

Crystal and Molecular Structure of the Orange and Red Allotropes of Chlorotris(triphenylphosphine)rhodium(I)

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The important catalytic compound chlorotris(triphenylphosphine)rhodium(I) $[\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3]$ crystallizes in orange and red forms. The crystal structures of both allotropes have been determined from three-dimensional x-ray data collected on a manual four-circle diffractometer at room temperature. The orange form crystallizes in the space group $Pna2_1$ with four molecules per unit cell ($\rho_{\text{obsd}} = 1.363$, $\rho_{\text{calcd}} = 1.367 \text{ g cm}^{-3}$). The axial parameters are $a = 19.470$ (3), $b = 12.689$ (2), $c = 18.202$ (3) Å. Least-squares refinement of absorption-corrected data converged at a conventional R factor of 0.047 based on 1417 significant reflections. The red form also crystallizes in the space group $Pna2_1$ ($Z = 4$, $\rho_{\text{obsd}} = 1.382$, $\rho_{\text{calcd}} = 1.379 \text{ g cm}^{-3}$) with axial parameters $a = 32.96$ (1), $b = 12.271$ (2), and $c = 11.007$ (2) Å. The least-squares refinement converged at a conventional R factor of 0.042 for 1469 significant reflections. The geometry around the rhodium atoms in both complexes may be described as square planar with a distortion toward tetrahedral geometry. This distortion is more marked in the red form. The two mutually trans rhodium-phosphorus distances (orange, $\text{Rh-P}(1) = 2.307$ (4), $\text{Rh-P}(3) = 2.348$ (4) Å; red, $\text{Rh-P}(1) = 2.334$ (3), $\text{Rh-P}(3) = 2.324$ (4) Å) are significantly longer than the other rhodium-phosphorus distance (orange, $\text{Rh-P}(2) = 2.228$ (4) Å; red, $\text{Rh-P}(2) = 2.214$ (4) Å). Close contacts are observed between the rhodium atoms and phenyl ortho hydrogen atoms in both complexes (orange, $\text{Rh-H}(222) = 2.84$ Å; red, $\text{Rh-H}(112) = 2.77$ Å).

Introduction

The complex chlorotris(triphenylphosphine)rhodium(I) crystallizes in red and orange forms depending upon the conditions of synthesis.^{1,2} A few details of the molecular structure of this important catalytic complex have appeared^{3,4} but a complete structural paper is not planned by the authors.⁵ We have undertaken complete structural analyses of both the red and orange forms to investigate the differences that are indicated by the spectroscopic properties and to provide data for comparison with the two dioxygen complexes $[\text{RhCl}(\text{O}_2)\text{P}(\text{C}_6\text{H}_5)_3]_2$ and $[\text{RhCl}(\text{O}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_3 \cdot 2\text{CH}_2\text{Cl}_2]$ that we have isolated.^{6,7}

Experimental Section

(a) Orange Form. $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$ was synthesized using the method outlined in the literature;² however the rate of addition of the ethanolic solution of rhodium trichloride was decreased substantially to encourage the formation of larger single crystals. Complete analyses⁸ were in excellent agreement. Anal. Calcd: C, 70.1; H, 4.9; Cl, 3.8; P, 10.0; Rh, 11.1. Found: C, 70.0; H, 4.9; Cl, 3.8; P, 10.2; Rh, 11.2. Crystal data were determined as follows: orthorhombic; space group $Pna2_1$ or $Pnam$ (systematic absences $0kl$ for $k + l = 2n + 1$, $h0l$ for $h = 2n + 1$), observed in the preliminary photographic study); unit cell dimensions at 22 °C $a = 19.470$ (3), $b = 12.689$ (2), $c = 18.202$ (3) Å; $\rho_{\text{obsd}} = 1.363 \text{ g cm}^{-3}$ (by flotation in aqueous potassium iodide), for 4 molecules per unit cell, $\rho_{\text{calcd}} = 1.367 \text{ g cm}^{-3}$. A crystal bounded by faces of the forms $\{100\}$, $\{010\}$, $\{001\}$, and $\{110\}$ and having approximate dimensions $0.22 \times 0.13 \times 0.05 \text{ mm}$ was mounted with its a axis coincident with the ϕ axis of a Picker manual four-circle diffractometer.

