

CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>(C<sub>8</sub>H<sub>14</sub>), 12184-53-1; [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)ReH-(CO)<sub>2</sub>SiPh<sub>3</sub>], 62598-40-7; *o*-IC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>, 444-29-1; [(η<sup>5</sup>-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub>], 12108-13-3; [(η<sup>5</sup>-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>THF], 51922-84-0; Cl<sup>-</sup>, 16887-00-6; Br<sup>-</sup>, 24959-67-9; I<sup>-</sup>, 20461-54-5; CN<sup>-</sup>, 57-12-5; SCN<sup>-</sup>, 302-04-5; **1d**, 73838-61-6; [*o*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>][BF<sub>4</sub>], 447-59-6; [*o*-FC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>][BF<sub>4</sub>], 446-46-8; [C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>][BF<sub>4</sub>], 369-57-3; [N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-

F][BF<sub>4</sub>], 459-45-0; [*p*-<sup>15</sup>N<sup>14</sup>NC<sub>6</sub>H<sub>4</sub>F][BF<sub>4</sub>], 73838-07-0.

**Supplementary Material Available:** Table VI, observed and calculated structure factors for [(η<sup>5</sup>-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>(*o*-N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)[BF<sub>4</sub>] (**1a**) (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

## Molecular Distortions in Sterically Congested Organometals. Crystal Structure of Bis(2,4,6-tri-*tert*-butylphenyl)mercury

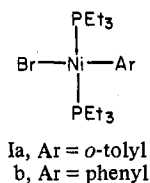
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(2,4,6-Tri-*tert*-butylphenyl)mercury chloride has been prepared and symmetrized to the title compound by treatment with metallic copper in pyridine. The structure of this sterically congested bis(aryl)mercury compound III, including the location of all of the hydrogen atoms, has been determined by an X-ray diffraction study at -155 °C. In contrast to those of coplanar diphenylmercury, the two aromatic rings in the present study lie perpendicular to one another, and moreover the molecule shows considerable distortion from idealized *D*<sub>2d</sub> symmetry. A description of the distortions present in the molecule was developed from idealized molecular parameters. The observed distortions are attributed to nonbonded H...H and H...Hg interactions. The extent of such contacts was assessed by means of idealized methyl groups generated with *d*<sub>C-H</sub> = 1.08 Å.

### Introduction

Ortho substituents are known to exert a profound influence on the chemistry of arylmetal compounds. An early demonstration of such an effect was provided by Chatt and Shaw,<sup>2</sup> who showed that the *o*-tolynickel complex, Ia, is completely



air stable. In contrast, the phenyl analogue Ib rapidly decomposes in air. More recently, an extensive series of mesityl transition-metal derivatives which exhibit remarkable stability have been prepared by Stolze and by Seidel and co-workers.<sup>3</sup>

In light of these effects and because of our continuing interest in steric effects on chemical reactivity,<sup>4</sup> we decided to examine the chemistry of arylmetal derivatives with larger ortho substituents. The 2,4,6-tri-*tert*-butylphenyl ligand was chosen for this study since the preparation of the corresponding bromide<sup>5</sup> and its conversion to an aryllithium derivative<sup>6</sup> had previously been reported. We found that both monoaryl- and diarylmercury compounds could be prepared, containing the tri-*tert*-butylphenyl substituent. However, structural characterization of the diaryl derivative shows it to be a severely

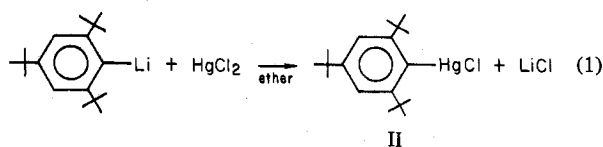
Table I. Bonded Distances in Angstroms for the Nonhydrogen Atoms in Bis(tri-*tert*-butylphenyl)mercury (III)

Hg(1)	C(1)	2.077 (6)	C(12)	C(121)	1.566 (9)
Hg(1)	C(7)	2.083 (6)	C(21)	C(22)	1.518 (9)
C(1)	C(2)	1.450 (9)	C(21)	C(23)	1.535 (10)
C(1)	C(6)	1.420 (8)	C(21)	C(24)	1.540 (10)
C(2)	C(3)	1.398 (10)	C(41)	C(42)	1.515 (10)
C(2)	C(21)	1.560 (9)	C(41)	C(43)	1.524 (11)
C(3)	C(4)	1.402 (9)	C(41)	C(44)	1.550 (10)
C(4)	C(5)	1.399 (9)	C(61)	C(62)	1.537 (10)
C(4)	C(41)	1.508 (9)	C(61)	C(63)	1.538 (9)
C(5)	C(6)	1.401 (9)	C(61)	C(64)	1.537 (10)
C(6)	C(61)	1.539 (9)	C(81)	C(82)	1.528 (10)
C(7)	C(8)	1.474 (9)	C(81)	C(83)	1.516 (10)
C(7)	C(12)	1.395 (9)	C(81)	C(84)	1.554 (9)
C(8)	C(9)	1.399 (9)	C(101)	C(102)	1.527 (10)
C(8)	C(81)	1.533 (9)	C(101)	C(103)	1.540 (11)
C(9)	C(10)	1.392 (9)	C(101)	C(104)	1.536 (11)
C(10)	C(11)	1.388 (9)	C(121)	C(122)	1.537 (9)
C(10)	C(101)	1.533 (9)	C(121)	C(123)	1.520 (10)
C(11)	C(12)	1.414 (9)	C(121)	C(124)	1.550 (10)

distorted molecule as a result of intramolecular steric strain. The nature of the strain and the resultant distortion is presented in this study.

### Results

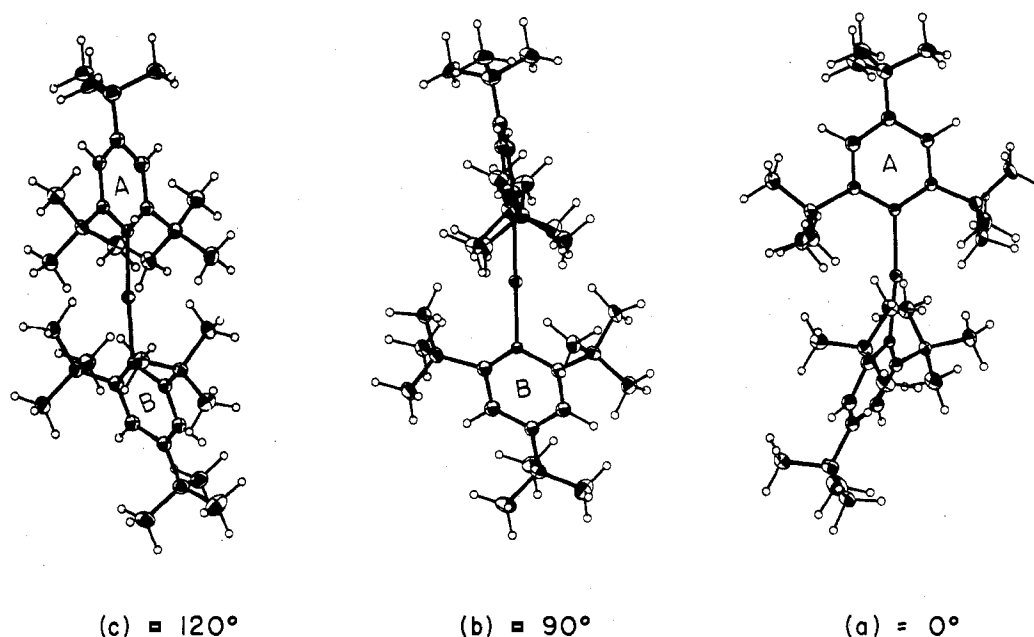
(2,4,6-Tri-*tert*-butylphenyl)mercury chloride, II, was prepared by reaction of the corresponding lithium reagent<sup>6</sup> with mercuric chloride (eq 1). II is a white solid which was in-



