11 (1)	−3 (1)
C(1)	59 (12)	42 (9)	38 (13)	−10 (8)	2 (9)	−1 (8)
C(2)	71 (14)	54 (10)	90 (17)	−10 (10)	−9 (12)	−4 (11)
C(3)	98 (17)	43 (10)	130 (22)	−27 (10)	0 (5)	5 (12)
C(4)	79 (15)	63 (11)	100 (19)	−21 (11)	−18 (13)	−18 (13)
C(5)	77 (14)	53 (10)	51 (15)	12 (10)	−22 (11)	−10 (10)
C(6)	50 (11)	39 (9)	84 (16)	13 (7)	−9 (10)	−3 (9)
C(7)	66 (13)	52 (10)	72 (16)	11 (9)	−26 (11)	6 (10)
C(8)	112 (18)	63 (12)	65 (17)	4(12)	8 (14)	−2 (11)
C(9)	135 (21)	83 (14)	78 (19)	−23 (14)	7 (16)	23 (13)
C(10)	128 (21)	55 (12)	148 (26)	−23 (13)	−23 (19)	23 (15)
C(11)	123 (20)	45 (10)	127 (23)	−14 (11)	−1 (17)	−6 (13)
C(12)	76 (15)	58 (11)	80 (17)	17 (10)	−26 (12)	6 (11)

[a] All parameters have been multiplied by 10^4. The anisotropic temperature factor expression is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The hydrogen atoms were assigned the fixed isotropic thermal parameters listed in Table IV, which is available as part of the supplementary material.

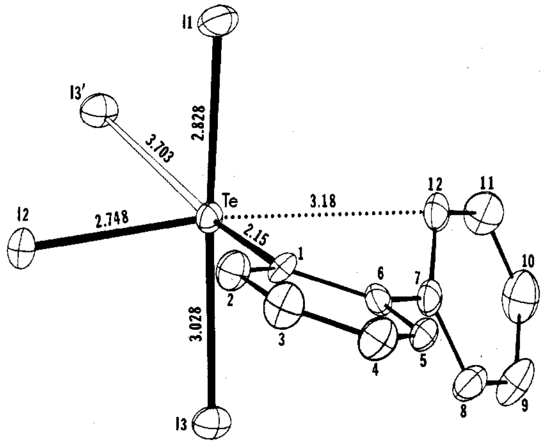

Figure 1. ORTEP plot of the 2-biphenylyltellurium triiodide molecule in the β crystal with thermal ellipsoids at the 25% probability level. Carbon atoms are indicated by the numbers 1–12 and hydrogen atoms are omitted. An octahedral interpretation of the coordination about tellurium includes an intermolecular bond to I(3)′ and a short intramolecular contact with C(12).

Table VII. Intramolecular Bond Distances and Angles in the β Crystal Modification of 2-Biphenylyltellurium Triiodide

(a) Distances, Å			
Te–I(1)	2.828 (1)	C(6)–C(1)	1.411 (17)
Te–I(2)	2.748 (1)	C(7)–C(8)	1.395 (20)
Te–I(3)	3.028 (1)	C(8)–C(9)	1.389 (22)
Te–C(1)	2.153 (12)	C(9)–C(10)	1.366 (24)
C(1)–C(2)	1.355 (18)	C(10)–C(11)	1.342 (24)
C(2)–C(3)	1.422 (19)	C(11)–C(12)	1.419 (21)
C(3)–C(4)	1.373 (21)	C(12)–C(7)	1.402 (20)
C(4)–C(5)	1.362 (20)	C(6)–C(7)	1.483 (19)
C(5)–C(6)	1.393 (18)		
(b) Bond Angles, Deg			
I(1)–Te–I(3)	176.02 (5)	C(1)–C(6)–C(7)	122.5 (1.2)
I(1)–Te–I(2)	95.29 (5)	C(5)–C(6)–C(7)	120.8 (1.2)
I(2)–Te–I(3)	88.53 (4)	C(6)–C(7)–C(8)	120.3 (1.4)
I(1)–Te–C(1)	91.1 (3)	C(6)–C(7)–C(12)	121.1 (1.3)
I(2)–Te–C(1)	98.1 (3)	C(8)–C(7)–C(12)	118.6 (1.5)
I(3)–Te–C(1)	89.5 (3)	C(7)–C(8)–C(9)	120.4 (1.5)
Te–C(1)–C(2)	119.4 (9)	C(8)–C(9)–C(10)	119.6 (1.6)
Te–C(1)–C(6)	117.5 (9)	C(9)–C(10)–C(11)	122.5 (1.6)
C(2)–C(1)–C(6)	123.1 (1.2)	C(10)–C(11)–C(12)	119.1 (1.6)
C(1)–C(2)–C(3)	117.5 (1.3)	C(11)–C(12)–C(7)	119.9 (1.5)
C(2)–C(3)–C(4)	120.9 (1.4)	C(3)···C(6)–C(7)	178.9 (9)[a]
C(3)–C(4)–C(5)	119.6 (1.3)	C(6)–C(7)···C(10)	178.3 (1.0)[a]
C(4)–C(5)–C(6)	122.2 (1.2)	C(4)···C(1)–Te	178.0 (7)[a]
C(5)–C(6)–C(1)	116.7 (1.2)		