The crystals show relatively poor ordering with virtually no data with $(\sin \theta)/\lambda$ exceeding 0.41. Intensity data were collected using the $\omega/2\theta$ scanning technique (2θ scan range $2\theta_{\text{calcd}} \pm 1^\circ$, 2θ scan speed $2^\circ/\text{min}$, background counts taken at the limits of the scan for 20 s). Data were collected using nickel foil filtered $\text{Cu K}\alpha$ X radiation within a single octant limited by $(\sin \theta)/\lambda \leq 0.46$ and were detected by a scintillation counter used in conjunction with a pulse height analyzer tuned to accept 95% of the $\text{Cu K}\alpha$ peak. The $h00$ reflections were scanned under varying conditions of ϕ to test the correctness of the subsequent absorption correction. The data were processed to yield 1412 significant observations ($I/\sigma(I) > 3.0$) assuming a linear interpretation of the background measurements. Only the significant data which were corrected for Lorentz-polarization and absorption effects ($\mu_{\text{CuK}\alpha} = 47.6 \text{ cm}^{-1}$, transmission factor range 0.550–0.805) were used in subsequent structure determination. Estimated standard deviations of the structure amplitudes included a p factor⁹ of 0.03.

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Internal consistency of the $h00$ ϕ scan data was $\pm 3\%$ after correction for absorption.

(b) Red Form. Red chunky crystals were prepared using the method outlined by Wilkinson et al.² Carbon and hydrogen analyses¹⁰ are in acceptable agreement. Anal. Calcd: C, 70.1; H, 4.9. Found: C, 70.6; H, 4.9. Crystal data were determined as follows: orthorhombic; space group $Pna2_1$ or $Pnam$ (systematic absences $0kl$ for $k + l = 2n + 1$, $h0l$ for $h = 2n + 1$); unit cell dimensions $a = 32.96$ (1), $b = 12.271$ (2), $c = 11.007$ (2) Å (obtained from least-squares refinement of setting angles of 12 reflections accurately centered on a Picker manual four-circle diffractometer, $\lambda(\text{Cu K}\alpha_1) 1.54051$ Å); $\rho_{\text{obsd}} = 1.382 \text{ g cm}^{-3}$, $\rho_{\text{calcd}} = 1.379 \text{ g cm}^{-3}$ for four molecules per unit cell.

A crystal with faces of the forms $\{100\}$, $\{210\}$, and $\{201\}$ and of approximate dimensions $0.17 \times 0.21 \times 0.14 \text{ mm}$ was mounted with its b axis coincident with the diffractometer ϕ axis and 1469 significant observations were obtained with $(\sin \theta)/\lambda < 0.46$ and experimental conditions and procedure as outlined for the orange form. The range of transmission factors for the study crystal was 0.566–0.683.

Structure Solution and Refinement

(a) Orange Form. The solution of the Patterson map yielded approximate coordinates for the rhodium, phosphorus, and chlorine atoms. This solution was consistent only with the space group $Pna2_1$. Carbon atoms were located in subsequent electron density maps. During the refinement the z coordinate of the rhodium atom was fixed at 0.250 to define the origin of the unit cell in this direction. The least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(|F_o|)$. Structure factors were calculated using scattering factors of Cromer and Mann¹¹ (except those for hydrogen which were from Mason and Robertson¹²) and included terms for the real and imaginary corrections for anomalous dispersion¹³ for the rhodium, phosphorus, and chlorine scattering factors. The relatively low number of observations imposed constraints on the number of parameters to be varied so the six carbon atoms of each phenyl group were treated as rigid planar groups of D_{6h} symmetry with carbon-carbon bond lengths fixed at 1.392 Å. Hydrogen atoms were included at their calculated positions assuming carbon-hydrogen bond lengths of 1.0 Å and temperature factors set at 10% greater than those of the attached carbon atoms. Anisotropic thermal parameters were introduced for the rhodium, phosphorus, and chlorine atoms only and the refinement converged to give $R_1 = 0.047$ and $R_2 = 0.053$ where the R factors are defined as

$$R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

$$R_2 = \left(\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right)^{1/2}$$

