The Structure of Acetylcarbonyltris(triphenylantimony)rhodium(I)

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

Department of Chemistry, University of the Orange Free State, Bloemfontein 9301, South Africa

(Received May 12, 1986)

A previous paper [1] dealt with the preparation and structure of 1,3-diphenyl-1,3-propandionatobis(triphenylantimony) diphenylrhodium(III) dibenzene, [Rh(DPD)$(SbPh_3)_2Ph_2 \cdot 2(C_6H_5)$], which was synthesized by means of the reaction between [Rh(DPD)$(CO)_2$] and $SbPh_3$ (1:3.5 mole ratio) in an acetone or hexane medium. In order to account for the unexpected oxidation of Rh(I) to Rh(III) during the latter reaction, the investigation was continued using methanol as reaction medium, upon which a monocarbonyl compound (ν(C≡O) at 1982 cm^{-1}) crystallised out of solution. With the expectation that the monocarbonyl compound was an intermediate compound (during the process where the above-mentioned Rh(III)-compound was formed) the crystal and molecular structure of the monocarbonyl compound was determined. The structure investigation, however, revealed a five coordinated rhodium(I) compound, acetylcarbonyltris(triphenylantimony)-rhodium(I), [Rh$(SbPh_3)_3(COCH_3)$(CO)] of which the structure is presented in this article.

Experimental

The Rh(I) β-diketone complex, [Rh(DPD)$(CO)_2$], was prepared by methods described previously [1–3]. Each of [Rh(DPD)$(CO)_2$] and $SbPh_3$ (1:3.5 mole ratio) was dissolved in the minimum amount of methanol. About 5 min after the two methanol solutions were added together, the title compound, being insoluble in methanol, started to precipitate out of solution from where it was removed by filtration and purified by recrystallisation from a chloroform methanol mixture (80:20 volume ratio).

Crystal Data

$C_{57}H_{48}O_2Sb_3Rh$, molecular mass 1233.16, monoclinic, space group $P2_1/n$, $a = 10.051$, $b = 24.035$, $c = 21.025$ Å, $\beta = 81.22°$, $Z = 4$, $D_{calc} = 1.63$ g cm^{-3}, μ(Mo Kα) = 19.21 cm^{-1}.

Three dimensional intensity data were collected and corrected as described earlier [1, 2]. No decomposition of the crystal was detectable during the data collection. A total of 7247 reflections were measured of which 4876 were considered as observed. The structure was solved by using direct methods to locate the positions of the Rh and Sb atoms.

The structure was further developed by successive Fourier and difference Fourier maps. Six cycles of blocked-cascade matrix least-squares refinement of all the positional and anisotropic thermal parameters resulted in a R value of 0.064. H atoms were not located. Final positional and thermal parameters are listed in Table I.

Results and Discussion

Figure 1 shows the molecular configuration of [Rh$(SbPh_3)_3(COCH_3)$(CO)] and the atomic nomenclature, while Tables II and III list selected bond lengths and selected bond angles respectively.

The coordination round the Rh atom forms a near ideal trigonal bipyramide (see Tables II and III) with the carbonyl and acetyl groups in axial positions. The trigonal plane, including the central Rh atom, is planar within the experimental error as proved by the calculation of the best plane through the atoms Rh(I), Sb(I), Sb(2) and Sb(3), while the angle between the normal of the latter plane and the straight line (within the experimental error) through C(55), Rh(I) and C(56) is 1.17°.

It seems that Rh(I) compounds with stibine ligands has a great tendency to stabilize penta coordination, since most of these compounds have been reported to be five coordinated species [4–7]. There is also direct evidence of a five coordinated reaction intermediate in the square-planar substitution reactions of a Rh(I)–antimony compound [8].

The nine phenyl rings in the molecule are planar within the experimental error and the average C–C bond distance and C–C–C bond angles in the phenyl rings are within the experimental error identical to the accepted values of 1.394 Å and 120° for phenyl rings [9].

The three Sb-atoms are approximately tetrahedrally surrounded by the Rh atom and three carbon atoms of phenyl rings. The mean Sb–C distance of 2.141 Å compares well with a previously reported value of 2.145 Å [1]. The average tetrahedral C–Sb–C angle is 98.8° in comparison with the average tetrahedral Rh–Sb–C angle of 118.6°.

