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Crystallographic Analysis of Two Rhodium(III) Hydride Complexes, Bis{1,1′-bis[*tert*-butyl(phenyl)phosphino]ferrocene-*P,P′*}-tri-μ-hydrido-dihydridodirhodium(III) Chlorate Methanol Solvate, $[\mathrm{Rh_2H_5\{Fe[P(C_4H_9)(C_5H_4)(C_6H_5)]_2\}_2]ClO_4.CH_3OH}$ (1), and Bis[1,1′-bis(di-*tert*-butylphosphino)ferrocene-*P,P′*]-tri-μ-hydrido-dihydridodirhodium(III) Chlorate, $[\mathrm{Rh_2H_5\{Fe[P(C_4H_9)_2(C_5H_4)]_2\}_2]ClO_4}$ (2)

BY F. W. B. EINSTEIN AND T. JONES

Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada V5A 1S6

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Abstract. $[(L\,L)\mathrm{HRh}(\mu\text{-H})_3\mathrm{RhH}(L\,L)]\mathrm{ClO_4}$ $\{(L\,L) = rac\text{-}\mathrm{Fe}[\eta^5\text{-}\mathrm{C_5H_4P(Ph)(CMe_3)}]_2\}$ (1): $M_r = 1371{\cdot}2$, monoclinic, $P2_1/n$, $a = 18{\cdot}708\ (4)$, $b = 14{\cdot}857\ (2)$, $c = 21{\cdot}853\ (4)$ Å, $\beta = 92{\cdot}95\ (2)°$, $V = 6065{\cdot}88$ Å^3, $Z = 4$, $D_x = 1{\cdot}501$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 11{\cdot}89$ cm^{-1}, $F(000) = 2824$, $T = 293$ K, final $R = 0{\cdot}045$ for 5732 observed reflections. $[(L'\,L')\mathrm{HRh}(\mu\text{-H})_3\mathrm{RhH}(L'\,L')]\mathrm{ClO_4}$ $\{(L'\,L') = \mathrm{Fe}[\eta^5\text{-}\mathrm{C_5H_4P(CMe_3)_2}]_2\}$ (2): $M_r = 1259{\cdot}2$, monoclinic, $P2_1/c$, $a = 15{\cdot}276\ (3)$, $b = 14{\cdot}751\ (2)$, $c = 25{\cdot}950\ (3)$ Å, $\beta = 90{\cdot}85\ (1)°$, $V = 5846{\cdot}83$ Å^3, $Z = 4$, $D_x = 1{\cdot}430$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 12{\cdot}26$ cm^{-1}, $F(000) = 2624$, $T = 293$ K, final $R = 0{\cdot}059$ for 4180 observed reflections. The structure of (1) contains an unusual RhPH skeletal structure in which each Rh atom (in the 3+ oxidation state) has three Rh—H bridging bonds [average 1·77 (8) Å], a single Rh—H terminal bond [average 1·56 (12) Å] and two Rh—P bonds. It is tentatively proposed that (2) contains a similar arrangement.

Introduction. In a recent communication (Butler, Cullen, Kim, Einstein & Jones, 1984), we reported the synthesis and crystallographic characterization of rhodium hydrides formed from cationic rhodium complexes $[(L\,L)\mathrm{RhNBD}]^+$ [where $L\,L$ is a bidentate ferrocenylphosphine ligand $\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4P}R_1R_2)$; $R_1 = \mathrm{Bu}^t$, $R_2 = \mathrm{Ph}$ or $R_1 = R_2 = \mathrm{Bu}^t$ and NBD = norbornadiene]. The present report describes, in more detail, the crystallographic aspects of this work.

Experimental. Crystal data for (1) and (2) are given in Table 1. Precession and Weissenberg photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) used to determine approximate cell dimensions and space group. Cell dimensions determined by least-squares refinement of diffractometer angles of 25 reflections, for both (1) ($25 < \theta < 34°$) and (2) ($20 < 2\theta < 29°$), Mo $K\alpha_1$ radiation. Data collected on Enraf–Nonius CAD-4F diffractometer. Background measurements made by extending scan range by 25% at each side of scan. 2 standard

Table 1. *Crystallographic data*

Function minimized: $\sum w(|F_o| - |F_c|)^2$.

