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## DIHYDRIDOBIS(TRIETHYLSILYL)PENTAMETHYLCYCLOPENTA- DIENYLIRIDIUM(V): NEUTRON DIFFRACTION AND PHOTOELECTRON SPECTROSCOPIC STUDIES

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### Summary

A low-temperature (20 K) neutron diffraction study of  $C_5Me_5Ir(H)_2(SiEt_3)_2$  has been undertaken in order accurately to compare its structural characteristics with those of the isomorphous rhodium analog. Crystal data: space group *Pbcm*,  $Z = 4$ ,  $a$  8.652(2),  $b$  16.040(3),  $c$  17.661(4) Å. The significant differences between the iridium and rhodium species are longer metal–ligand distances and larger bond angles for the iridium analog, so that the iridium atom has a radius ca. 0.01 Å larger than rhodium. The photoelectron spectrum of the compound was obtained using both He(I) and He(II) radiation. The first ionization energy was very close to that of  $C_5Me_5IrMe_4$ .

### Introduction

The title compound is one of a series of high oxidation state platinum metal complexes currently under investigation. The complex  $C_5Me_5Rh(H)_2(SiEt_3)_2$ , with rhodium formally in the unusual +5 oxidation state, was synthesized and studied by X-ray and low-temperature neutron diffraction techniques [1]. The iridium analog was prepared [2] and found to be isomorphous with the rhodium complex. The

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present neutron diffraction study was undertaken in order to characterize the bonding of iridium to hydrogen and to compare the iridium compound's structural characteristics with those of the rhodium species, while the photoelectron (PE) spectrum was measured to enable comparison with the related  $\text{Ir}^3$  derivative,  $\text{C}_5\text{Me}_5\text{IrMe}_4$ .

## Experimental

The synthesis of  $\text{C}_5\text{Me}_5\text{Ir}(\text{H})_2(\text{SiEt}_3)_2$  has been described elsewhere [2]. Preliminary examination by X-ray photographic methods showed this compound to be isomorphous with the rhodium analog whose neutron diffraction study at 20 K has been reported [1]. The crystal chosen for neutron diffraction was a diamond-shaped plate.

*Crystal data.*  $\text{C}_{22}\text{H}_{47}\text{IrSi}_2$ ,  $M_r$  560.0,  $a$  8.652(2),  $b$  16.040(3),  $c$  17.661(4) Å,  $V$  2451(1) Å<sup>3</sup> at 20.0(5) K,  $Z = 4$ , space group  $Pbcm$  (No. 57),  $D_x$  1.45 g cm<sup>-3</sup>. The specimen was mounted on an aluminum pin oriented along the 010 direction. The sample was sealed under a helium atmosphere in an aluminum container and placed in a closed-cycle helium refrigerator [3] mounted on a four-circle diffractometer [4,5] at the Brookhaven High Flux Beam Reactor. A beryllium (002) single-crystal monochromator was employed to produce a neutron beam of wavelength 1.0559(2) Å based on KBr ( $a_0 = 6.6000$  Å at  $T = 298$  K) [6]. A sample temperature of 20.0(5) K [7] was maintained during the experiment and unit-cell dimensions at this temperature were determined by a least-squares fit of the observed  $\sin^2\theta$  values of 32 reflections ( $45^\circ < 2\theta < 56^\circ$ ).

Three-dimensional intensity data were obtained over one octant of reciprocal space with  $2\theta \leq 113^\circ$  [ $(\sin \theta)/\lambda \leq 0.79$  Å<sup>-1</sup>] using  $\theta/2\theta$  step scans. Part of a second octant was sampled out to the same  $2\theta$  limit, but these data were not averaged with those from the complete octant because of extinction effects. The scan range was varied according to  $\Delta 2\theta = (1.96 + 0.86 \tan \theta)^\circ$  for the high-angle data ( $60^\circ \leq 2\theta \leq$

TABLE I  
EXPERIMENTAL DETAILS AND REFINEMENT PARAMETERS FOR  $\text{C}_5\text{Me}_5\text{Ir}(\text{H})_2(\text{SiEt}_3)_2$   
NEUTRON DATA AT 20 K

