

## Rhodium Complexes possessing the Unidentate Anion of 2,4-Pentanedione as a Ligand; X-Ray Crystal Structure of Carbonyl(2,4-pentanedionato-O)-bis(tri-isopropylphosphine)rhodium(I)†

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Rhodium complexes having the unidentate anion of 2,4-pentanedione as a ligand have been synthesized by the reaction of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  [ $\text{Hacac} = \text{acetylacetonate (2,4-pentanedione)}$ ] with highly basic tertiary phosphines. The X-ray crystallographic analysis revealed that the co-ordination chemistry about the Rh atom is square planar with two phosphine ligands in *trans* positions. The unidentate 2,4-pentanedionate ligand has a *trans* configuration with respect to the C=C bond. Proton n.m.r. studies indicated a singlet resonance for the methine of the pentanedione anion, which is widely accepted as a proof of the *cis* configuration. In the i.r. spectra absorptions characteristic of the unidentate pentanedionate were observed in the 1500–1620  $\text{cm}^{-1}$  region, but the ketonic absorptions were unusually low for  $\alpha,\beta$ -unsaturated carbonyls.

Metal complexes having the unidentate anion of 2,4-pentanedione as a ligand are known for Hg,<sup>1</sup> Pt,<sup>2,3</sup> Cu,<sup>4</sup> and Pd.<sup>5,6</sup> For Rh complexes it is known that triphenylphosphine substitutes only one carbonyl ligand of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  [ $\text{Hacac} = \text{acetylacetonate (2,4-pentanedione)}$ ] to form  $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ .<sup>7</sup> Recently the formation of  $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)_2]$  has been reported,<sup>8</sup> which was obtained by substitution of the chlorine ligand of  $[\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$  by sodium 2,4-pentanedionate. The geometry is assumed to be trigonal bipyramidal based on the spectral evidence. We have discovered that addition of highly basic tertiary phosphines(L) to  $[\text{Rh}(\text{acac})(\text{CO})_2]$  easily causes substitution of one carbonyl ligand and one bond of the 2,4-pentanedione anion to form  $[\text{Rh}(\text{acac}-\text{O})(\text{CO})\text{L}_2]$  which has a square-planar structure. To our knowledge this is the first example of a rhodium complex possessing the unidentate  $\beta$ -diketone ligand.

### Results and Discussion

Rhodium complexes possessing a unidentate anion of 2,4-pentanedione and two phosphine ligands are formed only when the phosphine has a highly basic and moderately bulky character. Neither 'ordinary' phosphines such as  $\text{PPh}_3$  or  $\text{PEt}_3$ , nor very bulky phosphines like  $\text{PBu}_3$  are able to co-ordinate two phosphine molecules to  $[\text{Rh}(\text{acac})(\text{CO})_2]$ .

Specific features of  $[\text{Rh}(\text{acac}-\text{O})(\text{CO})(\text{PPr}^i_3)_2]$  (1) have been compared in detail with  $[\text{Rh}(\text{acac})(\text{CO})(\text{PPr}^i_3)_2]$  (2) which has an ordinary square-planar structure with a  $\beta$ -diketone chelate ring. While complex (2) shows a sharp carbonyl absorption at 1962  $\text{cm}^{-1}$  and two comparable bands at 1585 and 1518  $\text{cm}^{-1}$  typical of the chelated structure of 2,4-pentanedionate, complex (1) shows absorption bands at 1950vs, 1613w, and 1515m  $\text{cm}^{-1}$ . The asymmetric absorption mode in the 1500–1620  $\text{cm}^{-1}$  region suggests a change in the co-ordination mode of the  $\beta$ -diketone. However, the free ketonic absorptions of the known unidentate  $\beta$ -diketone complexes are in the 1650–1680  $\text{cm}^{-1}$  region<sup>1–6</sup> characteristic of an  $\alpha,\beta$ -unsaturated carbonyl group. The lower ketonic band of complex (1) may suggest interaction of the carbonyl group

with other atoms, but the position of this band does not change either in the solid state (KBr) or in solution ( $\text{CH}_2\text{Cl}_2$ ), excluding the possibility of intermolecular interaction.

