

Crystal Structure of a Carbonylation Catalyst: Acetyldiiodo-1,3- bis(diphenylphosphino)propanerhodium(III)

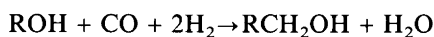
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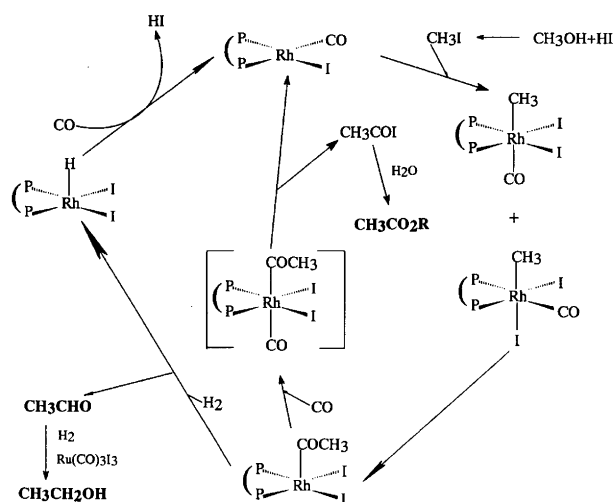
The structure of the carbonylation catalyst acetyldiiodo-1,3-bis(diphenylphosphino)propanerhodium(III)·0.5 methanol, $\text{RhI}_2(\text{COMe})(\text{dppp})\cdot 0.5 \text{ MeOH}$, has been prepared and investigated by X-ray diffraction techniques at $T = 120 \text{ K}$; $M_r = 828.2$, triclinic, $P1$, $a = 10.252(2)$, $b = 15.229(7)$, $c = 19.527(4) \text{ \AA}$, $\alpha = 99.19(2)$, $\beta = 92.31(3)$, $\gamma = 90.24(5)^\circ$, $V = 3007(2) \text{ \AA}^3$, $D_x = 1.82 \text{ g cm}^{-3}$, $\text{MoK}\alpha = 0.71073 \text{ \AA}$, $\mu = 27.2 \text{ cm}^{-1}$, $F(000) = 1604$, $Z = 4$, $R = 0.070$ for 6361 reflections. There are two independent complexes (I and II) in the asymmetric unit. In II the methyl carbon is disordered about two almost equally populated positions. The coordination geometry about the two rhodium(III) ions is approximately square pyramidal, the distortion of the coordination polyhedron being larger in I than in II.

Homologation or reductive carbonylation of alcohols according to



is a reaction of great industrial potential, because it allows the synthesis of any higher alcohol from carbon monoxide, hydrogen and methanol, which in turn can easily be synthesized from carbon monoxide and hydrogen by well known technology. Recently Moloy and Wegman¹ suggested a mechanism for the rhodiumdiphosphine catalyzed reductive carbonylation of methanol shown in Scheme 1. This scheme also contains the mechanism for the non-reductive carbonylation of methanol leading to acetic acid, and this reaction has previously been examined by Hjortkjær and Jensen,² who found the oxidative addition of methyl iodide to be the rate-determining step when there was no diphosphine present. However, in order to have *reductive* carbonylation it is necessary to 'remove' the rate-determining step, because only the complex just before the rate-determining step may be expected to be present in concentrations high enough to allow hydrogenation. This means that the acetyl complex should be stabilized against carbonylation and/or reductive elimination of acetyl iodide, and this stabilization may be established by coordination of 1,3-bis(diphenylphosphino)propane.

During our kinetic investigation of the catalytic reaction we have been able to isolate this acetyldiphosphine complex, allowing us to supplement our examination with a structure analysis of a very crucial complex from the catalytic cycle.



Scheme 1.

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Experimental

Preparation of the title compound. The compound was prepared according to the procedure described in Ref. 1. Found: C 43.00, H 3.80, I 28.53, P 7.51. Calcd. for C₂₉H₂₉I₂OP₂Rh: C 42.89, H 3.60, I 31.25, P 7.63. Calcd. for C₂₉H₂₉I₂OP₂Rh·¹/₂CH₃OH: C 42.78, H 3.77, I 30.64, P 7.48.

