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The Crystal Structure of Benzoyl-1,1,1-trifluoroacetonato(1,5-cyclooctadiene)-rhodium(I)

J. G. LEIPOLDT*, S. S. BASSON, G. J. LAMPRECHT, L. D. C. BOK and J. J. J. SCHLEBUSCH
Department of Chemistry, University of the Orange Free State, Bloemfontein, Republic of South Africa

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Benzoyl-1,1,1-trifluoroacetonato(1,5-cyclooctadiene)rhodium I, [Rh(TFBA)(COD)], crystallizes in the monoclinic space group $P2_1c$ with a = *10.966 Å,* b = *9.817 Å,* c = *17.004 Å, β = 113.2° and Z = 4. The compound was prepared by the reaction between [Rh(TFBA)(CO)$_2$] and cyclooctadiene. 2228 independent observed reflections were used for the structure determination. The final R value for all the reflections was 0.039. The results indicate that the oxygen atom nearest to the phenyl ring has the largest* trans-*effect.*

Introduction

β-diketone complexes of Rh(I) of the type [Rh(β-diketone)(D)$_2$] (where D are electron donors such as CO, ethylene and dienes) undergo substitution reactions with a large variety of ligands. To examine these reactions a knowledge of the relative *trans*-effect of the different ligands is necessary. In the case of symmetrical β-diketones like acetylacetone (acac), the oxygen atoms of the β-diketone are chemically equivalent if the other two ligands are identical. The results of the structure determination of [Rh(TTA)(CO)(PPh$_3$)] indicate that, in the compound [Rh(TTA)(CO)$_2$], the oxygen atom nearest to the CF$_3$-group has the smallest *trans*-effect [1, 2]. The *trans*-effect of the ligands normally has an influence on the metal–ligand bond strength and thus also on the bond lengths, as observed in the case of [Rh(acac)(CO)(PPh$_3$)] [3]. The crystal structure of [Rh(TFBA)(CO)$_2$] was determined to examine the effect of various substituents on the β-diketone on the relative Rh–ligand bond strengths. The standard deviation of the Rh–O and Rh–C bond lengths, however, were too large to draw any conclusions about the effect of the substituents on the β-diketone [4]. The crystal structure of [Rh(TFBA)(COD)] was determined in order to examine the effect of strong electron-attracting groups like CF$_3$ on the relative *trans*-effect of the two oxygen atoms. This complex has the following advantages: it is stable, well formed crystals are easily obtained, and the groups *trans* to the β-diketone are chemically equivalent. Therefore, cyclooctadiene will not influence the relative Rh–O bond lengths.

Experimental

A solution of [Rh$_2$Cl$_2$(CO)$_4$] was prepared by refluxing a solution of RhCl$_3$·3H$_2$O in dimethylformamide for approximately 30 minutes [5]. An equivalent amount of TFBA was added to the resulting yellow solution. The solution was diluted with water, and the resulting precipitate ([Rh(TFBA)(CO)$_2$]) was removed by centrifuging and washed with water. About 0.1 g cyclooctadiene was added to a solution of 0.1 g [Rh(TFBA)(CO)$_2$] in 5 cm^3 acetone. The solution was allowed to evaporate at room temperature. The resulting [Rh(TFBA)(COD)] was crystallized from petroleum ether (BP 60–80 °C). Well formed orange crystals were obtained.

Preliminary oscillation and Weissenberg photographs showed that the crystals were monoclinic, space group P2$_1$/c. Crystal data: $C_{18}H_{18}O_2F_3Rh$, molecular weight 426.2, monoclinic space group P2$_1$/c, a = 10.966 Å, b = 9.817 Å, c = 17.004 Å, β = 113.2°, d_{exp} = 1.68 g cm^{-3}, d_{calc} = 1.68 g cm^{-3}, $Z = 4$, μ(MoKα) = 10.3 cm^{-1}.

The three dimensional intensity data were measured with a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated MoKα radiation (λ = 0.7107 Å) for θ values between 3° and 23°. Three reflections were used as standards and remeasured after every 60 reflections. No decomposition of the crystal was detectable. 2474 independent reflections were measured, of which 2228 were considered as observed. Lorentz and polarization corrections were applied. A crystal with dimensions 0.5 × 0.4 × 0.5 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 rhodium atom was located from a three dimensional Patterson map. A subsequent Fourier map,

TABLE I. Fractional Atomic Coordinates and Thermal Parameters. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^3$).