Complex (1) is stable in air in the solid state over a month, but it tends to decompose in  $\text{CDCl}_3$  solution at room temperature yielding (2) and free phosphine. Therefore the proton n.m.r. spectra of (1) [two singlets at 1.93 and 2.20 p.p.m. ( $\text{acac}-\text{CH}_3$ ) and a singlet at 5.30 p.p.m. ( $\text{acac}-\text{CH}$ )] are always accompanied by a small portion of (2) [two singlets at 1.85 and 2.07 p.p.m. ( $\text{acac}-\text{CH}_3$ ) and a singlet at 5.46 p.p.m. ( $\text{acac}-\text{CH}$ )]. The two non-equivalent  $\text{acac CH}_3$  chemical shifts exclude certain symmetry modes which have a mirror plane passing through the centre of the  $\beta$ -diketone ligand. The singlet  $\text{acac CH}$  proton resonance has been considered to be proof of the *cis* configuration of the unidentate  $\beta$ -diketone ligand with respect to the C=C bond. This is based on the proton n.m.r. studies of *cis*- and *trans*- $\text{SiR}_3(\text{acac}-\text{O})$  complexes,<sup>9</sup> which are composed of two sets of signals assignable to two geometrical isomers; a multiplet methine for the *trans* isomer and a singlet methine for the *cis* isomer. If this is the general rule, the unidentate 2,4-pentanedionate ligand in (1) must have the *cis* configuration. However, the discrepancy in the determination of geometry between proton n.m.r. and X-ray analyses has already been pointed out.<sup>5</sup>

The  $^{31}\text{P}$  n.m.r. spectrum of complex (1) exhibits a simple doublet split by  $J(\text{RhP}) = 124.5$  Hz with a chemical shift of 47.35 p.p.m. The value of the coupling constant is analogous to those of the square-planar complexes *trans*- $[\text{RhX}(\text{CO})(\text{PPh}_3)_2]$ <sup>10</sup> ( $J = 123$ – $136$  Hz for a variety of unidentate anions, X) suggesting a similar configuration. On the other hand, complex (2) shows a doublet split by  $J(\text{RhP}) = 166.0$  Hz with a chemical shift of 69.19 p.p.m. These compared well with the data for  $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ <sup>11</sup> ( $J = 179.7$  Hz,  $\delta = 48.6$  p.p.m.).

The Figure shows a perspective view of a molecule of  $[\text{Rh}(\text{acac}-\text{O})(\text{CO})(\text{PPr}^i_3)_2]$  with the atom-numbering scheme. The selected bond lengths and angles are summarized in Table 1. The complex, as a whole, has an approximate mirror symmetry about the plane bisecting the P(1)–Rh–P(2) angle. The rhodium atom is four-co-ordinated by P(1), O(2), P(2), and C(1) and has a distorted square-planar environment with the two phosphine ligands in *trans* positions. The deviations from

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

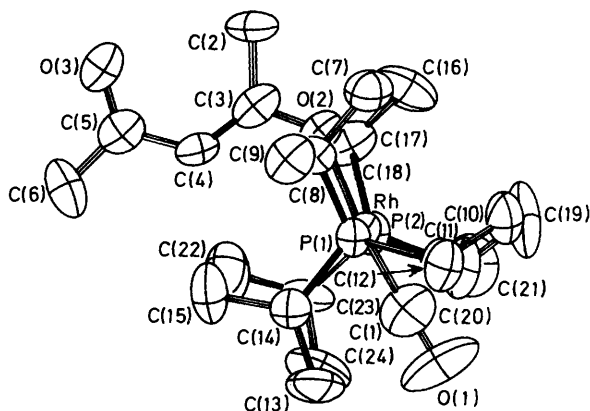


Figure. ORTEP (C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.) Drawing of  $[\text{Rh}(\text{acac}-\text{O})(\text{CO})(\text{PPr}_3)_2]$

