# The crystal and molecular structure of a new polymorph of carbonylhydridotris(triphenylphosphine)rhodium(I) having a Rh—H stretching absorption at 2013 cm<sup>-1</sup>

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A new polymorph of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, with a vRh—H of 2013 cm<sup>-1</sup>, has been isolated by crystallization from *tert*-butyl methyl ether/tetrahydrofuran. The crystals are monoclinic (space group  $P2_1/n$ ), with a = 21.48(2)Å, b = 14.92(2)Å, c = 14.52(1)Å,  $\beta = 107.95(8)^{\circ}$ . A final *R* value of 0.065 was obtained using 2243 reflections which had  $I_{net} > 2.5\sigma(I_{net})$ . The structure of the new polymorph has a similar coordination geometry to the known polymorph, but a different conformation of one of the phenyl rings.

### Introduction

Carbonylhydridotris(triphenylphosphine)rhodium-(1), HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, is usually prepared (Jardine, 1982) in ethanol and the crystalline material so obtained [polymorph A] is reported to have a Rh-H stretching absorption at 2040 cm<sup>-1</sup> when measured as a Nujol mull (Buckingham, 1984). During work on the reactions of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> we noted that, occasionally, samples of the compound had hydride stretching frequencies in Nujol considerably lower than 2040  $\rm cm^{-1}$ . Investigations showed that crystallization from solvents less polar than ethanol gave a material the Rh-H absorption of which was closer to 2004  $\text{cm}^{-1}$ , the value reported (Bath and Vaska, 1963) for the solution spectrum in benzene. Unfortunately, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> is only sparingly soluble in non-polar solvents such as cyclohexane, but we were eventually able to obtain single crystals [polymorph B] showing  $vRh-H = 2013 \text{ cm}^{-1}$  from a 2:1 mixture of tert-butyl methyl ether/tetrahydrofuran. The carbonyl absorptions are at 1918  $\pm$  2 cm<sup>-1</sup> in the Nujol spectra of both polymorphs. However, while the original polymorph A exhibits a  $\delta Rh - H$  at 784 cm<sup>-1</sup>, this band is absent in polymorph B, or, more probably, is obscured by the absorptions of the phenyl groups.

### Experimental

#### Preparation of $H-Rh(CO)(PPh_3)_3$

HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was prepared by a slight modification of the method described in Inorganic Syntheses (Ahmad et al., 1974). The original method sometimes results in the coprecipitation of some (PPh<sub>3</sub>)<sub>2</sub>Rh(CO)Cl. A solution of sodium ethoxide was prepared by dissolving sodium metal (0.7 g) in ethanol (25 cm<sup>3</sup>). Rhodium trichloride trihydrate (0.5 g) in hot ethanol  $(25 \text{ cm}^3)$  was added down the condenser to a stirred solution of PPh<sub>3</sub> (5 g) in ethanol (250 cm<sup>3</sup>) under reflux. After 15 sec 40% aqueous formaldehyde (20 cm<sup>3</sup>) followed immediately by the hot sodium ethoxide solution were added down the condenser. Heating was continued for 1 min during which time precipitation commences. The mixture was then allowed to cool to room temperature. The bright yellow product was then filtered off, washed with ethanol, water, ethanol, and hexane and dried in vacuo. Yield 1.3 g, 75%.

# X-ray data collection, structure solution and refinement

An automated Picker diffractometer was used with Zr-filtered Mo K $\alpha$  radiation to collect the data for polymorph B. 2808 reflections were measured in the range  $2^{\circ} < 2\theta < 35^{\circ}$  of which 2243 had  $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$ .

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The intensities were corrected for extinction and absorption. The rhodium atom was located from the Patterson function and the remaining nonhydrogen atoms by Fourier difference synthesis using the NRCVAX program package (Gabe et al., 1989). The phenyl hydrogen atoms were placed in calculated positions (C-H = 1.08Å) and included as fixed contributions during the refinement. The structure was refined with anisotropic temperature factors for the rhodium, phosphorus, and carbonyl group atoms, and isotropic temperature factors for the phenyl atoms. The final refinement which was carried out by full matrix least squares with 105 atoms and 317 parameters, converged to an R of 0.065. A comparison of the crystallographic data of the two polymorphs is given in Table 1. Atomic coordinates and thermal parameters of polymorph B are given in Table 2.