Crystal vol. (mm <sup>3</sup> )	7.34
Crystal boundary faces	{110}, {001}
Calculated transmission range ( $\mu$ 3.613 cm <sup>-1</sup> )	0.472–0.667
Number of reflections measured	8131 <sup>c</sup>
Number of independent reflections ( $n$ )	7143 <sup>b</sup>
Agreement factor for averaging <sup>b</sup>	
$R_c = \sum_{hkl}  F_o^2 - F_c^2  / \sum_{hkl} F_o^2$	0.008
Number of parameters refined ( $m$ )	335
Final indices of fit	
$R(F^2) = \sum  F_o^2 - (k^2 F_c^2)  / \sum  F_o^2 $	0.072
$R_w(F^2) = [\sum w(F_o^2 - (k^2 F_c^2))^2 / \sum w F_o^4]^{1/2}$	0.074 <sup>c</sup>
$S = [\sum w(F_o^2 - (k^2 F_c^2))^2 / (n - m)]^{1/2}$	1.369

<sup>a</sup> One complete octant was measured out to  $(\sin \theta/\lambda) 0.79$  Å<sup>-1</sup> and a second was partially sampled over the same range. <sup>b</sup> Repeated measurements of the same reflection were averaged. <sup>c</sup> Weights were chosen as  $w = (\sigma^2(F_o^2))^{-1} = (\sigma_{\text{count}}^2(F_o^2) + (0.015 F_o^2)^2)^{-1}$ .

113°) and  $\Delta 2\theta = 2.8^\circ$  for low-angle data. The step size was adjusted to give between 65 and 98 steps per scan, and counts were accumulated for approximately 2.3 s at each step, the exact time interval being determined by monitoring the incident beam intensity. The intensities of two monitor reflections were measured every 200 reflections and showed no significant variation over the course of data collection.

TABLE 2

ATOMIC PARAMETERS FOR  $C_5Me_5Ir(H)_2(SiEt_3)_2$ <sup>a,b</sup>

Atom	x	y	z	$U_{iso}$ (Å <sup>2</sup> )
Ir	17371(7)	18265(4)	25000	44(1)
Si	20730(12)	9856(7)	36053(6)	45(2)
C(1)	28631(8)	-1100(5)	34632(4)	72(1)
C(2)	32362(9)	-5690(5)	42048(4)	91(1)
C(3)	34444(8)	14755(5)	43167(4)	76(1)
C(4)	51305(8)	15275(5)	40501(4)	110(1)
C(5)	1956(8)	8104(5)	41387(4)	73(1)
C(6)	-10790(8)	3638(5)	36905(4)	100(1)
C(7)	-2421(11)	27807(7)	25000	56(2)
C(8)	6880(8)	29307(5)	31593(4)	56(1)
C(9)	22207(7)	31420(5)	29080(4)	55(1)
C(10)	-19448(12)	26001(7)	25000	88(2)
C(11)	1086(8)	30021(5)	39547(4)	85(1)
C(12)	35229(8)	34628(5)	33802(4)	82(1)
H(1)	7304(31)	9951(18)	25000	236(6)
H(2)	34263(28)	14276(19)	25000	244(6)
H(101)	-26049(31)	31802(21)	25000	347(9)
H(102)	-22873(22)	22429(16)	20054(13)	332(5)
H(111)	-1398(31)	36540(13)	40842(12)	325(5)
H(112)	9496(23)	27870(16)	43657(10)	301(5)
H(113)	-9586(21)	26592(15)	40395(12)	302(5)
H(121)	34424(26)	32618(16)	39652(11)	325(5)
H(122)	46326(19)	32607(16)	31653(12)	308(5)
H(123)	35268(26)	41435(13)	33742(14)	318(5)
H(11)	39026(21)	-839(13)	31065(10)	241(4)
H(12)	20112(23)	-4696(13)	31353(11)	241(4)
H(21)	42196(24)	-2910(15)	44948(12)	302(5)
H(22)	22665(23)	-5689(14)	45985(12)	283(5)
H(23)	35328(27)	-12239(13)	41058(12)	285(5)
H(31)	33754(22)	10945(13)	48339(10)	236(4)
H(32)	30275(22)	20968(12)	44755(11)	242(4)
H(41)	52236(23)	18733(15)	35224(12)	318(5)
H(42)	58766(23)	18312(18)	44645(13)	365(6)
H(43)	56095(24)	9113(14)	39472(15)	342(6)
H(51)	-2493(22)	13983(12)	43618(11)	243(4)
H(52)	5084(22)	4415(14)	46418(10)	250(4)
H(61)	-15584(24)	7696(15)	32558(12)	307(5)
H(62)	-20321(22)	1666(15)	40539(12)	312(5)
H(63)	-6479(24)	-1913(14)	34026(14)	317(5)