the least-squares plane of the co-ordinating atoms are  $-0.08$ ,  $+0.07$ ,  $-0.08$ , and  $+0.08$  Å for P(1), O(2), P(2), and C(1) respectively, and  $-0.04$  Å for Rh. The angle C(1)–Rh–O(2) is  $172.6(4)^\circ$ . Short intramolecular distances of  $3.38(2)$ ,  $3.39(3)$ ,  $3.28(2)$ , and  $3.27(1)$  Å for C(1)···C(13), C(1)···C(24), C(1)···C(11), and C(1)···C(20) respectively are observed. The 2,4-pentanedionate acts as a unidentate ligand and has a *trans* configuration with respect to the C(3)–C(4) bond. The same configuration is also seen in the Pd complex.<sup>5</sup> The ketonic bond length of C(5)–O(3) [ $1.240(14)$  Å] is slightly longer (not significantly so) than that of the Pd complex [ $1.217(12)$  Å], which is probably reflected in the unusually low ketonic i.r. absorption. But the ketonic oxygen atom in the crystal lattice is more than 7 Å from the adjacent Rh atom, so intermolecular interaction is clearly prevented.

The high basicity and moderate bulkiness of the phosphines examined here may be the cause of the formation of novel unidentate rhodium–pentanedione complexes. The anomaly in the low ketonic i.r. absorption and the singlet methine proton resonance cannot be reasonably rationalized. The multiplet methine resonance in the *trans* geometry has been explained by the long-range coupling between the methine proton and one of the methyl protons on C(2) in the so-called W-arrangement.<sup>12</sup> The best possible explanation of the singlet methine resonance for the *trans* configuration may be that the long-range coupling is hindered by the presence of the Rh–O(2)–C(3) bonds between them. It is concluded that the determination of the geometry of the unidentate pentanedionate ligand in the metal complexes, solely on the basis of proton n.m.r. resonance, may be erroneous and should be compared with the crystallographic data.

## Experimental

**Preparation of Complexes.**—Reactions were carried out in a dry nitrogen atmosphere using dried solvents. Tertiary phosphines which have different alkyl groups were synthesized by the stepwise reaction of  $\text{PCl}_3$  with the corresponding Grignard reagents.<sup>13,14</sup>

**Carbonyl(2,4-pentanedionato-O)bis(tri-isopropylphosphine)-rhodium(I)**,  $[\text{Rh}(\text{acac}-\text{O})(\text{CO})(\text{PPr}_3)_2]$ . To a diethyl ether suspension ( $10 \text{ cm}^3$ ) of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (258 mg, 1 mmol),  $\text{PPr}_3$  (1 mmol) was added dropwise at room temperature. The solution became homogeneous indicating formation of  $[\text{Rh}(\text{acac})(\text{CO})(\text{PPr}_3)]$ . To this solution, a further quantity of  $\text{PPr}_3$  (1 mmol) was added. Rapid precipitation of yellow crystals was observed. The precipitate (0.53 g, 92%) was washed with dry diethyl ether, and recrystallized from a dimethoxy-

Table 1. Bond distances (Å) and angles ( $^\circ$ ) with estimated standard deviations in parentheses

Rh–P(1)	2.359(2)	C(1)–O(1)	1.146(19)
Rh–P(2)	2.355(2)	C(2)–C(3)	1.492(17)
Rh–O(2)	2.056(6)	C(3)–O(2)	1.290(11)
Rh–C(1)	1.782(13)	C(3)–C(4)	1.370(13)
P(1)–C(8)	1.846(9)	C(4)–C(5)	1.431(15)
P(1)–C(11)	1.864(9)	C(5)–C(6)	1.515(22)
P(1)–C(14)	1.858(10)	C(5)–O(3)	1.240(14)
P(2)–C(17)	1.860(11)		
P(2)–C(20)	1.863(17)		
P(2)–C(23)	1.861(13)		
P(1)–Rh–O(2)	94.4(2)	Rh–C(1)–O(1)	177.9(13)
P(1)–Rh–C(1)	88.5(4)	Rh–O(2)–C(3)	134.7(6)
P(2)–Rh–O(2)	90.4(2)	O(2)–C(3)–C(2)	115.2(9)
P(2)–Rh–C(1)	89.0(4)	O(2)–C(3)–C(4)	121.7(8)
P(1)–Rh–P(2)	176.9(1)	C(2)–C(3)–C(4)	123.2(9)
O(2)–Rh–C(1)	172.6(4)	C(3)–C(4)–C(5)	127.7(9)
Rh–P(1)–C(8)	113.3(3)	C(4)–C(5)–C(6)	116.5(11)
Rh–P(1)–C(11)	111.2(3)	C(4)–C(5)–O(3)	127.1(10)
Rh–P(1)–C(14)	114.2(3)	C(6)–C(5)–O(3)	116.4(11)
Rh–P(2)–C(17)	113.0(3)		
Rh–P(2)–C(20)	112.5(5)		
Rh–P(2)–C(23)	113.3(4)		