The mean Rh–Sb bond distance is 2.568 Å, while Rh–Sb bond distances in a Rh(III) complex were reported as 2.588 and 2.551 Å [1].

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

TABLE 1. Fractional Atomic Coordinates with Standard Deviations in Parentheses

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Rh(1)	0.7681(1)	0.2833(1)	0.2975(1)	C(16)	0.5311(23)	0.0488(9)	0.1516(10)	C(37)	0.9563(18)	0.3722(8)	0.1767(8)
Sb(1)	0.7620(1)	0.1781(10)	0.3127(1)	C(17)	0.6599(23)	0.0373(9)	0.1810(11)	C(38)	1.0676(21)	0.3389(11)	0.1724(12)
Sb(2)	0.7610(1)	0.3524(10)	0.3904(1)	C(18)	0.7287(19)	0.0743(7)	0.2263(9)	C(39)	1.1916(24)	0.3645(12)	0.1706(11)
Sb(3)	0.7718(1)	0.3295(0)	0.1871(1)	C(19)	0.9478(16)	0.3962(6)	0.4127(8)	C(40)	1.2049(27)	0.4213(14)	0.1753(11)
O(1)	1.0719(15)	0.2735(6)	0.3272(10)	C(20)	1.0255(17)	0.4009(7)	0.3638(8)	C(41)	1.0990(36)	0.4529(13)	0.1819(15)
O(2)	0.4904(13)	0.2790(6)	0.2295(8)	C(21)	1.1524(19)	0.4264(8)	0.3750(9)	C(42)	0.9699(23)	0.4288(9)	0.1810(12)
C(1)	0.9619(17)	0.1430(7)	0.3255(8)	C(22)	1.2024(18)	0.4472(7)	0.4370(9)	C(43)	0.6279(17)	0.3883(7)	0.1399(8)
C(2)	1.0260(22)	0.1313(8)	0.3876(10)	C(23)	1.1227(20)	0.4438(7)	0.4861(10)	C(44)	0.6235(21)	0.4432(8)	0.1680(12)
C(3)	1.1616(24)	0.1140(10)	0.3967(13)	C(24)	0.9951(17)	0.4189(7)	0.4726(8)	C(45)	0.5355(25)	0.4832(11)	0.1366(14)
C(4)	1.2344(27)	0.1128(11)	0.3445(16)	C(25)	0.6260(15)	0.4220(7)	0.3790(7)	C(46)	0.4509(27)	0.4680(11)	0.0786(14)
C(5)	1.1678(27)	0.1233(12)	0.2852(18)	C(26)	0.6287(17)	0.4621(7)	0.4294(9)	C(47)	0.4530(25)	0.4140(12)	0.0580(12)
C(6)	1.0314(20)	0.1398(9)	0.2749(10)	C(27)	0.5526(19)	0.5096(8)	0.4189(9)	C(48)	0.5381(20)	0.3739(9)	0.0869(10)
C(7)	0.6827(18)	0.1434(7)	0.3927(8)	C(28)	0.4688(19)	0.5192(7)	0.3605(10)	C(49)	0.7658(18)	0.2742(7)	0.1074(7)
C(8)	0.6624(23)	0.0855(9)	0.3966(10)	C(29)	0.4658(21)	0.4798(8)	0.3107(10)	C(50)	0.7383(22)	0.2196(7)	0.1165(8)
C(9)	0.6048(23)	0.0644(9)	0.4489(10)	C(30)	0.5414(17)	0.4311(8)	0.3212(9)	C(51)	0.7282(21)	0.1808(9)	0.0653(10)
C(10)	0.5676(21)	0.1010(10)	0.4955(11)	C(31)	0.7413(17)	0.3270(7)	0.4855(7)	C(52)	0.7442(20)	0.1996(8)	0.0060(9)
C(11)	0.5947(25)	0.1555(10)	0.4918(11)	C(32)	0.6226(20)	0.3359(8)	0.5109(9)	C(53)	0.7769(27)	0.2539(10)	−0.0037(11)
C(12)	0.6498(20)	0.1786(9)	0.4395(9)	C(33)	0.6137(26)	0.3147(11)	0.5736(11)	C(54)	0.7894(24)	0.2925(9)	0.0484(9)
C(13)	0.6653(18)	0.1222(7)	0.2429(8)	C(34)	0.7228(28)	0.2868(10)	0.6081(10)	C(55)	0.9600(21)	0.2784(7)	0.3148(10)
C(14)	0.5348(19)	0.1356(8)	0.2119(9)	C(35)	0.8401(25)	0.2791(9)	0.5827(11)	C(56)	0.5573(10)	0.2831(6)	0.2792(8)
C(15)	0.4660(21)	0.0969(9)	0.1660(10)	C(36)	0.8507(21)	0.2985(7)	0.5214(8)	C(57)	0.5010(14)	0.2871(7)	0.3341(7)