	(1)	(2)
Crystal dimensions (mm)	0·28 × 0·17 × 0·43*	0·28 × 0·08 × 0·31
Scan type	ω–2θ	ω–2θ
ω scan speed(s) (° min^{-1})	0·7–5·0	1·0
Scan range (° in ω)	(0·7 + 0·36 tanθ)	(0·7 + 0·36 tanθ)
Data collected	$\pm h,k,l$	$\pm h,k,l$
Range of $\|h,k,l\|$	0–20, 0–15, 0–23	0–16, 0–16, 0–27
$2\theta_{max}$(°)	45	45
Crystal decay (correction applied) (%)	11	17
Measured reflections	8033	7627
Observed reflections $[I > 2{\cdot}3\sigma(I)]$	5732	4180
R	0·045	0·059
R_w	0·054	0·063
$(\Delta/\sigma)_{max}$ (mean)	0·8 (<0·1)	1·4 (< 0·1)†
$\sigma(\rho)$ e Å^{-3}	0·08	0·14

* The crystal dimensions are only approximate, the shape of the crystal was irregular.

† Max. shift was for U_{23} of C(222).

reflections every 60 min allowed correction for crystal decay. Lorentz and polarization corrections for (I) and (II), absorption corrections for (2) [transmission coefficients 0·77 to 0·94; for (1), ψ scans indicated absorption (±4%) was not a major effect]. Structures solved by conventional Patterson and Fourier methods. All non-hydrogen atoms easily located. Perchlorate anion in both compounds disordered in a similar manner, *viz* three oxygen atoms of a ClO_4^- each take up two alternative positions related by rotation about 'ordered' Cl—O(1) bond. For (1), a molecule of methanol of crystallization was also located.

Compound (1). All alkyl and aryl hydrogens clearly revealed during difference maps. Following difference map [based on all data ($2\theta \leq 45°$) and employing phases determined without H(226) in the model] gave two large peaks (1·5 and 2·0 e Å^{-3}) each approximately 1 Å from one of the Rh atoms. Next three largest peaks (0·6–0·7 e Å^{-3}) also near Rh atoms, sixth highest peak (0·6 e Å^{-3}) due to H(226). Same difference map was also determined with limited data set ($\sin\theta \leq 0{\cdot}35$): coordinates of highest eight peaks correspond to those found in previous map, but the relative magnitudes changed markedly (peaks 1 and 2 0·63 and 0·58 e Å^{-3}, respectively; peaks 3–8 0·53–0·35 e Å^{-3}). These results suggested peaks 3–7 were due to hydride ligands. Molecular diagrams further indicated that these positions, three of which were assigned as bridging hydrides and two as terminal hydrides, were structurally feasible. Isotropic temperature factors for hydride ligands were determined by refinement with their coordinates fixed. Positions of hydride ligands were then allowed to refine with B's fixed. During this refinement H(B2) became unstable and had to be fixed in its previously derived (ΔF synthesis) position; all other hydride ligands were well behaved. Block-diagonal least-squares refinement with anisotropic temperature factors for selected non-hydrogen atoms (Table 2), fixed isotropic temperature factors and variable positional parameters for H(T1), H(T2), H(B1) and H(B3) and all remaining hydrogen atoms included as fixed contributions [$B = B$ (parent carbon)] gave final agreement factors of $R = 0{\cdot}045$ and $R_w = 0{\cdot}054$ for 595 variables. Weighting scheme, on the basis of trends in $w\Delta^2$ *versus* F_o and $\sin\theta/\lambda$, was $1/[\sigma^2(F) + 0{\cdot}0004F^2]$. Final difference map was featureless apart from aforementioned peaks close to Rh atoms.

Compound (2). Location of hydrogen atoms in this structure proved more troublesome. Positions of ferrocenyl hydrogen atoms were calculated and subsequent difference maps revealed some but not all *tert*-butyl hydrogens; positions of remaining *tert*-butyl hydrogens calculated. With regard to possible location of hydride ligands, a similar procedure to that outlined for (1) was followed. A large peak of similar intensity close to each Rh atom was observed plus a number of smaller peaks in Rh—Rh vicinity; however, assignment of these latter peaks as hydride ligands was not immediately obvious, even using the structure of (1) as model. Block-diagonal least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and hydrogen atoms in fixed positions [$B = B$ (parent carbon)] gave final agreement factors of $R = 0{\cdot}059$ and $R_w = 0{\cdot}063$ for 578 variables. Unit weights. Final difference map was clean apart from peaks in the vicinity of Rh atoms.

Atomic scattering factors including anomalous dispersion were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). The computer programs used here are those belonging to the *NRC VAX* 750/780 *Crystal Structure System* (Gabe, Larson, Lee & Le Page, 1984) and *CRYSTALS* crystallographic suite (Watkin, 1984).

