

The Structure of 1,3-Diphenyl-1,3-propanedionatobis(triphenylantimony)-diphenylrhodium(III)dibenzene

G. J. LAMPRECHT*, J. G. LEIPOLDT and C. P. VAN BILJON

Department of Chemistry, University of the Orange Free State, Bloemfontein, South Africa

Received January 4, 1984

*1,3-Diphenyl-1,3-propanedionatobis(triphenylantimony)diphenylrhodium(III)dibenzene, $[\text{Rh}(\text{DPD})(\text{SbPh}_3)_2\text{Ph}_2] \cdot 2(\text{C}_6\text{H}_6)$ has been isolated as the product of the reaction between the Rh(I) complex $[\text{Rh}(\text{DPD})(\text{CO})_2]$, and triphenylantimony in acetone and in *n*-hexane medium. The crystal and molecular structure was determined from single crystal X-ray diffractometer data. The unit cell is triclinic with $a = 19.083$, $b = 13.167$, $c = 13.536$ Å, $\alpha = 81.81^\circ$, $\beta = 111.59^\circ$, $\gamma = 100.49^\circ$, $Z = 2$ and space group $P\bar{1}$. The structure was refined to a *R*-value of 0.079 for 6637 contributing reflections. The coordination polyhedron can be described as a slightly distorted octahedron in which the Rh-atom is coordinated by two phenyl groups, two oxygen atoms of a chelate ring, which are in *cis* position to one another, and two antimony-atoms of the two SbPh_3 ligands, which are in *trans* positions.*

Introduction

The crystal and molecular structure of 1,3-diphenyl-1,3-propanedionatobis(triphenylantimony)diphenylrhodium(III) dibenzene, $[\text{Rh}(\text{DPD})(\text{SbPh}_3)_2(\text{Ph})_2] \cdot 2(\text{C}_6\text{H}_6)$, was determined as part of a study of the substitution and oxidative addition reactions of rhodium(I) complexes of the type $[\text{Rh}(\text{LL}')(\text{CO})_2]$, $\text{LL}' =$ singly charged bidentate ligands such as the β -diketone DPD = 1,3-diphenyl-1,3-propanedione in the present case and $\text{SbPh}_3 =$ triphenylantimony.

Complexes of the type $[\text{Rh}(\text{LL}')(\text{CO})_2]$ give substitution reactions where only one carbonyl group is substituted by triphenylphosphine and triphenylarsine [1–3] and where both carbonyl groups are substituted by triphenylphosphite [4].

Bonati and Wilkinson [1] reported the six-coordinated Rh(I)-complex $[\text{Rh}(\text{acac})(\text{SbPh}_3)_3\text{CO}]$ to be the substitution product of the reaction between $[\text{Rh}(\text{acac})(\text{CO})_2]$ and SbPh_3 where acac = 1,3-dimethyl-1,3-propanedione, while Garrou and

Hartwell [5] reported the five-coordinated Rh(I)-complex $[\text{Rh}(\text{acac})(\text{SbPh}_3)_2\text{CO}]$. The best way to solve this discrepancy was to determine the molecular structure of the substitution product.

Unfortunately the substitution product of the reaction between $[\text{Rh}(\text{acac})(\text{CO})_2]$ and SbPh_3 has not yet been recrystallized so as to yield single crystals suitable for X-ray diffraction. Subsequently the β -diketone was changed from acac to the mentioned DPD which yielded ideal crystals of the title compound. The subsequent structure determination revealed a six-coordinated Rh(III)-complex of which the crystal and molecular structure is presented.

Experimental

The Rh(I) β -diketone complex $[\text{Rh}(\text{DPD})(\text{CO})_2]$ was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, *N,N*-dimethylformamide and 1,3-diphenyl-(1,3)-propanedione by methods described previously [2, 6]. The title compound was prepared from $[\text{Rh}(\text{DPD})(\text{CO})_2]$ and SbPh_3 (1:3.5 mol ratio) by following a method identical to that prescribed by Garrou and Hartwell [5] for their compound $[\text{Rh}(\text{acac})(\text{SbPh}_3)_2\text{CO}]$. Carrying out the experiment in the presence or absence of an inert atmosphere (argon) and in a hexane or an acetone medium yields the same product, namely the title compound. The complex was recrystallized from petroleum ether mixtures with boiling points 40–60 °C and 60–80 °C in a 50:50 volume ratio.