X-Ray techniques. Two crystalline phases have been found for the compound. One form is monoclinic, and the other crystal form is triclinic. Because of a breakdown during the collection of data for the monoclinic form, the crystal structure is too poor for publication. On the other

hand we got some information from the data (8637 reflections measured out of 12435 reflections). The space group is *P*2₁/*n* with *a* = 10.261(4), *b* = 10.189(4), *c* = 27.118(4) and β = 95.08(3)°, *Z* = 4.

The synthesis of the compound was repeated several times, changing temperature and pressure. Each time a few crystals of the sample were used to obtain a Gandolfi X-ray photograph. It was found that the triclinic phase was the most frequently occurring crystal form.

Crystal and experimental data for the triclinic form are listed in Table 1. The possible space groups were established from rotation and Weissenberg photographs using Cu radiation. The reflecting power of the crystals was rather poor, and furthermore it was not possible to get a

Table 1. Crystal and experimental data.

| | |
|---|--|
| Formula | C ₂₉ H ₂₉ I ₂ OP ₂ Rh · 0.5 CH ₄ O |
| Formula weight | 828.2 |
| Crystal system | Triclinic |
| Space group | <i>P</i> 1 |
| Unit-cell dimensions/Å | <i>a</i> = 10.252(4) <i>b</i> = 15.229(7) <i>c</i> = 19.527(4) α = 99.19(2) β = 92.31(3) γ = 90.24(5) |
| Unit-cell volume, V/Å ³ | 3007(2) |
| Formula units per unit cell, <i>Z</i> | 4 |
| <i>F</i> (000) | 1604 |
| Calculated density, <i>D</i> _x /g cm ³ | 1.82 |
| Radiation | MoKα |
| Wavelength, λ/Å | 0.71073 |
| Linear absorption coefficient/cm ⁻¹ | 27.2 |
| Temperature, <i>T</i> /K | 120 |
| Crystal description | Orange needles |
| Crystal size/mm | 0.20 × 0.08 × 0.05 |
| Diffractometer | Enraf–Nonius CAD-4F |
| Unit-cell determination | |
| No. of reflections used | 25 |
| θ-Range/° | 5.4–15.0 |
| Intensity data collection | |
| θ _{max} /° | 30 |
| Range of <i>h</i> | 0–14 |
| Range of <i>k</i> | –21–21 |
| Range of <i>l</i> | –27–27 |
| Scan mode | ω |
| Scan range, Δω | 1.00 + 0.35 tan θ |
| Total number of reflections | 18847 |
| No. of independent reflections, [<i>I</i> > 3σ(<i>I</i>)] | 6461 |
| No. reflections used in refinement | 6361 |
| Corrections | Lorenz-polarization and absorption |
| Transmission factors | 0.4304–0.4731 |
| Structure refinement: | |
| Minimization of | Σw(<i>F</i> _o – <i>F</i> _c) ² |
| No. of refined parameters | 412 (215 + 197) |
| Weighting scheme | [σ ² (<i>F</i> _o) + 0.001 <i>F</i> _o ²] ⁻¹ |
| <i>R</i> = Σ <i>F</i> _o – <i>F</i> _c / Σ <i>F</i> _o | 0.070 |
| <i>R</i> _w = [Σw(<i>F</i> _o – <i>F</i> _c) ² / Σw <i>F</i> _o ²] ^{1/2} | 0.079 |
| <i>S</i> = [Σw(<i>F</i> _o – <i>F</i> _c) ² / (N _{obs} – N _{var})] ^{1/2} | 1.53 |
| Final (Δ/θ) _{max} | 0.32 |
| Final Δ <i>ρ</i> _{min} and Δ <i>ρ</i> _{max} /e Å ⁻³ | –1.43 and 2.29 |

