Inorganica Chimica Acta, 119 (1986) L9–L11

Crystal Structure of *cis*-Diiodo(2,4-pentanedionato-*O,O'*)bis(triphenylphosphine)rhodium(III)

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(Received May 21, 1986)

The mechanism [1, 2] for the oxidative addition of iodomethane to [Rh(acac)(CO)(PX_3)] complexes (acac = 2,4-pentanedionato anion; X = ϕ-PhCl, Ph or ϕ-PhOMe) has been shown to proceed according to Scheme 1. All forward steps in the **A** → **D** conversion are slow. Attempts to prepare complex **D** in several solvents gave mixtures of **C** and **D** at infinite reaction times. [Rh(acac)(CO)(CH_3)(I)(PPh_3)] could, however, be extracted with Et_2O from the residue of an acetone preparation. This complex, when dissolved in 1,2-dichloroethane, is partially converted to the Rh(I) derivative, according to Scheme 1. The **D** → **C** carbonyl insertion reaction can thus be considered as a slow solvent assisted process. A kinetic study (to be published) showed no enhancement of the **D** → **C** conversion rate upon addition of PPh_3, but gave instead a fast substitution equilibrium with the 5-coordinated acetyl derivative **C**. Subsequent slow reactions of this substitution product led to the final isolation of [Rh(acac)$(I)_2$(PPh_3)$_2$] for which the structural results are reported here.

Experimental

[Rh(acac)(CO)(PPh_3)] was prepared from [Rh(acac)$(CO)_2$] as described previously [3]. The starting material **I**, consisting of a mixture of [Rh(acac)($COCH_3$)(I)(PPh_3)] and [Rh(acac)(CO)(CH_3)(I)(PPh_3)], was prepared as follows: [Rh(acac)(CO)(PPh_3)] (0.4 g) was dissolved with gentle heating in 20 cm^3 acetone containing 0.8 g CH_3I. The yellow solution gradually obtained an orange colour. Water (2 cm^3) was added after 1 h, followed by immediate solvent evaporation, using a strong air-current blowing on top of the solution. The mustard-yellow precipitate was dried *in vacuo* for 24 h. IR spectra (ν_{CO} = 2056 and 1724 cm^{-1}, KBr disk, [2]) confirmed the mixture's compositon.

[Rh(acac)$(I)_2$(PPh_3)$_2$] (**II**) was prepared as follows: to 50 mg of **I**, dissolved in 1.5 cm^3 acetone, was added 21 mg PPh_3 (total Rh:P = 1:1). The solution, covered with a perforated plastic film, was allowed to evaporate slowly (6 h) to give ruby-red monoclinic crystals of **II**. Single crystals for the structure determination were obtained by recrystallization from a 1:1 dichloromethane/acetone solution.

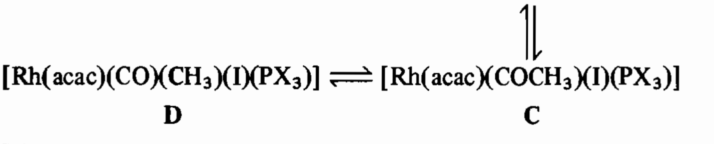
Crystal Data

$RhC_{41}H_{37}O_2I_2P_2$, molecular weight 980.3, space group $P2_1/c$, a = 13.038(4), b = 18.481(2), c = 17.082(6) Å, β = 113.57(4)°, Z = 4, V = 3772.8 Å^3, D_m = 1.72 g cm^{-3}, μ = (Mo Kα) = 22.1 cm^{-1}. Mo K$\bar{\alpha}$ radiation (graphite monochromator) λ = 0.71073 Å, $3 \leqslant \theta \leqslant 25°$, crystal dimensions 0.18 × 0.04 × 0.25 mm was used for intensity data collection. Final R and R_w values were 0.129 and 0.146 respectively for 2378 observed reflections [$I > 3\sigma(I)$] of 6793 independent reflections measured on an Enraf-Nonius CAD4F diffractometer. The intensity data were corrected for Lorentz, polarization and absorption effects.

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 function and all the other non-hydrogen atoms from a series of difference Fourier syntheses interspersed with least-squares refinement cycles. Scattering factors [4] were corrected for anomalous dispersion in the case of rhodium and iodine. Final atomic coordinates are listed in Table I.

Results and Discussion

The structural packing consists of discrete molecules, each having the stereochemistry shown in Fig. 1 and bond distances and angles as given in Tables II and III respectively. The bond distances of the



Scheme 1.