Table 2. Final positional parameters ( $\times 10^4$ ) for complex (I)

Atom	x	y	z
Rh	3 703	3 863	2 781(1)
P(1)	5 547(1)	3 798(1)	2 705(2)
P(2)	1 861(1)	3 924(1)	2 721(2)
O(1)	3 738(8)	4 499(6)	141(13)
O(2)	3 662(4)	3 523(3)	4 778(6)
O(3)	3 688(6)	1 811(3)	6 001(9)
C(1)	3 733(7)	4 242(5)	1 161(12)
C(2)	3 629(11)	2 981(5)	6 846(11)
C(3)	3 653(5)	3 026(4)	5 269(8)
C(4)	3 676(6)	2 575(4)	4 390(11)
C(5)	3 685(6)	2 003(4)	4 783(11)
C(6)	3 695(15)	1 589(6)	3 580(20)
C(7)	5 987(8)	3 890(6)	5 606(11)
C(8)	6 140(5)	3 516(4)	4 348(9)
C(9)	7 282(7)	3 324(6)	4 294(14)
C(10)	5 735(9)	4 952(4)	3 177(14)
C(11)	6 147(6)	4 478(3)	2 261(10)
C(12)	7 341(8)	4 493(5)	2 239(15)
C(13)	5 766(14)	3 524(8)	–178(14)
C(14)	6 038(7)	3 334(4)	1 295(10)
C(15)	5 642(13)	2 740(6)	1 516(18)
C(16)	1 555(12)	4 139(10)	5 619(17)
C(17)	1 258(6)	3 738(5)	4 439(11)
C(18)	57(8)	3 632(8)	4 382(17)
C(19)	1 927(17)	5 079(7)	3 025(43)
C(20)	1 388(8)	4 615(5)	2 117(18)
C(21)	205(10)	4 694(7)	2 072(23)
C(22)	1 427(13)	2 846(6)	1 883(24)
C(23)	1 233(8)	3 443(5)	1 422(11)
C(24)	1 596(15)	3 545(13)	–69(18)

ethane solution (Found: C, 52.8; H, 9.2; P, 11.3; Rh, 18.4.  $\text{C}_{24}\text{H}_{49}\text{O}_3\text{P}_2\text{Rh}$  requires C, 52.4; H, 9.0; P, 11.3; Rh, 18.2%). I.r. spectrum in KBr: 1 950vs, 1 613w, and 1 515m  $\text{cm}^{-1}$ .

The following compounds were prepared by a similar method.

**Carbonylbis(di-isopropylphenylphosphine)(2,4-pentanedionato-O)rhodium(I)**,  $[\text{Rh}(\text{acac}-\text{O})(\text{CO})(\text{PPr}^i_2\text{Ph})_2]$ . Yield, 69% (Found: C, 57.2; H, 6.9; P, 10.2; Rh, 15.8.  $\text{C}_{30}\text{H}_{45}\text{O}_3\text{P}_2\text{Rh}$  requires C, 58.2; H, 7.3; P, 10.0; Rh, 16.6%). I.r. spectrum in KBr: 1 954vs, 1 619w, and 1 518m  $\text{cm}^{-1}$ .

*Carbonylbis(di-isopropylmethylphosphine)(2,4-pentanedionato-O)rhodium(I)*, [Rh(acac-O)(CO)(PMePr<sup>i</sup>)<sub>2</sub>]. Yield, 82% (Found: C, 44.4; H, 7.4; P, 12.2; Rh, 19.8. C<sub>20</sub>H<sub>41</sub>O<sub>3</sub>P<sub>2</sub>Rh requires C, 48.6; H, 8.4; P, 12.5; Rh, 20.8%). I.r. spectrum in KBr: 1 957vs, 1 614w, and 1 519m cm<sup>-1</sup>.