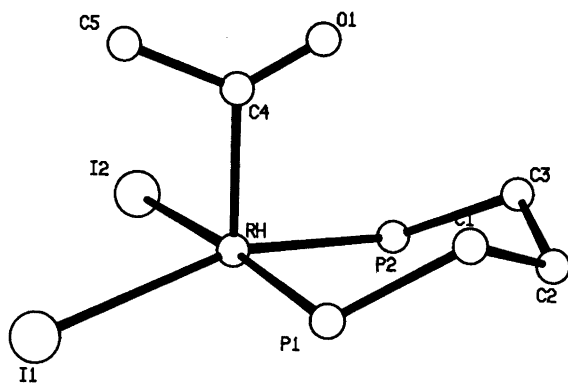


Fig. 1. The inner coordination sphere of $\text{RhI}_2(\text{COMe})(\text{dppp}) \cdot 0.5 \text{ MeOH}$.

good single crystal. The crystal was cooled to 120 K using the Cryostream nitrogen gas cooler system.³ The unit-cell parameters were derived from a least-squares fit of refined diffractometer setting angles for 25 reflections. Four standards were measured for intensity and orientation control after every 200 reflections; no fading was observed. The intensities were corrected for Lorentz, polarization and absorption (Gaussian integration) effects. The structure was solved by Patterson and Fourier methods. There are two independent complexes (**I** and **II**) and one molecule of methanol in the asymmetric unit. The structure was refined by a blocked least-squares technique with one block containing complex **I** and methanol (215 variables) and the other formed by complex **II**. Anisotropic thermal parameters were introduced for the Rh, I, P, O and C(1)–C(5), whereas the carbon atoms of the phenyl rings and the disordered carbon atoms were refined with isotropic temperature factors.

In the refinement the hydrogen atoms (except for the methyl groups and methanol) were at calculated positions using a riding model with $C-H = 1.08 \text{ \AA}$ and fixed thermal parameters [$U(H) \approx 1-1.2$ times U for attached C]. The methyl carbon [C(5)] in **II** and the carbon atom in methanol are both disordered about two almost equally populated positions. The structure refined well in the centrosymmetric space group $P\bar{1}$. Attempts to refine the structure in $P1$ did not yield any improvement in the defi-

nition of the methyl groups. The crystallographic computations were performed with SHELXS86⁴ and SHELX76.⁵ The atomic scattering factors were taken from Ref. 6. The PLUTO program⁷ was used for the illustrations and PLATON⁸ for molecular geometry calculations.

The final positional parameters are listed in Table 2. Anisotropic thermal parameters, positional parameters for the hydrogen atoms, bond lengths and angles for the phenyl ring and the methanol group and list of observed and calculated structure factors may be obtained from the authors on request. Also, data concerning the monoclinic form may be obtained.

Description and discussion of the structure

Selected bond lengths and bond angles are listed in Table 3. The structure consists of discrete molecules of $\text{RhI}_2(\text{CoMe})(\text{dppp})$ and of methanol. The labelling of the atoms in the coordination core is shown in Fig. 1. The numbering scheme used on the phenyl groups is C(6)–C(11) and C(12)–C(17) connected via C(6) and C(12) to P(1), and C(18)–C(23) and C(24)–C(29) connected via C(18) and C(24) to P(2).

In both **I** and **II** the coordination geometry about rhodium is approximately square pyramidal, with the acetyl group occupying the apical position. The arrangement is similar to that of $\text{RhCl}_2(\text{COPh})\text{dppp}$ ⁹ and $[\text{RhI}(\text{COEt})(\text{PPh}_3)(\text{mnt})]^-$ (mnt = maleonitriledithiolate)¹⁰ and appears to be the preferred coordination geometry for low-spin five-coordinated d^6 metal ions.

In the complexes **I** and **II** the four atoms (**I** and **P**) in the basal plane of the coordination polyhedrons are not strictly coplanar, the deviations of the atoms from the least-squares plane through them being less than 0.16 \AA for **I** and 0.03 \AA for **II**, respectively. The rhodium atom is displaced 0.25 \AA from this plane towards the acetyl group in both **I** and **II**.