Discussion. Final positional and B_{eq} thermal parameters for (1) and (2) are given in Tables 2 and 3, respectively,* and selected bond parameters for both compounds are given in Table 4. A view depicting the RhPH skeletal structure of (1) is shown in Fig. 1. Each Rh atom (which is in a 3+ oxidation state) lies in an irregular octahedral environment surrounded by two terminal P atoms, a terminal hydride ligand and three bridging hydride ligands. The average Rh—H distances, $Rh—H_T = 1{\cdot}56$ (12) and $Rh—H_B = 1{\cdot}177$ (8) Å, compare favourably with the values of $Rh—H_T = 1{\cdot}53$ (2) and $Rh—H_B = 1{\cdot}77$ (3) Å, reported for the Rh^{III} atom in $H_4Rh_2\{P[N(CH_3)_2]_3\}_4$ (Meir, Burch, Muetterties &

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* Lists of structure factors, anisotropic thermal parameters, mean planes, additional bond parameters, hydrogen, solvent and perchlorate parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39810 (97 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Day, 1982); Rh—P distances in (1) appear to be of two types, Rh(1)—P(2) and Rh(2)—P(3) are 2·300 (2) and 2·285 (2) Å, respectively, and are close to the values found in $H_4Rh_2\{P[N(CH_3)_2]_3\}$ [av. 2·288 (1) Å], whereas the values of 2·351 (2) and 2·377 (2) Å for Rh(1)—P(1) and Rh(2)—P(4), respectively, are somewhat longer; the cause of these differences is not immediately obvious. No direct comparison can be made between H_B—Rh—H_B angles in the two compounds; however, these angles are internally consistent in (1) and not surprisingly lower than the regular value of 90°, *viz* the average value about Rh(1) is 72 (3)°, whereas about Rh(2) it is 73 (3)°. The P—Rh—P angles of 103·50 (7) and 103·30 (7)° are consistent with the 'bulkiness' of the biphosphine ligand.

Table 2. *Final positional and thermal parameters for the cation* (1)