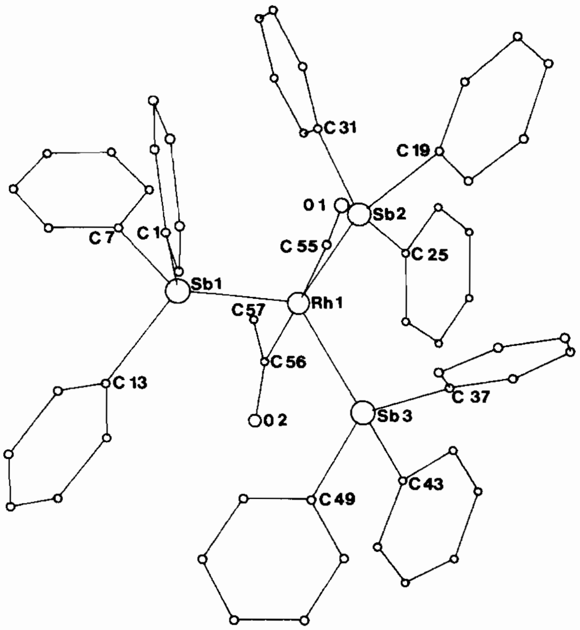

Fig. 1. Molecular configuration and atom numbering scheme for [Rh(SbPh$_3$)$_3$(COCH$_3$)(CO)].

TABLE II. Selected Interatomic Distances (Å) with Standard Deviations in Parentheses

Rh(1)–Sb(1)	2.552(2)	Sb(1)–C(1)	2.158(17)
Rh(1)–Sb(2)	2.572(2)	Sb(1)–C(7)	2.137(19)
Rh(1)–Sb(3)	2.579(2)	Sb(1)–C(13)	2.113(16)
Rh(1)–C(55)	1.911(20)	Sb(2)–C(19)	2.142(16)
Rh(1)–C(56)	2.095(16)	Sb(2)–C(25)	2.145(16)
C(55)–O(1)	1.121(25)	Sb(2)–C(31)	2.127(16)
C(56)–O(2)	1.156(22)	Sb(3)–C(37)	2.159(19)
C(56)–C(57)	1.365(24)	Sb(3)–C(43)	2.154(17)
		Sb(3)–C(49)	2.131(16)

As a result of the relatively short C(56)–C(57) bond distance (1.365(24) Å), some doubt existed as to whether the group *trans* with respect to the metal carbonyl bond was an acetyl or carboxyl group; that means whether the C(57) site in Fig. 1 was occupied by a carbon atom (of a –CH$_3$ group) or an oxygen atom (of an –OH group). After it was established that the compound possessed no organic acid properties, ^{1}H NMR spectra (CDCl$_3$, Brucker AM 300 NMR spectrometer) were used to identify the atom in the C(57) site (Singlet δ 2.4) as a methyl group adjacent to a carbonyl group. The ratio of methyl protons to aromatic protons (δ 7.133–6.453) was 15.05:1, which further proved the existence of a –CH$_3$ group and thus in fact an acetyl group *trans* with respect to the metal carbonyl bond.

The structure of an almost identical trigonal bipyramidal Rh(I)–phosphine complex [Rh(PPh$_3$)$_3$-H(CO)], has been reported [10]. The Rh(I)–C(55) and C(55)–O(1) bond distances (Table II) compare favourably with the corresponding distances of 1.81(2) Å and 1.18(3) Å in the mentioned phosphine complex [10] and with the corresponding distances of 1.809(6) Å and 1.145(8) Å in the Rh(I) complex [Rh(BPHA)(CO)(PPh$_3$)] [2].