At convergence (maximum shift/ $\sigma = 0.12$) the standard deviation

Table I. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3^a$

(i) Refined Parameters								
Atom	Orange form				Red form			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Rh	0.063 04 (5)	0.028 92 (9)	0.2500	2.38	0.112 98 (3)	0.122 04 (7)	-0.2500	2.25
Cl	-0.050 8 (2)	0.072 6 (3)	0.2088 (3)	3.88	0.077 0 (1)	0.089 5 (3)	-0.4336 (4)	5.07
P(1)	0.080 0 (2)	0.208 5 (3)	0.2555 (4)	2.91	0.12326 (9)	-0.066 2 (2)	-0.2471 (6)	2.28
P(2)	0.172 3 (2)	-0.019 9 (3)	0.2607 (4)	2.81	0.165 5 (1)	0.168 9 (3)	-0.1363 (4)	2.39
P(3)	0.015 4 (2)	-0.136 2 (3)	0.2757 (2)	2.71	0.072 9 (1)	0.276 7 (3)	-0.2305 (5)	2.61
(ii) Calculated Parameters								
Atom ^c	Orange form				Red form			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
C(111)	0.0247 (6)	0.273 (1)	0.3240 (6)	3.0 (4)	0.0719 (2)	-0.1234 (8)	-0.2267 (7)	2.4 (3)
C(112)	0.0372 (5)	0.377 (1)	0.3439 (5)	7.6 (7)	0.0441 (3)	-0.0622 (6)	-0.1603 (9)	4.3 (4)
C(113)	-0.0054 (7)	0.4268 (7)	0.3945 (8)	8.4 (7)	0.0055 (3)	-0.1035 (7)	-0.1377 (8)	4.5 (4)
C(114)	-0.0605 (6)	0.373 (1)	0.4253 (6)	5.8 (5)	-0.0053 (2)	-0.2059 (8)	-0.1815 (7)	4.6 (4)
C(115)	-0.0730 (5)	0.268 (1)	0.4054 (5)	4.8 (4)	0.0225 (3)	-0.2671 (6)	-0.2478 (9)	4.7 (3)
C(116)	-0.0305 (7)	0.2184 (7)	0.3548 (8)	4.0 (4)	0.0611 (3)	-0.2258 (7)	-0.2704 (8)	3.1 (3)
C(121)	0.0606 (6)	0.278 (1)	0.1699 (6)	3.4 (4)	0.1443 (3)	-0.1377 (9)	-0.3768 (7)	2.0 (4)
C(122)	0.0657 (6)	0.2186 (7)	0.1059 (8)	3.9 (4)	0.1535 (3)	-0.2484 (8)	-0.3710 (8)	3.2 (4)
C(123)	0.0549 (7)	0.266 (1)	0.0379 (6)	6.2 (5)	0.1722 (3)	-0.2995 (6)	-0.469 (1)	5.6 (5)
C(124)	0.0389 (7)	0.373 (1)	0.0339 (6)	5.7 (5)	0.1819 (3)	-0.2400 (9)	-0.5726 (7)	4.6 (5)
C(125)	0.0338 (6)	0.4322 (7)	0.0979 (8)	6.4 (6)	0.1728 (3)	-0.1293 (8)	-0.5784 (8)	4.4 (4)
C(126)	0.0446 (7)	0.385 (1)	0.1659 (6)	5.6 (6)	0.1540 (3)	-0.0782 (6)	-0.481 (1)	3.7 (4)
C(131)	0.1620 (8)	0.2692 (8)	0.2818 (9)	2.6 (4)	0.1510 (5)	-0.1328 (7)	-0.121 (2)	2.1 (4)
C(132)	0.201 (1)	0.3252 (9)	0.2308 (6)	3.2 (4)	0.1303 (6)	-0.1529 (7)	-0.0126 (9)	3.0 (4)
C(133)	0.2614 (8)	0.3746 (8)	0.253 (1)	5.3 (4)	0.1503 (8)	-0.2012 (7)	0.085 (2)	4.0 (4)
C(134)	0.2830 (8)	0.3680 (8)	0.3254 (9)	4.6 (5)	0.1911 (5)	-0.2294 (7)	0.074 (2)	4.0 (4)
C(135)	0.244 (1)	0.3119 (8)	0.3763 (6)	6.1 (5)	0.2118 (6)	-0.2093 (7)	-0.0335 (9)	3.0 (3)
C(136)	0.1837 (8)	0.2625 (8)	0.355 (1)	5.7 (5)	0.1918 (8)	-0.1611 (7)	-0.131 (2)	2.9 (3)
C(211)	0.2396 (6)	0.0633 (8)	0.220 (1)	2.9 (4)	0.2107 (3)	0.0905 (6)	-0.183 (3)	2.7 (4)
C(212)	0.232 (1)	0.0852 (8)	0.1451 (7)	3.8 (4)	0.2409 (8)	0.0560 (9)	-0.104 (1)	4.3 (4)
C(213)	0.282 (1)	0.1424 (8)	0.1081 (8)	5.7 (5)	0.2751 (6)	0.0026 (8)	-0.149 (2)	3.6 (4)
C(214)	0.3401 (6)	0.1777 (8)	0.146 (1)	4.8 (5)	0.2790 (3)	-0.0163 (6)	-0.273 (3)	3.5 (4)
C(215)	0.348 (1)	0.1559 (8)	0.2201 (7)	3.1 (4)	0.2488 (8)	0.0182 (9)	-0.352 (1)	6.1 (5)
C(216)	0.298 (1)	0.0987 (8)	0.2571 (8)	3.5 (3)	0.2146 (6)	0.0716 (8)	-0.308 (2)	4.3 (5)
