The Crystal Structure of 1,1,1-Trifluoro-5,5-Dimethylpentanedionatocarbonyltriphenylphosphinerhodium(I)

J. G. LEIPOLDT*, S. S. BASSON and J. T. NEL

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

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1,1,1-Trifluoro-5,5-dimethylpentanedionatocarbonyltriphenylphosphinerhodium(I), [Rh(TFDMAA)(CO)(PPh$_3$)], was synthesized by means of the reaction between [Rh(TFDMAA)(CO)$_2$] and PPh$_3$. It crystallizes in the triclinic space group $P\bar{1}$ *with* a = *9.215* Å, b = *10.584* Å, c = *13.760* Å, *α = 107.61°, β = 104.79°, γ = 83.54° and with two molecules per unit cell. The crystal structure was determined from 2980 observed reflections that were obtained with an automated diffractometer. The final* R *value was 0.046.*

The result of this structure determination indicates that the oxygen atom nearest to the CF$_3$-group has a larger trans *influence than the other oxygen atom of the β-diketone since it was the carbonyl group* trans *to the first mentioned oxygen atom that was substituted during the reaction with PPh$_3$. This result contradicts other similar structure determinations.*

Introduction

The crystal structure of 1,1,1-trifluoro-5,5-dimethylpentanedionatocarbonyltriphenylphosphinerhodium(I) [Rh(TFDMAA)(CO)(PPh$_3$)], was determined as part of a program for the study of the relative *trans* effects of the different ligands in square planar complexes of rhodium(I) and the factors that have an influence on the *trans* effects in these compounds. The fact that only one of the carbonyl groups in complexes of the type [Rh(LL′)(CO)$_2$] (where LL′ = singly charged bidentate ligands like β-diketones and 8-hydroxyquinoline) can be substituted by neutral ligands such as triphenylphosphine [1, 2] was used to determine the relative *trans* influence of the two bonding atoms of the chelating ligands thenoyltrifluoroacetone (TTA) [3], N-benzoyl-N-phenylhydroxylamine (BPHA) [4], and 8-hydroxyquinoline (oxine) [5] by means of crystal structure determinations of [Rh(TTA)(CO)(PPh$_3$)], [Rh(oxine)(CO)(PPh$_3$)] and [Rh(BPHA)(CO)(PPh$_3$)], since it can be assumed that the carbonyl group which is situated *trans* to the atom which has the largest *trans* influence will be substituted by the PPh$_3$ group. The latter complexes were accordingly synthesized by the following reaction: [Rh(LL′)(CO)$_2$] + PPh$_3$ → [Rh(LL′)(CO)(PPh$_3$)] + CO. It was also demonstrated by means of the crystal structure determination of [Rh(TFBA)(COD)] [6] and [Rh(oxine)(COD)] [7] that the relative *trans* influence of the bonded atoms of the chelating ligand may be obtained from the rhodium–ligand bond distances in complexes of the type [Rh(LL′)(COD)], where COD = 1,5-cyclooctadiene.

All the results of these structure determinations [3–7] showed that the most electronegative atom (or in the case of β-diketones the oxygen atom nearest to the strongest electron attracting group, like a CF$_3$ group) has the smallest *trans* influence. These results are in agreement with the polarization theory [8] and the σ-*trans* effect [9] since the oxygen atom nearest to the most electronegative group will be the least polarizable and also a weaker σ-donor. The crystal structure of [Rh(TFDMAA)(CO)(PPh$_3$)], synthesized according to the following reaction:

$$[\mathrm{Rh(TFDMAA)(CO)_2}] + \mathrm{PPh_3} \rightarrow [\mathrm{Rh(TFDMAA)(CO)(PPh_3)}] + \mathrm{CO} \qquad (1)$$

has been determined to lend extra support to the above mentioned conclusions about the *trans* influences of the different ligands in square planar complexes of rhodium(I).

Experimental

[Rh(TFDMAA)(CO)$_2$] was prepared by adding an equivalent amount of 1,1,1-trifluoro-5,5-dimethyl-

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*Author to whom correspondence should be addressed.