Table 1. Crystallographic data of polymorphs A and B of  $$C_{55}H_{46}OP_3Rh$$ 

	Polymorph A (La Placa and Ibers)	Polymorph B (this work)
M <sub>r</sub>	918.78	918.78
a, Å	10.11(5)	21.48(2)
b, Å	33.31(5)	14.92(2)
c, Å	13.33(7)	14.52(1)
β, deg	90.0(1)	107.95(8)
$V Å^3$	4489(33)	4430(8)
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
Z	4	4
$D_c \text{ g cm}^{-3}$	1.36	1.38
radiation used	Cu Ka	Μο Κα
$\mu m, cm^{-1}$	44.5	5.21
transm. coeff	$\max/\min = 1.18$	0.901-0.781
λ, Å	1.5418	0.7107
temp, K	296	298
R	0.072	0.065
R <sub>w</sub>	_	0.074
$R = \Sigma   F_o  -  F_c   / \Sigma  F_o $	$R_{w} = [(\Sigma w ( F_{o}  -  F_{c} )^{2} / \Sigma w F_{o}^{2}]^{1/2}]$	$w = 1/\sigma^2( F_o )$

**Table 2.** Fractional coordinates and equivalent isotropic thermalparameters for Polymorph  $B^a$ 

Atom	x	у	z.	Beq
Rh	0.39348(6)	0.19981(8)	0.16883(9)	2.7(1)
P1	0.4561(2)	0.2528(3)	0.3181(3)	2.9(2)
P2	0.4210(2)	0.2336(3)	0.0336(3)	3.1(2)
P3	0.3279(2)	0.0748(3)	0.1590(3)	2.9(2)
C55	0.326(1)	0.282(1)	0.153(1)	3.5(10)
0	0.284(1)	0.333(1)	0.145(1)	6.6(8)

