Inorganica Chimica Acta, 126 (1987) 25–28

The Crystal Structure of Thioacetylacetonatocarbonyltriphenylphosphinerhodium(I)

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(Received June 25, 1986)

Abstract

Thioacetylacetonatocarbonyltriphenylphosphinerhodium(I) was synthesized by means of the reaction between [Rh(Sacac)(CO)$_2$] and PPh$_3$. It crystallized in the triclinic space group $P\bar{1}$ with $a = 8.820(3)$, $b = 10.812(2)$, $c = 13.569(3)$ Å, $\alpha = 67.41(2)°$, $\beta = 72.90(2)°$ and $\gamma = 85.48(2)°$. The structure was determined from 2811 observed reflections. The final R value was 0.045. The carbonyl group *trans* to the sulphur atom was substituted during the reaction. This result as well as the Rh–P bond length indicated that the sulphur atom of Sacac has a greater *trans* influence than the oxygen atom.

Introduction

The fact that only one of the carbonyl groups in complexes of the type [Rh(LL′)(CO)$_2$] (where LL′ = monocharged bidentate ligands such as β-diketones, 8-hydroxyquinoline and 2-picolinic acid) can be substituted by triphenylphosphine [1] was used to determine the relative *trans* influence of the two bonded atoms of LL′ for a number of bidentate ligands [2–11] since it may be assumed that the carbonyl group *trans* to the atom with the largest *trans* influence will be substituted by PPh$_3$. The results in general indicated that the less electronegative donor atom of LL′ has the greater *trans* influence. This is the expected result according to the σ-*trans* effect [12] since the most electronegative atom will be the weaker σ-electron donor.

The crystal structure determination of compounds **9**–**12** (see Table IV) indicate that the nitrogen atom of the chelate ring has a larger *trans* influence than the oxygen atom. The crystal structure determination of the corresponding β-diketone complexes however indicated that when there is a relative small difference in the bonding capability of the two donor atoms (such as in non-symmetrical β-diketones) the electronic effect may be dominated by steric hindrance caused by large substituent groups on the β-diketone [5–8].

The conclusions based on the determination of the specific isomer formed during the substitution of one of the CO groups in [Rh(LL′)(CO)$_2$] by PPh$_3$ were also confirmed by determination of the two Rh–S distances in [Rh(Ox)(COD)] and [Rh(TFBA)(COD)] [13, 14], where S is the centre of the carbon–carbon double bonds in 1,5-cyclooctadiene. The Rh–S distance *trans* to the nitrogen atom (in the case of Ox) and *trans* to the oxygen atom nearest to phenyl group (in the case of TFBA) was significantly longer than the other Rh–S distance indicating that these atoms have the largest *trans* influence.

The average Rh–P bond distance (P *trans* to an oxygen atom) is 2.240(3) Å [2–8] while this distance is 2.265(3) Å when the phosphorous atom is *trans* to a nitrogen atom [9–12]. These results thus indicated that the nitrogen atom has a greater *trans* influence than an oxygen atom. The crystal structure of [Rh(Sacac)(CO)(PPh$_3$)] has been determined to correlate the relative *trans* influences of oxygen, nitrogen and sulphur atoms in these type of complexes and also to observe which specific isomer will be formed in the latter complex.

Experimental

[Rh(Sacac)(CO)$_2$] was prepared by adding a slight excess of HSacac (synthesized by the method of Duus and Anthonsen [15]) to a solution of [Rh$_2$Cl$_2$(CO)$_4$] in dimethylformamide, obtained by refluxing a solution of 0.3 g RhCl$_3$·3H$_2$O in 30 ml DMF for 30 min [16]. Cold water was added to this solution to precipitate the red reaction product [Rh(Sacac)(CO)$_2$]. The precipitate was removed by centrifuging and washed with water to remove the DMF and excess HSacac. [Rh(Sacac)(CO)(PPh$_3$)] was prepared by adding an equivalent amount of triphenylphosphine to a solution of [Rh(Sacac)(CO)$_2$] in acetone. The resulting yellow crystals were recrystallized from acetone to yield well-shaped crystals suitable for X-ray analysis. A microscopic examination of the crystals at a stage of nearly complete evaporation of the solvent clearly showed that only one isomer formed during the reaction. Crystal data: RhC$_{24}$H$_{22}$O$_2$SP, molecular mass 508.38, triclinic

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0020-1693/87/$3.50

space group $P\bar{1}$, $a = 8.820(3)$, $b = 10.812(2)$, $c = 13.569(3)$ Å, $\alpha = 67.41(2)°$, $\beta = 72.90(2)°$, $\gamma = 85.48(2)°$, $Z = 2$, $D_m = 1.471$ g cm^{-3}, μ(Mo Kα) = 8.99 cm^{-1}. The three-dimensional intensity data were collected for θ values between 3 and 25° using Mo Kα radiation. A crystal with dimensions 0.70 × 0.37 × 0.24 mm was used for the data collection. Three reflections were used as standards and remeasured after every 60 reflections. The crystal remained stable during the data collection and 3907 reflections were measured of which 2811 were considered as observed. The data were corrected for Lorentz and polarization effects.