	x	y	z	B_{eq}† or B
Rh(1)	0·96730 (3)	0·22027 (4)	0·20792 (3)	2·42 (3)
Rh(2)	1·08485 (3)	0·20188 (4)	0·15116 (3)	2·32 (3)
Fe(1)	0·78032 (5)	0·17225 (7)	0·30535 (5)	2·83 (6)
Fe(2)	1·28737 (5)	0·23748 (7)	0·07374 (4)	2·43 (6)
P(1)	0·8615 (1)	0·1465 (1)	0·1738 (1)	2·6 (1)
P(2)	0·9436 (1)	0·2664 (1)	0·3053 (1)	2·4 (1)
P(3)	1·1892 (1)	0·1267 (1)	0·1746 (1)	2·2 (1)
P(4)	1·1198 (1)	0·3158 (1)	0·0824 (1)	2·0 (1)
C(11)*	0·8718 (4)	0·0433 (5)	0·1253 (4)	3·6 (2)
C(111)*	0·9130 (5)	0·0627 (6)	0·0674 (4)	4·9 (2)
C(112)*	0·9126 (5)	−0·0264 (6)	0·1639 (4)	4·6 (2)
C(113)*	0·7972 (5)	0·0078 (6)	0·1039 (4)	5·1 (2)
C(121)*	0·8074 (4)	0·2242 (5)	0·1252 (3)	3·0 (2)
C(122)	0·8419 (5)	0·2692 (7)	0·0814 (4)	5·2 (7)
C(123)	0·8058 (5)	0·3290 (7)	0·0410 (4)	5·9 (7)
C(124)	0·7346 (5)	0·3462 (7)	0·0456 (4)	5·8 (7)
C(125)	0·7013 (5)	0·3036 (7)	0·0909 (5)	6·8 (8)
C(126)	0·7366 (5)	0·2441 (6)	0·1301 (4)	5·0 (7)
C(131)*	0·8064 (4)	0·1005 (5)	0·2316 (3)	2·9 (2)
C(132)	0·8406 (4)	0·0640 (5)	0·2871 (4)	3·5 (5)
C(133)	0·7882 (5)	0·0366 (6)	0·3271 (4)	5·0 (7)
C(134)	0·7215 (4)	0·0544 (6)	0·2982 (4)	4·3 (6)
C(135)	0·7312 (4)	0·0934 (5)	0·2400 (4)	3·7 (6)
C(21)*	0·9750 (4)	0·3851 (5)	0·3225 (3)	3·2 (2)
C(211)*	1·0563 (5)	0·3864 (6)	0·3329 (4)	4·5 (2)
C(212)*	0·9522 (5)	0·4447 (6)	0·2683 (4)	4·5 (2)
C(213)*	0·9393 (5)	0·4259 (6)	0·3793 (4)	4·6 (2)
C(221)*	0·9847 (4)	0·1930 (5)	0·3649 (3)	3·0 (2)
C(222)	0·9870 (4)	0·2123 (5)	0·4282 (3)	4·2 (6)
C(223)	1·0185 (5)	0·1530 (7)	0·4707 (4)	5·3 (8)
C(224)	1·0484 (5)	0·0752 (7)	0·4508 (5)	6·3 (8)
C(225)	1·0463 (6)	0·0556 (7)	0·3901 (5)	6·3 (8)
C(226)	1·0154 (4)	0·1146 (6)	0·3466 (4)	4·2 (6)
C(231)*	0·8507 (4)	0·2719 (5)	0·3229 (3)	2·4 (2)
C(232)	0·7951 (4)	0·3024 (5)	0·2809 (3)	2·8 (4)
C(233)	0·7295 (4)	0·2940 (5)	0·3087 (4)	3·4 (5)
C(234)	0·7418 (4)	0·2615 (5)	0·3684 (4)	3·6 (5)
C(235)	0·8170 (4)	0·2468 (5)	0·3781 (3)	3·1 (5)
C(31)*	1·1789 (4)	0·0010 (5)	0·1864 (3)	2·8 (2)
C(311)*	1·1405 (4)	−0·0387 (6)	0·1294 (4)	4·1 (2)
C(312)*	1·1360 (5)	−0·0198 (6)	0·2422 (4)	4·4 (2)
C(313)*	1·2534 (4)	−0·0423 (5)	0·1956 (4)	3·7 (2)
C(321)*	1·2307 (4)	0·1657 (5)	0·2479 (5)	2·4 (2)
C(322)	1·1836 (4)	0·1825 (6)	0·2931 (4)	4·6 (7)
C(323)	1·2082 (5)	0·2069 (7)	0·3516 (4)	5·6 (8)
C(324)	1·2798 (5)	0·2160 (6)	0·3648 (4)	4·5 (7)
C(325)	1·3265 (4)	0·2029 (6)	0·3197 (4)	5·0 (6)
C(326)	1·3024 (4)	0·1793 (6)	0·2609 (4)	3·8 (6)
C(331)*	1·2539 (4)	0·1268 (5)	0·1155 (3)	2·4 (2)
C(332)	1·3310 (4)	0·1284 (5)	0·1165 (3)	3·4 (5)
C(333)	1·3529 (4)	0·1299 (6)	0·0560 (4)	3·7 (6)
C(334)	1·2919 (4)	0·1269 (5)	0·0172 (3)	3·2 (5)
C(335)	1·2309 (4)	0·1248 (5)	0·0519 (3)	2·6 (4)
C(41)*	1·0850 (4)	0·4323 (5)	0·1006 (3)	2·7 (2)
C(411)*	1·0034 (4)	0·4309 (5)	0·0945 (4)	3·7 (2)
C(412)*	1·1115 (4)	0·4556 (5)	0·1662 (3)	3·3 (2)
C(413)*	1·1129 (4)	0·5038 (5)	0·0586 (4)	3·8 (2)
C(421)*	1·0828 (4)	0·2955 (5)	0·0037 (3)	2·4 (2)
C(422)	1·0323 (4)	0·2285 (5)	−0·0047 (4)	3·7 (5)
C(423)	1·0005 (4)	0·2104 (6)	−0·0623 (4)	4·5 (6)
C(424)	1·0204 (4)	0·2580 (6)	−0·1118 (3)	4·2 (6)
C(425)	1·0694 (4)	0·3249 (6)	−0·1050 (4)	3·9 (6)
C(426)	1·1006 (4)	0·3450 (5)	−0·0478 (3)	3·1 (5)
C(431)*	1·2149 (3)	0·3369 (4)	0·0770 (3)	2·4 (2)
C(432)	1·2625 (4)	0·3389 (5)	0·1306 (3)	2·6 (4)
C(433)	1·3330 (4)	0·3508 (5)	0·1130 (4)	3·7 (6)
C(434)	1·3317 (4)	0·3573 (5)	0·0488 (4)	3·9 (6)
C(435)	1·2590 (4)	0·3492 (5)	0·0248 (3)	2·9 (5)
H(*T*1)	0·916 (3)	0·310 (4)	0·207 (3)	3·0
H(*T*2)	1·104 (3)	0·139 (4)	0·102 (2)	1·5
H(*B*1)	1·036 (3)	0·133 (4)	0·191 (3)	2·7
H(*B*2)	1·051	0·269	0·213	4·0
H(*B*3)	0·993 (3)	0·229 (4)	0·131 (3)	3·6

* Atom was refined isotropically.