soluble in hexane and CCl<sub>4</sub> and had only limited solubility in chloroform and benzene. Conversion of II to bis(2,4,6-tri-

- (1) Central Research and Development Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, DE 19898.
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- (3) (a) Stolze, G. *J. Organomet. Chem.* **1966**, *6*, 383. (b) Stolze, G.; Hahle, J. *Ibid.* **1967**, *7*, 301. (c) Seidel, W.; Kreisel, G. *Z. Chem.* **1974**, *14*, 25. (d) Seidel, W.; Bürger, I. *J. Organomet. Chem.* **1979**, *177*, C19.
- (4) (a) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. (b) For recent studies on the oxidative addition of 2,4,6-tri-*tert*-butylphenyl bromide to nickel(0) see: Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.
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- (6) Betts, E. E.; Barclay, L. R. C. *Can. J. Chem.* **1955**, *33*, 1768.

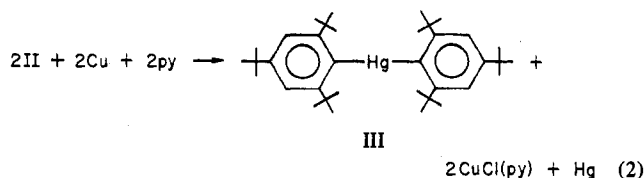


**Figure 1.** ORTEP drawing of bis(2,4,6-tri-*tert*-butylphenyl)mercury shown in three perspectives with (a) ring A flat, followed by (b) 90° rotation and (c) 120° rotation of the molecule. Note the severe distortion with ring B.

**Table II.** Bonded Angles in Degrees for the Nonhydrogen Atoms of III

C(1)	Hg(1)	C(7)	173.4 (2)	C(4)	C(41)	C(44)	109.1 (6)
C(2)	C(1)	C(6)	116.6 (5)	C(42)	C(41)	C(43)	109.9 (6)
C(1)	C(2)	C(3)	119.5 (6)	C(42)	C(41)	C(44)	107.9 (6)
C(1)	C(2)	C(21)	122.4 (5)	C(43)	C(41)	C(44)	107.8 (7)
C(3)	C(2)	C(21)	118.1 (6)	C(6)	C(61)	C(62)	111.9 (5)
C(2)	C(3)	C(4)	124.5 (7)	C(6)	C(61)	C(63)	112.6 (6)
C(3)	C(4)	C(5)	114.6 (6)	C(6)	C(61)	C(64)	109.9 (5)
C(3)	C(4)	C(41)	121.2 (6)	C(62)	C(61)	C(63)	104.9 (6)
C(5)	C(4)	C(41)	124.1 (6)	C(62)	C(61)	C(64)	110.5 (6)
C(4)	C(5)	C(6)	124.3 (6)	C(63)	C(61)	C(64)	106.8 (6)
C(1)	C(6)	C(5)	120.4 (6)	C(8)	C(81)	C(82)	112.2 (5)
C(1)	C(6)	C(61)	121.5 (5)	C(8)	C(81)	C(83)	112.9 (5)
C(5)	C(6)	C(61)	117.9 (6)	C(8)	C(81)	C(84)	108.9 (5)
C(8)	C(7)	C(12)	117.6 (6)	C(82)	C(81)	C(83)	106.0 (6)
C(7)	C(8)	C(9)	118.2 (6)	C(82)	C(81)	C(84)	110.9 (6)
C(7)	C(8)	C(81)	122.2 (6)	C(83)	C(81)	C(84)	105.8 (6)
C(9)	C(8)	C(81)	119.4 (6)	C(10)	C(101)	C(102)	112.6 (6)
C(8)	C(9)	C(10)	123.5 (6)	C(10)	C(101)	C(103)	110.2 (6)
C(9)	C(10)	C(11)	117.5 (6)	C(10)	C(101)	C(104)	109.1 (6)
C(9)	C(10)	C(101)	123.2 (6)	C(102)	C(101)	C(103)	108.4 (7)
C(11)	C(10)	C(101)	119.3 (6)	C(102)	C(101)	C(104)	107.4 (7)
C(10)	C(11)	C(12)	122.2 (6)	C(103)	C(101)	C(104)	109.0 (6)
C(7)	C(12)	C(11)	120.7 (6)	C(12)	C(121)	C(122)	115.2 (5)
C(7)	C(12)	C(121)	126.5 (6)	C(12)	C(121)	C(123)	111.3 (6)
C(11)	C(12)	C(121)	112.5 (6)	C(12)	C(121)	C(124)	108.2 (6)
C(2)	C(21)	C(22)	110.5 (6)	C(122)	C(121)	C(123)	108.2 (6)
C(2)	C(21)	C(23)	112.7 (6)	C(122)	C(121)	C(124)	104.5 (6)
C(2)	C(21)	C(24)	111.6 (5)	C(123)	C(121)	C(124)	109.0 (6)
C(22)	C(21)	C(23)	106.6 (6)	Hg(1)	C(1)	C(2)	119.5 (3)
C(22)	C(21)	C(24)	109.0 (6)	Hg(1)	C(1)	C(6)	119.5 (3)
C(23)	C(21)	C(24)	106.1 (6)	Hg(1)	C(7)	C(8)	118.8 (3)
C(4)	C(41)	C(42)	112.2 (6)	Hg(1)	C(7)	C(12)	121.0 (3)
C(4)	C(41)	C(43)	109.8 (6)				

*tert*-butylphenyl)mercury was accomplished by symmetrization (eq 2) using copper metal in pyridine. The white, crystalline



product III was soluble even in hydrocarbon solvents. The  $^{13}\text{C}$

NMR spectrum of III shows that both aryl ligands are equivalent on the NMR time scale at ambient temperatures.

The X-ray crystal structure of III, including the location of all of the hydrogen atoms, was determined at  $-155^\circ\text{C}$ . The resultant structure is shown in three perspectives in the ORTEP diagrams of Figure 1. The numbering scheme used in this study can be seen in the stick diagram in Figure 2. The bond lengths for all nonhydrogen atoms are listed in Table I, and bond angles are similarly given in Table II.

