

## Structure of Bis( $\mu$ -di-*tert*-butylphosphido)-bis(dicarbonylrhodium)(*Rh–Rh*) in $P\bar{1}$

BY RICHARD A. JONES\* AND THOMAS C. WRIGHT

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

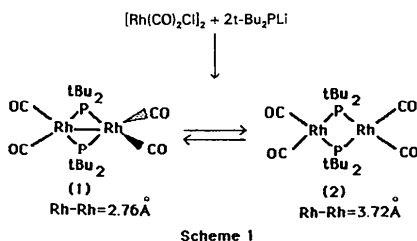
AND JERRY L. ATWOOD\* AND WILLIAM E. HUNTER

Department of Chemistry, The University of Alabama, University, Alabama 35486, USA

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**Abstract.**  $[\text{Rh}_2\{\text{P}(\text{C}_4\text{H}_9)_2\}_2(\text{CO})_4]$ ,  $M_r = 608.3$ , triclinic,  $P\bar{1}$ ,  $a = 8.592$  (5),  $b = 11.803$  (7),  $c = 13.717$  (7) Å,  $\alpha = 74.53$  (4),  $\beta = 77.90$  (5),  $\gamma = 75.88$  (4)°,  $V = 1284.5$  Å<sup>3</sup>,  $Z = 2$  (dimers),  $D_x = 1.57$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 13.93$  cm<sup>-1</sup>,  $F(000) = 616$ , ambient temperature,  $R = 0.026$  for 2635 unique observed reflections. The two Rh atoms adopt different coordination geometries: Rh(1) – pseudotetrahedral, Rh(2) – square planar [Rh–Rh = 2.7481 (6) Å]. The two *tert*-Bu<sub>2</sub>P<sup>-</sup> groups occupy asymmetric bridging positions Rh(1)–P(1)–Rh(2) = 71.49 (4), Rh(1)–P(2)–Rh(2) = 71.94 (4)°; Rh(1)–P(av.) = 2.234 (1), Rh(2)–P(av.) = 2.449 (1) Å and each Rh bears two CO ligands [Rh(1)–C(av.) = 1.908 (7), Rh(2)–C(av.) = 1.854 (7) Å]. Key angles to CO ligands: Rh(1)–Rh(2)–C(av.) = 134.6 (2), Rh(2)–Rh(1)–C(av.) = 125.0 (2)°.

**Introduction.** We recently described the unusual dinuclear Rh<sup>I</sup> system based on two isomers of the di-*tert*-butylphosphido-bridged (*tert*-Bu<sub>2</sub>P<sup>-</sup>) complex  $[\text{Rh}(\mu\text{-tert-Bu}_2\text{P})(\text{CO})_2]_2$  (Jones, Wright, Atwood & Hunter, 1983). The interesting feature of this system is a facile reversible metal–metal-bond cleavage accompanied only by a geometric isomerization (Scheme 1). After crystals of (1) and (2) had been characterized we isolated a third form of this compound, (3), which was different in both color (lighter orange) and crystalline shape from either (1) or (2). A single-crystal X-ray diffraction study showed that (3) had virtually the same molecular structural parameters as (1) but had crystallized in a different space group from (1) ( $P\bar{1}$  vs  $P2_1$ ).



\* Authors to whom correspondence should be addressed.

**Experimental.** Crystals of (3) were isolated from the reaction of *tert*-Bu<sub>2</sub>PLi and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  previously reported, which also yields (1) and (2). Crystals of all three compounds were grown from hexane solutions and separated by hand. Crystals of (3) were sealed in Lindemann capillaries and mounted on a CAD-4 diffractometer. Unit-cell parameters obtained from 25 strong-intensity reflections ( $2 < 2\theta < 26^\circ$ ) collected in the automated search mode. After suitable refinement of these values data collected in  $\omega$ - $2\theta$  scan mode. Other relevant data: graphite monochromator, crystal dimensions 0.40 × 0.30 × 0.20 mm (prism-shaped), scan width (°) 0.8 + 0.2tan $\theta$ , standard reflections 300, 030, 003, decay of standards <3%, *hkl* range:  $\pm h$  (–8 to +9),  $\pm k$  (–11 to +12),  $l$  (0 to 14).