† B_{eq} (Å^2) is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table 3. *Final positional and thermal parameters for the cation* (2)

	x	y	z	B_{eq}*
Rh(1)	−0·24471 (6)	0·06060 (8)	0·85010 (4)	4·00 (5)
Rh(2)	−0·25529 (7)	0·21168 (8)	0·90983 (4)	4·31 (5)
Fe(1)	−0·2352 (2)	−0·2109 (2)	0·7833 (1)	7·6 (2)
Fe(2)	−0·2729 (2)	0·4798 (2)	0·9789 (1)	8·3 (2)
P(1)	−0·1356 (2)	−0·0534 (2)	0·8649 (1)	3·7 (2)
P(2)	−0·3479 (3)	−0·0086 (4)	0·7931 (1)	6·4 (3)
P(3)	−0·3297 (2)	0·2520 (3)	0·9840 (1)	5·0 (2)
P(4)	−0·1902 (3)	0·3516 (3)	0·8795 (2)	5·2 (2)
C(11)	−0·145 (1)	−0·105 (1)	0·932 (0)	5 (1)
C(111)	−0·233 (1)	−0·151 (1)	0·934 (1)	6 (1)
C(112)	−0·146 (1)	−0·030 (1)	0·972 (0)	5 (1)
C(113)	−0·073 (1)	−0·170 (1)	0·948 (1)	7 (1)
C(12)	−0·018 (1)	−0·013 (1)	0·855 (0)	5 (1)
C(121)	0·014 (1)	0·037 (1)	0·902 (1)	6 (1)
C(122)	−0·016 (1)	0·049 (1)	0·808 (0)	5 (1)
C(123)	0·045 (1)	−0·089 (1)	0·844 (1)	7 (1)
C(131)	−0·136 (1)	−0·149 (1)	0·820 (1)	6 (1)
C(132)	−0·131 (1)	−0·136 (1)	0·766 (1)	6 (1)
C(133)	−0·124 (1)	−0·221 (1)	0·742 (1)	9 (1)
C(134)	−0·127 (1)	−0·286 (1)	0·779 (1)	11 (2)
C(135)	−0·132 (1)	−0·244 (1)	0·829 (1)	8 (1)
C(21)	−0·347 (1)	0·046 (2)	0·727 (1)	10 (2)
C(211)	−0·350 (1)	0·146 (2)	0·731 (1)	12 (2)
C(212)	−0·260 (1)	0·024 (1)	0·701 (1)	8 (2)
C(213)	−0·419 (2)	0·015 (2)	0·691 (1)	13 (3)
C(22)	−0·462 (1)	−0·002 (2)	0·821 (1)	10 (2)
C(221)	−0·454 (1)	−0·027 (1)	0·877 (1)	8 (1)
C(222)	−0·527 (1)	−0·067 (2)	0·795 (1)	17 (4)
C(223)	−0·497 (1)	0·092 (2)	0·815 (1)	13 (3)
C(231)	−0·338 (1)	−0·132 (1)	0·782 (1)	9 (1)
C(232)	−0·350 (1)	−0·194 (1)	0·821 (1)	9 (1)
C(233)	−0·345 (1)	−0·284 (1)	0·799 (1)	11 (2)
C(234)	−0·341 (1)	−0·270 (2)	0·746 (1)	12 (2)
C(235)	−0·334 (1)	−0·180 (2)	0·736 (1)	12 (2)
C(31)	−0·300 (1)	0·176 (1)	1·041 (1)	6 (1)
C(311)	−0·340 (1)	0·083 (1)	1·035 (1)	8 (1)
C(312)	−0·205 (1)	0·166 (1)	1·043 (1)	8 (1)
C(313)	−0·333 (2)	0·215 (1)	1·093 (1)	11 (2)
C(32)	−0·453 (1)	0·251 (1)	0·972 (1)	9 (2)
C(321)	−0·478 (1)	0·325 (1)	0·936 (1)	12 (2)
C(322)	−0·480 (1)	0·164 (1)	0·949 (1)	11 (2)
C(323)	−0·506 (1)	0·261 (1)	1·021 (1)	12 (2)
C(331)	−0·306 (1)	0·363 (1)	1·013 (1)	7 (1)
C(332)	−0·221 (1)	0·390 (1)	1·029 (1)	8 (1)
C(333)	−0·227 (1)	0·475 (1)	1·052 (1)	10 (2)
C(334)	−0·312 (2)	0·503 (1)	1·053 (1)	10 (2)
C(335)	−0·364 (1)	0·437 (1)	1·029 (1)	8 (1)
C(41)	−0·067 (1)	0·353 (1)	0·888 (1)	7 (1)
C(411)	−0·044 (1)	0·356 (1)	0·945 (1)	9 (1)
C(412)	−0·029 (1)	0·269 (1)	0·864 (1)	9 (2)
C(413)	−0·020 (1)	0·432 (1)	0·862 (1)	9 (1)
C(42)	−0·217 (1)	0·374 (1)	0·809 (1)	8 (1)
C(421)	−0·201 (2)	0·471 (1)	0·791 (1)	12 (2)
C(422)	−0·313 (1)	0·356 (1)	0·802 (1)	10 (1)
C(423)	−0·170 (1)	0·308 (1)	0·773 (1)	8 (1)
C(431)	−0·227 (1)	0·461 (1)	0·907 (1)	8 (1)
C(432)	−0·319 (1)	0·485 (1)	0·906 (1)	10 (1)
C(433)	−0·329 (2)	0·567 (2)	0·928 (1)	15 (2)
C(434)	−0·245 (2)	0·600 (1)	0·943 (1)	15 (2)
C(435)	−0·180 (1)	0·534 (1)	0·931 (1)	9 (1)