C(221)	0.1885 (8)	-0.1394 (8)	0.2047 (9)	2.9 (4)	0.1842 (3)	0.3102 (6)	-0.164 (1)	1.6 (3)
C(222)	0.1481 (7)	-0.1499 (9)	0.1420 (6)	4.4 (5)	0.1737 (3)	0.3948 (9)	-0.0855 (7)	3.1 (3)
C(223)	0.1593 (9)	-0.233 (1)	0.0939 (5)	6.3 (5)	0.1869 (3)	0.5004 (7)	-0.1094 (9)	4.1 (4)
C(224)	0.2109 (8)	-0.3064 (8)	0.1085 (9)	6.5 (5)	0.2106 (3)	0.5214 (6)	-0.212 (1)	4.2 (4)
C(225)	0.2513 (7)	-0.2959 (9)	0.1712 (6)	5.9 (5)	0.2211 (3)	0.4368 (9)	-0.2896 (7)	5.5 (5)
C(226)	0.2401 (9)	-0.212 (1)	0.2193 (5)	5.0 (5)	0.2079 (3)	0.3312 (7)	-0.2657 (9)	4.7 (4)
C(231)	0.204 (2)	-0.044 (1)	0.356 (1)	3.7 (4)	0.1657 (8)	0.1601 (9)	0.0305 (7)	2.9 (3)
C(232)	0.268 (1)	-0.087 (1)	0.372 (1)	7.3 (6)	0.1326 (5)	0.1091 (8)	0.084 (2)	3.8 (4)
C(233)	0.2879 (6)	-0.104 (1)	0.445 (2)	7.8 (6)	0.1292 (4)	0.1059 (7)	0.210 (2)	5.7 (5)
C(234)	0.244 (2)	-0.076 (1)	0.502 (1)	6.5 (6)	0.1591 (8)	0.1536 (9)	0.2825 (7)	6.9 (5)
C(235)	0.180 (1)	-0.032 (1)	0.486 (1)	7.2 (6)	0.1992 (5)	0.2045 (8)	0.229 (2)	5.6 (4)
C(236)	0.1601 (6)	-0.016 (1)	0.413 (2)	5.1 (5)	0.1955 (4)	0.2078 (7)	0.103 (2)	4.2 (4)
C(311)	-0.0533 (6)	-0.1085 (9)	0.3436 (8)	2.9 (4)	0.0767 (3)	0.3751 (9)	-0.105 (1)	2.8 (4)
C(312)	-0.0379 (5)	-0.0402 (8)	0.401 2 (5)	3.5 (4)	0.0794 (3)	0.3329 (6)	0.012 (1)	3.4 (4)
C(313)	-0.0876 (8)	-0.0167 (8)	0.453 7 (7)	4.5 (4)	0.0834 (3)	0.403 (1)	0.1107 (9)	5.4 (4)
C(314)	-0.1527 (6)	-0.0613 (9)	0.448 6 (8)	4.8 (5)	0.0846 (3)	0.5151 (9)	0.092 (1)	6.9 (6)
C(315)	-0.1682 (5)	-0.1295 (8)	0.391 1 (5)	4.2 (4)	0.0819 (3)	0.5573 (6)	-0.025 (1)	7.9 (6)
C(316)	-0.1185 (8)	-0.1531 (8)	0.338 5 (7)	3.6 (4)	0.0779 (3)	0.487 (1)	-0.1235 (9)	4.8 (4)
C(321)	0.0649 (6)	-0.2422 (8)	0.3208 (8)	3.6 (4)	0.0700 (5)	0.3672 (8)	-0.361 (1)	3.4 (4)
C(322)	0.0965 (6)	-0.320 (1)	0.2785 (4)	3.6 (4)	0.0363 (3)	0.432 (1)	-0.384 (1)	5.7 (5)
C(323)	0.1365 (6)	-0.3968 (8)	0.3121 (8)	4.8 (5)	0.0366 (6)	0.5048 (8)	-0.4815 (9)	6.0 (5)
C(324)	0.1449 (6)	-0.3965 (8)	0.3880 (8)	4.7 (5)	0.0707 (5)	0.5120 (8)	-0.556 (1)	5.0 (5)
C(325)	0.1133 (9)	-0.319 (1)	0.4304 (4)	6.2 (5)	0.1044 (3)	0.447 (1)	-0.533 (1)	7.0 (5)
C(326)	0.0733 (6)	-0.2419 (8)	0.3968 (8)	4.6 (4)	0.1040 (3)	0.3743 (8)	-0.4358 (9)	4.6 (4)
C(331)	-0.0278 (6)	-0.212 (1)	0.2037 (6)	3.9 (4)	0.0202 (3)	0.2307 (7)	-0.212 (4)	3.3 (4)
C(332)	-0.0329 (6)	-0.1672 (7)	0.1340 (9)	5.0 (5)	0.003 (1)	0.2158 (9)	-0.098 (3)	4.4 (4)
C(333)	-0.0650 (7)	-0.222 (1)	0.0775 (6)	8.0 (6)	-0.037 (1)	0.175 (1)	-0.089 (1)	6.4 (5)
C(334)	-0.0921 (6)	-0.322 (1)	0.0906 (6)	7.7 (6)	-0.0585 (3)	0.1501 (7)	-0.193 (4)	5.9 (5)
C(335)	-0.0870 (6)	-0.3669 (7)	0.1603 (9)	5.5 (5)	-0.041 (1)	0.1650 (9)	-0.307 (3)	11.3 (8)
C(336)	-0.0549 (7)	-0.312 (1)	0.2168 (6)	4.4 (4)	-0.002 (1)	0.205 (1)	-0.316 (1)	7.3 (6)
H(112)	0.077	0.416	0.322	8.3	0.051	0.011	-0.129	4.7
H(113)	0.004	0.501	0.410	9.4	-0.014	-0.060	-0.090	5.0
H(114)	-0.091	0.408	0.462	6.5	-0.033	-0.236	-0.165	5.1
H(115)	-0.112	0.229	0.427	5.2	0.015	-0.341	-0.279	5.2
H(116)	-0.039	0.144	0.340	4.2	0.081	-0.270	-0.318	3.4