The carbon-mercury bond lengths in III are 2.077 (6) and 2.083 (6) Å. These values are similar to the C-Hg bond length

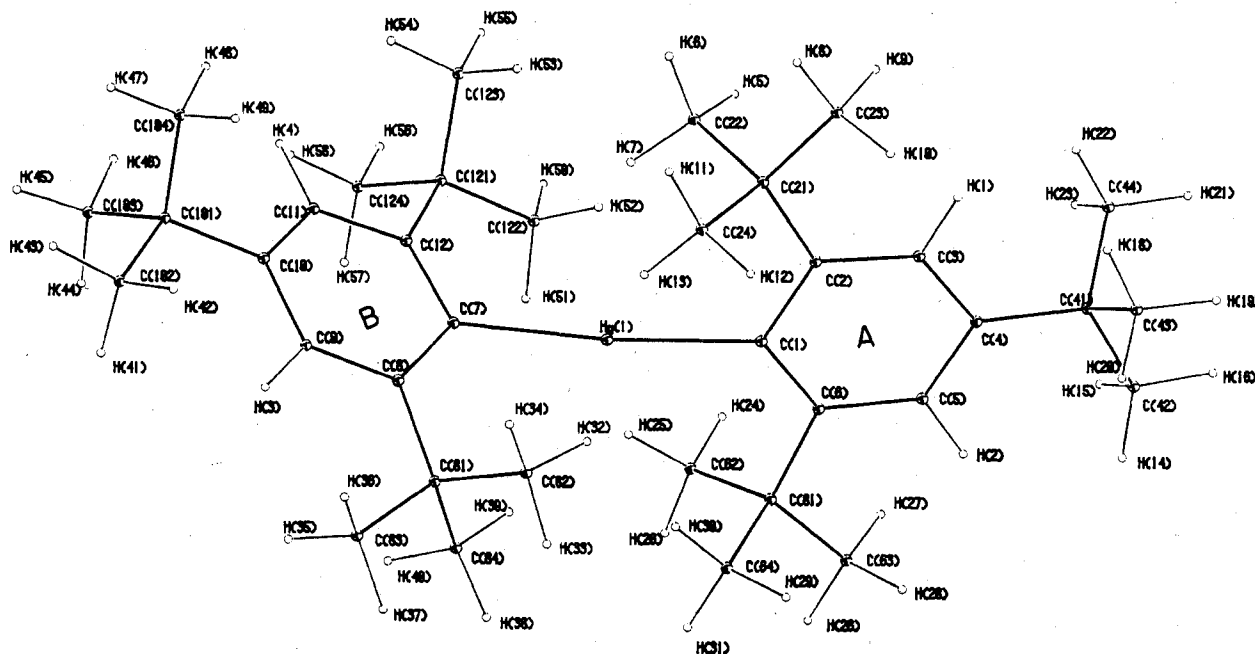


Figure 2. Stick drawing showing numbering scheme for III.

of 2.085 (7) Å reported for diphenylmercury.<sup>7</sup> The most obvious difference between the structures of III and diphenylmercury involves the relative position of the phenyl rings. In  $\text{Ph}_2\text{Hg}$  the two phenyl rings are essentially coplanar with one another and with the mercury atom. In III the two aryl rings lie roughly perpendicular to one another. The C–Hg–C angle of 176.9 (4)° in diphenylmercury is closer to linearity than that in III where C(1)–Hg–C(7) = 173.4 (2)°. The C–C bond lengths in diphenylmercury all fall in the range 1.373 (14)–1.389 (13) Å. Ten of the twelve ring C–C distances in III fall in a comparable range [1.388 (9)–1.420 (8) Å]. However, each ring of III additionally exhibits one extraordinarily long C–C bond involving the ipso carbon [C(1)–C(2) = 1.450 (9) Å, C(7)–C(8) = 1.474 (9) Å]. The ring C–C–C angles also vary over a wider range in III [114.6 (6)–124.5 (7)°] than in diphenylmercury [117.5 (7)–122.4 (5)°].

That the structure of III is severely distorted from  $D_{2d}$  symmetry can be discerned from Figures 1 and 2. The magnitude of this distortion is underscored by the least-squares analysis of the planes defined by the two phenyl rings in Table III. Of the two tri-*tert*-butylphenyl ligands, the one containing ring A [i.e., C(1), C(2), C(3), C(4), C(5), and C(6)] is the less distorted, all six ring carbon atoms falling within ca. 0.01 Å of the least-squares plane. The quaternary carbon atoms of the three *tert*-butyl groups, i.e., C(21), C(41), and C(61), deviate from the least-squares plane by –0.01, +0.05, and –0.05 Å, respectively. However, even for ring A the mercury atom falls 0.27 Å off the least-squares plane.

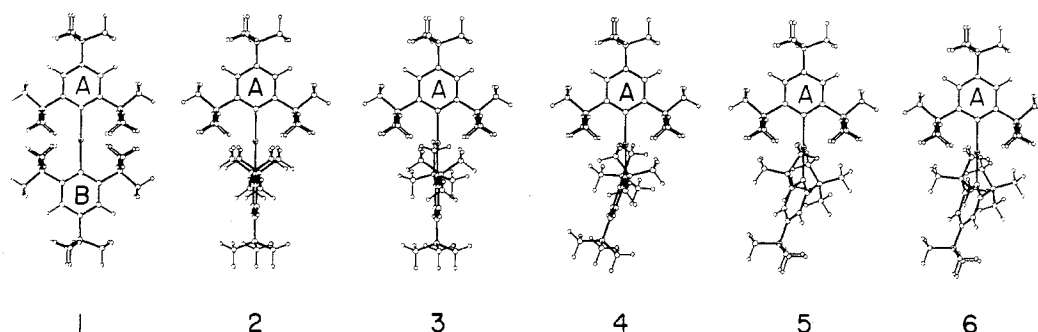
The distortion is more severe for the ligand containing ring B [C(7), C(8), C(9), C(10), C(11), and C(12)]. The mercury atom is displaced fully 0.78 Å from the least-squares planes defined by these carbon atoms. Moreover, the ortho quaternary carbons, C(81) and C(121), lie +0.18 and +0.26 Å from the plane, while the para quaternary carbon C(101) is –0.08 Å from coplanarity. In fact, the data suggest a slight puckering of ring B itself, as evidenced by deviations of the ring carbon atoms of up to 0.04 Å from the least-squares plane. However, the magnitude of the esd's (typically 0.01 Å for the C–C bonds) clouds the interpretation of this effect.