* B_{eq} (Å^2) is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table 4. *Selected bond parameters* (Å, °) *for* (1) *and* (2)

	(1)	(2)		(1)	(2)
Rh(1)–Rh(2)	2·5943 (9)	2·720 (2)	P(1)–C(11)	1·878 (8)	1·89 (1)
Rh(1)–P(1)	2·351 (2)	2·394 (3)	P(1)–C(12)		1·91 (1)
Rh(1)–P(2)	2·300 (2)	2·376 (4)	P(1)–C(121)	1·836 (7)	
Rh(1)–H(*T*1)	1·64 (6)		P(1)–C(131)	1·806 (7)	1·82 (1)
Rh(1)–H(*B*1)	1·87 (6)		P(2)–C(21)	1·890 (8)	1·89 (2)
Rh(1)–H(*B*2)	1·72		P(2)–C(22)		1·89 (2)
Rh(1)–H(*B*3)	1·77 (6)		P(2)–C(221)	1·837 (7)	
Rh(2)–P(3)	2·285 (2)	2·325 (4)	P(2)–C(231)	1·802 (7)	1·86 (2)
Rh(2)–P(4)	2·377 (2)	2·426 (4)	P(3)–C(31)	1·897 (7)	1·90 (2)
Rh(2)–H(*T*2)	1·47 (5)		P(3)–C(32)		1·91 (2)
Rh(2)–H(*B*1)	1·65 (5)		P(3)–C(321)	1·836 (7)	
Rh(2)–H(*B*2)	1·81		P(3)–C(331)	1·815 (7)	1·84 (2)
Rh(2)–H(*B*3)	1·79 (6)		P(4)–C(41)	1·898 (7)	1·88 (2)
			P(4)–C(42)		1·89 (2)
Fe(1)–Cp(1)*	1·645	1·61	P(4)–C(421)	1·846 (7)	
Fe(1)–Cp(2)*	1·639	1·63	P(4)–C(431)	1·817 (7)	1·85 (1)
Fe(2)–Cp(3)*	1·639	1·63			
Fe(2)–Cp(4)*	1·631	1·64			

	(1)	(2)
P(1)–Rh(1)–P(2)	103·50 (7)	104·6 (2)
P(3)–Rh(2)–P(4)	103·30 (7)	105·0 (1)
Cp(1)–Fe(1)–Cp(2)	177	177
Cp(3)–Fe(2)–Cp(4)	177	178

* Cp refers to the midpoint of the cyclopentadienyl ring.