The coordinates of the rhodium atom were determined from a three-dimensional Patterson function. The positional parameters of the non-hydrogen atoms were deduced from a subsequent Fourier map. A full matrix least squares refinement, using all the observed reflections and anisotropic temperature parameters for all the atoms resulted in a R-value of 0.045. The atomic scattering factors were those tabulated by Cromer and Waber [17]. The final atomic coordinates with their standard deviations are listed in Table I. See also 'Supplementary Material'.

TABLE I. Final Positional Parameters (×10^4) with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z
Rh	1621.7(7)	−217.1(6)	2704.9(5)
P	896(2)	1823(2)	1614(1)
S	2334(3)	−2288(2)	3748(2)
O(1)	1891(5)	580(4)	3773(4)
O(2)	1493(9)	−1257(6)	1019(5)
C(1)	3587(12)	−3551(9)	5463(7)
C(2)	2970(9)	−2199(8)	4799(6)
C(3)	2998(9)	−1141(8)	5088(6)
C(4)	2455(8)	162(7)	4615(6)
C(5)	2509(10)	1172(8)	5117(7)
C(6)	1502(10)	858(7)	1679(7)
C(11)	1401(8)	3257(6)	1854(6)
C(12)	2448(8)	4296(7)	1020(6)
C(13)	2856(10)	5344(8)	1275(8)
C(14)	2252(11)	5373(9)	2326(8)
C(15)	1191(11)	4332(9)	3162(8)
C(16)	767(8)	3284(7)	2927(6)
C(21)	1814(7)	2243(6)	136(5)
C(22)	3415(8)	1894(7)	−202(6)
C(23)	4192(9)	2193(8)	−1331(7)
C(24)	3388(10)	2887(9)	−2126(7)
C(25)	1814(11)	3232(9)	−1793(7)
C(26)	1030(9)	2940(8)	−672(6)
C(31)	−1221(7)	1977(7)	1751(5)
C(32)	−1983(8)	3179(7)	1707(6)
C(33)	−3635(9)	3234(9)	1856(6)
C(34)	−4509(9)	2096(9)	2038(6)
C(35)	−3742(10)	919(9)	2076(7)
C(36)	−2105(8)	839(8)	1933(6)

Results and Discussion

The system of numbering of the atoms in the molecule is shown in Fig. 1 while the bond lengths and bond angles are given in Tables II and III respectively. The structure consists of well-separated molecular units. The X-ray powder photographs of [Rh(acac)(CO)(PPh$_3$)] and [Rh(Sacac)(CO)(PPh$_3$)] proved them to be isomorphous.

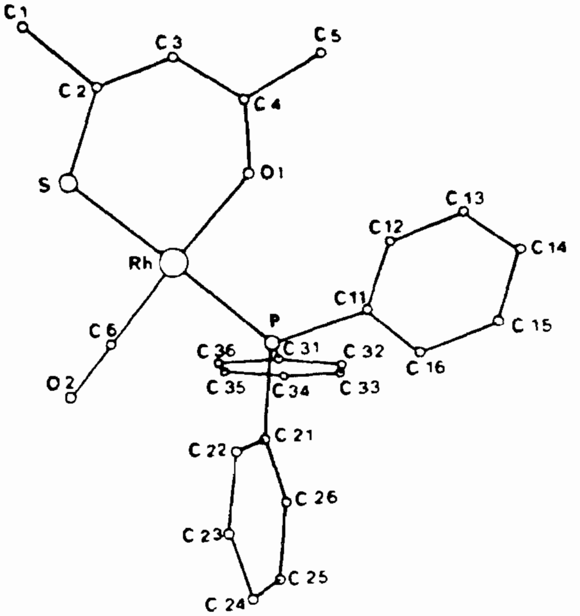


Fig. 1. Perspective view of the molecule with atom numbering scheme.

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

Rh–P	2.300(2)	P–C(31)	1.822(7)
Rh–O(1)	2.023(6)	S–C(2)	1.716(10)
Rh–C(6)	1.808(11)	C(1)–C(2)	1.547(12)
Rh–S	2.297(2)	C(2)–C(3)	1.348(14)
C(6)–O(2)	1.135(14)	C(3)–C(4)	1.416(10)
P–C(21)	1.813(7)	C(4)–C(5)	1.504(14)
P–C(11)	1.814(9)	C(4)–O(1)	1.288(10)

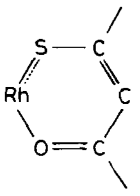
TABLE III. Bond Angles (°) with Estimated Standard Deviations in Parentheses