Table 1. Final atomic parameters for (3)

The form of the anisotropic thermal parameter is:  $\exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hkaU_{12} + 2hlcU_{13} + 2klcU_{23})]$  where  $a, b$ , and  $c$  are reciprocal lattice constants.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (Å <sup>2</sup> )
Rh(1)	0.89970 (5)	0.73037 (4)	0.15788 (3)	0.031 (3)
Rh(2)	0.72945 (5)	0.66357 (4)	0.35013 (3)	0.036 (4)
P(1)	0.8754 (2)	0.5402 (1)	0.2277 (1)	0.032 (4)
P(2)	0.7741 (2)	0.8619 (1)	0.2538 (1)	0.036 (6)
C(1)	1.0588 (7)	0.4237 (5)	0.2724 (4)	0.040 (7)
C(2)	1.1861 (7)	0.4092 (6)	0.1769 (5)	0.052 (10)
C(3)	1.0265 (8)	0.2997 (5)	0.3307 (5)	0.055 (13)
C(4)	1.1293 (8)	0.4749 (6)	0.3413 (5)	0.056 (4)
C(5)	0.7333 (7)	0.4646 (5)	0.1884 (4)	0.043 (5)
C(6)	0.6031 (8)	0.5640 (6)	0.1404 (6)	0.078 (33)
C(7)	0.6472 (8)	0.3827 (6)	0.2775 (5)	0.061 (3)
C(8)	0.8272 (8)	0.3936 (6)	0.1083 (5)	0.065 (4)
C(9)	0.8960 (8)	0.9258 (5)	0.3195 (5)	0.054 (6)
C(10)	0.978 (1)	1.0187 (7)	0.2394 (7)	0.099 (39)
C(11)	0.800 (1)	0.979 (1)	0.4078 (8)	0.144 (46)
C(12)	1.0268 (8)	0.8232 (6)	0.3618 (5)	0.073 (1)
C(13)	0.5858 (8)	0.9758 (5)	0.2161 (5)	0.053 (16)
C(14)	0.4771 (8)	0.9083 (6)	0.1872 (6)	0.068 (27)
C(15)	0.639 (1)	1.0683 (7)	0.1210 (7)	0.091 (28)
C(16)	0.488 (1)	1.0419 (8)	0.2959 (7)	0.121 (8)
C(17)	1.1259 (8)	0.7359 (5)	0.1320 (5)	0.047 (1)
O(1)	1.2557 (6)	0.7444 (5)	0.1053 (4)	0.077 (29)
C(18)	0.8131 (8)	0.7844 (5)	0.0331 (5)	0.047 (5)
O(2)	0.7795 (6)	0.8198 (4)	–0.0473 (4)	0.074 (20)
C(19)	0.7092 (7)	0.5177 (6)	0.4408 (5)	0.045 (1)
O(3)	0.6960 (6)	0.4331 (4)	0.5044 (3)	0.063 (15)
C(20)	0.596 (1)	0.7456 (6)	0.4441 (6)	0.072 (27)
O(4)	0.509 (1)	0.7860 (5)	0.5060 (5)	0.144 (69)

Full details of data-collection procedures have been published (Jones & Wright, 1983). 3155 reflections measured in  $2\theta$  range  $1\text{--}44^\circ$ , of these 2635 unique reflections with  $I > 2\sigma(I)$  considered observed,  $\sigma(I) = [\sigma^2 + (0.05I)^2]^{1/2}$  with  $\sigma$  calculated from counting statistics. The space group was chosen as  $P\bar{1}$ , and this was confirmed on the basis of successful refinement. All calculations performed using *SHELX76* (Sheldrick, 1976) on a Univac 1100/60 computer system. Heavy atoms located by *MULTAN* (Germain, Main & Woolfson, 1971) and remainder by subsequent difference Fourier synthesis. Unit weights used throughout and no correction made for either decay or absorption since none was warranted (decay  $< 2\%$ , trans. min. 92%). Anisotropic refinement of all non-H atoms gave  $R = 0.026$  and  $wR = 0.030$  with a  $\text{GOF} = 1.37$ , function minimized  $\sum w(|F_o| - |F_c|)^2$ . H atoms placed in calculated positions but not refined. No chemically significant peaks observed in final difference map (max. and min. electron density  $+0.6$  and  $-0.3 \text{ e } \text{\AA}^{-3}$  respectively).  $(\Delta/\sigma)_{\text{max}} < 0.01$ . Scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final atomic parameters for (3) are given in Table 1.\* Fig. 1 is a perspective drawing of the molecule and a view of the unit cell is given in Fig. 2.