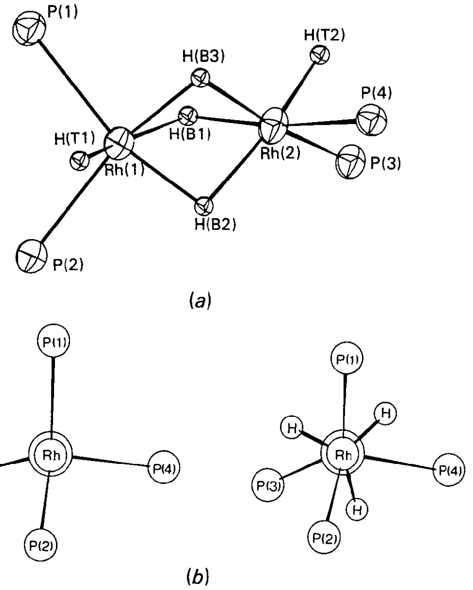

Fig. 1. (*a*) A view (*SNOOPI*; Davies, 1984) depicting the RhPH skeletal structure of (1). (*b*) Comparison of the RhP arrangement in (1) and (2).

The unusual triply hydride-bridged arrangement found here was previously postulated from NMR evidence for $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$ (Crabtree, Felkin & Morris, 1977); a crystallographic study (Crabtree, Felkin, Morris, King & Richards, 1976) did not locate the hydride ligands and could not be completed ($R = 0{\cdot}129$) owing to serious 'disorder'. The revised bonding description for $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$ (Crabtree, Felkin & Morris, 1977), which treats each hydride bridge as a three-centre two-electron Ir–H–Ir bond, is also adopted here for (1); however, the possibility of some Rh–Rh interaction should not be ruled out in view of the relatively short Rh–Rh distance of 2·5943 (9) Å (Sherwood & Hall, 1982).

As mentioned in the *Experimental*, hydride ligands for (2) could not satisfactorily be located; this we feel was due to difficulty in selecting a suitable crystal and deterioration of crystal quality during the data collection. However, a view along the Rh···Rh vector for (1) and (2) (Fig. 1*b*) indicates a similar arrangement of Rh and P atoms and suggests that (2) may have a similar structure to (1). As previously noted (Butler, Cullen, Kim, Einstein & Jones, 1984), this would also seem reasonable from a chemical standpoint. The Rh–P bond parameters in (2) are uniformly larger than in (1), consistent with the replacement of a phenyl group with a *tert*-butyl group at the P atoms of the biphosphine

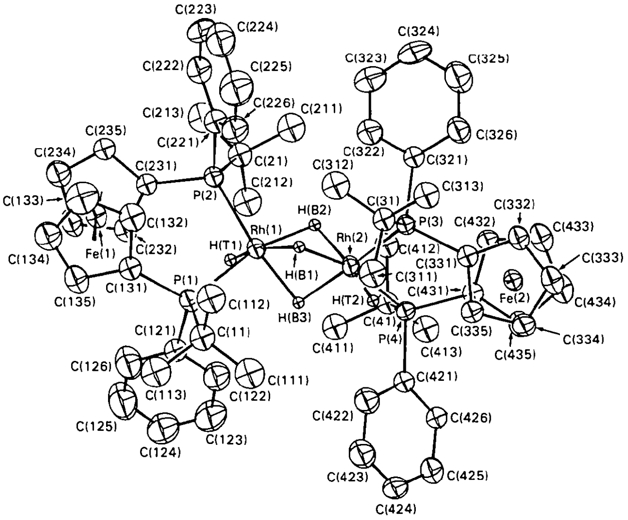

Fig. 2. Molecular diagram (*SNOOPI*; Davies, 1984) of the cationic moiety of (1) (50% probability contours for all atoms; alkyl and aryl hydrogens have been omitted for clarity).

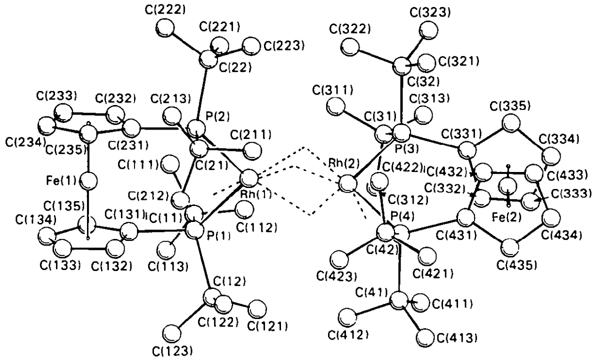

Fig. 3. Molecular diagram (*SNOOPI*; Davies, 1984) of the cationic moiety of (2) (alkyl and aryl hydrogens have been omitted for clarity; the dashed lines are a schematic representation of the hydride ligands, which could not be located).