[a] Nonbonded angle given to show distortion from ideal 180° value.

Table VIII. Some Additional Distances and Angles of Interest about the Heavy Atoms in β-$C_{12}H_9TeI_3$[a]

(a) Distances, Å			
Te···I(3)′	3.703 (1)	Te→C(12)	3.18 (1)
I(3)···I(2)″	3.337 (1)		
(b) Angles about Tellurium, Deg			
I(1)–Te···I(3)′	84.65 (3)	I(1)–Te→C(12)	88.6 (3)
1(2)–Te···I(3)′	85.41 (3)	I(2)–Te→C(12)	167.2 (3)
I(3)–Te···I(3)′	94.54 (3)	I(3)–Te→C(12)	87.9 (3)
C(1)–Te···I(3)′	174.7 (3)	C(1)–Te→C(12)	69.6 (4)
C(12)→Te···I(3)′	170.2 (3)		
(c) Angles about Iodine, Deg			
Te″–I(2)″···I(3)	174.03 (5)	Te–I(3)···Te′	85.46 (3)
Te–I(3)···I(2)″	104.06 (4)	I(2)″···I(3)···Te′	151.94 (4)

[a] Intermolecular bonds are indicated here and in Figure 8 by means of dotted lines. A short intramolecular contact between Te and C(12) is indicated by means of an arrow. Unprimed atoms are in symmetry position A of the origin cell, (000); atoms with a single prime are in position B of cell $(\bar{1}00)$; and doubly primed atoms are in position D of cell (010). The coordinates of the symmetry positions are given in Table I.

The final atomic positional and thermal parameters are listed in Tables II and III. Table IV[4] gives the calculated positional parameters and assigned isotropic thermal parameters for the hydrogen atoms and Table V[4] lists the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids together with the corresponding *B* values. The observed structure factors and those calculated on the basis of the tabulated parameters are available as Table VI.[4] The atomic scattering factors used were from Table 2.2A of ref 5 and the real and imaginary components of anomalous dispersion from Table 2.3.1 of ref 5 were applied to the scattering factors for iodine and tellurium atoms. An analysis of the values of $d = ||F_o| - |F_o||/\sigma(F_o)$ for the 1066 reflections for which $I < 3\sigma(I)$ showed the following distribution: d = 0–1, 79.1%; d = 1–2, 15.9%; d = 2–3, 2.9%; d = 3–4, 1.1%. Four reflections had values of d greater than 4, with a maximum of 4.4.

