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The Crystal Structure of Benzoyl-1,1,1-trifluoroacetonatodicarbonylrhodium(I)

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β-Diketones have proved to be one of the most versatile groups of ligands available in the study of coordination compounds. In many cases these complexes have provided examples of interesting stereochemical arrangements. The complex [Rh(acac)-$(CO)_2$] was first prepared by Bonati and Wilkinson [1], and the crystal structure was determined by Huq and Skapski [2]. The structural analysis of the complex [Rh(TFBA)$(CO)_2$] was undertaken to obtain a better knowledge of the rhodium–ligand interactions in this type of compounds and as a partial study of the effects that the different substituents in non-symmetrical β-diketones have on the kinetics of substitution reactions of these compounds.

Experimental

A solution of $[Rh_2Cl_2(CO)_4]$ was prepared by refluxing a solution of $RhCl_3 \cdot 3H_2O$ in dimethylformamide for approximately 30 minutes [3]. A slight excess of benzoyl-1,1,1-trifluoroacetone was added to the resulting light yellow solution. The solution was diluted with water, and the precipitate was removed by centrifuging and washed with petroleum ether. Crystallization from acetone gave orange–red crystals which were orthorhombic, space group Pbca, with a = 30.486 Å, b = 12.086 Å, c = 7.047 Å, Z = 8, d_c = 1.90 g cm^{-3} and d_{exp} = 1.88 g cm^{-3} (flotation in aqueous NaI solution). The three-dimensional intensity data were measured with a Philips four circle single crystal X-ray diffractometer, using Mo(K_α) radiation. 881 observed reflections were measured. No evidence of crystal decomposition could be detected during the intensity data collection. Lorentz and polarization corrections were applied.

The crystal 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 function. All the other non-hydrogen atoms were located from successive Fourier functions. A full-matrix least squares refinement, using all the observed reflections and anisotropic temperature parameters for all the atoms, gave R = 0.078 after four cycles. A table of the observed and calculated structure factors may be obtained from the authors. The final atomic parameters with their standard deviations are listed in Table I.

TABLE I. Fractional Atomic Coordinates $\times 10^4$ and Anisotropic Thermal Parameters $\times 10^3$ with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	848(0)	2373(2)	−242(3)	75(1)	84(1)	64(1)	3(1)	−4(1)	−2(1)
C(1)	793(13)	5889(29)	−362(53)	114(26)	111(29)	85(23)	22(25)	11(24)	13(22)
C(2)	999(13)	4757(23)	−376(40)	141(31)	67(21)	61(19)	19(21)	−6(21)	20(17)
C(3)	1447(9)	4723(21)	−594(34)	68(17)	80(19)	59(17)	16(16)	−15(14)	−8(14)
C(4)	1659(8)	3693(24)	−683(28)	61(17)	91(22)	29(12)	6(17)	−3(12)	−16(15)
C(5)	2142(8)	3711(19)	−935(30)	90(20)	48(15)	41(14)	4(15)	−2(13)	22(13)
C(6)	2403(8)	4628(19)	−452(32)	76(19)	70(18)	54(14)	−4(14)	3(14)	4(14)
C(7)	2876(9)	4588(21)	−583(35)	91(20)	78(19)	56(16)	−15(16)	10(15)	12(15)
C(8)	3074(9)	3627(22)	−1351(31)	100(20)	75(18)	40(14)	0(17)	−9(14)	4(14)
C(9)	2812(8)	2724(23)	−1915(29)	81(17)	101(22)	37(13)	−19(18)	9(13)	9(15)
C(10)	2348(8)	2750(20)	−1616(31)	74(16)	70(19)	58(15)	− 4(16)	6(13)	−5(14)
C(11)	284(9)	2012(22)	78(37)	86(19)	93(20)	57(16)	−9(16)	−16(16)	−8(16)
C(12)	961(7)	900(24)	−355(36)	51(16)	102(21)	60(16)	−17(15)	10(14)	2(17)
O(1)	708(6)	4010(17)	−171(23)	92(13)	107(15)	51(11)	14(11)	0(10)	17(11)
O(2)	1492(5)	2736(14)	−588(21)	86(11)	75(13)	59(10)	2(10)	−5(9)	−5(10)
O(3)	−81(7)	1744(18)	356(30)	92(15)	142(18)	106(16)	−14(13)	3(15)	−1(15)
O(4)	1030(6)	−41(17)	−407(33)	111(15)	79(13)	128(19)	0(12)	−1(15)	1(15)
F(1)	559(11)	6100(21)	1047(35)	352(40)	166(22)	138(20)	135(26)	82(25)	7(17)
F(2)	494(10)	6997(20)	−1631(34)	250(30)	171(22)	156(21)	128(23)	−75(22)	−12(17)
F(3)	1046(8)	6694(17)	−579(60)	151(19)	85(14)	483(56)	37(14)	52(32)	17(25)

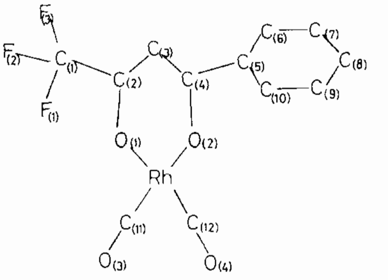

Figure.