*Carbonyl(2,4-pentanedionato-O)bis(1-t-butylphosphacyclohexane)rhodium(I)*. Yield, 84% (Found: C, 52.7; H, 8.1; P, 11.8; Rh, 19.0. C<sub>24</sub>H<sub>45</sub>O<sub>3</sub>P<sub>2</sub>Rh requires C, 52.7; H, 8.3; P, 11.3; Rh, 18.8%). I.r. spectrum in KBr: 1 947vs, 1 618w, and 1 509m cm<sup>-1</sup>.

*Carbonyl(2,4-pentanedionato-O)bis(1-t-butylphosphacyclopentane)rhodium(I)*. Yield, 82% (Found: C, 50.6; H, 7.9; P, 12.6; Rh, 20.2. C<sub>22</sub>H<sub>41</sub>O<sub>3</sub>P<sub>2</sub>Rh requires C, 51.0; H, 8.0; P, 12.0; Rh, 19.9%). I.r. spectrum in KBr: 1 954vs, 1 619w, and 1 518m cm<sup>-1</sup>.

*Spectral Analysis*.—I.r. spectra were recorded on a Nicolet 170SX FT-IR spectrometer either in the solid state (KBr disc) or in solution (CH<sub>2</sub>Cl<sub>2</sub>). Proton n.m.r. spectra were recorded on a JEOL FX-270 (270 MHz) spectrometer. <sup>31</sup>P N.m.r. spectra were recorded on a JEOL 90Q (36.4 MHz) spectrometer.

*X-Ray Analysis of [Rh(acac-O)(CO)(PPr<sup>i</sup>)<sub>2</sub>]*.—The orange hexagonal prism (0.24 × 0.24 × 0.56 mm) was obtained from recrystallization of the product from a dimethoxyethane solution.

*Crystal data*. C<sub>24</sub>H<sub>49</sub>O<sub>3</sub>P<sub>2</sub>Rh, *M* = 550.507, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 12.759(4), *b* = 24.186(12), *c* = 9.433(4) Å, β = 90.88(4)°, *U* = 2 911(2) Å<sup>3</sup>, *D*<sub>c</sub> = 1.26 g cm<sup>-3</sup>, *Z* = 4, *F*(000) = 1 168, μ(Mo-K<sub>α</sub>) = 7.02 cm<sup>-1</sup>.

The three dimensional intensity data were collected with a Rigaku AFC-4 four-cycle diffractometer, using graphite monochromated Mo-K<sub>α</sub> radiation (λ = 0.710 69 Å) at room temperature. Intensities of 7 155 reflections were measured with 2θ values in the range 3–55°. 5 081 independent reflections [|*F*<sub>o</sub>| ≥ 3.0σ(|*F*<sub>o</sub>|)] were obtained and used in the analysis. The structure was solved by the Monte Carlo method.<sup>15</sup> Anisotropic thermal parameters were assumed for all non-hydrogen atoms. Forty hydrogen atoms were located in the differential Fourier synthesis and the remaining nine were placed at calculated positions. Thermal parameters for hydrogen atoms were kept fixed at the isotropic values of the parent atoms. The final full-matrix least-squares refinement led to an *R* value of 0.078 and *R*' value of 0.086 employing the weighting scheme of *w* = [1.7 × 10<sup>2</sup>(sinθ/λ)<sup>2</sup> - 2.0 × 10<sup>2</sup>(sinθ/λ) + 60]<sup>-1</sup>. An absorption correction following the method of Busing and Levy<sup>16</sup> was applied. All computations were carried out on a

FACOM M-380 computer using the UNICS III system.<sup>17</sup> The atomic scattering factors for non-hydrogen atoms and for hydrogen atoms were taken from refs. 18 and 19, respectively. Table 2 gives the final atomic co-ordinates for the complex. Additional material available from the Cambridge Crystallographic Data Centre comprises the H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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