Table I (Continued)

Atom ^c	(ii) Calculated Parameters (Continued)							
	Orange form				Red form			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
H(122)	0.077	0.142	0.109	4.2	0.147	-0.291	-0.296	3.5
H(123)	0.059	0.223	-0.008	6.7	0.179	-0.379	-0.464	6.1
H(124)	0.031	0.407	-0.015	6.4	0.196	-0.277	-0.643	5.1
H(125)	0.022	0.509	0.095	6.9	0.180	-0.087	-0.653	5.9
H(126)	0.041	0.427	0.212	6.3	0.147	-0.001	-0.485	4.1
H(132)	0.186	0.331	0.179	3.5	0.101	-0.132	-0.005	3.3
H(133)	0.290	0.416	0.218	5.9	0.135	-0.215	0.162	4.4
H(134)	0.326	0.403	0.343	5.9	0.205	-0.264	0.144	4.4
H(135)	0.259	0.305	0.429	6.6	0.241	-0.230	-0.041	3.3
H(136)	0.155	0.221	0.391	6.3	0.207	-0.147	-0.208	3.2
H(212)	0.190	0.060	0.118	4.0	0.238	0.070	-0.014	4.7
H(213)	0.277	0.158	0.054	6.0	0.297	-0.022	-0.091	4.0
H(214)	0.376	0.219	0.119	5.2	0.303	-0.055	-0.305	3.8
H(215)	0.390	0.181	0.247	3.3	0.252	0.005	-0.441	6.7
H(216)	0.303	0.083	0.310	4.0	0.193	0.097	-0.365	4.7
H(222)	0.111	-0.097	0.132	4.8	0.157	0.380	-0.012	3.4
H(223)	0.130	-0.241	0.049	6.7	0.179	0.561	-0.053	4.5
H(224)	0.219	-0.366	0.074	7.1	0.220	0.597	-0.229	4.6
H(225)	0.288	-0.349	0.181	6.9	0.238	0.452	-0.363	6.1
H(226)	0.269	-0.205	0.264	5.5	0.216	0.270	-0.322	5.2
H(232)	0.300	-0.107	0.331	7.5	0.111	0.075	0.033	4.2
H(233)	0.334	-0.135	0.457	8.6	0.106	0.069	0.249	6.3
H(234)	0.257	-0.087	0.554	7.1	0.157	0.151	0.373	7.6
H(235)	0.148	-0.012	0.527	7.6	0.214	0.239	0.280	6.2
H(236)	0.114	0.015	0.402	5.6	0.219	0.245	0.064	4.6
H(312)	0.009	-0.008	0.405	3.8	0.079	0.252	0.025	3.7
H(313)	-0.077	0.032	0.495	4.7	0.085	0.372	0.195	5.9
H(314)	-0.188	-0.045	0.486	5.1	0.087	0.565	0.164	7.6
H(315)	-0.215	-0.162	0.387	4.8	0.082	0.638	-0.037	8.7
H(316)	-0.130	-0.202	0.297	4.0	0.076	0.518	-0.207	5.3
H(322)	0.091	-0.321	0.224	4.0	0.012	0.427	-0.330	6.3
H(323)	0.160	-0.453	0.283	5.2	0.012	0.552	-0.498	6.6
H(324)	0.173	-0.451	0.414	5.2	0.071	0.564	-0.626	5.5
H(325)	0.119	-0.318	0.486	6.7	0.129	0.452	-0.587	7.7
H(326)	0.050	-0.186	0.427	5.1	0.128	0.327	-0.420	5.1
H(332)	-0.013	-0.096	0.124	5.6	0.018	0.234	-0.023	4.9
H(333)	-0.069	-0.191	0.027	9.0	-0.049	0.165	-0.007	7.1
H(334)	-0.115	-0.363	0.050	8.5	-0.087	0.121	-0.186	6.5
H(335)	-0.107	-0.439	0.170	6.4	-0.057	0.147	-0.382	12.4
H(336)	-0.051	-0.343	0.267	4.7	0.011	0.216	-0.398	8.1