TABLE II. Interatomic Distances (Å) with Estimated Standard Deviations in Parenthesis.

Rh–C(11)	1.788(26)	C(1)–C(2)	1.51(5)
Rh–C(12)	1.815(29)	C(4)–C(5)	1.48(3)
Rh–O(1)	2.024(20)	C(1)–F(1)	1.25(5)
Rh–O(2)	2.024(16)	C(1)–F(2)	1.28(5)
C(11)–O(3)	1.18(3)	C(1)–F(3)	1.25(4)
C(12)–O(4)	1.16(4)	C(6)–C(7)	1.45(4)
C(2)–O(1)	1.28(4)	C(7)–C(8)	1.42(4)
C(4)–O(2)	1.27(3)	C(8)–C(9)	1.41(4)
C(2)–C(3)	1.38(5)	C(5)–C(6)	1.41(3)
C(3)–C(4)	1.41(4)	C(5)–C(10)	1.40(3)
		C(9)–C(10)	1.43(3)

Results and Discussion

The system of numbering the atoms in the molecule is shown in Figure 1. The bond lengths and bond angles are given in Tables II and III respectively. The rhodium atom has a square planar coordination with the two Rh–O distances equal (2.024 Å) and the two Rh–C distances 1.788 Å and 1.815 Å. The angles C–Rh–C and O–Rh–O are 87.0° and 89.8° respectively. The Rh–O and Rh–C bond lengths are, within the experimental error, the same as in $[Rh(acac)(CO)_2]$ [2]. The calculation of the best plane through the atoms of the polyhedron, *i.e.* Rh, C(11), C(12), O(1) and O(2) showed no significant deviation from a flat plane. The molecules are stacked in the [001] direction in such a way that the rhodium atoms of neighbouring molecules occupy the two remaining pseudo-octahedral positions. The Rh.....Rh distance is 3.537 Å. This separation is incompatible with normal bonding but is an evidence that some metal–metal interaction occurs in this direction. The Rh.....Rh stacking direction forms an angle of about 86° with the least squares plane through the coordination polyhedron.

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 in $[Rh(acac)(CO)_2]$ and indicates a conjugation which forms a pseudo-aromatic system. The calculation of the best plane through the atoms of the chelate ring showed that it is nearly planar.

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

O(1)–Rh–O(2)	89.8(7)
C(11)–Rh–C(12)	87.0(11)
Rh–C(11)–O(3)	177.0(23)
Rh–C(12)–O(4)	179.1(23)
C(2)–C(3)–C(4)	119.2(24)
C(2)–O(1)–Rh	122.8(19)
C(5)–C(6)–C(7)	121.4(22)
C(4)–O(2)–Rh	126.6(15)
C(5)–C(10)–C(9)	120.6(22)
O(1)–C(2)–C(3)	133.2(27)
O(2)–C(4)–C(3)	128.4(22)
C(6)–C(5)–C(10)	118.9(22)
C(6)–C(7)–C(8)	118.6(23)
C(7)–C(8)–C(9)	120.0(23)
C(8)–C(9)–C(10)	120.2(23)
F(1)–C(1)–F(2)	97.3(32)
F(2)–C(1)–F(3)	105.4(33)
F(1)–C(1)–F(3)	106.9(34)

The C–C bond lengths of the phenyl ring is slightly longer than for an aromatic C–C bond (mean 1.419 Å), but the standard deviations indicate that the observed difference is insignificant. The phenyl ring is planar within the experimental error and is at an angle of 23.0° to the plane through the chelate ring.

The standard deviations of the Rh–O and Rh–C bond lengths are too large to draw any conclusions about the relative bond lengths and the effect of substituents of the β-diketones. One could, however, assume that the oxygen atom nearest to the phenyl ring will have the largest *trans* effect. This is in agreement with the polarization theory [4] since the atom nearest to the CF_3-group will be least polarizable as a result of electron-attracting power of the CF_3-group. In reactions of the type [1]

$$[Rh(\beta\text{-diketone})(CO)_2] + P \rightarrow [Rh(\beta\text{-diketone})(CO)(P)] + CO$$

where only one carbonyl group is displaced, it can thus be assumed that the group C(11)–O(3), see Figure 1, would be displaced. This is in agreement with the results of the structure determination of $[Rh(TTA)(CO)(PPh_3)]$ [5].

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