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	901.2(5)	6448.0(5)	3376.6(3)	39.7(5)	44.4(6)	41.7(5)	6.2(2)	21.3(3)	10.2(2)
O(1)	2218(4)	4968(4)	4045(3)	41(2)	45(3)	44(3)	8(2)	21(2)	11(2)
O(2)	1978(4)	6786(5)	2637(3)	46(3)	54(3)	46(3)	7(2)	26(2)	13(2)
C(1)	3631(7)	6595(7)	2119(4)	50(4)	58(5)	54(4)	−1(3)	31(3)	7(4)
C(2)	3030(6)	6132(6)	2752(4)	42(4)	43(4)	38(4)	−6(3)	21(3)	−4(3)
C(3)	3683(6)	5106(6)	3319(4)	47(4)	38(4)	42(4)	−2(3)	24(3)	−2(3)
C(4)	3245(6)	4570(6)	3941(4)	38(3)	35(3)	36(3)	−2(3)	13(3)	−4(3)
C(5)	4004(6)	3455(6)	4525(4)	42(3)	35(3)	35(3)	1(3)	13(3)	−6(3)
C(6)	3400(7)	2784(8)	5001(5)	59(4)	53(5)	61(5)	12(4)	31(4)	20(4)
C(7)	4071(8)	1741(8)	5569(5)	71(5)	55(5)	73(5)	16(4)	32(4)	20(4)
C(8)	5346(8)	1369(8)	5667(5)	75(5)	46(4)	54(4)	12(4)	18(4)	−1(4)
C(9)	5955(7)	2039(7)	5196(4)	61(4)	51(4)	49(4)	13(4)	14(3)	−9(3)
C(10)	5286(6)	3089(7)	4623(4)	46(4)	47(4)	42(4)	5(3)	14(3)	−11(3)
C(11)	309(7)	6668(8)	4409(4)	56(4)	66(5)	54(4)	9(4)	38(4)	10(4)
C(12)	−451(7)	5635(8)	3857(5)	51(4)	62(5)	62(5)	5(4)	40(4)	17(4)
C(13)	−1898(7)	5794(10)	3209(5)	37(4)	98(7)	77(5)	−5(4)	20(4)	21(5)
C(14)	−2096(8)	6773(12)	2505(7)	41(5)	138(10)	131(9)	0(5)	14(5)	77(8)
C(15)	−828(7)	7354(8)	2453(5)	42(4)	60(5)	68(5)	19(4)	13(4)	27(4)
C(16)	−51(8)	8361(8)	3000(5)	68(5)	49(5)	69(5)	24(4)	31(4)	24(4)
C(17)	−312(14)	9016(10)	3736(7)	226(14)	71(7)	107(8)	58(8)	109(9)	15(6)
C(18)	−196(9)	8116(9)	4455(5)	96(6)	71(6)	70(5)	23(5)	49(5)	4(5)
F(1)	3997(6)	7867(5)	2235(4)	180(6)	67(3)	139(5)	−33(4)	124(5)	−8(3)
F(2)	4689(5)	5904(6)	2169(3)	104(4)	122(4)	125(4)	40(3)	90(4)	46(4)
F(3)	2790(5)	6485(8)	1334(3)	88(3)	231(7)	47(3)	−42(4)	31(2)	9(4)

phased by the rhodium atom gave the positions of all the remaining non-hydrogen atoms. Four cycles of full matrix least squares refinement of all the positional and isotropic thermal parameters resulted in the residual factor $R = \Sigma\|F_o| - |F_c\| \div \Sigma|F_o|$ of 9.5%. Further five cycles of refinement with anisotropic thermal parameters converged to R = 3.9%. In the final cycle no positional parameter exhibited shifts of more than 0.3 times its standard deviation.

The atomic scattering factors used were those tabulated by Cromer and Waber [6]. A list of the observed and calculated structure factors may be obtained from the authors. The final positional and thermal parameters are listed in Table I. The estimated standard deviations in the last significant figure are given in parentheses.