^a Values in parentheses in this and the following tables represent the standard deviation of the least significant digit(s). ^b These values are equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters given in Table III. ^c The numbering of the carbon atom C(*ijk*) proceeds as follows: *i*, phosphine number; *j*, ring number; *k*, atom number within phenyl ring.

of an observation of unit weight was 1.55. A final electron density difference map showed no systematic residual peaks with the largest positive and negative peaks being +0.44 and -0.36 e Å⁻³, respectively (cf. carbon peak at ~3 e Å⁻³). Refinement of the *x*, *y*, *z* solution gave rise to significantly worse agreement ($R_1 = 0.052$; $R_2 = 0.064$).

(a) **Red Form.** The initial stages of the solution and refinement of the red form were essentially the same as those described for the orange allotrope. However certain anomalies appeared during the later stages of the refinement. In particular the thermal parameters of the chlorine atom and the unusual pattern of the thermal parameters for phenyl carbon ring 33 (especially the high *B* values for carbon atoms C(335) and C(366)) gave cause for concern. These areas were studied carefully by means of electron density difference maps with and without D_{6h} constraints on this ring. No interpretable pattern was found in the residual peaks. Similar difficulties were experienced in the independent study by Mason and Hitchcock.⁵ We conclude that the structure is probably disordered in this region but that the extent of the disorder is relatively small.

The model incorporating a rigid-body description of the phenyl groups refined to $R_1 = 0.044$ and $R_2 = 0.047$. An alternate solution *x*, *y*, *z* gives significantly better agreement, converging at $R_1 = 0.042$ and $R_2 = 0.044$. In the final cycle of refinement the maximum shift in a parameter was equal to less than one-fifth of its standard deviation and the standard deviation of an observation of unit weight was equal to 1.60. Residual features in the final electron density difference map

ranged from -0.20 to +0.38 e Å⁻³ (cf. a typical carbon peak at ~3 e Å⁻³).

Programs used in these studies included SFLS5HR,¹⁵ GONOS,¹⁶ ORFFE II,¹⁷ FORDAP,¹⁸ and ORTEP.¹⁹

Results

Table I gives the refined and derived positional coordinates of the atoms and their isotropic thermal parameters in the two structures. Table II gives the refined phenyl ring rigid-body parameters while Table III contains the anisotropic thermal parameters for the central atoms. Other tables give selected interatomic distances (Table IV), interatomic angles (Table V), and intra- and intermolecular nonbonded contacts (Tables VI and VII, respectively). A comparison of the weighted mean molecular planes is given in Table VIII. Comparisons of ($|F_o|$) and ($|F_c|$) (electrons × 10) are available (see paragraph at end of paper regarding supplementary material).

Discussion

The molecular structure in the orange and red allotropes can be described in terms of square-planar coordination to a first approximation. Figures 1 and 2 show the structures of the orange and red forms projected onto the mean molecular plane. However there is a distortion toward tetrahedral

