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The Crystal Structure of Acetylacetonatocarbonyltriphenylphosphinerhodium(I)

J. G. LEIPOLDT, S. S. BASSON, L. D. C. BOK and T. I. A. GERBER

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

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It is well known that one of the carbonyl groups in complexes of the type [Rh(β-diketone)(CO)$_2$] can be substituted by triphenylphosphine and -arsine [1]. The two Rh–O bond distances in [Rh(acac)(CO)$_2$] are equal within experimental error [2], while the Rh–O bond distance (oxygen atom *trans* to the PPh$_3$ group) in [Rh(TTA)(CO)(PPh$_3$)] is longer by 0.033Å (more than 3σ) than the other Rh–O bond distance [3]. Because thenoyltrifluoroacetone (TTA) is not a symmetrical β-diketone, it is difficult to determine whether this difference is due to the effect of the different substituents of the β-diketone or the relative *trans* effects of CO and PPh$_3$. The crystal structure of acetylacetonatocarbonyltriphenylphosphinerhodium-(I), [Rh(acac)(CO)(PPh$_3$)], has been determined as part of a project for the study of substitution reactions of compounds of the type of [Rh(β-diketone)-(CO)$_2$] and to determine the relative effects of PPh$_3$ and CO on the Rh–O (β-diketone) bond strengths.

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 [4]. An equimolar amount of acetylacetone was added to the resulting yellow solution. The solution was diluted with water, and the precipitate ([Rh(acac)(CO)$_2$]) was removed by centrifuging and washed with petroleum ether. [Rh(acac)(CO)(PPh$_3$)] was prepared from [Rh(acac)(CO)$_2$] as described by Bonati and Wilkinson [1], and chromatographed on alumina using chloroform as eluant. Crystallization from

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

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	2392.0(5)	–46.7(5)	672.4(6)	39(1)	35(1)	32(1)	11(0)	12(0)	4(0)
P	3421(1)	1945(2)	2433(2)	36(1)	32(1)	26(1)	10(1)	13(1)	7(1)
C(1)	–286(7)	1157(9)	–2812(11)	57(5)	66(6)	72(6)	26(4)	3(4)	25(5)
C(2)	369(6)	220(7)	–2046(9)	35(4)	57(5)	44(4)	10(3)	14(3)	15(4)
C(3)	13(6)	–1144(8)	–2833(9)	40(4)	52(5)	56(5)	7(4)	16(4)	8(4)
C(4)	526(6)	–2099(7)	–2242(9)	36(4)	50(4)	43(4)	1(3)	17(4)	–2(3)
C(5)	4(6)	–3572(8)	–3198(10)	53(5)	47(5)	69(6)	–1(4)	14(4)	–17(4)
C(6)	3481(7)	–744(7)	1808(9)	54(5)	36(4)	49(4)	7(4)	14(4)	2(3)
C(7)	3219(5)	2178(6)	4372(7)	30(4)	43(4)	29(3)	4(3)	15(3)	5(3)
C(8)	3122(6)	1091(7)	5139(8)	46(4)	50(4)	42(4)	11(3)	19(3)	15(3)
C(9)	2928(7)	1233(8)	6600(9)	59(5)	66(5)	38(4)	10(4)	23(4)	15(4)
C(10)	2840(6)	2456(8)	7270(9)	46(5)	73(6)	35(4)	4(4)	15(3)	1(4)
C(11)	2951(7)	3547(8)	6542(9)	56(5)	60(5)	38(4)	10(4)	21(4)	–1(4)
C(12)	3147(6)	3414(7)	5070(8)	47(4)	41(4)	35(4)	6(3)	19(3)	–2(3)
C(13)	3138(6)	3414(6)	1635(7)	51(4)	33(4)	26(3)	18(3)	17(3)	10(3)
C(14)	4003(7)	4418(6)	1512(8)	75(5)	30(4)	33(4)	7(3)	24(4)	6(3)
C(15)	3731(8)	5512(7)	850(9)	86(6)	41(4)	42(4)	16(4)	25(4)	9(3)
C(16)	2618(8)	5587(8)	299(9)	99(7)	41(5)	44(4)	28(5)	25(5)	11(4)
C(17)	1770(7)	4593(8)	441(10)	75(6)	55(5)	52(5)	37(5)	20(4)	15(4)
C(18)	2032(6)	3513(7)	1114(8)	53(5)	49(4)	36(4)	27(4)	17(3)	7(3)
C(19)	4948(6)	2273(6)	3091(8)	42(4)	35(4)	38(4)	12(3)	22(3)	14(3)
C(20)	5698(6)	2828(7)	4725(9)	43(5)	45(4)	44(4)	11(3)	14(3)	4(3)
C(21)	6857(7)	3004(9)	5189(11)	42(5)	69(6)	69(6)	14(4)	16(4)	12(4)
C(22)	7274(7)	2630(9)	4007(12)	52(5)	62(5)	86(7)	17(4)	35(5)	26(5)
C(23)	6525(7)	2094(8)	2371(11)	60(6)	62(5)	69(6)	23(4)	38(5)	25(4)
C(24)	5367(6)	1902(7)	1910(9)	59(5)	45(4)	50(4)	19(4)	32(4)	16(3)
O(1)	1230(4)	778(5)	–703(6)	42(3)	46(3)	42(3)	15(2)	4(2)	6(2)
O(2)	1415(4)	–1904(5)	–942(6)	51(3)	42(3)	50(3)	14(2)	16(3)	–2(2)
O(3)	4204(5)	–1173(6)	2486(8)	68(4)	56(4)	97(5)	29(3)	–1(4)	23(3)