It is very difficult to account for the presence of the acetyl group (C(57)–C(56)–O(2)) in the molecule. The title compound, in which there is no β-diketone ligand, is formed only when the reaction between [Rh(DPD)(CO)$_2$] and SbPh$_3$ is carried out in a methanol medium. DPD is the β-diketone 1,3diphenyl-1,3propandione. When the reaction is carried out in an acetone or hexane medium, the β-diketone ligand is retained in the molecule and the Rh(III) complex [Rh(DPD)(SbPh$_3$)$_2$(Ph)$_2$] [1] is formed. A possible explanation for the formation of the title compound is that methanol, being a more

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

Sb(1)–Rh(1)–Sb(2)	122.7(1)	Rh(1)–Sb(1)–C(13)	124.1(4)
Sb(2)–Rh(1)–Sb(3)	114.4(1)	C(1)–Sb(1)–C(7)	101.6(7)
Sb(1)–Rh(1)–Sb(3)	122.9(1)	C(1)–Sb(1)–C(13)	99.2(7)
Sb(3)–Rh(1)–C(55)	92.5(6)	C(7)–Sb(1)–C(13)	96.4(7)
Sb(2)–Rh(1)–C(55)	93.3(6)	Rh(1)–Sb(2)–C(19)	110.9(5)
Sb(1)–Rh(1)–C(55)	87.6(5)	Rh(1)–Sb(2)–C(25)	120.6(4)
Sb(3)–Rh(1)–C(56)	89.4(5)	Rh(1)–Sb(2)–C(31)	123.1(4)
Sb(2)–Rh(1)–C(56)	89.8(4)	C(19)–Sb(2)–C(25)	99.1(6)
Sb(1)–Rh(1)–C(56)	88.7(4)	C(19)–Sb(2)–C(31)	98.1(6)
Rh(1)–C(55)–O(1)	176.3(18)	C(25)–Sb(2)–C(31)	100.4(6)
C(55)–Rh(1)–C(56)	176.3(6)	Rh(1)–Sb(3)–C(37)	115.2(4)
Rh(1)–C(56)–C(57)	112.5(11)	Rh(1)–Sb(3)–C(43)	126.6(5)
C(57)–C(56)–O(2)	120.7(16)	Rh(1)–Sb(3)–C(49)	115.9(5)
Rh(1)–C(56)–O(2)	126.8(15)	C(37)–Sb(3)–C(43)	99.7(7)
Rh(1)–Sb(1)–C(1)	111.3(4)	C(37)–Sb(3)–C(49)	98.0(7)
Rh(1)–Sb(1)–C(7)	120.2(5)	C(43)–Sb(3)–C(49)	96.4(6)

protic solvent than acetone or hexane, caused the β-diketone ligand to split off and that the acetyl group is formed by some disproportionation of the β-diketone ligand.

Acknowledgements

The authors thank the University of the Orange Free State for financial support and Dr. P. H. van Rooyen of the South African C.S.I.R. for the data collection.

References

1 G. J. Lamprecht, J. G. Leipoldt and C. P. van Biljon, *Inorg. Chim. Acta, 88*, 55 (1984).
2 J. G. Leipoldt and E. C. Grobler, *Inorg. Chim. Acta, 60*, 141 (1982)
3 Yu. S. Varsharskii and T. G. Cherkasova, *Russ. J. Inorg. Chem., 12*, 899 (1967).
4 D. F. Steele and T A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 2162 (1972).
5 R. Ugo, F. Bonati and S Cenini, *Inorg. Chim. Acta, 3*, 220 (1969).
6 P. E. Garrou and G. E. Hartwell, *J. Organomet Chem., 69*, 445 (1974).
7 W. Hieber and V. Frey, *Chem. Ber., 99*, 2614 (1966).
8 L. Cattalini, R. Ugo and A. Orio, *J. Am. Chem. Soc., 90*, 4800 (1968).
9 L. E. Sutin, 'Tables of Interatomic Distances and Configuration in Molecules and Ions', Suppl. 1956–59, The Chemical Society, London, 1965, p. 5165.
10 S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc., 85*, 3501 (1963).