Table II. Refined Rigid-Body Parameters^a

Group	x	y	z	D	E	F
Orange Form						
11	-0.0179 (4)	0.3226 (7)	0.3746 (4)	0.318 (8)	0.669 (8)	5.783 (9)
12	0.0497 (4)	0.3254 (6)	0.1019 (5)	6.061 (7)	1.632 (8)	3.599 (8)
13	0.2225 (4)	0.3186 (5)	0.3036 (4)	0.979 (6)	1.97 (1)	5.34 (1)
21	0.2899 (4)	0.1205 (5)	0.1826 (4)	1.017 (6)	2.01 (1)	4.58 (1)
22	0.1997 (4)	-0.2229 (6)	0.1566 (4)	2.548 (7)	2.239 (9)	4.305 (9)
23	0.2240 (5)	-0.0599 (6)	0.4289 (5)	1.986 (8)	1.51 (1)	5.91 (2)
31	-0.1030 (4)	-0.0849 (5)	0.3961 (4)	0.887 (7)	0.51 (1)	5.94 (1)
32	0.1049 (3)	-0.3194 (5)	0.3544 (4)	2.521 (7)	1.691 (9)	5.239 (9)
33	-0.0599 (4)	-0.2672 (7)	0.1471 (5)	3.566 (7)	1.851 (8)	3.725 (9)
Red Form						
11	0.0333 (2)	-0.1646 (5)	-0.2041 (6)	0.431 (6)	0.374 (7)	0.412 (6)
12	0.1631 (2)	-0.1888 (6)	-0.4747 (6)	6.065 (6)	1.162 (6)	2.662 (7)
13	0.1710 (2)	-0.1811 (4)	-0.0231 (6)	5.154 (5)	0.66 (1)	1.47 (1)
21	0.2448 (2)	0.0371 (4)	-0.2281 (8)	5.210 (5)	1.79 (2)	1.74 (2)
22	0.1974 (2)	0.4158 (5)	-0.1875 (6)	3.311 (6)	0.996 (5)	1.906 (6)
23	0.1624 (2)	0.1568 (5)	0.1565 (7)	4.186 (5)	1.54 (1)	6.22 (1)
31	0.0806 (2)	0.4451 (6)	-0.0064 (8)	3.183 (6)	1.658 (7)	0.665 (8)
32	0.0703 (2)	0.4396 (6)	-0.4586 (7)	2.351 (6)	0.567 (9)	2.00 (1)
33	-0.0191 (2)	0.1904 (4)	-0.2027 (7)	1.203 (5)	1.49 (2)	1.42 (2)

^a The center of gravity of the ring is described by the x, y, and z coordinates, while the inclination is described by the angles D, E, and F (in radians).

Table III. Anisotropic Temperature Factors ($\text{Å}^2 \times 10^3$)^a

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Orange Form						
Rh	24.6 (6)	27.3 (6)	38.6 (7)	-0.4 (6)	0 (1)	0 (1)
Cl	30 (3)	48 (3)	69 (3)	1 (2)	-11 (3)	6 (2)
P(1)	32 (3)	34 (2)	45 (3)	-1 (2)	-3 (4)	-5 (4)
P(2)	26 (2)	35 (2)	46 (4)	0 (2)	3 (3)	-3 (4)
P(3)	34 (3)	25 (2)	44 (4)	-3 (2)	0 (3)	0 (2)
Red Form						
Rh	29.6 (5)	25.0 (5)	31.0 (6)	1.1 (6)	-5 (1)	-3 (1)
Cl	75 (3)	53 (3)	64 (3)	13 (2)	-43 (3)	-13 (3)
P(1)	28 (2)	28 (2)	30 (2)	0 (1)	-1 (3)	-5 (5)
P(2)	32 (2)	27 (2)	32 (3)	2 (2)	0 (2)	-2 (2)
P(3)	35 (2)	32 (2)	32 (3)	2 (2)	3 (3)	1 (3)

^a Anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2 + a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k lb^*c^*)]$.

Table IV. Selected Interatomic Distances

Atoms	Distance, Å			
	Orange form		Red form	
Rh-Cl	2.404 (4)	2.416 (4) ^a	2.376 (4)	2.398 (4) ^a
Rh-P(1)	2.304 (4)	2.307 (4) ^a	2.334 (3)	2.334 (3) ^a
Rh-P(2)	2.225 (4)	2.228 (4) ^a	2.214 (4)	2.214 (4) ^a
Rh-P(3)	2.338 (4)	2.341 (4) ^a	2.322 (4)	2.324 (4) ^a
P(1)-C(111)	1.841 (10)		1.842 (9)	
P(1)-C(121)	1.831 (10)		1.815 (10)	
P(1)-C(131)	1.836 (9)		1.859 (9)	
P(2)-C(211)	1.841 (9)		1.847 (9)	
P(2)-C(221)	1.852 (10)		1.864 (9)	
P(2)-C(231)	1.871 (10)		1.839 (10)	
P(3)-C(311)	1.856 (9)		1.837 (10)	
P(3)-C(321)	1.847 (9)		1.820 (9)	
P(3)-C(331)	1.832 (10)		1.838 (9)	

^a Value corrected for riding.

geometry which is more marked in the case of the red allotrope. This is clearly shown by the deviations from the mean molecular planes (Table 8). This can be compared with a pyramidal distortion observed²⁰ in RhLCl (where L is the tridentate phosphine ligand $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_3\text{H}_6)_2\text{P}(\text{C}_6\text{H}_5)$).