ligand. The conformations of the complex cations for (1) and (2) are shown in Figs. 2 and 3, respectively. In the case of (1), Fig. 2 shows one of the two enantiomorphs present in the unit cell, *i.e.* the ferrocene groups have the *S,S* conformer. For (2) (Fig. 3) the conformation is *S,R*. Bond parameters associated with the biphosphine ligands are not unusual and compare favourably with those found for these ligands in $[(L\ L)\mathrm{RhNBD}]\mathrm{ClO}_4$ complexes (Cullen, Kim, Einstein & Jones, 1984), *viz* P—C distances show a similar trend, *i.e.* P—C(Cp) < P—C(Ph) < P—C(Bu^t); the deviations of P atoms out of their associated Cp ring planes are in agreement with the equivalent deviations in the $[(L\ L)\mathrm{RhNBD}]\mathrm{ClO}_4$ series (Cullen, Kim, Einstein & Jones, 1984) and can be explained in the same way. The closest contact between the 'disordered' perchlorate anions and their respective cations is 2·62 Å between O(1)* and H(135) in (1) and 2·43 Å between O(5) and H(111*C*) in (2). Intramolecular distances are not unusual.

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* O(1) denotes the ordered oxygen atom of the perchlorate group while O(2)–O(7) denote the disordered oxygen atoms (see *Experimental*). The hydrogen-atom numbering schemes are such that their serial numbers are the same as the parent carbon, with additional letters *A*, *B* or *C* in the case of methyl hydrogens.

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Structure of Tetraphenylphosphonium Triiodomercurate(II), $[\mathrm{P(C_6H_5)_4}][\mathrm{HgI_3}]$

By Boulos Zacharie, James D. Wuest, Marc J. Olivier and André L. Beauchamp*

Département de Chimie, Université de Montréal, CP 6210, *Succ. A, Montréal, Québec, Canada H*3*C* 3*V*1

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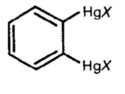
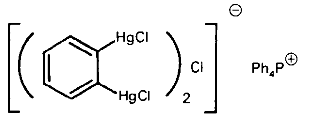
Abstract. $M_r = 920{\cdot}70$, triclinic, $P\bar{1}$, $a = 9{\cdot}163\ (7)$, $b = 10{\cdot}921\ (3)$, $c = 13{\cdot}300\ (7)$ Å, $\alpha = 85{\cdot}04\ (3)$, $\beta = 76{\cdot}57\ (5)$, $\gamma = 85{\cdot}84\ (4)$°, $V = 1287{\cdot}9$ Å^3, $Z = 2$, $D_x = 2{\cdot}374$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}54178$ Å (graphite-monochromated), $\mu = 40{\cdot}74$ mm^{-1}, $F(000) = 836$, $T = 293$ K. Final $R = 0{\cdot}043$ for 3754 unique non-zero reflections. The unit cell contains two $[\mathrm{P(C_6H_5)_4}]^+$ cations and one centrosymmetric $[\mathrm{Hg_2I_6}]^{2-}$ anion. In the anion, two iodines bridge two $\mathrm{HgI_2}$ units, and the coordination about mercury is approximately tetrahedral. The main distances are: Hg—I(terminal) = 2·707 (1) and 2·690 (1) Å, Hg—I(bridge) = 2·864 (1) and 2·962 (1) Å, mean P—C = 1·789 (8) Å.

Introduction. Treatment of *μ-o*-phenylene-bis[chloromercury(II)] (1) and *μ-o*-phenylene-bis[bromomercury(II)] (2) with a variety of phosphonium and ammonium halides produces salts of anionic complexes like structure (4) (Wuest & Zacharie, 1985). We were surprised to find that analogous reactions of *μ-o*-phenylene-bis[iodomercury(II)] (3) do not yield similar complexes, but give instead the products of redistribution reactions. For example, X-ray crystallographic study has shown that the salt formed from equimolar amounts of compound (3) and tetraphenylphosphonium iodide is in fact tetraphenylphosphonium triiodomercurate(II). The structure of this salt is described below.



(1) (*X* = Cl)
(2) (*X* = Br)
(3) (*X* = I)



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* Author to whom correspondence should be addressed.