Table III. Least-Squares Analysis of Planes and Lines in III

Equation of Plane 1					
–0.99479X + 8.7181Y + 9.1283Z = 1.6077					
Atoms Defining Plane 1 and Deviations (Å)					
C(1)	–0.001	C(4)	0.016		
C(2)	0.003	C(5)	–0.014		
C(3)	–0.011	C(6)	0.007		
Other Atoms and Deviations (Å)					
Hg(1)	0.274	C(41)	0.054		
C(21)	–0.014	C(61)	–0.047		
Equation of Plane 2					
9.7661X – 1.2651Y + 9.2616Z = 11.784					
Atoms Defining Plane 2 and Deviations (Å)					
C(7)	–0.041	C(10)	–0.033		
C(8)	0.018	C(11)	0.010		
C(9)	0.019	C(12)	0.028		
Other Atoms and Deviations (Å)					
Hg(1)	–0.778	C(101)	–0.081		
C(81)	0.183	C(121)	0.256		
Atoms in the Lines					
3	Hg(1) C(1)	8	C(41) C(4)		
4	Hg(1) C(7)	9	C(61) C(6)		
5	C(1) C(4)	10	C(81) C(8)		
6	C(7) C(10)	11	C(101) C(10)		
7	C(21) C(2)	12	C(121) C(12)		
Angles (Deg) between Planes and Lines					
1 2	70.77	2 3	26.85		
1 3	7.61	2 4	20.71		
1 4	8.04	2 5	25.87		
1 5	–0.33	2 6	0.16		
1 6	0.61	2 10	–6.20		
1 7	–0.65	2 11	–1.80		
1 8	–1.46	2 12	8.37		
1 9	–2.02				

The data do unambiguously show that rings A and B do not lie perfectly perpendicular to one another, the angle between the least-squares planes being 70.8°. It is noteworthy that a line defined by the ipso and para carbon atoms of ring A [i.e., C(1) and C(4)] intersects the least-squares plane of ring B at 25.9°. In contrast, the line defined by C(7) and C(10) is nearly coplanar with ring A, the angle of intersection being 0.6°.

(7) Grdenić, D.; Kamenar, B.; Nagl, A. *Acta Crystallogr., Sect. B* 1977, B33, 587.



**Figure 3.** Pictorial representation of computer-generated structures of bis(2,4,6-tri-*tert*-butylphenyl)mercury carried out by stepwise transformations: (1) phenyl ligands A and B parallel, all *tert*-butyl groups anti to Hg; (2) phenyl ligand B rotated 90° with respect to A; (3) one *tert*-butyl group in B rotated 60° to be syn to Hg; (4) phenyl ligand B "tilted" by 20°; (5) phenyl ligand B rotated about C(7) by 20°; (6) unique syn *tert*-butyl group rotated 10° out of idealized syn position.

**Table IV.** Important Nonbonded H...H and H...Hg Contacts (Å)

A. Mercury-Hydrogen Distances					
Hg(1)	H(25)	2.346	Hg(1)	H(52)	2.531
Hg(1)	H(32)	2.403	Hg(1)	H(39)	2.699
Hg(1)	H(13)	2.444	Hg(1)	H(30)	2.716
Hg(1)	H(7)	2.459	Hg(1)	H(51)	2.823
B. Hydrogen-Phenyl Hydrogen Distances					
H(1)	H(10)	2.063	H(3)	H(35)	2.125
H(1)	H(9)	2.104	H(3)	H(36)	2.126
H(1)	H(18)	2.197	H(3)	H(41)	2.257
H(1)	H(22)	2.257	H(3)	H(42)	2.193
H(2)	H(28)	2.026	H(4)	H(56)	2.018
H(2)	H(27)	2.102	H(4)	H(54)	2.124
H(2)	H(14)	2.195	H(4)	H(45)	2.245
H(2)	H(15)	2.241	H(4)	H(48)	2.258
C. Other Hydrogen-Hydrogen Contacts					
H(7)	H(52)	2.241	H(25)	H(51)	2.390
H(30)	H(39)	2.300	H(13)	H(32)	2.415
D. Intermolecular Contacts					
H(27)	H(34)	2.292	$x$	$-1/2 - y$	$z$
H(14)	H(28)	2.300	$1 - x$	$-1 - y$	$1 - z$
H(47)	H(58)	2.310	$x$	$1/2 - y$	$-1 + z$
H(23)	H(42)	2.361	$x$	$-1/2 - y$	$z$
H(5)	H(12)	2.364	$1 - x$	$1/2 + y$	$-z$
H(44)	H(51)	2.388	$2 - x$	$-y$	$1 - z$
H(17)	H(28)	2.394	$1 - x$	$-1 - y$	$1 - z$
H(41)	H(47)	2.404	$2 - x$	$-1/2 + y$	$-z$
H(21)	H(24)	2.411	$1 - x$	$-y$	$1 - z$
H(33)	H(54)	2.451	$x$	$-1 + y$	$z$
H(40)	H(56)	2.475	$2 - x$	$-y$	$1 - z$
H(19)	H(49)	2.478	$1 - x$	$-1/2 + y$	$-z$
H(18)	H(53)	2.483	$1 - x$	$-1/2 + y$	$-z$
H(9)	H(12)	2.484	$1 - x$	$1/2 + y$	$-z$

A final mode of distortion in III relates to the conformation of the ortho *tert*-butyl groups. In ring A, both *tert*-butyl groups adopt an essentially anti conformation with respect to the mercury atom. Thus, the dihedral angles for the most nearly coplanar methyl group in each case is  $\angle C(1)-C(2)-C(21)-C(23) = 174.07^\circ$  and  $\angle C(1)-C(6)-C(61)-C(63) = 178.16^\circ$ . However, ring B contains one anti and one syn ortho *tert*-butyl group. The relevant dihedral angles are  $\angle C(7)-C(8)-C(81)-C(83) = 169.10^\circ$  and  $\angle C(7)-C(12)-C(121)-C(122) = 2.59^\circ$ . A listing of other important torsion angles for III is given in the supplementary material.

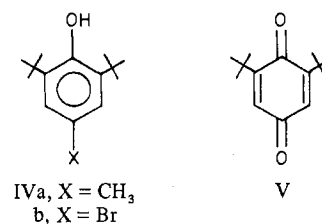
In order to describe the distortions present in III, we attempted to generate the observed structure using idealized molecular parameters. A reasonable approximation of the observed structure was obtained by the following stepwise sequence.<sup>8</sup> (1) The structure was first generated with the two

phenyl rings parallel to one another and all *tert*-butyl groups anti with respect to mercury. (2) One phenyl group was turned 90° with respect to the other. (3) One *tert*-butyl group was rotated to lie in a syn position relative to mercury. This ring then corresponds to ring B in the description above. (4) Ring B was then tilted 20° [i.e., it was turned such that the position of its ipso carbon atom was held constant and its para carbon atom was moved in the plane of ring A]. (5) Ring B was then rotated 20° on an axis containing its ipso and para carbon atoms. (6) The unique syn *tert*-butyl group was then rotated 10° out of the idealized syn position.

The proper rotations for steps 4 and 5 above were ascertained by examining hydrogen contacts while various tilts were applied to the phenyl group. The final values adopted gave the closest fit to those observed in the crystallographic study. While the final structure arrived at in step 6 remains a simplification of the actual structure, it reproduces all of the essential features described above. The final structure from step 6 is shown at the extreme right in Figure 3, and a reasonable agreement with the crystal structure can be seen by comparison with Figure 1c.