Description and Discussion of the Structure

The 2-biphenylyltellurium triiodide molecule in the β modification and a view of the β crystal structure down the *b* axis are shown in Figures 1 and 2, respectively. Intramolecular bond distances and angles are given in Table VII and some additional intramolecular and intermolecular distances and angles about the heavy atoms are listed in Table VIII. The molecular structures in the two modifications are very similar. While there are differences in the distances and angles about tellurium that are significant from the standpoint

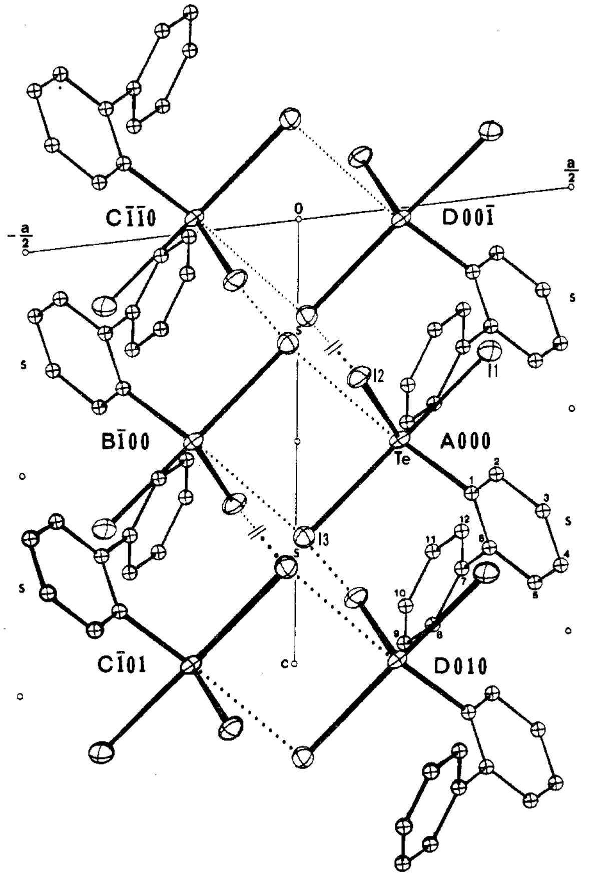

Figure 2. Projection down the b axis of a selected portion of the structure of the β crystal centered about 0, 0, $^1/_2$. Intermolecular bonds are indicated by means of dotted lines and 2_1 screw axes are indicated by means of the letter "s". See Tables I and VIII for the meaning of the symbols A(000), etc., used to designate individual molecules.

Table IX. Comparison of Some Bond Distances (Å) and Bond Angles (deg) about Tellurium in the α and β Modifications of $C_{12}H_9TeI_3$

	α form	β form	Diff ($\alpha - \beta$)
Te-I(1)	2.833 (1)	2.828 (1)	0.005
Te-I(2)	2.769 (1)	2.748 (1)	0.021
Te-I(3)	3.099 (1)	3.028 (1)	0.071
I(1)-Te-I(3)	176.54 (4)	176.02 (5)	0.52
I(2)-Te-C(1)	100.4 (3)	98.1 (3)	2.3

Table X. Comparison of Distances and Angles about I(3) in the α and β Modifications of $C_{12}H_9TeI_3$[a]

(a) Distances, Å

α modification			β modification		
Bond	Dist	Bond order[b]	Bond	Dist	Bond order[b]
I(3)–Te	3.099	0.27	I(3)–Te	3.028	0.34
I(3)···I(2)′	3.239	0.15	I(3)···I(2)″	3.337	0.11
I(3)···I(1)″	3.772	0.03	I(3)···Te′	3.703	0.04
		0.45			0.49

(b) Angles, Deg

α modification		β modification	
Te–I(3)···I(1)″	170.09 (4)	Te–I(3)···I(2)″	104.06 (4)
Te–I(3)···I(2)′	75.48 (4)	Te–I(3)···Te′	85.46 (3)
I(2)′···I(3)···I(1)″	98.09 (4)	I(2)″···I(3)···Te′	151.94 (4)

[a] See Table VIII for the significance of the primes on some of the atoms. [b] See ref 6.