Crystal data: $\text{C}_{75}\text{H}_{63}\text{O}_2\text{Sb}_2\text{Rh}$, molecular mass 1342.24, triclinic, space group $P\bar{1}$, $a = 19.083$, $b = 13.167$, $c = 13.536$ Å, $\alpha = 81.81^\circ$, $\beta = 111.59^\circ$, $\gamma = 100.49^\circ$, $Z = 2$, $d_{\text{calc}} = 1.44$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 11.81$ cm⁻¹.

Three dimensional intensity data were collected with a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.7107$ Å) for θ values between 3° and 23°. Three reflections were used as standards and were re-measured after every 60 reflections. No decomposition of the crystal was detectable during the data collection. A total of 8589 reflections were

*Author to whom correspondence should be addressed.

TABLE I. Positional and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with Standard Deviations.

Atom	x	y	z	U	Atom	x	y	z	U
Rh	0.3048(1)	0.2261(1)	0.6329(1)	33(0)	C(56)	0.1555(11)	-0.1749(15)	0.6625(16)	67(5)
Sb(1)	0.2408(1)	0.0974(1)	0.4910(1)	37(0)	C(57)	0.0783(12)	-0.1866(17)	0.6077(17)	76(6)
Sb(2)	0.3835(1)	0.3394(1)	0.7892(1)	38(0)	C(58)	0.0465(12)	-0.1257(16)	0.5173(17)	73(6)
O(1)	0.2424(6)	0.3490(8)	0.5465(8)	45(3)	C(59)	0.0905(11)	-0.0459(16)	0.4795(16)	66(5)
O(2)	0.2152(6)	0.1756(8)	0.6980(8)	39(2)	C(64)	0.3645(9)	0.3026(12)	0.9379(13)	43(4)
C(1)	0.1613(8)	0.2293(11)	0.6825(12)	37(4)	C(65)	0.4256(12)	0.2878(16)	1.0320(16)	68(5)
C(2)	0.1854(9)	0.3731(12)	0.5573(12)	40(4)	C(66)	0.4101(13)	0.2609(18)	1.1278(18)	82(6)
C(3)	0.1463(10)	0.3212(14)	0.6210(14)	56(5)	C(67)	0.3371(14)	0.2480(19)	1.1293(19)	89(7)
C(4)	0.1078(10)	0.1777(13)	0.7410(13)	49(4)	C(68)	0.2775(13)	0.2640(18)	1.0323(18)	82(6)
C(5)	0.0978(11)	0.0719(15)	0.7602(15)	62(5)	C(69)	0.2906(12)	0.2897(16)	0.9361(16)	67(5)
C(6)	0.0490(12)	0.0220(17)	0.8153(17)	74(6)	C(74)	0.3792(9)	0.2856(12)	0.5541(12)	39(4)
C(7)	0.0125(12)	0.841(17)	0.8537(17)	74(6)	C(75)	0.4567(9)	0.2846(12)	0.5937(13)	45(4)
C(8)	0.0242(12)	0.1885(17)	0.8348(17)	76(6)	C(76)	0.5056(11)	0.3320(15)	0.5383(15)	62(5)
C(9)	0.0720(10)	0.2381(14)	0.7788(14)	55(4)	C(77)	0.4717(13)	0.3779(17)	0.4332(18)	80(6)
C(14)	0.1590(9)	0.4730(13)	0.4925(13)	46(4)	C(78)	0.3949(11)	0.3780(16)	0.3933(16)	68(5)