There are some distortions from ideal square pyramidal geometry in the two complexes, especially in **I**. The difference between the I(2)–Rh–P(1) angle and the I(1)–Rh–P(2) angle is 13.9 and 2.6° for **I** and **II**, respectively,

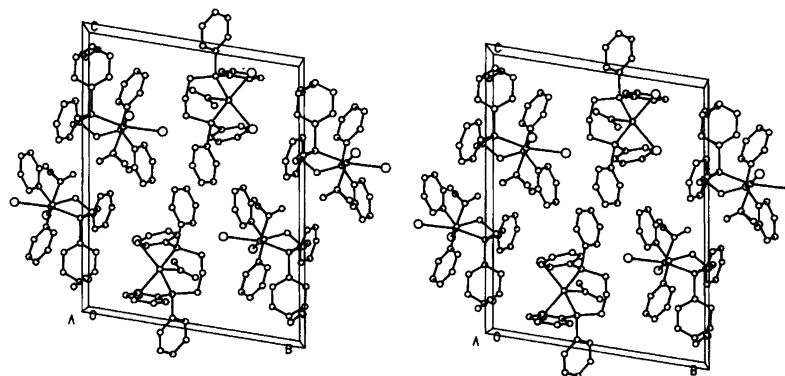


Fig. 2. A stereo view of the unit cell of $\text{RhI}_2(\text{COMe})(\text{dppp}) \cdot 0.5 \text{ MeOH}$.

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters (in Å²).

