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Structure of Acetylacetonato(carbonyl)bis(tricyclohexylphosphine)rhodium(I)

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Abstract. [Rh($C_5H_7O_2$)($C_{18}H_{33}P$)$_2$(CO)], $M_r = 790.9$, triclinic, $P\bar{1}$, $a = 10.449$ (2), $b = 11.968$ (2), $c = 19.469$ (4) Å, $\alpha = 71.13$ (0.01), $\beta = 71.11$ (0.01), $\gamma = 67.29$ (0.01)°, $V = 2069.3$ Å^3, $Z = 2$, D_m not measured, $D_x = 1.269$ g cm^{-3}, λ(Mo $K\alpha$) = 0.70173 Å, $\mu = 5.154$ cm^{-1}, $F(000) = 848$, $T = 293$ (2) K, $R = 0.060$ for 4491 observed reflections [$(F_o)^2 > 2.0\sigma(F_o)^2$], $\sin\theta \geq 0.05$. The complex has a central Rh atom in a slightly tetrahedrally distorted planar four-coordinate environment with the pairs of *trans* positioned tricyclohexylphosphine (Cy$_3$P) ligands, the enolate O of the non-chelated acac ligand and C of the linear carbonyl ligand. Rh—C = 1.786 (9), Rh—O = 2.052 (5), Rh—P(1) = 2.361 (2), Rh—P(2) = 2.348 (2) Å.

Introduction. The title compound is an intermediate in the *in situ* synthesis of Cy$_3$P/Rh complex catalysts used during hydroformylation processes.

Experimental. Material derived *via* the ligand exchange of rhodium dicarbonyl acetylacetonate with excess tricyclohexylphosphine; crystallized from toluene under dry nitrogen. Data collected on an Enraf–Nonius

CAD-4 diffractometer; structure solved with the *SDP* package (Frenz, 1982) on a PDP 11/60 computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). During the least-squares

Table 1. *Crystal data and experimental parameters*

Crystal shape and size	~0.3 × 0.25 × 0.1 mm, mounted in glass capillary
Absorption corrections applied (max./min. values)	ψ scan. μ = 5.154 cm⁻¹ (1–0.97)
Number of reflections used for cell constants	25
θ range for cell constants	10.2–18.4°
Max. θ for data collection	30°
Scan mode	ω–θ
Scan speed	2–13° variable speed
Range of *hkl* measured	h = (−11, +11) k = (−13, +13) l = (−2, −26) (up to limit of 12 859 reflections)
Standard reflections (variations)	5,1̄,10 155 5̄18 <3% <3% <5%
Decay correction	2.2% throughout correction period
Number of unique reflections measured	10 359
Number of observed reflections	4491 [|F_o|² > 2σ(F_o²)]; sinθ > 0.05
Hydrogen atoms	Calculated positions. Not refined.
Parameters refined (LS based on F)	433; Rh, P, C, O (all anisotropic). scale factor
Final R	0.060
Final wR	0.074
S	1.008
Final Δ/σ	< 0.02
Max. height of final difference electron density map	0.21 e Å⁻³