The molecule is a dimer in which the coordination geometry about each Rh is different. Excluding the metal-metal interaction Rh(1) is pseudotetrahedral, and Rh(2) is square planar. There is a notable asymmetry in the Rh-P bond lengths with  $\text{Rh}(1)\text{--P}(\text{av.}) = 2.234(1) \text{ \AA}$ , while  $\text{Rh}(2)\text{--P}(\text{av.}) = 2.449(1) \text{ \AA}$ . This asymmetry has been shown by calculations to be a major factor responsible for the stabilization of the molecule (Kang, Albright, Jones & Wright, 1985). The Rh-Rh distance is well within the range expected for a bond order of one.

Table 2 gives pertinent bond lengths and angles for (3) as well as for the structure of (1) solved in  $P2_1$ . It is interesting to note that there are no chemically significant differences in the two structures. Discussion of this unusual type of structure has been made elsewhere (Jones, Wright, Atwood & Hunter, 1983).

Although polymorphism is well documented, it is relatively rare for organometallic complexes (Bernal, Brunner & Wachter, 1984). Also, the structural features of compounds studied having more than one space group inevitably differ substantially from one another. In most cases, the different morphologies result from changing the conditions under which the compound is crystallized (*e.g.* solvent, temperature,

pressure, *etc.*) with each form simply representing the most stable configuration of the molecule under a certain set of conditions. Often these different forms are capable of existing under the same conditions, even though one must be more thermodynamically stable than the other. However, in the case of (1) and (3) the molecular structures of both forms are virtually identical to within experimental error. The molecules are simply packed differently, such that one is triclinic [(3)] while the other is monoclinic [(1)]. This is even more unusual since both forms may be obtained from the same hexane solution. Clearly the energy difference between the two forms (1) and (3) is very small and a combination of other factors which are not normally of major significance, such as packing forces, could make both forms kinetically accessible.

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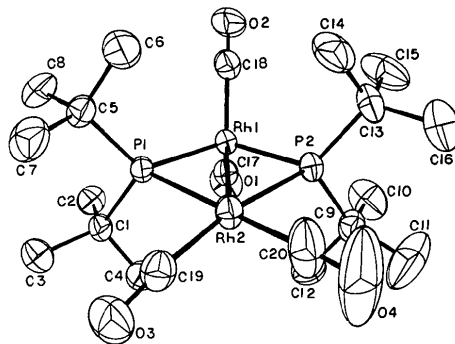


Fig. 1. ORTEP view (Johnson, 1976) of (3). The atom-labeling scheme is the same as that used for (1) (Jones, Wright, Atwood & Hunter, 1983). H atoms have been omitted for clarity.

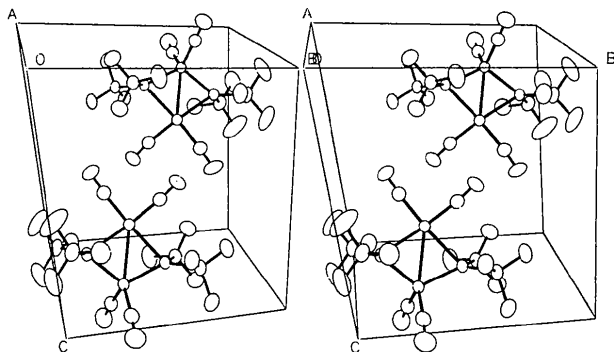


Fig. 2. Stereoview of the unit cell for (3).