acetone gave stable yellow crystals which were triclinic, space group $P\bar{1}$ with a = 13.20Å, b = 10.45Å, c = 8.90Å, α = 97.05°, β = 110.85°, γ = 103.15° and Z = 2. The three dimensional intensity data were measured with a Philips four single crystal X-ray diffractometer, using Mo(Kα) radiation. 3030 reflections were measured, of which 2493 were considered as observed. A crystal with the dimensions 0.12 X 0.13 X 0.16 mm^3 was used for the data collection. Lorentz and polarization corrections were applied.

The structure was solved using the X-ray 72 system of programs on a Univac 1100 computer. The rhodium atom was located form a three dimensional Patterson function. All the other non-hydrogen atoms were located from successive Fourier analyses. A full-matrix least squares refinement, using all the observed reflections and anisotropic temperature factors for all the atoms, gave R = 0.043 after four cycles.

A table of the observed and calculated structure factors may be obtained from the authors. The final atomic and thermal parameters and their standard deviations are listed in Table I.

Results and Discussion

The system of numbering of the atoms in the molecule is shown in Figure 1. The bond lengths and bond angles are given in Tables II and III respectively.

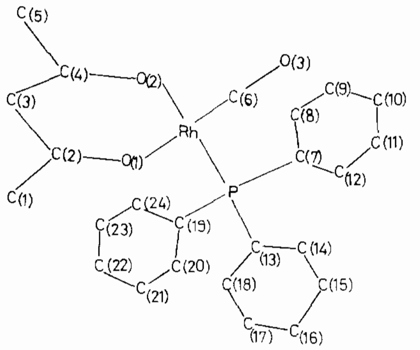

Figure 1. System of numbering of the atoms in the molecule.

The rhodium atom has a square planar coordination with the two Rh–O (acac) bond distances 2.087Å and 2.029Å. The Rh–C and Rh–P bond distances are 1.801Å and 2.244Å respectively. The calculation of the best plane through the atoms of the coordination polyhedron, *i.e.* Rh, O(1), O(2), C(6) and P showed no significant deviation from a flat plane. The O–Rh–O and C–Rh–P bond angles, 87.9° and 87.8° respectively, are about the same as in [Rh(TTA)(CO)(PPh$_3$)]. The Rh–C–O chain is approximately linear, 176.8°, with the C–O bond distance of 1.153Å, which is the same as found in [Rh(TTA)(CO)(PPh$_3$)] and [Rh(acac)(CO)$_2$].