Table 2. *Positional parameters and their estimated standard deviations*

	x	y	z	$B_{eq}\dagger(\text{Å}^2)$		x	y	z	$B_{eq}\dagger(\text{Å}^2)$
Rh(1)	0·79492 (7)	0·16987 (5)	0·73048 (3)	1·70 (1)	C(19)	0·6766 (7)	−0·0478 (7)	0·7024 (4)	2·3 (2)
P(1)	0·8240 (2)	−0·0352 (2)	0·7294 (1)	1·98 (4)	C(20)	0·6609 (8)	0·0365 (7)	0·6250 (4)	3·1 (2)
P(2)	0·7661 (2)	0·3750 (2)	0·7292 (1)	2·05 (4)	C(21)	0·5433 (9)	0·0226 (8)	0·6012 (4)	3·3 (2)
O(1)	1·0240 (7)	0·1815 (6)	0·5960 (4)	5·1 (2)	C(22)	0·4012 (9)	0·0506 (8)	0·6574 (5)	3·6 (2)
O(2)	0·6193 (5)	0·1621 (4)	0·8163 (3)	2·7 (1)	C(23)	0·4187 (8)	−0·0327 (8)	0·7345 (5)	3·3 (2)
O(3)	0·5458 (7)	0·1469 (6)	1·0488 (3)	5·1 (2)	C(24)	0·5326 (8)	−0·0179 (7)	0·7601 (4)	3·1 (2)
C(1)	0·9339 (9)	0·1800 (7)	0·6483 (4)	3·1 (2)	C(25)	0·7644 (7)	0·4757 (6)	0·6340 (4)	2·2 (2)
C(2)	0·5888 (8)	0·1513 (6)	0·8874 (4)	2·5 (2)	C(26)	0·7447 (9)	0·6138 (7)	0·6260 (4)	3·0 (2)
C(3)	0·4422 (9)	0·1528 (8)	0·9249 (5)	3·7 (2)	C(27)	0·773 (1)	0·6782 (7)	0·5435 (5)	4·1 (3)
C(4)	0·6874 (9)	0·1347 (7)	0·9257 (5)	3·2 (2)	C(28)	0·682 (1)	0·6669 (9)	0·5038 (5)	4·3 (3)
C(5)	0·662 (1)	0·1294 (8)	1·0029 (5)	3·7 (2)	C(29)	0·693 (1)	0·5331 (9)	0·5132 (5)	4·3 (3)
C(6)	0·790 (1)	0·099 (1)	1·0322 (6)	6·0 (3)	C(30)	0·6626 (9)	0·4661 (8)	0·5953 (5)	3·6 (2)
C(7)	0·8265 (7)	−0·1392 (6)	0·8225 (4)	2·2 (2)	C(31)	0·9167 (8)	0·3924 (6)	0·7515 (4)	2·3 (2)
C(8)	0·9376 (8)	−0·1381 (7)	0·8571 (4)	2·7 (2)	C(32)	0·9433 (9)	0·3088 (7)	0·8273 (4)	3·2 (2)
C(9)	0·9156 (9)	−0·2048 (8)	0·9397 (4)	3·6 (2)	C(33)	1·0633 (9)	0·3266 (8)	0·8465 (5)	3·7 (2)
C(10)	0·9132 (9)	−0·3365 (8)	0·9510 (4)	3·5 (2)	C(34)	1·1989 (9)	0·3056 (7)	0·7876 (5)	3·6 (2)
C(11)	0·8095 (9)	−0·3399 (7)	0·9142 (5)	3·3 (2)	C(35)	1·1750 (9)	0·3872 (8)	0·7120 (5)	3·8 (2)
C(12)	0·8319 (9)	−0·2710 (6)	0·8312 (4)	3·1 (2)	C(36)	1·0560 (8)	0·3710 (8)	0·6913 (5)	3·2 (2)
C(13)	0·9800 (8)	−0·1038 (6)	0·6594 (4)	2·4 (2)	C(37)	0·6068 (8)	0·4428 (6)	0·7977 (4)	2·7 (2)
C(14)	0·9851 (9)	−0·2145 (8)	0·6367 (5)	3·9 (2)	C(38)	0·4687 (8)	0·4773 (7)	0·7744 (5)	3·3 (2)
C(15)	1·108 (1)	−0·2396 (8)	0·5691 (5)	4·5 (2)	C(39)	0·340 (1)	0·5157 (8)	0·8365 (6)	4·6 (3)
C(16)	1·250 (1)	−0·2618 (9)	0·5816 (6)	5·2 (3)	C(40)	0·339 (1)	0·6234 (8)	0·8620 (5)	4·9 (3)
C(17)	1·2479 (9)	−0·1545 (9)	0·6091 (5)	4·4 (3)	C(41)	0·476 (1)	0·5926 (9)	0·8856 (6)	5·1 (3)
C(18)	1·1246 (8)	−0·1286 (7)	0·6770 (5)	3·1 (2)	C(42)	0·6075 (9)	0·5548 (7)	0·8220 (5)	3·3 (2)

† Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = (4/3)\,[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$, where a, b, c are direct cell constants and $B(i,j)$ values have been deposited.

refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$ with a value $P = 0\cdot08$ (program weight: Frenz, 1982). Other experimental parameters are listed in Table 1. Atomic coordinates and equivalent isotropic thermal factors are in Table 2.*

Discussion. A labeled diagram of the complex (minus H atoms) is shown in Fig. 1, and major bond lengths and angles are given in Table 3. Surprisingly, it was found that the complex is of a non-chelating character, in spite

$$\text{CH}_3\text{COCH=C} \underset{\text{Cy}_3\text{P}}{\overset{\text{CH}_3}{\underset{|}{-\text{CO}}}} \overset{\text{PCy}_3}{\underset{\text{Rh}}{\diagdown}} \text{CO}$$
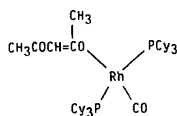
of the presence of the acetylacetonate, a group of highly chelating tendency as shown in the (acac) complexes [Rh(acac)(PPh₃)] (I) (Leipoldt, Basson, Bok & Gerber, 1978) and [Rh(acac)(CO)₂] (II) (Huq & Skapski, 1974). It is linked to Rh(1) through O(2) only. The central Rh atom has an almost planar four-coordination with C(1) from a linear carbonyl; O(2), a carbonyl oxygen from the acac ligand; P(1), P(2), two *trans* positioned P atoms from the two tricyclohexyl-phosphine groupings. This minimizes steric interaction between the bulky PCy₃ ligands. Rh(1) lies

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and additional bond angles and distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43064 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
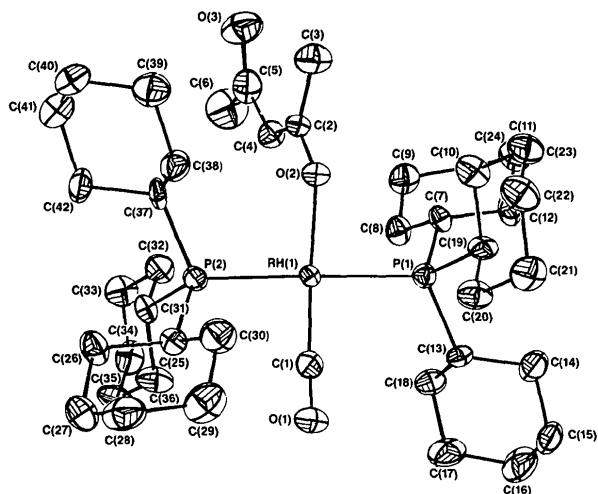

Fig. 1. Molecular configuration and atomic labeling.

Table 3. *Bond distances (Å) and angles (°)*

Rh(1)–P(1)	2·361 (2)		C(2)–C(3)	1·464 (12)
Rh(1)–P(2)	2·348 (2)		C(2)–C(4)	1·378 (13)
Rh(1)–O(2)	2·052 (5)		C(4)–C(5)	1·423 (13)
Rh(1)–C(1)	1·7869 (7)		C(5)–C(6)	1·497 (15)
C(1)–O(1)	1·142 (10)		C(5)–O(3)	1·238 (12)
C(2)–O(2)	1·291 (9)			
P(1)–Rh(1)–P(2)	178·9 (1)		O(2)–C(2)–C(3)	114·8 (8)
P(1)–Rh(1)–C(1)	91·1 (3)		O(2)–C(2)–C(4)	122·9 (8)
P(1)–Rh(1)–O(2)	87·5 (2)		C(3)–C(2)–C(4)	122·5 (8)
P(2)–Rh(1)–C(1)	88·15		C(2)–C(4)–C(5)	126·8 (9)
P(2)–Rh(1)–O(2)	93·2 (2)		C(4)–C(5)–C(6)	116·1 (10)
P(2)–Rh(1)–C(1)	172·9 (4)		C(4)–C(5)–O(3)	127·9 (11)
Rh(1)–C(1)–O(1)	177·2 (8)		C(6)–C(5)–O(3)	116·0 (10)
Rh(1)–O(2)–C(2)	136·0 (6)			