Table 2. Continued

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Atom	<i>x</i>	у	Z	B <sub>eq</sub>	
C1	0.489(1)	0.366(1)	0.321(1)	3.0(3)	
C2	0.484(1)	0.410(1)	0.237(1)	3.6(4)	
C3	0.509(1)	0.497(1)	0.237(1)	4.8(4)	
C4	0.538(1)	0.538(1)	0.325(1)	4.6(4)	
C5	0.544(1)	0.498(1)	0.409(1)	5.0(4)	
C6	0.519(1)	0.411(1)	0.412(1)	4.6(4)	
C7	0.416(1)	0.265(1)	0.410(1)	2.5(3)	
C8	0.361(1)	0.319(1)	0.393(1)	3.6(4)	
C9	0.327(1)	0.327(1)	0.459(1)	4.3(4)	
C10	0.345(1)	0.281(1)	0.544(1)	4.6(4)	
C11	0.399(1)	0.226(1)	0.562(1)	4.4(4)	
C12	0.434(1)	0.219(1)	0.498(1)	3.8(4)	
C13	0.527(1)	0.183(1)	0.380(1)	2.9(3)	
C14	0.568(1)	0.035(1)	0.440(1)	5.3(4)	
C15	0.514(1)	0.093(1)	0.388(1)	4.1(4)	
C16	0.628(1)	0.070(1)	0.477(1)	5.9(5)	
C17	0.642(1)	0.156(1)	0.467(1)	6.1(5)	
C18	0.590(1)	0.217(1)	0.418(1)	4.6(4)	
C19	0.385(1)	0.338(1)	-0.024(1)	3.6(4)	
C20	0.318(1)	0.342(1)	-0.061(1)	4.9(4)	
C21	0.285(1)	0.423(1)	-0.096(1)	5.7(5)	
C22	0.322(1)	0.499(1)	-0.092(1)	5.6(5)	
C23	0.388(1)	0.496(1)	-0.057(1)	5.6(5)	
C24	0.421(1)	0.414(1)	-0.023(1)	4.1(4)	
C25	0.509(1)	0.248(1)	0.046(1)	3.4(4)	
C26	0.530(1)	0.258(1)	-0.035(1)	4.3(4)	
C27	0.599(1)	0.264(1)	-0.024(1)	5.6(5)	
C28	0.642(1)	0.260(1)	0.068(1)	5.0(4)	
C29	0.622(1)	0.250(1)	0.148(1)	4.8(4)	
C30	0.554(1)	0.244(1)	0.136(1)	3.6(4)	
C31	0.403(1)	0.152(1)	-0.067(1)	3.1(4)	
C32	0.371(1)	0.173(1)	-0.162(1)	5.9(5)	
C33	0.359(1)	0.106(2)	-0.236(2)	7.0(5)	
C34	0.384(1)	0.026(2)	-0.211(2)	6.5(5)	
C35	0.416(1)	0.002(1)	-0.119(1)	5.7(5)	
C36	0.424(1)	0.068(1)	-0.045(1)	4.6(4)	
C37	0.366(1)	-0.033(1)	0.208(1)	2.4(3)	
C38	0.331(1)	-0.097(1)	0.242(1)	3.9(4)	
C39	0.362(1)	-0.179(1)	0.275(1)	5.2(4)	
C40	0.422(1)	-0.196(1)	0.274(1)	4.7(4)	
C41	0.458(1)	-0.136(1)	0.239(1)	4.9(4)	
C42	0.428(1)	-0.053(1)	0.205(1)	3.9(4)	
C43	0.264(1)	0.081(1)	0.216(1)	3.3(4)	
C44	0.280(1)	0.109(1)	0.309(1)	4.4(4)	
C45	0.236(1)	0.107(1)	0.361(1)	5.0(4)	
C46	0.172(1)	0.079(1)	0.316(1)	5.5(4)	
C47	0.156(1)	0.054(1)	0.224(1)	3.0(4)	
C48	0.198(1)	0.053(1)	0.1/2(1)	3.9(4)	
C49	0.281(1)	0.043(1)	0.034(1)	5,1(5) 1 6(1)	
C50	0.236(1)	0.109(1)	-0.01/(1)	4.0(4)	
C51	0.199(1)	0.089(1)	-0.113(1)	5.3(3) 5.0(4)	
C52	0.211(1) 0.256(1)	-0.013(1)	-0.130(1)	5.0(4)	
C54	0.230(1)	-0.031(1)	-0.010(1)	3.8(4)	
0.54	0.2220(1)	0.051(1)	0.010(1)	5.0(4)	

<sup>a</sup> Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as  $B_{\rm eq} = 8\pi^2/3\Sigma_i\Sigma_j U_{ij}a_i^*a_i^*(a_i \cdot a_j)$ .

### **Results and discussion**

The molecules of both polymorphs have the same basic geometry, with the three phosphorus atoms in the equatorial plane of a trigonal bipyramid. The Figure shows the molecules of polymorph A and polymorph B viewed down the Rh-C-O vector. The atomic numbering system adopted is that used by the Cambridge Crystallographic Database, so that the carbonyl carbon is C55. The carbon atoms of the phenyl groups attached to P1 are C1-C18, those attached to P2 are C19-C36, and those attracted to P3 are C37-C54. It can be seen from Figure 1 that the orientations of the phenyl groups attached to P1 and P3 are very similar in both molecules. However, there is a considerable difference in the orientation of one of the phenyl groups attached to P2. In Polymorph A, P2 and Rh are roughly coplanar with carbon atoms C19-C24 of the phenyl ring, but in polymorph B the corresponding phenyl group is twisted through about 90°. The Rh-P2 distance in polymorph B (2.276(5)A) is somewhat shorter than the corresponding distance in polymorph A (2.316(9)Å). Not surprisingly, in view of this, the volume per triphenylphosphine molecule is lower in polymorph B,369 Å<sup>3</sup>, compared with 374  $Å^3$  for polymorph A. Both these volumes are slightly less than that found in the isoelectronic ruthenium nitrosyl complex RuH(NO)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub> (378 Å<sup>3</sup>) (Pierpoint and Eisenberg, 1972), and polymorph B approaches the value of triphenylphosphine itself (364 Å<sup>3</sup>) (Daly, 1964). A comparison of the bond lengths and interbond angles in the coordination sphere of both polymorphs is given in Table 3. Although our final R of 0.065 is better than the 0.072 achieved by La Placa and Ibers (1965) using photographic data, we do not feel confident about the position of the hydride hydrogen atom. The final difference map showed several peaks in the vicinity of the rhodium atom, but none could