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TABLE I. Fractional Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations in Parentheses. Positional Parameters (×10^4) and Thermal Parameters (×10^3).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	2019.7(6)	38.6(5)	2607.8(4)	56(1)	46(1)	53(1)	3(1)	18(1)	13(1)
P	1206(2)	1956(2)	3586(2)	41(1)	43(1)	52(1)	−1(1)	12(1)	12(1)
O(1)	2203(6)	842(5)	1459(4)	81(3)	64(3)	67(3)	3(2)	28(3)	25(3)
O(2)	2612(6)	−1799(5)	1665(4)	84(3)	55(3)	55(3)	12(2)	23(2)	9(2)
O(3)	1922(9)	−1153(6)	4261(5)	175(7)	71(4)	83(4)	6(4)	55(4)	31(3)
C(1)	2885(10)	−3491(8)	179(6)	89(6)	76(5)	62(5)	1(4)	24(4)	2(4)
C(2)	2684(8)	−2004(8)	709(6)	62(4)	66(5)	59(5)	4(4)	17(3)	12(4)
C(3)	2612(9)	−1139(8)	−139(6)	84(5)	70(5)	64(5)	0(4)	30(4)	18(4)
C(4)	2445(9)	244(8)	560(6)	66(5)	85(6)	58(5)	−3(4)	16(4)	25(4)
C(5)	2632(12)	1107(10)	−130(8)	113(7)	96(7)	102(7)	−15(6)	12(6)	57(6)
C(6)	1172(12)	1654(13)	−547(10)	82(6)	189(12)	151(10)	−20(7)	−9(6)	120(9)
C(7)	3654(11)	2262(10)	538(8)	101(6)	109(7)	103(7)	−36(6)	15(5)	45(6)
C(8)	1946(9)	−667(7)	3616(8)	78(5)	48(4)	70(5)	8(3)	28(4)	9(4)
C(9)	−843(7)	2091(7)	3402(5)	40(3)	56(4)	45(3)	−4(3)	7(3)	10(2)
C(10)	−1636(8)	3305(8)	3397(6)	50(4)	69(5)	78(5)	9(3)	17(4)	18(4)
C(11)	−3220(9)	3367(9)	3248(7)	53(4)	98(6)	86(6)	9(4)	18(4)	22(5)
C(12)	−3966(9)	2242(10)	3119(7)	50(4)	114(7)	73(5)	−9(4)	15(4)	21(5)
C(13)	−3171(9)	1051(10)	3122(7)	62(5)	106(7)	94(6)	−22(5)	21(4)	25(5)
C(14)	−1592(8)	959(8)	3256(7)	55(4)	75(5)	87(5)	−14(4)	17(4)	26(4)
C(15)	1650(7)	3432(6)	3320(6)	48(4)	43(3)	65(4)	3(3)	21(3)	10(3)
C(16)	2656(8)	4345(7)	4066(6)	60(4)	54(4)	81(5)	−9(3)	18(4)	15(4)
C(17)	3005(9)	5459(8)	3810(8)	77(5)	64(5)	101(6)	−15(4)	25(5)	20(5)
C(18)	2363(10)	5630(8)	2821(8)	92(6)	58(5)	99(6)	3(4)	44(5)	24(5)
C(19)	1347(10)	4721(8)	2085(7)	93(6)	58(5)	82(5)	5(4)	35(5)	26(4)
C(20)	1003(9)	3616(7)	2335(6)	75(5)	57(4)	64(4)	7(4)	20(4)	24(4)
C(21)	1936(7)	2271(6)	4999(5)	47(4)	46(3)	53(4)	−1(3)	11(3)	13(3)
C(22)	1030(8)	2830(7)	5703(6)	66(4)	65(4)	54(4)	6(3)	17(3)	11(3)
C(23)	1650(10)	3084(9)	6787(6)	93(6)	87(6)	61(5)	8(5)	15(4)	18(4)
C(24)	3171(11)	2778(9)	7148(7)	89(6)	88(6)	65(5)	−7(5)	3(5)	21(4)
C(25)	4065(9)	2215(9)	6450(7)	65(5)	84(6)	74(5)	−14(5)	−2(4)	27(4)
C(26)	3458(8)	1942(7)	5366(6)	51(4)	70(5)	67(6)	−5(3)	7(3)	23(4)
F(1)	3997(7)	−4058(6)	707(5)	138(5)	96(4)	118(4)	43(3)	−2(4)	−11(3)
F(2)	1675(7)	−4140(5)	112(5)	142(5)	86(3)	128(4)	−24(3)	42(4)	7(3)
F(3)	3013(8)	−3767(4)	−790(4)	205(6)	101(4)	78(3)	−3(4)	65(4)	−2(3)