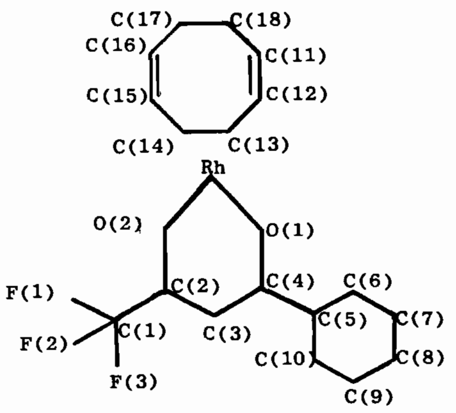

Fig. 1. System of numbering of the atoms in the molecule.

Results and Discussion

The system of numbering of the atoms in the molecule is shown in Fig. 1. The bond lengths and bond angles with their estimated standard deviations are given in Tables II and III respectively.

As in other β-diketone complexes an enolate type of resonance is found in the chelate ring with the C–O and C–C bonds of intermediate order. These bond lengths compare well with those found in $[Rh(TTA)(CO)(PPh_3)]$ [1], and $[Rh(acac)(CO)_2]$ [7], and indicate a conjugation which formed a pseudo-aromatic system. The calculation of the best plane through the atoms of the chelate ring showed no significant deviation from a plane. The slight shortening of the C(4)–C(5) bond (1.494 Å) indicates a certain conjugation with the phenyl ring. That this is an incomplete conjugation is reflected in the angle between the best planes through the chelate and phenyl ring, 12.9°. The average C–C

TABLE II. Interatomic Distances (A) with Estimated Standard Deviations in Parentheses.

Rh–O(1)	2.050(4)	C(1)–F(3)	1.295(7)
Rh–O(2)	2.066(5)	C(4)–C(5)	1.494(8)
Rh–S(1)	2.004(7)	C(5)–C(6)	1.397(11)
Rh–S(2)	1.989(7)	C(6)–C(7)	1.402(10)
Rh–C(11)	2.110(9)	C(7)–C(8)	1.394(13)
Rh–C(12)	2.115(9)	C(8)–C(9)	1.395(13)
Rh–C(15)	2.126(7)	C(9)–C(10)	1.410(9)
Rh–C(16)	2.122(8)	C(11)–C(12)	1.410(10)
O(2)–C(2)	1.269(8)	C(12)–C(13)	1.545(9)
C(2)–C(3)	1.384(8)	C(13)–C(14)	1.482(15)
C(3)–C(4)	1.423(11)	C(14)–C(15)	1.541(13)
C(4)–O(1)	1.272(9)	C(15)–C(16)	1.395(10)
C(1)–C(2)	1.537(11)	C(16)–C(17)	1.532(17)
C(1)–F(1)	1.303(9)	C(17)–C(18)	1.472(15)
C(1)–F(2)	1.319(10)	O(1)–O(2)	2.914(6)

bond distance in the phenyl ring (1.400 Å) is in good agreement with the normal value (1.394 Å) for the aromatic C–C bond [8]. All the bond angles are 120° within the experimental error. The phenyl ring is planar within the experimental error. The C–F distance (mean 1.306 Å) are about the same as that found in [Rh(TTA)(CO)(PPh_3)] [1].

The cyclooctadiene ligand has a boat like conformation. The carbon atoms participating in the bonding are virtually in a plane. The remaining set of four atoms are also nearly planar. The double bonds (C(11)–C(12) and C(15)–C(16)) are nearly perpendicular to the plane of the chelate ring; they form angles of 3.4° and 3.6°, with the normal of the chelate ring, respectively. These C=C bonds (1.410 Å and 1.395 Å) are slightly extended which corresponds to a decrease in the π-electron density as a result of bonding with the rhodium atom. The C–C bond lengths are about the same as in 1-phenyl-1,2-butanedionato(1,6-dichloro-1,5-cyclooctadiene)rhodium(I) [9].