## Discussion

Several structures have previously been reported for aromatic compounds in which two *tert*-butyl groups were located ortho to a heteroatom substituent.<sup>9-11</sup> Of these the most relevant to the present discussion is 2,6-di-*tert*-butyl-4-methylphenol, IVa.<sup>9</sup> The structure of IVa is, in fact, com-



IVa, X = CH<sub>3</sub>  
b, X = Br

parable to that of the less distorted ring of III. The ring C-C-C bond angles of IVa [116.8 (6)-123.5 (6)°] are roughly in the same range as those in III. The ring C-C bond lengths of IVa fall in the range 1.390 (9)-1.405 (9) Å as do four of the six ring C-C bonds of ring A in III. [However, the C-C bonds involving the ipso carbon of III are somewhat longer, being 1.420 (8) and 1.450 (9) Å]. A least-squares analysis

(8) Using a locally modified program based on Hildebrandt's algorithm [Hildebrandt, R. L. *J. Chem. Phys.* **1969**, *51*, 1654]. Available on request.

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Table V. Fractional Coordinates of Atoms and Isotropic Thermal Parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>
Hg(1)	0.72193 (1)	-0.13033 (2)	0.40930 (1)	<i>a</i>	H(12)	0.537 (5)	-0.201 (8)	0.205 (5)	2.8 (8)
C(1)	0.6198 (4)	-0.1740 (6)	0.4097 (4)	1.25 (5)	H(13)	0.622 (5)	-0.146 (8)	0.258 (5)	2.3 (7)
C(2)	0.5461 (4)	-0.1171 (6)	0.3479 (4)	1.54 (7)	H(14)	0.440 (5)	-0.373 (7)	0.499 (5)	2.6 (8)
C(3)	0.4794 (4)	-0.1329 (6)	0.3541 (4)	1.98 (7)	H(15)	0.455 (4)	-0.236 (6)	0.547 (4)	0.5 (8)
C(4)	0.4783 (4)	-0.1976 (6)	0.4187 (4)	1.78 (8)	H(16)	0.371 (5)	-0.269 (7)	0.502 (5)	0.5 (8)
C(5)	0.5498 (4)	-0.2535 (6)	0.4765 (4)	1.57 (7)	H(17)	0.355 (4)	-0.350 (7)	0.342 (4)	1.3 (9)
C(6)	0.6194 (4)	-0.2413 (6)	0.4749 (4)	1.44 (6)	H(18)	0.329 (5)	-0.226 (8)	0.294 (6)	4.1 (8)
C(7)	0.8163 (4)	-0.0734 (6)	0.3971 (4)	1.04 (4)	H(19)	0.291 (5)	-0.283 (8)	0.348 (5)	3.8 (8)
C(8)	0.8463 (4)	-0.1642 (6)	0.3594 (4)	1.51 (6)	H(20)	0.417 (5)	-0.014 (9)	0.477 (6)	4.5 (8)
C(9)	0.8871 (4)	-0.1130 (6)	0.3235 (4)	1.74 (6)	H(21)	0.332 (5)	-0.068 (9)	0.435 (6)	4.2 (8)
C(10)	0.9008 (4)	0.0190 (6)	0.3215 (4)	1.71 (7)	H(22)	0.375 (3)	-0.014 (5)	0.387 (4)	0.2 (8)
C(11)	0.8771 (4)	0.1020 (7)	0.3624 (4)	1.88 (6)	H(23)	0.803 (4)	-0.252 (6)	0.636 (4)	0.6 (9)
C(12)	0.8365 (4)	0.0571 (6)	0.4011 (4)	1.81 (5)	H(24)	0.751 (8)	-0.146 (11)	0.616 (9)	8.5 (11)
C(21)	0.5376 (4)	-0.0411 (6)	0.2724 (4)	<i>a</i>	H(25)	0.780 (5)	-0.185 (9)	0.557 (6)	3.8 (8)
C(22)	0.5847 (5)	0.0838 (7)	0.3000 (5)	<i>a</i>	H(26)	0.721 (5)	-0.413 (8)	0.645 (5)	2.9 (8)
C(23)	0.4525 (5)	-0.0024 (9)	0.2111 (5)	<i>a</i>	H(27)	0.661 (4)	-0.309 (7)	0.636 (5)	2.2 (9)
C(24)	0.5650 (5)	-0.1227 (7)	0.2235 (5)	<i>a</i>	H(28)	0.650 (5)	-0.435 (8)	0.588 (5)	3.2 (8)
C(41)	0.4044 (4)	-0.2059 (7)	0.4227 (5)	<i>a</i>	H(29)	0.671 (4)	-0.491 (7)	0.473 (4)	2.1 (8)
C(42)	0.4071 (5)	-0.2784 (8)	0.4982 (5)	<i>a</i>	H(30)	0.715 (5)	-0.390 (7)	0.458 (5)	2.7 (9)
C(43)	0.3398 (5)	-0.2711 (8)	0.3454 (6)	<i>a</i>	H(31)	0.763 (4)	-0.456 (7)	0.550 (5)	2.6 (9)
C(44)	0.3765 (5)	-0.0668 (7)	0.4262 (6)	<i>a</i>	H(32)	0.718 (4)	-0.320 (6)	0.327 (4)	0.6 (8)
C(61)	0.6931 (4)	-0.3101 (6)	0.5426 (4)	<i>a</i>	H(33)	0.751 (4)	-0.456 (7)	0.313 (5)	2.2 (8)
C(62)	0.7614 (4)	-0.2149 (8)	0.5903 (4)	<i>a</i>	H(34)	0.731 (6)	-0.338 (9)	0.266 (6)	4.3 (9)
C(63)	0.6799 (5)	-0.3729 (7)	0.6083 (5)	<i>a</i>	H(35)	0.938 (5)	-0.368 (6)	0.355 (5)	1.8 (8)
C(64)	0.7174 (5)	-0.4193 (7)	0.5048 (5)	<i>a</i>	H(36)	0.863 (5)	-0.372 (6)	0.276 (5)	1.7 (8)
C(81)	0.8396 (4)	-0.3117 (6)	0.3642 (4)	<i>a</i>	H(37)	0.887 (5)	-0.476 (8)	0.342 (5)	3.4 (8)
C(82)	0.7552 (4)	-0.3593 (6)	0.3107 (5)	<i>a</i>	H(38)	0.865 (6)	-0.448 (11)	0.452 (6)	5.9 (10)
C(83)	0.8876 (5)	-0.3856 (7)	0.3357 (5)	<i>a</i>	H(39)	0.849 (4)	-0.315 (6)	0.485 (4)	0.7 (9)
C(84)	0.8734 (5)	-0.3512 (7)	0.4555 (4)	<i>a</i>	H(40)	0.931 (5)	-0.334 (7)	0.485 (5)	2.7 (8)
C(101)	0.9431 (4)	0.0748 (7)	0.2793 (4)	<i>a</i>	H(41)	0.996 (4)	-0.073 (7)	0.270 (5)	1.8 (8)
C(102)	0.9649 (6)	-0.0295 (8)	0.2372 (6)	<i>a</i>	H(42)	0.915 (4)	-0.085 (8)	0.193 (5)	2.4 (8)
C(103)	1.0185 (5)	0.1453 (8)	0.3426 (5)	<i>a</i>	H(43)	0.991 (6)	-0.002 (9)	0.204 (6)	5.7 (9)
C(104)	0.8886 (5)	0.1718 (8)	0.2130 (5)	<i>a</i>	H(44)	1.052 (4)	0.079 (6)	0.379 (4)	1.2 (9)
C(121)	0.8254 (4)	0.1656 (6)	0.4522 (4)	<i>a</i>	H(45)	1.005 (5)	0.221 (9)	0.361 (5)	4.0 (9)
C(122)	0.7918 (5)	0.1193 (7)	0.5053 (4)	<i>a</i>	H(46)	1.050 (4)	0.166 (6)	0.323 (4)	0.9 (8)
C(123)	0.7738 (5)	0.2748 (7)	0.3972 (5)	<i>a</i>	H(47)	0.912 (3)	0.204 (5)	0.183 (4)	0.4 (8)
C(124)	0.9073 (5)	0.2211 (8)	0.5148 (5)	<i>a</i>	H(48)	0.878 (4)	0.241 (6)	0.236 (4)	1.2 (8)
H(1)	0.431 (4)	-0.090 (7)	0.312 (5)	2.1 (8)	H(49)	0.842 (6)	0.139 (8)	0.171 (6)	3.9 (8)
H(2)	0.554 (4)	-0.296 (7)	0.520 (4)	1.8 (8)	H(50)	0.795 (4)	0.193 (7)	0.547 (5)	2.6 (9)
H(3)	0.907 (3)	-0.171 (6)	0.299 (4)	0.3 (8)	H(51)	0.825 (4)	0.037 (6)	0.542 (4)	2.0 (9)
H(4)	0.886 (5)	0.195 (8)	0.362 (5)	3.5 (8)	H(52)	0.742 (4)	0.106 (6)	0.473 (4)	0.5 (8)
H(5)	0.577 (5)	0.124 (7)	0.333 (5)	2.3 (9)	H(53)	0.725 (4)	0.253 (6)	0.357 (4)	1.9 (8)
H(6)	0.571 (4)	0.136 (5)	0.259 (4)	1.1 (8)	H(54)	0.795 (5)	0.311 (8)	0.368 (5)	2.9 (8)
H(7)	0.641 (4)	0.062 (6)	0.333 (4)	1.4 (7)	H(55)	0.773 (5)	0.335 (9)	0.432 (6)	3.7 (8)
H(8)	0.452 (5)	0.032 (9)	0.160 (6)	4.3 (9)	H(56)	0.930 (4)	0.258 (6)	0.487 (4)	1.4 (8)
H(9)	0.432 (5)	0.047 (8)	0.235 (5)	3.4 (9)	H(57)	0.938 (4)	0.151 (6)	0.547 (4)	1.3 (8)
H(10)	0.424 (5)	-0.067 (10)	0.197 (6)	4.1 (8)	H(58)	0.905 (5)	0.299 (9)	0.553 (6)	4.8 (10)
H(11)	0.557 (4)	-0.073 (7)	0.179 (5)	2.1 (8)					