| Atom | x | y | z | U_{eq}^a |
|--------------------|--------------|------------|-------------|------------|
| I | | | | |
| I(1) | 0.17902(10) | 0.23185(8) | 0.27027(7) | 0.0549(5) |
| I(2) | 0.12338(11) | 0.23684(7) | 0.07691(7) | 0.0562(4) |
| Rh | 0.25397(11) | 0.34104(7) | 0.18137(7) | 0.0313(4) |
| P(1) | 0.3781(3) | 0.4212(3) | 0.2695(2) | 0.0328(13) |
| P(2) | 0.3703(3) | 0.4003(2) | 0.1021(2) | 0.0289(13) |
| O(1) | 0.1373(10) | 0.5061(7) | 0.1712(6) | 0.042(4) |
| C(1) | 0.4147(15) | 0.5345(9) | 0.2575(8) | 0.036(5) |
| C(2) | 0.5003(14) | 0.5406(9) | 0.1950(7) | 0.030(5) |
| C(3) | 0.4243(14) | 0.5148(8) | 0.1244(7) | 0.026(4) |
| C(4) | 0.1157(15) | 0.4364(9) | 0.1870(7) | 0.031(5) |
| C(5) | -0.0075(14) | 0.4064(10) | 0.2136(8) | 0.037(5) |
| C(6) | 0.3086(15) | 0.4409(10) | 0.3547(8) | 0.035(4) |
| C(7) | 0.2027(15) | 0.4935(10) | 0.3681(8) | 0.038(4) |
| C(8) | 0.1467(17) | 0.5071(11) | 0.4333(9) | 0.044(4) |
| C(9) | 0.2009(18) | 0.4661(12) | 0.4863(10) | 0.054(5) |
| C(10) | 0.3065(19) | 0.4130(13) | 0.4749(10) | 0.060(5) |
| C(11) | 0.3595(18) | 0.3980(12) | 0.4112(9) | 0.050(4) |
| C(12) | 0.5343(15) | 0.3721(10) | 0.2834(8) | 0.037(4) |
| C(13) | 0.5523(18) | 0.2823(12) | 0.2601(9) | 0.050(4) |
| C(14) | 0.6756(18) | 0.2441(12) | 0.2652(9) | 0.055(5) |
| C(15) | 0.7754(17) | 0.2964(11) | 0.2974(9) | 0.044(4) |
| C(16) | 0.7607(17) | 0.3842(11) | 0.3234(9) | 0.043(4) |
| C(17) | 0.6379(15) | 0.4220(10) | 0.3149(8) | 0.038(4) |
| C(18) | 0.2965(15) | 0.3992(10) | 0.0143(8) | 0.036(4) |
| C(19) | 0.1970(16) | 0.4582(11) | 0.0069(9) | 0.042(4) |
| C(20) | 0.1363(18) | 0.4601(12) | -0.0584(10) | 0.055(5) |
| C(21) | 0.1748(17) | 0.4008(11) | -0.1174(9) | 0.046(4) |
| C(22) | 0.2751(17) | 0.3468(11) | -0.1078(9) | 0.049(4) |
| C(23) | 0.3384(16) | 0.3445(10) | -0.0422(8) | 0.041(4) |
| C(24) | 0.5164(15) | 0.3352(10) | 0.0852(8) | 0.034(3) |
| C(25) | 0.6357(16) | 0.3717(11) | 0.0734(8) | 0.041(4) |
| C(26) | 0.743(2) | 0.3190(12) | 0.0638(10) | 0.058(5) |
| C(27) | 0.7358(19) | 0.2311(12) | 0.0616(10) | 0.056(5) |
| C(28) | 0.618(2) | 0.1907(15) | 0.0748(11) | 0.073(6) |
| C(29) | 0.507(2) | 0.2447(14) | 0.0861(11) | 0.070(6) |
| II | | | | |
| I(1) | -0.10846(12) | 0.63839(6) | 0.33450(6) | 0.0423(4) |
| I(2) | -0.38503(11) | 0.78309(8) | 0.30478(11) | 0.0899(7) |
| Rh | -0.13359(10) | 0.81439(7) | 0.33967(6) | 0.0253(3) |
| P(1) | 0.0883(3) | 0.8304(2) | 0.34901(18) | 0.0220(11) |
| P(2) | -0.1562(4) | 0.9559(2) | 0.3167(2) | 0.0366(13) |
| O(1) | -0.1034(11) | 0.9206(7) | 0.4717(6) | 0.052(4) |
| C(1) | 0.1487(13) | 0.9415(9) | 0.3854(8) | 0.031(5) |
| C(2) | 0.1044(14) | 1.0165(9) | 0.3464(9) | 0.036(5) |
| C(3) | -0.0375(13) | 1.0388(9) | 0.3588(9) | 0.039(5) |
| C(4) | -0.1500(19) | 0.8578(10) | 0.4401(9) | 0.054(6) |
| C(5) ^b | -0.198(5) | 0.786(3) | 0.484(2) | 0.062(16) |
| C(5') ^b | -0.273(4) | 0.811(3) | 0.463(2) | 0.049(15) |
| C(6) | 0.1780(14) | 0.7682(9) | 0.4066(8) | 0.033(3) |
| C(7) | 0.135(2) | 0.7657(15) | 0.4716(12) | 0.082(7) |
| C(8) | 0.206(3) | 0.7275(16) | 0.5226(14) | 0.090(7) |
| C(9) | 0.325(2) | 0.6920(16) | 0.5019(13) | 0.084(7) |
| C(10) | 0.370(2) | 0.6881(14) | 0.4387(11) | 0.071(6) |
| C(11) | 0.2964(17) | 0.7276(11) | 0.3877(9) | 0.048(4) |
| C(12) | 0.1597(15) | 0.8042(10) | 0.2647(8) | 0.039(4) |
| C(13) | 0.2788(17) | 0.8437(11) | 0.2501(9) | 0.046(4) |
| C(14) | 0.327(2) | 0.8195(13) | 0.1848(11) | 0.066(6) |
| C(15) | 0.270(2) | 0.7605(14) | 0.1347(12) | 0.069(6) |
| C(16) | 0.152(2) | 0.7241(16) | 0.1473(13) | 0.084(7) |
| C(17) | 0.096(2) | 0.7442(14) | 0.2121(11) | 0.068(6) |
| C(18) | -0.3100(17) | 1.0130(11) | 0.3403(9) | 0.047(4) |
| C(19) | -0.330(2) | 1.0440(15) | 0.4063(13) | 0.083(7) |
| C(20) | -0.452(2) | 1.0891(16) | 0.4222(14) | 0.089(7) |
| C(21) | -0.538(2) | 1.0949(15) | 0.3689(12) | 0.082(7) |

Table 2. (continued).