<sup>a</sup> Positional parameters  $\times 10^5$  and equivalent isotropic thermal parameters  $\times 10^4$ . Esd's in parentheses. Atoms Ir, C(7), C(10), H(1), H(2), and H(101) lie on a mirror plane and have  $z$  fixed at 0.25. <sup>b</sup> Tables of anisotropic thermal parameters (Table 6) and squared structure factors (Table 7) have been deposited with NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017.

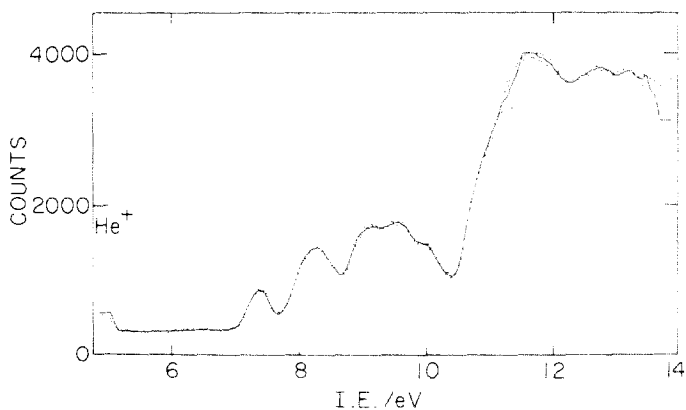


Fig. 1. He(I) PE spectrum of  $C_5Me_5Ir(H)_2(SiEt_3)_2$  in the low IE region.

Integrated intensities were obtained with the first and last tenth of each scan taken as background. Absorption corrections ( $\mu$   $3.613 \text{ cm}^{-1}$ ) calculated by means of numerical integration over a Gaussian grid of points [8] were applied to yield squared structure factors,  $F_o^2$ , for 7143 reflections. Further details are given in Table 1.

Initial coordinates for all atoms were taken from the results of the 20 K neutron diffraction study of the isomorphous rhodium structure [1]. Least-squares refinements were carried out by a full-matrix procedure [9], minimizing  $\sum w(F_o^2 - (k^2 F_c^2))^2$ , with weights taken as  $w = 1/\sigma^2(F_o^2)$ , where  $\sigma^2(F_o^2) = \sigma_{\text{count}}^2 + (0.015 F_o^2)^2$ . The final model included positional and anisotropic thermal parameters for all 39 atoms, except where fixed by symmetry, a scale factor  $k$ , and a type I isotropic-extinction parameter [10], for a total of 335 variable parameters. The most significant extinction correction factor was 1.28 multiplying  $F_o^2$  for reflections 110,  $\bar{1}10$ , and 002.

Neutron scattering lengths were taken to be  $b_{Ir}$   $1.0600 \times 10^{-12}$ ,  $b_{Si}$   $0.4149 \times 10^{-12}$ ,  $b_C$   $0.6648 \times 10^{-12}$ , and  $b_H$   $-0.3741 \times 10^{-12}$  cm [11]. The refinement was terminated when the maximum shift/esd for positional and thermal parameters was less than 0.02. Final indices of fit are included in Table 1, while positional and equivalent isotropic thermal parameters for all atoms are given in Table 2.