<sup>a</sup> The atom was refined anisotropically.

of IVa further underscores its similarities with ring A of III. The ortho quaternary carbons and the unique methyl fall within +0.08, +0.04, and -0.12 Å of the plane defined by the six ring carbons. The ring carbons themselves deviate by no more than 0.03 Å from coplanarity. However, the oxygen atom of IVa lies only 0.05 Å out of the ring plane, a much smaller deviation than that (0.27 Å) shown by the mercury atom in III.

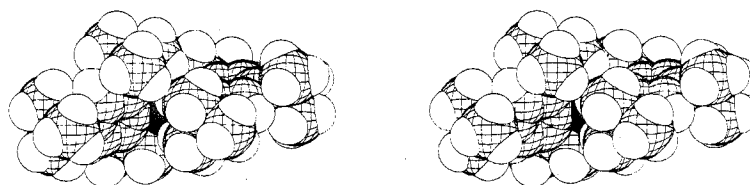
The *tert*-butyl groups of IVa lie anti to the phenolic oxygen atom. Similarly, the anti conformation is observed for the *tert*-butyl groups of both IVb and V.<sup>10,11</sup> Thus, the presence of the syn *tert*-butyl group in ring B of III is apparently associated with the presence of a second bulky tri-*tert*-butylphenyl group in this molecule. We attribute this distortion as well as the other modes of distortion enumerated above to the avoidance of nonbonded hydrogen-hydrogen contacts.

In order to assess the extent of such contacts in III, we calculated idealized positions for the hydrogen atoms. For this purpose the program HYDRA<sup>12</sup> was utilized, and idealized

methyl groups with C-H = 1.08 Å were fitted to the observed hydrogen positions.

This approach was considered valid on basis of the fact that the hydrogen atoms in III appear well determined as shown by the average C-H distance of 0.95 ± 0.07 Å and well-behaved thermal parameters. While using "idealized" hydrogen distances of 1.08 Å leads to more realistic internuclear contact distances, the ideal sp<sup>3</sup> geometry invoked precludes the examination of possible distortion of the actual hydrogen position. Complete calculations of the bond distances and angles with both the observed and idealized hydrogen are given in the supplementary material.

A complete listing of nonbonded distances to 3.0 Å was prepared by using the idealized hydrogen positions. The significant distances are summarized in Table IV, and a complete tabulation is available in the supplementary material. These data confirmed the supposition that nonbonded H...H and H...Hg contacts are responsible for the distorted structure of III. Thus, a total of eight distances of less than 3.5 Å were found for Hg...H contacts, of which five are significantly less than the combined van der Waals radii (2.75 Å). There are numerous H...H contacts less than 2.5 Å in the molecule. The



**Figure 4.** Steroscopic view of the space-filling model of bis(tri-*tert*-butylphenyl)mercury computer generated from SPACE.<sup>13</sup> Note the nonbonded hydrogen-hydrogen contacts between ortho *tert*-butyl groups across the mercury.

shortest, of course, are those involving adjacent hydrogens on the various methyl groups, which are 1.764 Å as defined by the ideal  $sp^3$  geometry used. These distances are followed by a total of 16 contacts of less than 2.3 Å arising from the interaction of phenyl hydrogens with the methyl hydrogens of the *tert*-butyl groups. We note that 9 of the 10 H...H distances involving a phenyl hydrogen and a methyl hydrogen (in which the *tert*-butyl group is syn to the phenyl hydrogen) are less than the six H...H distances where the *tert*-butyl group is anti to the phenyl hydrogen. There are five H...H contacts of less than 2.5 Å where the hydrogens are on *tert*-butyl groups on either side of the mercury. Two of these, [H(7)...H(52)] and [H(30)...H(39)], are certainly less than the combined van der Waals radii for hydrogen (2.4 Å). There are also 18 contacts involving hydrogens on the same *tert*-butyl group but on a different methyl group, and these range from 2.315 to 2.485 Å. Fourteen intermolecular contact distances of less than 2.5 Å are present, the shortest of which is 2.292 Å [H(27)...H(34);  $x, -1/2 - y, z$ ].