P–Rh–S	177.8(1)	S–C(2)–C(3)	128.8(6)
P–Rh–O(1)	90.4(1)	C(2)–C(3)–C(4)	128.1(9)
P–Rh–C(6)	88.1(2)	C(3)–C(4)–C(5)	119.1(8)
S–Rh–O(1)	91.7(1)	C(3)–C(4)–O(1)	125.6(9)
S–Rh–C(6)	89.7(2)	C(4)–O(1)–Rh	134.5(5)
O(1)–Rh–C(6)	176.0(3)	Rh–P–C(31)	115.4(2)
Rh–C(6)–O(2)	177.1(8)	Rh–P–C(21)	113.1(2)
Rh–S–C(2)	110.6(3)	Rh–P–C(11)	115.4(2)
S–C(2)–C(1)	112.0(7)		

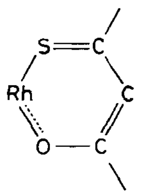
The Rh–C–O chain is linear and the Rh–C and C–O bond lengths are about the same as in similar complexes. The phosphorous atom is tetrahedrally surrounded by the rhodium atom and three carbon atoms of the phenyl rings. The P–C bond distances are about the same as found in [Rh(acac)(CO)(PPh$_3$)] [2]. The phenyl rings are planar within the experimental error while the bond lengths and angles within the rings (average C–C bond distance is 1.402(12) Å and C–C–C bond angle is 120.0(8)°) are the same as in other phenyl compounds.

All the ligand–rhodium–ligand angles are nearly 90° and the calculation of the best plane through the atoms of the coordination polyhedron showed it to be planar within the experimental error as can be expected for a dsp^2 square planar hybridization of metal orbitals.

The bond distances within the chelate ring compare well with those found in tris[benzoyl(thiobenzoyl)methanato]indium(III) [18]. All the carbon atoms of the chelate ring are of the sp^2 type as is evident from the sum of the bond angles and the planarity of the chelate ring. The rhodium atom is however displaced by a significant 0.19 Å out of the best plane through the chelate ring-atoms. The chelate ring forms an angle of 8.4° with the best plane through the four metal-bonded ligand atoms of the coordination polyhedron. Two resonance forms A and B are possible:



A



B

The C(2)–C(3) and C(3)–C(4) bond distances differ by a significant 0.068 Å, indicating that the resonance form A contributes more significantly to the structure than B. This may be explained by the fact that the sulphur atom has the capability to form a π-bond with the rhodium atom.

This crystal structure determination showed that the carbonyl group *trans* to the sulphur atom was substituted during the reaction [Rh(Sacac)(CO)$_2$] + PPh$_3$ → [Rh(Sacac)(CO)(PPh$_3$)] + CO. This result indicates that the sulphur atom has a larger *trans* influence than the oxygen atom. The larger *trans* influence of the sulphur atom (relative to the oxygen atom) may be explained by its π-bonding capability which results in a weakening of the *trans* orientated Rh–C bond in agreement with the π-*trans* effect [12].

The large *trans* influence of the sulphur atom is also observed in the rhodium–phosphorous bond distance. The Rh–P bond distances for a number of similar structures are listed in Table IV. These compounds can be divided into three groups according to the Rh–P bond distances. The average Rh–P bond distance *trans* to an oxygen atom (compounds **1**–**8**) is 2.240(3) Å while the average Rh–P bond distance *trans* to a nitrogen atom (compounds **9**–**12**) is 2.265(3) Å and that *trans* to a sulphur atom 2.300(2) Å as in the present case. These significant differences clearly indicate that the order of the *trans* influence of these atoms is S > N > O. This order may be explained as follows: The sulphur atom is the only atom capable of forming a strong π-bond with the rhodium atom (it is expected that a π-*trans* effect is greater than a σ-*trans* effect [12]) while the nitrogen atom being less electronegative than an oxygen atom is the better σ-donor of the two thus having a larger σ-*trans* effect than the oxygen atom.

TABLE IV. Rh–P Bond Distances in Complexes of the Type [Rh(LL')(CO)(PPh$_3$)]

Compound	LL'	Distance (Å)	Reference
1	acac	2.244(2)	2
2	BPHA	2.232(1)	3
3	TTA	2.245(3)	4
4	TROP	2.232(2)	5
5	TFTMAA	2.238(3)	6
6	TFDMAA	2.239(2)	7
7	TFHD[a]	2.252(3)	8
8	TFAA[b]	2.231(2); 2.243(2)	8
9	Ox	2.261(2)	9
10	Sal-NR	2.281(2)	10
11	Qui[c]	2.258(2)	d
12	Pic	2.262(2)	11
13	Sacac	2.300(3)	this work

[a] 1,1,1-Trifluoro-2,4-hexanedionate. [b] 1,1,1-Trifluoro-2,4-pentanedionate. [c] 2-Carboxyquinolinate. [d] Unpublished results.

Supplementary Material

A list of the observed and calculated structure factors and of the anisotropic thermal parameters may be obtained from the authors.

Acknowledgements

We thank the South African C.S.I.R. and the Research Fund of this University for financial support as well as Dr P. H. van Rooyen of the South African C.S.I.R. for the data collection.

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