0·079 Å from the plane defined by C(1), P(1), P(2). P(1)—Rh(1)—P(2) is 178·9 (1)° and is similar to the 178·6° found in other square-planar complexes, C₃₃H₃₈F₆P₃Rh (Alcock, Brown & Jeffrey, 1977), but greater than that in [C₂₉H₂₈ClP₂O₂Rh]₂.xCH₂Cl₂ (Alcock, Brown & Jeffrey, 1977), C₃₃H₃₈O₅F₆P₃Rh (Alcock, Brown & Jeffery, 1976) and C₁₉H₃₄OP₂Rh (Young, 1983), where P—Rh—P angles of 172·9, 165·9, 174·3 and 164·1° are found respectively. Corresponding Rh—P and Rh—C(carbonyl) distances are similar also.

The acac ligand is almost planar. The dihedral angle between its mean plane and that through the distorted square-planar coordinations around Rh is 75·1°. The carbonyl bonds are *trans*, which differs from the acac complexes (I) and (II) above where both carbonyl oxygens have a chelated *cis* configuration within the distorted square-planar configuration around Rh. The Rh—O distances are 2·052 (5) Å in this compound, 2·06 and 2·05 Å in (I) and 2·029 and 2·087 Å in (II). Within the acac ligand, an enolate-type resonance is found, with the coordinated C—O distance being 1·291 (9) Å and intermediate-bond-order backbone C—C bonds of 1·378 (13), 1·423 (13) Å respectively. These are similar to the corresponding values of 1·281 (6), 1·377 (5), 1·379 Å found in (I) and 1·274, 1·275, 1·385, 1·399 Å in (II). The C—O value for the uncoordinated end, however, is much shorter:

1·238 (12) Å, and similar to the value of 1·23 Å for a ketonic C=O bond (*International Table for X-ray Crystallography*, 1962). The pairs of carbonyl oxygens and methyl groups are in *cis* positions relative to the C(2)—C(4)—C(5) backbone. The bulky trisubstituted phosphine ligands are in a *trans* arrangement which minimizes intramolecular steric interactions. Distances and angles within the six chair-shaped cyclohexane groups are normal. There are no unusually short intermolecular distances.

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Structure of (2,2'-Bipyridyl)salicylaldehydatocopper(II) Perchlorate

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Abstract. [Cu(C₇H₅O₂)(C₁₀H₈N₂)]ClO₄, $M_r = 440·3$, triclinic, $P\bar{1}$, $a = 8·513$ (5), $b = 9·453$ (8), $c = 11·826$ (6) Å, $\alpha = 77·93$ (5), $\beta = 69·71$ (6), $\gamma = 83·10$ (4)°, $V = 872$ (1) Å³, $Z = 2$, $D_x = 1·677$ g cm⁻³, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14·504$ cm⁻¹, $F(000) = 446$, $T = 291$ K. Final $R = 0·051$ for 2381 unique observed reflections. The structure consists of a dimeric unit involving two (2',2'-bipyridyl)salicylaldehydato-copper(II) cations and two perchlorate anions. The coordination sphere of copper can be described as an elongated octahedron due to the Jahn–Teller effect. The basal plane is formed by the two N atoms of the 2,2'-bipyridyl and by the two O atoms of the salicylaldehydate. Two large apical Cu—O distances are found, one towards the O atom of the perchlorate anion and the other towards the O atom of the nearest salicylaldehyde molecule.

Introduction. Among the ternary complexes containing 3d ions, those with copper(II) have been by far the best studied in solution (Sigel, 1973). Some ligand combinations lead to a discriminating behaviour and an