The influence of the hydrogen contacts is apparent not only in the overall distortion mentioned previously, but also in the relative position of the *tert*-butyl groups with respect to the phenyl rings. The angle of the tertiary carbon with respect to the carbons of the phenyl ring is always "bent" away from the mercury position, with deviation of 1.4–2.15° for the three *tert*-butyl groups anti to the mercury and by 7° for the group syn to the mercury.

The extent of the steric congestion in III is underscored by the computer-generated space-filling model shown in Figure 4.<sup>13</sup> Figure 4 was generated by using the idealized hydrogen positions described above.

In principle, it should be possible to predict the structure of III by using appropriate molecular mechanics calculations. An unfortunate complication in this approach is that present molecular mechanics programs cannot accommodate the ring deformations present in III. However, by disregarding these ring deformations, we made an attempt to calculate the optimal geometry for III. Molecular mechanics calculations predicted a C–Hg–C angle for III of 174.6°, in fair agreement with 173.4° observed in the crystal structure.<sup>14</sup> Modified extended Hückel calculations<sup>15</sup> (including a term for two-body repulsion) were used to compare the energy of the observed structure with various idealized structures of higher symmetry. It is noteworthy that, despite the crudeness of this approach, the observed structure proved to be the lowest energy geometry of the structures investigated.<sup>16</sup>

## Conclusion

It is seen from the above discussion that the severe distortions in III are the direct result of nonbonded hydrogen-hydrogen contacts between the two aryl ligands. The message which clearly evolves from these results is that the considerable stability associated with mesityl transition-metal derivatives<sup>3</sup> cannot necessarily be extended to aryl derivatives with bulkier ortho substituents. Stabilization due to shielding the M–C bond and an increased barrier toward reductive elimination will be offset to some extent by intramolecular steric effects. As for the tri-*tert*-butylphenyl group itself, space-filling models suggest that it is unlikely that more than two such groups could be bonded to the same metal atom (see Figure 4). Indeed, one of the most remarkable aspects of III is that the molecule can be synthesized at all. All of the various mechanisms which have been proposed<sup>17</sup> for symmetrization of arylmercuric halides involve three-coordinate mercury at some stage. A species in which mercury is bonded to two tri-*tert*-butylphenyl groups as well as to a third atom (either chlorine, copper, or a second mercury atom) can be expected to be even more sterically congested than III itself.<sup>18</sup>

## Experimental Section

**Materials.** 2,4,6-Tri-*tert*-butylbromobenzene was prepared by treatment of tri-*tert*-butylbenzene with bromine and silver nitrate according to the procedure of Zimmerman and Dodd.<sup>5</sup> For large-scale preparations of this material, we found that triple recrystallization from ethanol was a useful alternative to column chromatographic purification. Pyridine and the solvents used in this work were sparged with dry nitrogen and stored over 4A molecular sieves. All other chemicals were reagent grade materials and were used as received.

**(Tri-*tert*-butylphenyl)mercuric Chloride, II.** To a solution of 4.0 g of tri-*tert*-butylbromobenzene in 10 mL of hexane was added 4.8 mL of 2.6 M butyllithium in hexane.<sup>19</sup> After 1 h, 50 mL of ether was added to the stirred solution followed by the gradual addition of 4.0 g of finely divided mercury(II) chloride. Stirring was continued for 1 h, and then the mixture was quenched with 50 mL of H<sub>2</sub>O and washed into a separatory funnel with 200 mL of additional ether. The ether layer was filtered and dried (MgSO<sub>4</sub>). Distillation of the solvent afforded a white product which was ca. 50% II by NMR. Most of the impurity was removed by washing the product with 50 mL of pentane. II was further purified by recrystallization from ethanol; mp 167–169 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.47 (2 H, s,  $J_{199\text{Hg}-^1\text{H}} = 70$  Hz, aryl), δ 1.64 (18 H, s, ortho *tert*-butyl), δ 1.34 (9 H, s, para *tert*-butyl).

**Bis(tri-*tert*-butylphenyl)mercury, III.** The symmetrization procedure used was essentially the general procedure of Hein and Wagler.<sup>20</sup> To a solution of 2.0 g of II in 10.0 mL of pyridine was added 5.0 g of electrolytic copper dust. The mixture was stirred for 48 h with rigorous exclusion of oxygen. The pyridine was removed by vacuum distillation; III was extracted from the solid residue with pentane and was purified by recrystallization from ethanol; mp 177–179 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.45 (4 H, s, aryl), 1.59 (36 H, s, ortho *tert*-butyl), 1.35 (18 H, s,

(13) Using the SPACE program [Smith, G. M.; Gund, P. *J. Chem. Inf. Comput. Sci.* **1978**, *18*, 207].

(14) (a) We wish to thank Dr. D. A. Pensak of E. I. du Pont de Nemours and Co. for carrying out these calculations. (b) Allinger, N. L. "MM1", Program No. 318; available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.

(15) Using local modifications of Anderson's programs. See: Anderson, A. B. *J. Chem. Phys.* **1975**, *62*, 1187.

(16) For instance, one may consider the various structures in the six-step generation of the simplified structure of III given in the Results. The calculated energies (in eV) for the structures achieved after these six steps were respectively (1) –3411.1933, (2) –3435.0598, (3) –3434.6884, (4) –3435.3282, (5) –3433.2288, and (6) –3432.7515. In contrast, the observed geometry of the crystal structure gave an energy of –3442.2207 eV.

(17) Makarova, L. G.; Nesmeyanov, A. N. "Methods of Elemento-Organic Chemistry"; Nesmeyanov, A. N., Kocheshkov, W. A., Eds.; North-Holland Publishing Co.: Amsterdam, 1967; Vol. 4.

(18) Nevertheless, a tetrahedrally coordinated phosphorus compound in which two tri-*tert*-butylphenyl groups are bonded to a single phosphorus atom has recently been reported. See: Yoshifuji, M.; Shima, I.; Inamoto, N. *Tetrahedron Lett.* **1979**, 3963.

(19) Compare ref 6.

(20) Hein, F.; Wagler, K. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 1499.

para *tert*-butyl).  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) showed resonances at the following chemical shifts in ppm from internal standard tetramethylsilane: 31.52, 34.64, 34.96, 37.43, 121.40, 148.11, 158.25, and 159.68. The highest *m/e* fragment observed was the tri-*tert*-butylphenyl radical cation at *m/e* 245 (44.9%) and 246 (9.1%).