C(15)	0.1085(11)	0.5243(15)	0.5078(16)	66(5)	C(79)	0.3485(9)	0.3337(13)	0.4537(13)	46(4)
C(16)	0.0909(12)	0.6203(17)	0.4482(17)	77(6)	C(84)	0.1672(10)	0.1529(13)	0.3409(14)	50(4)
C(17)	0.1232(13)	0.6609(17)	0.3779(18)	77(6)	C(85)	0.1674(11)	0.1216(15)	0.2481(15)	62(5)
C(18)	0.1772(13)	0.6132(18)	0.3583(19)	83(7)	C(86)	0.1197(12)	0.1585(17)	0.1440(17)	76(6)
C(19)	0.1929(12)	0.5154(16)	0.4199(17)	72(6)	C(87)	0.0717(12)	0.2244(17)	0.1443(17)	74(6)
C(24)	0.3707(9)	0.4987(12)	0.7627(13)	43(4)	C(88)	0.0670(13)	0.2545(18)	0.2342(18)	82(6)
C(25)	0.3596(12)	0.5455(16)	0.6588(16)	69(6)	C(89)	0.1141(12)	0.2146(16)	0.3341(16)	69(5)
C(26)	0.3484(13)	0.6512(18)	0.6383(18)	83(6)	C(94)	0.5033(9)	0.3458(13)	0.8441(13)	46(4)
C(27)	0.3524(13)	0.7079(17)	0.7178(18)	77(6)	C(95)	0.5352(10)	0.2525(13)	0.8759(14)	52(4)
C(28)	0.3643(12)	0.6603(16)	0.8189(17)	74(6)	C(96)	0.6163(11)	0.2592(15)	0.9033(16)	66(5)
C(29)	0.3730(11)	0.5554(15)	0.8428(16)	65(5)	C(97)	0.6606(13)	0.3554(18)	0.8996(18)	81(6)
C(34)	0.3086(9)	0.0190(13)	0.4404(13)	47(4)	C(98)	0.6282(11)	0.4441(16)	0.8707(16)	67(5)
C(35)	0.3666(11)	0.0795(15)	0.4119(15)	60(5)	C(99)	0.5502(10)	0.4409(14)	0.8438(14)	57(5)
C(36)	0.4144(13)	0.0261(18)	0.3790(18)	80(6)	C(114)	0.0638(15)	0.5347(20)	0.7650(21)	97(8)
C(37)	0.3980(13)	-0.0801(17)	0.3753(18)	82(6)	C(115)	0.0278(15)	0.4987(21)	0.8387(22)	105(8)
C(38)	0.3400(13)	-0.1376(17)	0.4020(18)	79(6)	C(116)	0.1427(15)	0.5442(21)	0.7998(21)	101(8)
C(39)	0.2919(11)	-0.0878(16)	0.4339(16)	66(5)	C(117)	0.1820(15)	0.5051(21)	0.8963(22)	105(8)
C(44)	0.3614(9)	0.1090(12)	0.7239(13)	42(4)	C(118)	0.1471(17)	0.4679(23)	0.9682(24)	121(9)
C(45)	0.4121(9)	0.0615(12)	0.7005(12)	42(4)	C(119)	0.0684(16)	0.4631(23)	0.9440(23)	114(9)
C(46)	0.4499(9)	-0.0181(13)	0.7702(13)	47(4)	C(124)	0.2265(16)	-0.0699(22)	1.1135(22)	111(9)
C(47)	0.4395(10)	-0.0490(13)	0.8659(14)	51(4)	C(125)	0.1800(17)	-0.1545(24)	1.1348(25)	124(10)
C(48)	0.3876(10)	-0.0036(14)	0.8883(14)	57(5)	C(126)	0.1489(17)	-0.2330(23)	1.0666(23)	117(9)
C(49)	0.3497(8)	0.0739(11)	0.8209(12)	38(4)	C(127)	0.1599(16)	-0.2167(23)	0.9660(23)	114(9)
C(54)	0.1701(9)	-0.0307(13)	0.5374(13)	45(4)	C(128)	0.2034(18)	-0.1246(24)	0.9447(25)	127(10)
C(55)	0.2014(11)	-0.0924(15)	0.6292(15)	62(5)	C(129)	0.2352(17)	-0.0531(23)	1.0175(24)	118(9)