pentanedione to a solution of $[Rh_2Cl_2(CO)_4]$ (obtained by refluxing a solution of 0.2 g $RhCl_3 \cdot 3H_2O$ in 20 cm^3 dimethylformamide for approximately 30 minutes) in dimethylformamide. About 50 cm^3 cold water was added to this solution to precipitate the reaction product, $[Rh(TFDMAA)(CO)_2]$. The precipitate was removed by centrifuging and washed with water. It was recrystallized from acetone. $[Rh(TFDMAA)(CO)(PPh_3)]$ was prepared by adding an equivalent amount of triphenylphosphine to a solution of $[Rh(TFDMAA)(CO)_2]$ in acetone. The product was recrystallized from petroleum benzine (boiling point 50–70 °C). Yellow crystals, suitable for X-ray analysis, were obtained. Crystal data: $C_{26}H_{23}O_3F_3PRh$, molecular weight 575.35, triclinic space group $P\bar{1}$, a = 9.215 Å, b = 10.584 Å, c = 13.760 Å, α = 107.61°, β = 104.79°, γ = 83.54°, $Z = 2$, μ(MoKα) = 7.17 cm^{-1}. The three dimensional intensity data were collected for θ values between 3° and 23° on a Philips PW 1100 four circle single crystal X-ray diffractometer using graphite monochromated MoKα radiation (λ = 0.7107 Å). A crystal with dimensions 0.25 × 0.28 × 0.30 mm^3 was used for the data collection. Three reflections were used as standards and remeasured after every 60 reflections to monitor any possible changes. No decomposition of the crystal was detectable during the data collection. A total of 3408 independent reflections were measured. 2980 of these were considered as observed. Only Lorentz and polarization corrections were applied.

The coordinates of the rhodium atom were determined from a three dimensional Patterson function. A subsequent Fourier map, phased by the rhodium atom, gave the positions of all the remaining non-hydrogen atoms. A full matrix least squares refinement, using all the observed reflections and anisotropic temperature parameters for all the atoms,

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

Rh–O(1)	2.057(6)	C(9)–C(10)	1.406(10)
Rh–O(2)	2.089(4)	C(10)–C(11)	1.418(10)
Rh–P	2.239(2)	C(11)–C(12)	1.383(14)
Rh–C(8)	1.781(9)	C(12)–C(13)	1.386(13)
O(1)–C(4)	1.271(9)	C(13)–C(14)	1.415(11)
C(4)–C(5)	1.552(15)	C(14)–C(9)	1.387(11)
C(5)–C(6)	1.451(14)	C(15)–C(16)	1.401(8)
C(5)–C(7)	1.537(13)	C(16)–C(17)	1.418(13)
C(3)–C(4)	1.409(11)	C(17)–C(18)	1.397(14)
C(2)–C(3)	1.360(13)	C(18)–C(19)	1.399(11)
C(2)–O(2)	1.285(9)	C(19)–C(20)	1.404(13)
C(2)–C(1)	1.534(10)	C(20)–C(15)	1.397(10)
C(1)–F(1)	1.298(10)	C(21)–C(22)	1.393(10)
C(1)–F(2)	1.344(11)	C(22)–C(23)	1.407(11)
C(1)–F(3)	1.308(10)	C(23)–C(24)	1.398(12)
C(8)–O(3)	1.159(12)	C(24)–C(25)	1.381(13)
P–C(9)	1.835(6)	C(25)–C(26)	1.404(11)
P–C(15)	1.820(8)	C(26)–C(21)	1.407(9)
P–C(21)	1.826(6)		

TABLE III. Bond angles (degrees) with Estimated Standard Deviations in Parentheses.

P–Rh–C(8)	87.2(2)
P–Rh–O(1)	93.7(1)
O(1)–Rh–O(2)	87.5(2)
O(2)–Rh–C(8)	91.7(3)
C(4)–O(1)–Rh	128.4(5)
C(3)–C(4)–O(1)	126.0(9)
C(3)–C(4)–C(5)	116.4(7)
C(5)–C(4)–O(1)	117.6(7)
C(4)–C(5)–C(6)	109.1(10)
C(4)–C(5)–C(7)	109.9(8)
C(6)–C(5)–C(7)	108.4(8)
C(2)–C(3)–C(4)	122.7(7)
C(2)–O(2)–Rh	123.5(5)
C(3)–C(2)–O(2)	130.8(6)
C(1)–C(2)–C(3)	118.5(7)
C(1)–C(2)–O(2)	110.7(7)
F(1)–C(1)–C(2)	113.0(6)
F(2)–C(1)–C(2)	110.6(7)
F(3)–C(1)–C(2)	113.9(8)
Rh–P–C(9)	113.2(2)
Rh–P–C(15)	114.8(2)
Rh–P–C(21)	115.0(2)
Rh–C(8)–O(3)	178.2(7)
P–C(9)–C(10)	121.0(6)
C(10)–C(9)–C(14)	120.8(6)
C(9)–C(10)–C(11)	119.3(7)
C(10)–C(11)–C(12)	120.0(7)
C(11)–C(12)–C(13)	120.1(7)
C(12)–C(13)–C(14)	121.0(9)
C(13)–C(14)–C(9)	118.8(7)
P–C(15)–C(16)	121.3(6)
C(16)–C(15)–C(20)	120.3(7)
C(15)–C(16)–C(17)	119.2(7)
C(16)–C(17)–C(18)	120.1(7)
C(17)–C(18)–C(19)	120.3(9)
C(18)–C(19)–C(20)	119.7(8)
C(19)–C(20)–C(15)	120.4(6)
P–C(21)–C(22)	121.7(4)
C(22)–C(21)–C(26)	120.3(6)
C(21)–C(22)–C(23)	119.7(6)
C(22)–C(23)–C(24)	119.7(8)
C(23)–C(24)–C(25)	120.5(7)
C(24)–C(25)–C(26)	120.3(7)
C(21)–C(26)–C(25)	119.4(7)

resulted in the residual factor *R* = 4.6% after 6 cycles.