X-ray quality crystals of III were grown by dissolving the compound in a 10:1 pentane/octane mixture. Slow evaporation of this solution afforded colorless hexagonal plates of III. The crystals were protected from light since III rapidly darkened on exposure to sunlight. The crystal selected for X-ray diffraction measured  $0.05 \times 0.15 \times 0.15$  mm.

**X-ray Structure Analysis.** The crystal was mounted on a goniometer head by using silicone grease. The diffractometer utilized was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator (Mo  $K\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$ ) is interfaced to a TI980 mini-computer, with Slo-Syn stepping motors to drive the angles. Centering is accomplished by using automated top/bottom-left/right slit assemblies. The minicomputer is interfaced by low-speed data lines to a CYBER172-CDC6600 multi-mainframe system where all computations are performed. In the present case the crystal system, space group, and approximate unit-cell dimensions were determined during a preliminary investigation. The quality of the crystal was shown to be adequate on the basis of  $\omega$  scans which showed the peak width at half-height to be ca.  $0.20^\circ$ . The unit-cell dimensions were subsequently refined from the Bragg angles of 23 reflections [ $\text{C}_{36}\text{H}_{58}\text{Hg}$ ,  $M_r = 691.44$ , monoclinic, space group  $P2_1/c$ ; at  $-155^\circ\text{C}$ ,  $a = 19.830$  (15)  $\text{\AA}$ ,  $b = 10.309$  (7)  $\text{\AA}$ ,  $c = 18.919$  (13)  $\text{\AA}$ ,  $\beta = 120.69$  (6) $^\circ$ ,  $Z = 4$ ,  $V = 3326 \text{ \AA}^3$ ,  $D_{\text{calcd}} = 1.381 \text{ g cm}^{-3}$ , linear absorption coefficient =  $46.45 \text{ cm}^{-1}$ ].

Intensity data were collected by using the  $2\theta$  scan technique ( $4^\circ < 2\theta < 55^\circ$ ; scan rate =  $2.0^\circ \text{ min}^{-1}$ ; single background time at extremes of scan = 15 s). The scan width was  $2.0^\circ$  plus dispersion; 6418

reflections were recorded at  $-155^\circ$ . Due to the size of the crystal and the linear absorption coefficient, an absorption correction was made which ranged from 0.359 to 0.638.

The structure was solved by using a combination of direct methods and Patterson techniques. The structure was refined by the full-matrix least-squares method using 5259 reflections for which  $F > 2.33\sigma(F)$ . The atomic scattering factors were taken from the tabulations of Cromer and Waber;<sup>21a</sup> anomalous dispersion corrections were by Cromer.<sup>21b</sup> The standard deviations of the observed structure factors  $\sigma(F_o)$  were based on counting statistics and an "ignorance factor",  $p$ , of 0.02.<sup>22</sup> The Hg and *tert*-butyl C atoms were refined with anisotropic thermal parameters; the H and phenyl C atoms were refined with isotropic thermal parameters. The final residuals were  $R(F) = 0.037$  and  $R_w(F) = 0.043$ .

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**Registry No.** II, 74063-08-4; III, 74063-09-5.

**Supplementary Material Available:** Tables of the anisotropic thermal parameters, the hydrogen distances, the hydrogen bond angles, the torsion angles, the bonded and nonbonded distances, the idealized hydrogen positions, and the bonded and nonbonded contacts as well as the idealized coordinates (60 pages). Ordering information is given on any current masthead page.

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 (22) Corfield, B. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

Contribution No. 3505 from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

## A Donor Semibridge? Molecular Structures of Dicyclopentadienyldivanadium Tetracarbonyl Triphenylphosphine and Dicyclopentadienyldivanadium Pentacarbonyl

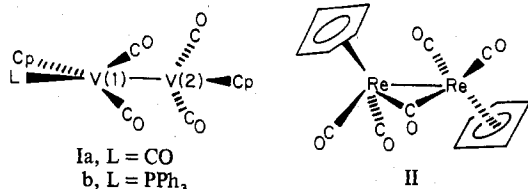
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The compound  $\text{Cp}_2\text{V}_2(\text{CO})_4\text{PPh}_3$ , Ib, has been synthesized by photochemical substitution on the parent carbonyl,  $\text{Cp}_2\text{V}_2(\text{CO})_5$ , Ia. The crystal and molecular structure of the phosphine derivative has been determined at  $-130^\circ\text{C}$ . The space group is  $P\bar{1}$  with cell constants  $a = 8.225$  (2)  $\text{\AA}$ ,  $b = 16.806$  (4)  $\text{\AA}$ ,  $c = 10.193$  (3)  $\text{\AA}$ ,  $\alpha = 102.13$  (2) $^\circ$ ,  $\beta = 101.91$  (2) $^\circ$ , and  $\gamma = 83.84$  (1) $^\circ$ . Full-matrix least-squares refinement of 3989 reflections resulted in  $R(F) = 0.088$ . For comparison, the crystal structure of  $\text{Cp}_2\text{V}_2(\text{CO})_5$  has been redetermined at  $-150^\circ\text{C}$ . The metal-metal bond length in Ib, 2.466 (1)  $\text{\AA}$ , is essentially identical with that in the parent carbonyl and is indicative of a multiple bond. The overall molecular structure of Ib is similar to that of the parent carbonyl. A detailed comparison of the bond lengths and angles at the semibridging carbonyls in Ib with those in the parent carbonyl was made in an attempt to evaluate whether or not the semibridging interaction in both compounds involves a donation of electron density from the CO bond to a neighboring electron-deficient vanadium. This attempt is precluded by asymmetry at the carbonyl semibridges in Ia. The origin of this asymmetry is traced to end-to-end nonbonded contacts in these sterically crowded dimers.

### Introduction

The compound  $\text{Cp}_2\text{V}_2(\text{CO})_5$ , Ia, is noteworthy in several



respects.<sup>1</sup> It is not the obvious extension of the homologous series  $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ ,  $\text{Cp}_2\text{Co}_2(\text{CO})_3$ ,  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ ,  $\text{Cp}_2\text{Re}_2$

$(\text{CO})_5$ ,  $\text{Cp}_2\text{Cr}_2(\text{CO})_6$ . Although Ia has a formula related to  $\text{Cp}_2\text{Re}_2(\text{CO})_5$ , II, the structures differ markedly.<sup>2</sup> The rhenium dimer has only one bridging carbonyl, which is symmetrically disposed with respect to the metal atoms. The vanadium dimer has no symmetric CO bridges;<sup>3</sup> it may be roughly described as consisting of  $\text{CpV}(1)(\text{CO})_3$  and  $\text{CpV}(2)(\text{CO})_2$  units, held together by a short (2.46  $\text{\AA}$ ) metal-metal bond and two asymmetrically bridging CO groups. The asymmetric bridges are disposed in a noncompensating fashion,<sup>4</sup> and both of the carbonyl ligands involved are strongly

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