measured, of which 6637 were considered as contributing reflections. The data were corrected for Lorentz and polarization effects. A crystal with dimensions $0.1 \times 0.2 \times 0.2 \text{ mm}^3$ was used for the data collection.

The structure was solved using the X-ray 72 system of programs on a Univac 1100 computer. The Rh and Sb atoms were located from a three dimensional Patterson synthesis. The positional parameters of the non-hydrogen atoms were deduced from successive Fourier and difference-Fourier synthesis. Six cycles of blocked-cascade matrix least-squares refinement of all the positional and isotropic thermal parameters resulted in an R value of 0.079. Four additional cycles of refinement with anisotropic thermal parameters converged R to 0.071. A significance test carried out with the theory of linear hypothesis (as described by Hamilton [7]) showed that the decrease in R due to anisotropic refinement was insignificant. We therefore used the isotropic refined parameters to determine the molecular structure. In the final stage of refinement no parameter shifted more than 0.3σ , where σ is the standard deviation of the parameter.

The atomic scattering factors for Rh, Sb, O and C were taken from ref. [8]. The final difference-Fourier maps contained no significant peaks. Final positional and isotropic thermal parameters are listed in Table I.

Results and Discussion

The molecular structure of $[\text{Rh}(\text{DPD})(\text{SbPh}_3)_2\text{Ph}_2] \cdot 2(\text{C}_6\text{H}_6)$ and the system of numbering the atoms is shown in Fig. 1. Bond lengths and bond angles are given in Tables II and III respectively.

The six atoms Sb(1), Sb(2), O(1), O(2), C(44) and C(74) form a slightly distorted octahedron with the

TABLE II. Selected Interatomic Distances (Å) with Standard Deviation.

Rh—O(1)	2.132(10)	C(2)—C(3)	1.374(23)
Rh—O(2)	2.161(12)	C(1)—C(4)	1.525(26)
Rh—Sb(1)	2.551(2)	C(2)—C(14)	1.530(22)
Rh—Sb(2)	2.588(2)	Sb(1)—C(34)	2.133(21)
Rh—C(44)	2.036(16)	Sb(1)—C(54)	2.132(17)
Rh—C(74)	2.059(18)	Sb(1)—C(84)	2.118(15)
O(2)—C(1)	1.290(20)	Sb(2)—C(24)	2.120(17)
O(1)—C(2)	1.249(23)	Sb(2)—C(64)	2.147(19)
C(1)—C(3)	1.380(23)	Sb(2)—C(94)	2.118(17)

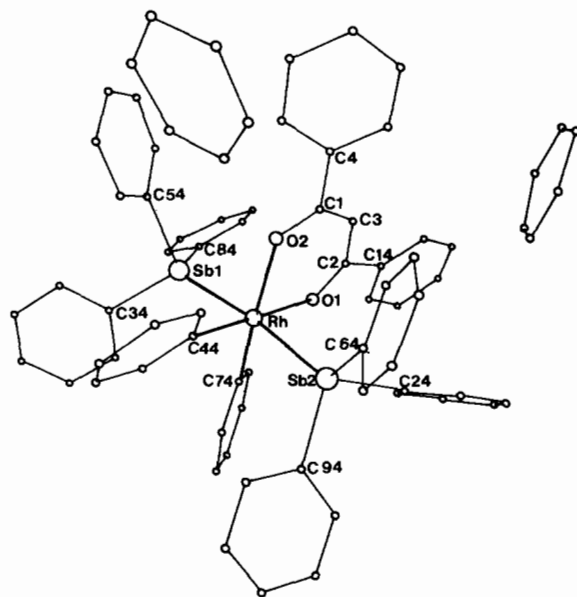


Fig. 1. Molecular configuration and atom numbering scheme for $[\text{Rh}(\text{DPD})(\text{SbPh}_3)_2\text{Ph}_2] \cdot 2(\text{C}_6\text{H}_6)$.

TABLE III. Selected Bond Angles (deg.) with Standard Deviations.

Sb(1)—Rh—Sb(2)	172.1(1)	C(54)—Sb(1)—C(34)	100.9(7)
O(1)—Rh—C(44)	175.9(7)	C(34)—Sb(1)—C(84)	99.9(5)
O(2)—Rh—C(74)	171.9(5)	C(34)—Sb(1)—Rh	119.9(5)
O(1)—Rh—O(2)	86.8(4)	Rh—Sb(2)—C(64)	118.8(4)
O(2)—Rh—Sb(1)	89.9(3)	C(64)—Sb(2)—C(94)	100.0(6)
O(1)—Rh—Sb(1)	96.1(3)	C(94)—Sb(2)—C(24)	102.0(6)
Sb(1)—Rh—C(44)	86.0(4)	C(24)—Sb(2)—Rh	116.4(4)
C(44)—Rh—O(2)	89.7(6)	Rh—Sb(2)—C(94)	116.9(5)
O(2)—Rh—Sb(2)	92.2(3)	C(64)—Sb(2)—C(24)	100.0(6)
C(44)—Rh—Sb(2)	86.4(4)	Rh—O(2)—C(1)	122.7(9)
Sb(2)—Rh—O(1)	91.7(3)	Rh—O(1)—C(2)	127.0(9)
O(1)—Rh—C(74)	85.5(5)	O(2)—C(1)—C(3)	129.5(16)
Sb(1)—Rh—C(74)	88.2(4)	O(1)—C(2)—C(3)	127.3(15)
C(44)—Rh—C(74)	98.1(7)	C(1)—C(3)—C(2)	125.8(19)
Sb(2)—Rh—C(74)	90.7(4)	O(2)—C(1)—C(4)	111.7(12)
Rh—Sb(1)—C(84)	117.5(5)	C(3)—C(1)—C(4)	118.7(16)
C(84)—Sb(1)—C(54)	102.8(6)	O(1)—C(2)—C(14)	114.4(15)
Rh—Sb(1)—C(54)	113.3(5)	C(3)—C(2)—C(14)	118.3(16)