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42599 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) for (1) and (3)

	(1)	(3)		(1)	(3)		(1)	(3)
Rh(1)—Rh(2)	2.7610 (9)	2.7481 (6)	P(1)—C(5)	1.90 (1)	1.908 (5)	C(9)—C(11)	1.52 (2)	1.510 (9)
Rh(1)—P(1)	2.241 (2)	2.236 (1)	P(2)—C(9)	1.91 (1)	1.904 (6)	C(9)—C(12)	1.50 (1)	1.517 (9)
Rh(1)—P(2)	2.244 (2)	2.232 (1)	P(2)—C(13)	1.90 (1)	1.900 (6)	C(13)—C(14)	1.53 (1)	1.533 (9)
Rh(1)—C(17)	1.88 (1)	1.915 (7)	C(1)—C(2)	1.55 (1)	1.539 (8)	C(13)—C(15)	1.51 (2)	1.529 (9)
Rh(1)—C(18)	1.90 (1)	1.900 (7)	C(1)—C(3)	1.52 (1)	1.530 (8)	C(13)—C(16)	1.51 (1)	1.50 (1)
Rh(2)—P(1)	2.446 (2)	2.459 (1)	C(1)—C(4)	1.51 (1)	1.532 (8)	C(17)—O(1)	1.16 (1)	1.119 (7)
Rh(2)—P(2)	2.458 (2)	2.439 (1)	C(5)—C(6)	1.52 (1)	1.523 (8)	C(18)—O(2)	1.13 (1)	1.141 (7)
Rh(2)—C(19)	1.86 (1)	1.858 (6)	C(5)—C(7)	1.51 (2)	1.521 (8)	C(19)—O(3)	1.13 (1)	1.149 (7)
Rh(2)—C(20)	1.85 (1)	1.849 (7)	C(5)—C(8)	1.54 (2)	1.533 (8)	C(20)—O(4)	1.15 (1)	1.133 (8)
P(1)—C(1)	1.89 (1)	1.910 (5)	C(9)—C(10)	1.53 (2)	1.524 (9)			
Rh(2)—Rh(1)—P(1)	57.43 (6)	58.03 (4)	Rh(1)—P(1)—Rh(2)	72.02 (7)	71.49 (4)	C(6)—C(5)—C(7)	105 (1)	107.4 (5)
Rh(2)—Rh(1)—P(2)	57.73 (6)	57.53 (4)	Rh(1)—P(1)—C(1)	120.7 (3)	119.8 (2)	P(1)—C(5)—C(8)	108.5 (8)	110.0 (4)
P(1)—Rh(1)—P(2)	115.15 (9)	115.55 (5)	Rh(2)—P(1)—C(1)	114.0 (3)	114.6 (2)	C(6)—C(5)—C(8)	108 (1)	108.8 (5)
Rh(2)—Rh(1)—C(17)	125.7 (3)	123.7 (2)	Rh(1)—P(1)—C(5)	119.9 (3)	123.1 (2)	C(7)—C(5)—C(8)	110.0 (9)	109.6 (5)
P(1)—Rh(1)—C(17)	106.9 (3)	108.0 (2)	Rh(2)—P(1)—C(5)	112.7 (4)	111.7 (2)	P(2)—C(9)—C(10)	109.1 (8)	108.5 (5)
P(2)—Rh(1)—C(17)	108.9 (3)	107.0 (2)	C(1)—P(1)—C(5)	111.3 (4)	110.0 (2)	P(2)—C(9)—C(11)	112.3 (8)	115.3 (5)
Rh(2)—Rh(1)—C(18)	122.7 (3)	126.3 (2)	Rh(1)—P(2)—Rh(2)	71.74 (7)	71.94 (4)	C(10)—C(9)—C(11)	111 (1)	110.1 (7)
P(1)—Rh(1)—C(18)	107.7 (3)	109.6 (2)	Rh(1)—P(2)—C(9)	121.2 (4)	120.4 (2)	P(2)—C(9)—C(12)	107.8 (7)	107.1 (4)
P(2)—Rh(1)—C(18)	106.7 (3)	106.6 (2)	Rh(2)—P(2)—C(9)	112.5 (3)	111.8 (2)	C(10)—C(9)—C(12)	109 (1)	108.3 (6)
C(17)—Rh(1)—C(18)	111.6 (4)	109.9 (3)	Rh(1)—P(2)—C(13)	120.7 (3)	119.9 (2)	C(11)—C(9)—C(12)	108 (1)	107.3 (6)
Rh(1)—Rh(2)—P(1)	50.54 (5)	50.48 (3)	Rh(2)—P(2)—C(13)	113.8 (4)	115.9 (2)	P(2)—C(13)—C(14)	107.0 (7)	107.1 (4)
Rh(1)—Rh(2)—P(2)	50.53 (6)	50.54 (4)	C(9)—P(2)—C(13)	110.6 (4)	111.0 (3)	P(2)—C(13)—C(15)	108.5 (8)	108.0 (5)
P(1)—Rh(2)—P(2)	101.07 (8)	101.01 (5)	P(1)—C(1)—C(2)	108.5 (8)	107.5 (4)	C(14)—C(13)—C(15)	106 (1)	108.3 (6)
Rh(1)—Rh(2)—C(19)	134.4 (3)	134.6 (2)	P(1)—C(1)—C(3)	116.9 (8)	116.2 (4)	P(2)—C(13)—C(16)	116.8 (8)	116.2 (5)
P(1)—Rh(2)—C(19)	83.9 (3)	84.8 (2)	C(2)—C(1)—C(3)	107.8 (9)	108.4 (5)	C(14)—C(13)—C(16)	110 (1)	108.9 (6)
P(2)—Rh(2)—C(19)	173.5 (3)	170.4 (2)	P(1)—C(1)—C(4)	108.2 (6)	107.4 (4)	C(15)—C(13)—C(16)	109 (1)	108.1 (7)
Rh(1)—Rh(2)—C(20)	136.4 (3)	134.6 (2)	C(2)—C(1)—C(4)	107 (1)	108.5 (5)	Rh(1)—C(17)—O(1)	171 (1)	171.8 (6)
P(1)—Rh(2)—C(20)	170.9 (4)	172.0 (3)	C(3)—C(1)—C(4)	108 (1)	108.6 (5)	Rh(1)—C(18)—O(2)	170.5 (9)	171.6 (6)
P(2)—Rh(2)—C(20)	86.2 (3)	84.4 (2)	P(1)—C(5)—C(6)	108.3 (7)	107.1 (4)	Rh(2)—C(19)—O(3)	173.2 (9)	173.2 (5)
C(19)—Rh(2)—C(20)	89.2 (4)	90.7 (3)	P(1)—C(5)—C(7)	117.1 (8)	113.9 (4)	Rh(2)—C(20)—O(4)	173 (1)	173.3 (7)