TABLE 3  
IONIZATION ENERGY DATA FOR  $C_5Me_5Ir(H)_2(SiEt_3)_2$

Vertical IE (eV)	Assignment
7.34	$d_{2z}$
8.22	$d_{xy} + e_1$ ( $C_5Me_5$ )
8.99	{ Ir-Si
9.44	
10.01	{ Ir-H
11.53	{ + Si-C
13.4	...

The PE spectrum was measured on a PES Laboratories 0078 spectrometer interfaced with a RML 380Z microprocessor. Both He(I) and He(II) radiation were used for spectral measurement. The He(I) spectrum in the low ionization energy (IE) region is shown in Fig. 1 and IE of key features are given in Table 3.

## Results and discussion

The molecular structure of  $C_5Me_5Ir(H)_2(SiEt_3)_2$  and its numbering scheme are illustrated in Fig. 2. Structural characteristics resemble closely those of the rhodium analog [1]. These include the pentagonal  $C_5Me_5$  ring which is  $\eta^5$ -bonded to the metal. The ring is bisected by a mirror plane containing the *trans* hydrides and reflecting the two triethylsilyl ligands. Thus the metal atom is formally in the +5 oxidation state with five uninegative ligands. The Ir–H distance is relatively short (average Ir–H, 1.594(3) Å) and is about the same as that found in  $[(PEt_3)_2Pt(\mu_2-H)_2IrH_2(PEt_3)_2]^+ [BPh_4]^-$  (terminal Ir–H, 1.589(3) Å) [12]. This bond distance is slightly longer than that of the rhodium analog (average Rh–H, 1.581(3) Å). A comparison of selected bond lengths and angles for the two structures is given in Table 4. The cone-angles for the  $C_5Me_5$  ligands are  $160^\circ$  for the iridium compound and  $161^\circ$  for rhodium, or somewhat smaller than was estimated previously [13]. With the exception of the average M–C distance, all of the ligand–metal bonds are significantly longer for iridium than for rhodium and suggest that the iridium atom is about 0.01 Å larger in radius than rhodium. The only other significantly different features between the two structures are the larger bond angles about the metal in the iridium complex. Angle H–Ir–H is  $99.5(2)^\circ$  vs. H–Rh–H,  $94.8(2)^\circ$ , and the remaining angles about the metal also are larger for iridium in each case. The increase in bond angles is reflected in larger intramolecular distances  $H \cdots H$  and  $H \cdots Si$  (Table 5). There are no unusual intermolecular contacts in the structure, the shortest such  $H \cdots H$  distance being 2.09 vs. 2.11 Å for the rhodium complex. For a view of the crystal packing the reader is referred to the isomorphous rhodium structure (Fig.

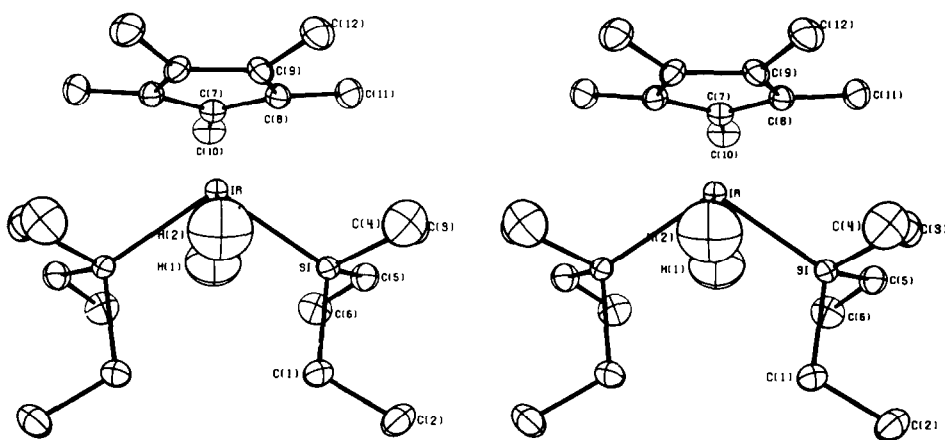


Fig. 2. Stereoview of the  $C_5Me_5Ir(H)_2(SiEt_3)_2$  molecule with thermal ellipsoids drawn to enclose 97% probability density [16]. Hydrogen atoms on the  $C_5Me_5$  and  $SiEt_3$  groups omitted for clarity.