Table XI. Results of Least-Squares Planes Calculations for β-$C_{12}H_9TeI_3$

(a) Distances of Atoms from Least-Squares Planes, Å[a]

Plane A		Plane B		Plane C	
C(1)	−0.001*	C(7)	0.000*	I(2)	0.000*
C(2)	0.008*	C(8)	0.002*	Te	0.000*
C(3)	−0.012*	C(9)	−0.002*	C(1)	0.000*
C(4)	0.009*	C(10)	0.001*	C(12)	0.187
C(5)	−0.003*	C(11)	0.000*	I(3)′	−0.255[c]
C(6)	−0.001*	C(12)	−0.001*		
Te	0.044	C(6)	−0.043		
C(7)	0.012	Rms dev[b]	0.001		
Rms dev[b]	0.007				

(b) Interplanar Angles, Deg

Plane A–Plane B	55.3 (5)	Plane A–Plane C	22.7 (5)

[a] Atoms used to define least-squares are indicated by asterisks. [b] The root-mean-square deviations (in Å) of the asterisked atoms from their respective least-squares planes. [c] For location of atom I(3)′, see footnote to Table VIII.

of the σ values involved, these differences are minor from a chemical point of view. Some of the more interesting distances and angles about tellurium in the molecules of the two forms are compared in Table IX. The main differences between the two structures are in the systems of intermolecular bonds between the heavy atoms. In the α structure, the strongest intermolecular bonds are between I(2) and I(3) atoms and chains are formed along 2_1 screw axes which consist of two molecules per cycle. Weaker intermolecular bonds between I(1) and I(3) atoms form chains parallel to the face-diagonal lattice-row line [101]. In the β structure, the strongest intermolecular bonds are again between I(2) and I(3) atoms along 2_1 screw axes. However, in this case atoms from four different molecules are involved in a cycle which also includes weaker intermolecular bonds between I(3) and Te atoms. The latter bonds also serve to hold pairs of molecules (for example, molecules A(000) and B(1̄00) of Figure 2) in dimeric relationships across centers of symmetry. It is interesting to note that the I(3) atoms are involved in all of the intermolecular bonds in both crystal modifications. The bonding arrangements about these atoms are compared in Table X which also gives the bond order of each bond calculated as suggested by Pauling.[6] In neither structure does I(3) form any really strong bonds to other atoms and in each case the total bond order is only 0.5. The possible significance of this with respect to tendencies toward an aryldiiodotellurium salt structure, $[ArI_2Te^+]I^-$, was mentioned in the discussion of the α structure.

The presence of Te···I intermolecular bonds in the β structure is of interest on two counts. The first of these concerns the coordination about tellurium, which becomes octahedral if one also includes C(12) because of a short intramolecular contact of 3.18 (1) Å with tellurium. The configuration about tellurium is shown in Figure 1 and an extended listing of distances and angles about the tellurium atom is included in Table VIII. The second point has to do with the "black" color of the α crystals and the "red" color of the β form. It has been suggested that Te–I and Te···I bonds tend to produce colors toward the orange and red while I···I bonds tend toward purple or darker colors.[7] While the β ("red") triiodide also includes I···I bonds (along with Te–I and Te···I bonds) these are weaker than the strongest I···I bonds in the α ("black") modification and there are only half as many of this type of bond in the β crystals. Thus there is some support for the above color hypothesis.

The least-squares planes calculations summarized in Table XI indicate greater planarity of the six-membered rings in the β crystals. Also, the atoms bonded to the rings, namely, Te and C(7) for ring 1 (or plane A) and C(6) for ring 2 or (plane B), show smaller displacements from the respective least-squares planes.

In all three of the 2-biphenylyltellurium trihalide structures investigated, short Te–C(12) intramolecular contacts have been observed. These are 2.945 (9) Å in the tribromide, 3.32 (1) Å in the α triiodide and 3.18(1) Å in the β triiodide. These distances may be compared with the shortest packing distances of 3.83 and 3.84 Å observed between Te and aromatic carbon atoms in dibenzotellurophene.[8] The significance of these short Te–C(12) contacts with respect to conversion of the 2-biphenylyltellurium trihalides to dibenzotellurophene dihalides has been discussed.[1]

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Supplementary Material Available: Table IV, the calculated (idealized) positions and assigned isotropic thermal parameters of the hydrogen atoms, Table V, the root-mean-square amplitudes of vibration, and Table VI, the observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Bonding of Hydrido Ligands in Transition Metal–Silyl Complexes: Terminal or Bridging? 1. Structure of Bis(μ-diethylsilicon)-bis(tricarbonyldihydridorhenium)(*Re*–*Re*), $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$