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## Structure of (5,10,15,20-Tetraphenylporphinato)cadmium(II)

BY ALAN HAZELL

*Institute of Chemistry, Århus University, DK-8000 Århus C, Denmark*

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**Abstract.**  $[\text{Cd}(\text{C}_{44}\text{H}_{28}\text{N}_4)]$ ,  $M_r = 781.2$ , triclinic,  $P\bar{1}$ ,  $a = 14.697$  (7),  $b = 10.096$  (4),  $c = 14.784$  (6) Å,  $\alpha = 56.31$  (2),  $\beta = 68.76$  (2),  $\gamma = 62.43$  (2)°,  $V = 1601$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.620$  (1) Mg m<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.7255$  (6) mm<sup>-1</sup>,  $F(000) = 736$ ,  $T = 294$  K,  $R(F) = 0.042$  for 3905 reflexions [ $I > 3\sigma(I)$ ] and 443 variables. The porphine skeleton is

non-planar, Cd being 0.578 (6) Å out of the plane of the N atoms and only 2.845 (5) Å from an  $\alpha$ -carbon of a pyrrole group of the centrosymmetrically related molecule. The mean Cd–N distance is 2.187 (2) Å, the mean N–C–N angles are 86.0 (1) and 149.3 (1)°. Although chemically equivalent bonds and angles do not differ significantly the molecule is flexible and