TABLE 4

COMPARISON OF SELECTED INTERATOMIC DISTANCES (Å)<sup>a,b</sup> AND BOND ANGLES (DEG)<sup>a,b</sup> IN C<sub>5</sub>Me<sub>5</sub>M(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub> (M = Rh, Ir)

	Rh	Ir
M-H(1)	1.578(3)	1.593(3)
M-H(2)	1.583(3)	1.595(3)
M-Si	2.379(2)	2.390(1)
M-C (ring)	1.930(2)	1.936(1)
M-C <sub>ax</sub>	2.283(9)	2.291(11)
Si-C <sub>ax</sub>	1.901(2)	1.900(1)
H(1)-M-H(2)	94.84(18)	99.50(16)
H(1)-M-Si	64.29(7)	66.04(6)
H(2)-M-Si	68.92(7)	70.27(6)
Si-M-Si'	107.90(8)	109.49(6)
C-C(ethyl) <sub>ax</sub>	1.536(2)	1.536(1)
C-C(ring) <sub>ax</sub>	1.435(1)	1.439(1)
C-C(ring-methyl) <sub>ax</sub>	1.500(1)	1.497(2)
C-H(methylene) <sub>ax</sub>	1.098(2)	1.098(2)
C-H(methyl) <sub>ax</sub>	1.089(2)	1.089(2)

<sup>a</sup> Estd's in parentheses. Atoms related by the mirror plane are primed. <sup>b</sup> Standard deviations of mean values are given as the larger of the individual esd's or  $\sigma(x_{av}) = [\sum_{i=1}^n (x_i - x_{av})^2 / (n(n-1))]^{1/2}$  where  $x_{av}$  is the mean value and  $x_i$  are the individual values. <sup>c</sup> Individual values of interatomic distances between non-hydrogen atoms for C<sub>5</sub>Me<sub>5</sub>Ir(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub> (Table 8) have been deposited.

2 of ref. 1).

The photoelectron spectrum may be assigned by comparison with that of C<sub>5</sub>Me<sub>5</sub>IrMe<sub>4</sub> [14], namely the first band to an  $a_1$  orbital, largely  $d_{z^2}$  in character, and the second to a combination of ionization from the non-bonding  $d_{xy}$  orbital and the C<sub>5</sub>Me<sub>5</sub> ring  $e_1$  orbitals. Subsequent bands occur at lower IE than in the tetramethyl compound and must include ionizations from the Ir-Si bonding orbitals. The lowest IE for bands associated with the SiEt<sub>3</sub> groups would be expected around 10 eV [15], and it is reasonable to assume that the Ir-H ionizations should also occur in this higher region.

Interestingly, the first IE of C<sub>5</sub>Me<sub>5</sub>Ir(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub> is within experimental error identical to that of C<sub>5</sub>Me<sub>5</sub>IrMe<sub>4</sub>, again demonstrating the capacity of the electron donating C<sub>5</sub>Me<sub>5</sub> ring to prevent the  $d$ -electrons being pulled into the core, even in relatively high oxidation state Group VIII metals.

TABLE 5

SELECTED INTRAMOLECULAR NON-BONDED DISTANCES (Å)

	Rh	Ir
H(1)···Si	2.212(2)	2.272(2)
H(2)···Si	2.336(2)	2.384(2)
H(1)···H(2)	2.328(4)	2.433(4)
M···Me <sub>5</sub> (ring)	2.131(2)	2.135(2)
Ring methyl hydrogen···Triethylsilyl hydrogen	2.115(3)	2.106(3)

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