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TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) with Estimated Standard Deviations in Parentheses for [$Rh(acac)(I)_2(PPh_3)_2$]

Atom[b]	x	y	z	U or U_{eq}
Rh	−2179(2)	1488(1)	2146(1)	15(1)[a]
I(1)	−2552(2)	197(1)	2589(2)	49(1)[a]
I(2)	−1350(3)	2017(2)	3711(2)	66(2)[a]
P(1)	−4034(6)	1830(4)	1960(4)	20(2)[a]
P(2)	−324(6)	1114(4)	2385(4)	22(2)[a]
O(1)	−2800(15)	1139(10)	893(12)	26(5)
O(2)	−1865(17)	2499(11)	1770(13)	32(5)
C(1)	−3342(35)	1100(23)	−607(27)	63(11)
C(2)	−2874(27)	1492(18)	238(21)	42(8)
C(3)	−2538(25)	2206(16)	274(19)	37(7)
C(4)	−2079(29)	2611(19)	1031(23)	46(9)
C(5)	−1798(30)	3464(21)	870(23)	55(10)
C(11)	−5010(26)	1644(17)	850(20)	37(8)
C(12)	−5349(25)	929(17)	603(20)	35(7)
C(13)	−6015(28)	812(18)	−219(21)	43(8)
C(14)	−6439(32)	1323(21)	−791(25)	61(10)
C(15)	−6078(31)	2033(20)	−566(24)	51(9)
C(16)	−5388(31)	2204(20)	287(23)	51(9)
C(21)	−4322(22)	2795(14)	2106(17)	24(6)
C(22)	−5338(29)	2974(20)	2198(22)	50(9)
C(23)	−5595(29)	3697(19)	2233(22)	47(9)
C(24)	−4930(26)	4217(17)	2167(19)	37(7)
C(25)	−3941(35)	4041(23)	2129(27)	65(11)
C(26)	−3659(31)	3323(21)	2058(24)	55(10)
C(31)	−4706(22)	1394(15)	2602(18)	26(6)
C(32)	−4051(27)	1312(17)	3486(20)	39(8)
C(33)	−4598(38)	1028(24)	3990(29)	74(12)
C(34)	−5730(36)	907(23)	3633(28)	66(11)
C(35)	−6326(32)	1025(21)	2817(25)	55(10)
C(36)	−2825(27)	1239(18)	2261(21)	42(8)
C(41)	629(25)	945(16)	3462(19)	32(7)
C(42)	1590(29)	1349(19)	3923(22)	47(9)
C(43)	2322(29)	1195(19)	4746(22)	46(8)
C(44)	2122(27)	602(18)	5121(21)	41(8)
C(45)	1201(28)	175(19)	4751(22)	45(8)
C(46)	431(27)	340(17)	3901(21)	40(8)
C(51)	376(23)	1822(15)	1995(18)	27(6)
C(52)	657(32)	1666(21)	1343(24)	56(10)
C(53)	1200(36)	2189(24)	1017(28)	68(12)
C(54)	1338(39)	2892(26)	1446(30)	76(13)
C(55)	1043(34)	3034(22)	2091(26)	62(11)
C(56)	513(29)	2466(19)	2399(22)	46(8)
C(61)	−198(22)	299(15)	1844(17)	25(6)
C(62)	−1046(39)	11(26)	1142(31)	76(13)
C(63)	−870(47)	−644(31)	679(35)	97(17)
C(64)	132(35)	−943(22)	1017(27)	64(11)
C(65)	883(41)	−777(27)	1725(32)	81(14)
C(66)	735(35)	−97(23)	2152(27)	66(11)

[a] Anisotropic refinement, $U_{eq} = (1/3)\Sigma_i\Sigma_j[U_{ij}(a_i^*a_j^*)(\bar{a}_i\bar{a}_j)]$.

[b] Carbon atom numbering, C(xy), with x = 1–3 refer to P(1)- and x = 4–6 to P(2)-bonded phenyl rings.

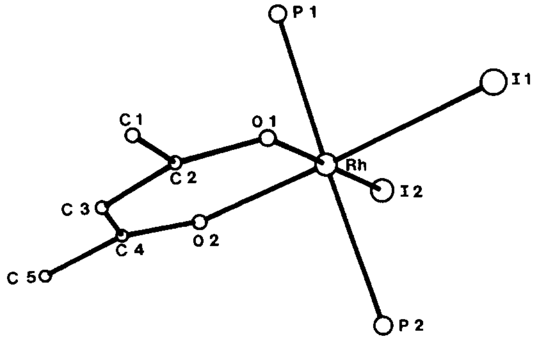

Fig. 1. Perspective view of the [$Rh(acac)(I)_2(PPh_3)_2$] molecule. Phenyl rings omitted for clarity.

acac ligand compare well with those of Rh(I) β-diketone complexes [3, 5–8] where the normal enolate type of resonance in the chelate ring gives C–O and C–C bonds of intermediate order. The two Rh–O bonds, being formed by a symmetrical ligand and each subjected to a small *trans* influence of iodine atoms, are thus of similar length and also comparable to those of the above Rh(I) complexes.