The atomic scattering factors were those tabulated by Cromer and Waber [10]. A list of the observed and calculated structure factors may be obtained from the authors. The final atomic coordinates and anisotropic thermal parameters with their standard deviations are listed in Table I.

Results and Discussion

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

The calculation of the best plane through the coordination polyhedron showed it to be planar as expected for dsp^2 hybridization. The C–C, C–F and C–O bond lengths within the β-diketonato ligand compare well with those found in other β-diketone complexes of rhodium(I) [3, 6, 11]. The calculation of the best plane through the atoms of the chelate ring showed no significant deviation from a plane. The Rh–O bond distances compare also well with those found in other complexes [3, 6, 11]. The two Rh–O bond distances differ by 0.032 Å, see Table II. The Rh–O bond *trans* to the triphenylphosphine group is thus significantly longer than the other Rh–O bond length. This indicates, in agree-

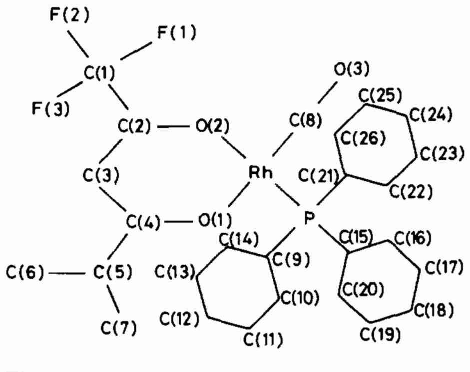

Fig. 1. The system of numbering of the atoms in the molecule.

ment with previous findings [11, 12], that the PPh_3 group has a larger *trans* influence than the carbonyl group.

The Rh–P bond distance is 2.239 Å which is in agreement with the Rh–P bond length found in [Rh(acac)(CO)(PPh_3)] [11], [Rh(BPHA)(CO)(PPh_3)] [4] and [Rh(TTA)(CO)(PPh_3)] [3]. These bond distances are however significantly shorter than the Rh–P bond length in [Rh(oxine)(CO)(PPh_3)] [5]. The PPh_3 group in the last mentioned complex is *trans* to the nitrogen atom of 8-hydroxyquinoline. These results indicate that the nitrogen atom in 8-hydroxyquinoline has a much larger *trans* influence than the oxygen atom of a β-diketone or β-diketone-like ligand.

The phosphorous atom is tetrahedrally surrounded by the rhodium atom and three carbon atoms of the phenyl rings. The calculation of the best planes through the atoms of the phenyl rings of the PPh_3 group showed that they are planar, within experimental error. The Rh–C–O chain is approximately linear, 178.2°, with the C–O bond distance 1.159 Å which is the same as found in other complexes of the same type [3–5].

This crystal structure determination showed that the carbonyl group *trans* to the oxygen atom nearest to the electronegative CF_3 group has been substituted by the PPh_3 ligand during the reaction:

$$[\mathrm{Rh(TFDMAA)(CO)_2}] + \mathrm{PPh_3} \rightarrow [\mathrm{Rh(TFDMAA)(CO)(PPh_3)}] + \mathrm{CO}$$

This result indicates, in contrast to the conclusions based upon the structure determinations of [Rh-TTA(CO)(PPh_3)], [Rh(BPHA)(CO)(PPh_3)] and [Rh-TFBA(CO)(PPh_3)], that the oxygen atom nearest to the electronegative CF_3 group has the largest *trans* influence. This result is also in contrast to the polarization theory and the *σ-trans* effect [8, 9] mentioned in the Introduction.

A possible explanation for this inconsistency may be found in the structure of the five coordinated reaction intermediate for the displacement of the carbonyl group according to reaction (1): the kinetic results of the substitution of the carbonyl groups in complexes of the type [Rh(β-diketone)($(CO)_2$)] indicated that these reactions proceed *via* an associative mechanism [14]. If the expected isomer (according to the results of the above mentioned structure determinations) is to be formed during this reaction, the oxygen atom next to the bulky $-CH(CH_3)_2$, leaving CO and incoming PPh_3 groups have to occupy the trigonal plane of the trigonal bipyramidal transition state. Such a reaction intermediate will probably be unstable due to steric hindrance between these bulky groups so that the other isomer (obtained *via* the intermediate with less steric hindrance) will be formed during this reaction.

This explanation will be investigated by means of further structure determinations on similar complexes containing more bulky substituents on the β-diketone ligands.

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