The Rh–O and Rh–C bond lengths correspond well with the usual values found in the literature. The position of the central rhodium atom with respect to the oxygen atoms of the chelate ring and the centres of the C–C double bonds of cyclooctadiene indicates a square planar dsp^2 hybridization in which the 5s, $4p_x$, $4p_y$ and $4d_{x^2-y^2}$ metal orbitals take part. The calculation of the best plane through O(1), O(2), Rh, S(1) and S(2) (S(1) and S(2) are the centres of the C(15)–C(16) and C(11)–C(12) bonds respectively) corresponds to a square planar coordination polyhedron. The S(1)–Rh–S(2) and O(1)–Rh–O(2) angles are 89.7° and 90.1° respectively. The last mentioned angle causes the increase in the bond angles at the oxygen and carbon atoms of the chelate ring compared to the normal 120° angle in aromatic systems.

TABLE III. Bond Angles (Degrees) with Estimated Standard Deviations in Parentheses.

O(1)–Rh–O(2)	90.1(2)	C(3)–C(4)–C(5)	120.1(6)
S(1)–Rh–S(2)	89.7(2)	C(11)–C(12)–C(13)	125.2(7)
Rh–O(2)–C(2)	122.1(4)	C(12)–C(13)–C(14)	115.1(7)
O(2)–C(2)–C(3)	131.8(7)	C(13)–C(14)–C(15)	116.0(6)
C(2)–C(3)–C(4)	123.5(7)	C(14)–C(15)–C(16)	123.7(9)
C(3)–C(4)–O(1)	124.7(5)	C(15)–C(16)–C(17)	125.4(9)
C(4)–O(1)–Rh	127.7(4)	C(16)–C(17)–C(18)	116.3(8)
C(5)–C(6)–C(7)	120.1(7)	C(17)–C(18)–C(11)	115.3(9)
C(6)–C(7)–C(8)	120.3(9)	C(12)–C(11)–C(18)	124.5(6)
C(7)–C(8)–C(9)	119.8(7)	C(1)–C(2)–C(3)	117.0(6)
C(8)–C(9)–C(10)	120.2(7)	C(2)–C(1)–F(1)	111.7(7)
C(6)–C(5)–C(10)	119.8(6)	C(2)–C(1)–F(2)	114.5(6)
C(9)–C(10)–C(5)	119.7(7)	C(2)–C(1)–F(3)	111.5(6)

The relative effect of the CF_3 and phenyl groups on the Rh–O bond strengths are reflected in the Rh–O bond lengths. The chemical equivalent oxygen atoms of the β-diketone in [Rh(acac)$(CO)_2$] results in the same (within the experimental error) Rh–O bond lengths of 2.040 and 2.044 Å. In the present structure the Rh–O(2) bond length is 0.016 Å longer than the Rh–O(1) bond length. This can be explained as a result of the electron attracting ability of the CF_3-group causing the Rh–O bond (oxygen atom nearest to the CF_3-group) to be weakened relative to the other Rh–O bond. This implies that O(1) has a greater *trans*-effect compared to O(2). This is in agreement with the polarization theory [10] and the σ-*trans*-effect [11] since the oxygen atom nearest to the CF_3-group will be least polarizable and a weaker σ-donor as a result of the electron attracting power of the CF_3-group.

The relative *trans*-effect of O(1) and O(2) is also noticeable in the Rh–S(1) and Rh–S(2) distances, see Table II. (O(1) and O(2) are *trans* with respect to S(1) and S(2) respectively). Although this difference (0.015 Å) is only about twice the standard deviation, it also indicates that O(1) has a larger *trans*-effect than O(2). The longer Rh–S(1) distance could imply that less π-electrons of the C(15)–C(16) bond, compared to the C(11)–C(12) bond, are used for bond formation with rhodium. This should result in a lengthening of the C(11)–C(12) bond compared to the C(15)–C(16) bond. This is in agreement with the observed bond lengths, although the difference (0.015 Å) is only 1½ times the standard deviation.

This smaller *trans*-effect of the oxygen atom nearest to the electron withdrawing CF_3-group was also illustrated by the reaction between [Rh(TTA)$(CO)_2$] and triphenylphosphine [1, 2]. In this case it was found that the CO-group *trans* with respect to the oxygen atom adjacent to the thenoyl-group was replaced.

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