| Atom | x | y | z | U_{eq}^a |
|---------------------|-------------|------------|------------|-------------------|
| C(22) | -0.521(2) | 1.0647(13) | 0.3037(11) | 0.065(5) |
| C(23) | -0.4036(18) | 1.0190(12) | 0.2840(10) | 0.054(5) |
| C(24) | 0.1366(17) | 0.9566(12) | 0.2242(9) | 0.049(4) |
| C(25) | -0.160(2) | 0.8798(16) | 0.1805(13) | 0.085(7) |
| C(26) | -0.140(3) | 0.876(3) | 0.1067(19) | 0.145(12) |
| C(27) | -0.099(3) | 0.956(2) | 0.0823(18) | 0.129(11) |
| C(28) | -0.080(2) | 1.0285(15) | 0.1294(11) | 0.073(6) |
| C(29) | -0.0983(18) | 1.0320(12) | 0.1984(10) | 0.054(5) |
| O | 0.4330(13) | 0.9988(7) | 0.1081(6) | 0.054(4) |
| C(Me) ^c | 0.289(9) | 0.998(6) | 0.096(4) | 0.16(4) |
| C(Me') ^c | 0.522(4) | 0.946(3) | 0.076(2) | 0.101(17) |

^a $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. ^b Population factors for C(5) and C(5') are 0.53(6) and 0.47(6), respectively. ^c Population factors for C(Me) and C(Me') are 0.51(5) and 0.49(5), respectively.

and the C(4)–Rh–I(1) angle (104.8° for **I** and 102.9° for **II**) is larger than the three other C(4)–Rh–X angles [X = I(2), P(1) and P(2)] (the average value of the three angles is 92.8° and 93.6° for **I** and **II**, respectively).

For pentacoordinated compounds two basic idealized geometric forms, the D_{3h} trigonal bipyramid (TBP) and the C_{4v} square pyramid (SP) appear. These two forms are most simply and symmetrically related by the Berry intramolecular ligand exchange process with the trigonal bipyramid as reference. If in the trigonal bipyramid the atoms 2, 3 and 4 occupy the equatorial sites and 1 and 5 the axial positions, then after the Berry rearrangement process the atoms 1, 2, 4 and 5 will form the equatorial square plane with atom 3 occupying the apical site. Greatly associated with the Berry exchange is the dihedral angle δ_{24} , which is the angle between the normals to the trigonal bipyramidal faces 124 and 245. δ_{24} is 53.1° for TBP and 0° for SP, respectively. Methods of describing this type of distortion from idealized geometries and crystal structure data on five-coordinated compounds with an indication of distortion relative to the Berry coordinate have been surveyed by Holmes.¹¹

A comparison between the coordination geometry about the rhodium ions of this structure and that of $\text{RhCl}_2(\text{COPh})\text{dppp}^9$ and $[\text{RhI}(\text{COEt})(\text{PPh}_3)(\text{mnt})]^{-10}$ is shown in Table 4.

The Rh–C bond lengths of 2.027(15) and 1.981(17) Å in the present structure are in the range of 1.93–2.06 Å reported for other Rh(III) complexes. The Rh–P bond lengths of 2.281–2.284 Å are close to those obtained in analogous compounds (2.274–2.388 Å). The Rh–I bond lengths of 2.661–2.718 Å found in the present complexes are in agreement with those observed for most Rh(III) iodide compounds (2.65–2.71 Å). Bond lengths and angles within the dppp ligands are normal.

The packing of the structure is shown in Fig. 2. The only intermolecular distance which may be shorter than the sum of the corresponding van der Waals radii is the C(5)–C(16)[$x - 1, y, z$] distance of 3.32(2) Å between two **I** complexes. The shortest distance between complexes **I** and **II** is the C(8)(**I**)–C(9)(**II**) distance of 3.41(3) Å. The molecule of methanol is about 3.5 Å from both **I** and **II**.

Table 3. Selected bond lengths (in Å) and bond angles (in °).