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The structure of $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ has been determined crystallographically and consists of one molecule of the complex, with symmetry $\bar{1}$, in the unit cell (space group $P\bar{1}$, reduced cell parameters $a = 8.768$ (3) Å, $b = 8.776$ (3) Å, $c = 8.357$ (3) Å, $\alpha = 97.76$ (3)°, $\beta = 112.88$ (3)°, $\gamma = 109.07$ (3)°, and $V = 533.9$ Å^3). Observed and calculated densities are 2.23 (2) and 2.25 g cm^{-3}, respectively. Based on 1510 independent reflections with $F_o^2 \geq 3\sigma(F_o^2)$, the data were refined by full-matrix, least-squares techniques to $R = 0.034$ and $R_w = 0.045$. The central cluster of the molecule consists of two rhenium and two silicon atoms in the shape of a rhombus, with like atoms at opposing corners. A bond joins the two rhenium atoms across the shorter diagonal. One carbonyl group on each rhenium atom lies along the Re–Re axis, while the other four lie above and below the plane of the rhombus, two on each rhenium atom. The ethyl groups are bonded, two on each silicon atom, above and below the rhombus plane giving the silicon atoms distorted tetrahedral environments. The Re–Re bond is 3.084 (1) Å, the two independent Re–Si distances are 2.534 (3) and 2.536 (3) Å, the Re–Re–Si angles average 52.53 (6)° and the Re–Si–Re′ angle is 74.95 (7)°. The hydride ligands are judged to occupy normal terminal positions; thus the rhenium coordination can be described as distorted hexagonal bipyramidal.

Introduction

The reactions of disubstituted silanes with dirhenium decacarbonyl and with both tungsten and molybdenum hexacarbonyls have produced an interesting series of silicon-bridged, metal–metal bonded species.[1,2] A systematic study of representative molecules from this series has been undertaken to elucidate the major structural characteristics of these systems. Ignoring the carbonyl groups, these molecules fall into five major classes: (I) no hydride ligands, e.g., $Re_2(CO)_8(Si(C_6H_5)_2)_2$;[3] (II) two hydride ligands, each on a different transition metal but both adjacent to the same silicon atom, e.g., $Re_2(CO)_8H_2Si(C_6H_5)_2$;[4,5] (III) two hydride ligands, each attached to a different transition metal and adjacent to different silicon atoms, e.g., $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$;[6] (IV) two hydride ligands attached to one transition metal and adjacent to different silicon atoms, e.g., $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$;[7] (V) four hydride ligands, two attached to each transition metal, with each silicon having two adjacent hydrogen atoms, e.g., $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$, the topic of this paper. These structural fragments are shown in Figure 1 using valence bond descriptions and normal terminal transition metal hydride formulation, with the exceptions of IIIb where bridging hydrogen atoms are indicated and IIIc where the terminal hydrogen atoms interact weakly with the silicon atoms. Our interest in this series has centered around the central cluster of transition metal and silicon atoms and hydride ligands to obtain information concerning the nature of the bonding of the hydride ligands.

It had been suggested, on the basis of spectroscopic evidence, that in these compounds the hydride ligands bridged the metal–silicon bonds rather than being bonded terminally to the metals.[1,4,5] The basis of this argument was the spectroscopic studies of Kaesz and co-workers[8,9] on the trimeric rhenium hydride $(HRe(CO)_4)_3$ and its deuteride $(DRe(CO)_4)_3$, in which the absence of a distinct metal–hydrogen stretching frequency in the infrared spectra was interpreted as evidence that the hydride ligands were bridging the Re–Re bonds. Since the terminal metal–hydrogen stretch should be visible in the infrared spectrum, its absence was postulated as a characteristic feature of M–H–M bridges. This postulate was extended to the series of transition metal–silicon hydrides where the metal–hydrogen stretch was again absent in the infrared spectra,[2] and consequently a M–H–Si bridge was postulated. In addition, in $Re_2(CO)_8H_2Si(CH_3)_2$, the methyl resonance