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

Rh–O(1)	2.029(5)	C (9)–C(10)	1.391(13)
Rh–O(2)	2.087(4)	C(10)–C(11)	1.393(12)
Rh–C(6)	1.801(8)	C(11)–C(12)	1.404(12)
Rh–P	2.244(2)	C (7)–C(12)	1.402(10)
C(1)–C(2)	1.517(13)	C(13)–C(14)	1.410(10)
C(2)–C(3)	1.399(10)	C(14)–C(15)	1.409(11)
C(3)–C(4)	1.385(12)	C(15)–C(16)	1.398(15)
C(4)–C(5)	1.533(10)	C(16)–C(17)	1.398(13)
C(4)–O(2)	1.275(8)	C(17)–C(18)	1.396(12)
C(2)–O(1)	1.274(7)	C(13)–C(18)	1.398(11)
C(6)–O(3)	1.153(11)	C(19)–C(20)	1.393(8)
P–C(7)	1.834(8)	C(20)–C(21)	1.397(12)
P–C(13)	1.828(7)	C(21)–C(22)	1.405(16)
P–C(19)	1.822(7)	C(22)–C(23)	1.391(11)
C(7)–C(8)	1.400(11)	C(23)–C(24)	1.392(12)
C(8)–C(9)	1.410(12)	C(19)–C(24)	1.404(12)

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

O(1)–Rh–O(2)	87.9(2)	C(4)–O(2)–Rh	125.6(5)
O(1)–Rh–P	92.0(1)	C(3)–C(4)–C(5)	119.1(6)
C(6)–Rh–P	87.8(2)	C(3)–C(2)–C(1)	119.7(6)
O(2)–Rh–C(6)	92.4(2)	Rh–C(6)–O(3)	176.8(9)
Rh–O(1)–C(2)	128.7(5)	Rh–P–C(7)	114.8(2)
O(1)–C(2)–C(3)	125.3(7)	Rh–P–C(13)	114.7(2)
C(2)–C(3)–C(4)	125.0(6)	Rh–P–C(19)	114.4(2)
C(3)–C(4)–O(2)	127.2(6)		

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(acac)(CO)$_2$] and indicate 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.

The phosphorus 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 three phenyl rings is planar within the experimental error, while the bond lengths between these carbon atoms are the same as in other phenyl compounds. The mean P–C distance is 1.828Å, the same as in [Rh(TTA)(CO)(PPh$_3$)].

The significant difference in the two Rh–O bond distances (Rh–O(1) = 2.029(5)Å and Rh–O(2) = 2.087(4)Å) indicates that the triphenylphosphine group has a larger *trans* effect than the CO group in this type of compounds. The effect of the PPh$_3$ group is also observed in comparing this difference in the Rh–O bond distances with those found in [Rh(acac)(CO)$_2$] where the two chemically equivalent Rh–O bond distances are the same within the experimental error, *i.e.* 2.040Å and 2.044Å.

The Rh–C bond distances in [Rh(TTA)(CO)(PPh$_3$)] and [Rh(acac)(CO)(PPh$_3$)] are 1.780(12) and 1.801(8)Å respectively. Although this difference is only about twice the standard deviation it indicates that the enolate oxygen nearest to a CH$_3$-group has a larger *trans* effect than an oxygen atom nearest to a CF$_3$-group. This is in agreement with the polarization theory [5], since the oxygen atom nearest to the CF$_3$-group will be least polarizable as a result of the electron-attracting power of a CF$_3$-group.

These conclusions about the relative *trans* effects in this type of compounds are important in the study of the substitution reactions of these compounds, and may give valuable information about the mechanism and structure of the products of such reactions.

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References

1 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).
2 F. Huq and A. C. Skapski, *J. Cryst. Mol. Struct.*, *4*, 411 (1974).
3 J. G. Leipoldt, L. D. C. Bok, J. S. van Vollenhoven and A. I. Pieterse, *J. Inorg. Nucl. Chem.*, (in the press, 1977).
4 Yu. S. Varshavskii and T. G. Cherkasova, *Russ. J. Inorg. Chem.*, *12*, 1709 (1967).
5 A. A. Grinberg, *Acta Physicochim. U.R.S.S.*, *3*, 573 (1945).