| | I | II |
|------------------|-----------|-----------|
| Rh–I(1) | 2.718(2) | 2.680(2) |
| Rh–I(2) | 2.683(2) | 2.661(2) |
| Rh–P(1) | 2.283(4) | 2.284(3) |
| Rh–P(2) | 2.284(4) | 2.281(3) |
| Rh–C(4) | 2.027(15) | 1.981(17) |
| P(1)–C(1) | 1.818(15) | 1.823(14) |
| P(1)–C(6) | 1.818(16) | 1.809(15) |
| P(1)–C(12) | 1.799(16) | 1.815(16) |
| P(2)–C(3) | 1.807(13) | 1.824(15) |
| P(2)–C(18) | 1.843(16) | 1.827(18) |
| P(2)–C(24) | 1.812(16) | 1.843(18) |
| C(4)–O(1) | 1.17(2) | 1.14(2) |
| C(1)–C(2) | 1.55(2) | 1.53(2) |
| C(2)–C(3) | 1.55(2) | 1.52(2) |
| C(4)–C(5) | 1.48(2) | 1.58(5) |
| C(4)–C(5') | | 1.56(5) |
| I(1)–Rh–I(2) | 89.68(7) | 87.18(7) |
| I(1)–Rh–P(1) | 89.3(1) | 89.7(1) |
| I(1)–Rh–P(2) | 161.4(1) | 166.7(1) |
| I(1)–Rh–C(4) | 104.8(4) | 102.9(5) |
| I(2)–Rh–P(1) | 175.3(1) | 169.5(1) |
| I(2)–Rh–P(2) | 89.5(1) | 89.6(1) |
| I(2)–Rh–C(4) | 92.5(4) | 98.6(6) |
| P(1)–Rh–P(2) | 90.1(2) | 91.2(1) |
| P(1)–Rh–C(4) | 92.1(4) | 91.8(6) |
| P(2)–Rh–C(4) | 93.7(4) | 90.3(5) |
| Rh–P(1)–C(1) | 114.6(5) | 115.4(5) |
| Rh–P(1)–C(6) | 117.0(5) | 118.1(5) |
| Rh–P(1)–C(12) | 113.2(5) | 111.1(5) |
| C(1)–P(1)–C(6) | 100.7(7) | 98.5(7) |
| C(1)–P(1)–C(12) | 105.2(7) | 105.5(7) |
| C(6)–P(1)–C(12) | 104.7(7) | 106.7(7) |
| Rh–P(2)–C(3) | 117.9(5) | 117.1(5) |
| Rh–P(2)–C(18) | 118.6(5) | 117.3(6) |
| Rh–P(2)–C(24) | 108.5(5) | 109.5(6) |
| C(3)–P(2)–C(18) | 101.4(7) | 100.6(7) |
| C(3)–P(2)–C(24) | 106.1(7) | 103.6(8) |
| C(18)–P(2)–C(24) | 102.7(7) | 107.4(8) |
| P(1)–C(1)–C(2) | 113.8(10) | 115.9(11) |
| C(1)–C(2)–C(3) | 112.5(12) | 110.9(12) |
| P(2)–C(3)–C(2) | 116.6(9) | 115.6(11) |
| Rh–C(4)–O(1) | 121.2(12) | 127.0(14) |
| Rh–C(4)–C(5) | 111.7(10) | 115.3(17) |
| Rh–C(4)–C(5') | | 106.9(17) |
| O(1)–C(4)–C(5) | 127.1(14) | 115(2) |
| O(1)–C(4)–C(5') | | 123(2) |

Table 4. Coordination about rhodium for some pentacoordinated compounds.

| 1-Rh-5 ^a | 2-Rh-4 | 2-Rh-3 | 3-Rh-4 | δ ₂₄ | %(TBP-SP) | Compound |
|---------------------|--------|--------|--------|-----------------|-----------|----------|
| 175.3 | 161.4 | 93.7 | 104.8 | 13.8 | 80.8 | I |
| 169.5 | 166.7 | 90.3 | 102.9 | 2.8 | 93.4 | II |
| 169.8 | 163.5 | 91.2 | 105.1 | 6.0 | 86.2 | Ref. 7 |
| 169.7 | 162.0 | 98.5 | 99.5 | 7.6 | 85.8 | Ref. 8 |

^a 1=P(1); 2=P(2); 4=I(1); 5=I(2); 3=C(4) for I and II. 1=P(1); 2=P(2); 4=Cl(1); 5=Cl(2); 3=C(1) for Ref. 7. 1=S(1); 2=S(2); 4=I; 5=P; 3=C(1) for Ref. 8.

In the monoclinic form there is no disorder of the methyl group, and no solvent molecule is found in the structure. The coordination geometry about rhodium is square pyramidal, with the acetyl group occupying the apical position. The distortion seems to be greater than for the triclinic form, the % (TBP-SP) being only about 66.

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