coordination atom Rh in the centre. The average twist angle ϕ , as described and defined by Muetterties and Guggenberger [9], has a value of 52.7° as compared with an ideal octahedron angle of 60° and an ideal trigonal prism angle of 0° . The deviation from an ideal octahedron can further be seen by considering the bond angles between the atoms describing the coordination polyhedron (Table III). The three equatorial planes of the octahedron O(1), O(2), C(44), C(47) and Sb(1), Sb(2), C(44), O(1) and Sb(1), Sb(2), C(74), O(2) make angles of 88.9° , 89.9° and 89.0° with each other. These planes are planar within experimental error, except for the last mentioned with a deviation of 0.15 Å of the atoms from the best plane through the atoms. In each of the three planes the Rh-atom lies within 0.015 Å from the best plane through the atoms.

Since the chemical environment of the two antimony atoms is identical, the significant difference between the two Rh–Sb bond distances (2.588 and 2.551 Å) cannot be accounted for. Average bond distances for Rh–P [10] and Rh–As [11] in similar Rh(III)-complexes are 2.35 Å and 2.44 Å respectively.

The chelate ring (Rh, O(1), O(2), C(1), C(2) and C(3)) is planar, within experimental error. The two phenyl rings of the β -diketone are not co-planar with the chelate ring but make angles of 33.4° and 14.1° with the chelate ring and an angle of 25.0° between one another.

The ten phenyl rings in the molecule are planar within experimental error, and the average C–C bond distance (1.394 Å) and average bond angles (120.0°) are identical to the accepted values for phenyl rings.

The two Sb-atoms are approximately tetrahedrally surrounded by the Rh-atom and three carbon atoms of phenyl rings. The mean Sb–C bond distance (2.145 Å) is (as expected) longer than the average P–C [2] bond distance (1.83 Å), and an average As–C [12] bond distance (1.94 Å) in similar compounds where P and As are bonded to phenyl carbons. The average tetrahedral C–Sb–C angle is 101.0° in comparison with the average tetrahedral C–Sb–Rh angle of 117.1° .

The absence or presence of atmospheric oxygen during the preparation of the title compound makes no difference as to the nature of the final product. This fact ruled out the possibility that Rh(I) was oxidized by oxygen. The only other possibility is that the Rh(I) was oxidized to Rh(III) by the excess SbPh_3 present to yield the two phenyl rings bonded to the Rh-atom with the subsequent reduction of SbPh_3 . Chemical kinetics to determine a possible

reaction mechanism, as well as structure work on similar compounds, is at present the subject of further research in order to account for the oxidation of Rh(I).

The presence of the two benzene molecules is also difficult to account for, since the complex was prepared in an acetone medium and recrystallized from petroleum ether free from aromatic hydrocarbons. The two benzene rings are planar within experimental error, and the average C–C bond distance (1.381 Å) and angles (119.9°) are in good agreement with the accepted values for benzene. The distance from the C-atoms of these benzene rings to other atoms in the structure (>3.80 Å) does not indicate any strong interaction. The relatively high thermal parameters of these benzene C-atoms (Table I) also indicate non-bonding. Ugo and co-workers [12] reported a clathrated benzene molecule in $[\text{RhCl}(\text{CO})(\text{SbPh}_3)_2] \cdot \text{C}_6\text{H}_6$, and proved that the compound did not lose any benzene while being heated at 100°C and 5 mm Hg for six days or by repeated washing with ether. The presence of benzene rings in the structure of $[\text{RhI}_2\text{Me}(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_6$ was also reported by Troughton and Skapski [10].

Acknowledgements

We thank Mr. Jon Albain of the South African C.S.I.R. for the data collection and the research fund of this University for financial support.

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