 
 Table 3. Comparison of bond lengths and interbond angles of Polymorphs A and B

Polymorph A (La Placa and Ibers)		Polymorph B (this work)	
Bond distances (Å)			
Rh-P1	2.336(8)	Rh-P1	2.311(4)
Rh-P2	2.316(9)	Rh-P2	2.276(5)
Rh-P3	2.315(8)	Rh-P3	2.315(5)
Rh-C55	1.83(3)	RhC55	1.86(2)
Bond angles (deg)			
P1-Rh-P2	115.8(2)	P1-Rh-P2	120.2(2)
P2-Rh-P3	120.5(3)	P1-Rh-P3	120.0(2)
P2-Rh-P3	116.7(3)	P2-Rh-P3	116.1(2)
P1-Rh-C55	94.8(8)	P1-Rh-C55	95.6(5)
P2-Rh-C55	104.0(8)	P2-Rh-C55	98.3(5)
P3-Rh-C55	97.8(8)	P3-Rh-C55	95.2(5)
Rh-C55-O	179(2)	Rh-C55-O	178(2)



Fig. 1. A comparison of the molecular conformation of polymorph A and polymorph B of  $HRh(CO)(PPh_3)_3$  viewed down the Rh-C-O axis.

be refined to give a sensible position for the hydride hydrogen atom. Pierpoint and Eisenberg, who achieved a residual R of 0.062, were also unable to locate the hydride in the ruthenium nitrosyl referred to above. While it is unfortunate that we were also unable to locate the hydride in polymorph B there is no doubt that the difference observed in the infra-red spectra of the two polymorphs is due to the different force fields experienced by the Rh-H bonds. The difference could be caused by either steric interactions with the ortho-hydrogen atoms of the phenyl groups, or to changes in the electronic state of the Rh atom arising from the slightly different coordination environment. The Rh-H stretching frequency of polymorph A is the more remarkable, as the frequency of 36  $cm^{-1}$  higher than the solution frequency. Generally solid state and solution frequencies differ by less than 20  $\text{cm}^{-1}$  (Hill and Rendall, 1975).

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### References

- Ahmad, N., Levison, J. J., Robinson, S. D., and Uttley, M. F. (1974) *Inorg. Synth.* 15, 59.
- Bath, S. S., and Vaska, L. (1963) J. Am. Chem. Soc. 85, 3500.
- Buckingham, J. (1984) (ed.) Dictionary of organometallic compounds, Vol. 2 (Chapman and Hall, London) p. 1737.
- Daly, J. J. (1964) J. Chem. Soc. 3799.
- Gabe, E. J., Le Page, Y., Charland, P. F., Lee, F. L., and White, P. S. (1989) J. Appl. Cryst. 22, 384.
- Hill, R. R., and Rendall, D. A. E. (1975) The interpretation of infrared spectra. (Heyden, London) p. 52.
- Jardine, F. H. (1982) Polyhedron 1, 569.
- La Placa, S. J., and Ibers, J. A. (1965) Acta Cryst. 18, 511.
- Pierpont, C. G., and Eisenberg, R. (1972) Inorg. Chem. 11, 1094.