The Rh–I bond distances differ significantly by 0.031 Å irrespective of the same *trans* influence of the two oxygen atoms. The O(1), O(2), I(2), I(1) array is also planar with the rhodium atom displaced only 0.02 Å from this plane. Significant distortion is, however, observable in the widening of the I(1)–Rh–I(2) and accompanying reduction

TABLE II. Selected Bond Distances (Å) for [$Rh(acac)(I)_2(PPh_3)_2$] with Estimated Standard Deviations in Parentheses

Type	Distance
Rh–O(1)	2.07(2)
Rh–O(2)	2.07(2)
Rh–I(1)	2.606(3)
Rh–I(2)	2.637(4)
Rh–P(1)	2.395(8)
Rh–P(2)	2.388(8)
C(2)–O(1)	1.26(4)
C(4)–O(2)	1.20(4)
C(1)–C(2)	1.51(5)
C(2)–C(3)	1.39(5)
C(3)–C(4)	1.40(5)
C(4)–C(5)	1.67(5)
P(1)–C(11)	1.84(3)
P(1)–C(21)	1.86(3)
P(1)–C(31)	1.84(3)
P(2)–C(41)	1.79(3)
P(2)–C(51)	1.86(3)
P(2)–C(61)	1.81(3)

TABLE III. Selected Bond Angles (°) for [Rh(acac)(I)$_2$(PPh$_3$)$_2$] with Estimated Standard Deviations in Parentheses

Atoms	Angle
O(1)–Rh–P(1)	89.3(6)
O(1)–Rh–P(2)	92.1(6)
O(2)–Rh–P(1)	92.0(6)
O(2)–Rh–P(2)	90.0(6)
O(1)–Rh–O(2)	90.2(8)
I(1)–Rh–P(1)	89.1(2)
I(1)–Rh–P(2)	88.9(2)
I(1)–Rh–I(2)	95.4(1)
I(2)–Rh–P(1)	91.1(2)
I(2)–Rh–P(2)	87.6(2)
I(1)–Rh–O(1)	88.5(5)
I(2)–Rh–O(2)	85.9(6)
P(1)–Rh–P(2)	177.5(3)
I(1)–Rh–O(2)	178.3(7)
I(2)–Rh–O(1)	176.1(6)

of the I(2)–Rh–O(2) and I(2)–Rh–P(2) angles. The displacement for the I(2) atom is more severe if the latter two angles are compared with those corresponding to I(1). Similarly the Rh–I(1) distance can be considered as one of the shortest bonds of this type reported if compared with those tabulated for other Rh(III) complexes [9–11]. We believe that the weakening of the Rh–I(2) bond and accompanying distortion from normal octahedral geometry are related to mutual repulsive forces between the iodine atoms. The I(1)–I(2) distance of 3.878(4) Å confirms this on the basis of a van der Waals radius of 2.15 Å for iodine [12].

The two Rh–P bond distances, being the result of a mutual *trans* influence of the phosphorous atoms, are within experimental error the same, but longer than the 2.350(4) Å in [Rh(I)$_2$(CH$_3$)(PPh$_3$)$_2$]·C$_6$H$_6$ [13] and 2.334(2) Å in the *trans*-[Rh(H)(Cl)(dppm)$_2$]$^+$ ion [14].

The most important feature of this structure determination is the presence of two iodine atoms in its formulation. Considering the parent acetyl complex (**C**, Scheme 1) on which PPh$_3$ substitution took place, it implies that the presence of the second iodine atom can be accounted for as either substitution by free I$^-$, or a dimerization step along one of the slow steps following the initial fast PPh$_3$ substitution step. The first possibility stems from the fact that [Fe(CO)(PMe$_3$)$_3$(COMe)(I)] can, for example, give displacement of iodine through methyl migration to form [Fe(CO)$_2$(PMe$_3$)$_3$(Me)]I [15]. We are currently concerned with structural analyses of two more products of the PPh$_3$ substitution reaction isolated from MeOH medium which we hope will further clarify the mechanistic details of this reaction.

Supplementary Material

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

Acknowledgements

We wish to thank Dr P. H. van Rooyen of the National Chemical Research Laboratory for the data collection and the South African C.S.I.R. for financial assistance.

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