A further difference in the metal coordination arises from the nonprimary valence interaction with ortho hydrogens of the phenyl groups in that the close contact in the red form is in a position pseudo-trans to P(3) whereas in the orange form the hydrogen contact is pseudo-trans to the chlorine atom. The

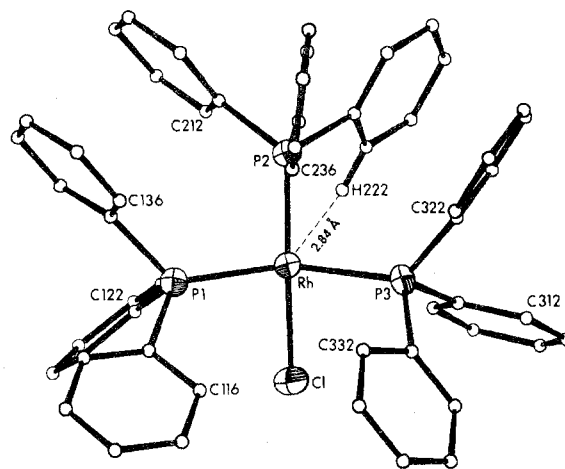


Figure 1. Perspective view of the orange allotrope.

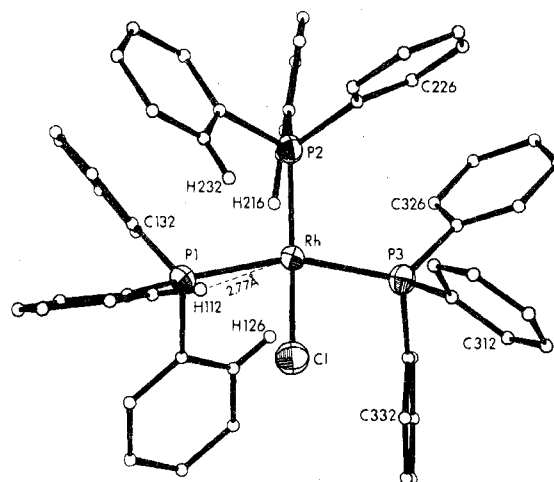


Figure 2. Perspective view of the red allotrope.

potential importance of these secondary interactions has been discussed elsewhere.²¹

The rhodium-ligand distances (uncorrected for thermal motion) of this study, the equivalent values of Mason et al.,^{3,4} and the relevant data on RhLCl are compared in Table IX. The two determinations of the red form are in excellent

Table V. Selected Interatomic Angles

Atoms	Angle, deg	
	Orange form	Red form
P(1)-Rh-P(2)	97.7 (1)	97.9 (2)
P(1)-Rh-P(3)	159.1 (2)	152.8 (1)
P(1)-Rh-Cl	85.3 (1)	85.2 (2)
P(1)-Rh-H(112)		67.2
P(1)-Rh-H(222)	122.9	
P(2)-Rh-P(3)	96.4 (2)	100.4 (1)
P(2)-Rh-Cl	166.7 (2)	156.2 (2)
P(2)-Rh-H(112)		115.1
P(2)-Rh-H(222)	66.1	
P(3)-Rh-Cl	84.5 (1)	86.1 (2)
P(3)-Rh-H(112)		86.7
P(3)-Rh-H(222)	77.1	
Cl-Rh-H(112)		88.0
Cl-Rh-H(222)	101.3	
Rh-P(1)-C(111)	112.5 (5)	104.3 (3)
Rh-P(1)-C(121)	114.3 (5)	121.5 (4)
Rh-P(1)-C(131)	123.4 (4)	121.1 (4)
Rh-P(2)-C(211)	119.0 (4)	109.7 (4)
Rh-P(2)-C(221)	109.9 (5)	114.1 (3)
Rh-P(2)-C(231)	116.4 (5)	123.5 (4)
Rh-P(3)-C(311)	104.4 (4)	124.7 (4)
Rh-P(3)-C(321)	122.3 (4)	117.1 (4)
Rh-P(3)-C(331)	120.6 (6)	107.2 (3)
P(1)-C(111)-C(114)	178.7 (8)	176.6 (7)
P(1)-C(121)-C(124)	175.1 (8)	176.0 (6)
P(1)-C(131)-C(134)	177.3 (6)	178.2 (6)
P(2)-C(211)-C(214)	174.6 (7)	174.9 (7)
P(2)-C(221)-C(224)	174.3 (8)	178.1 (6)
P(2)-C(231)-C(234)	176.4 (9)	175.0 (7)
P(3)-C(311)-C(314)	177.6 (7)	176.7 (8)
P(3)-C(321)-C(324)	177.4 (7)	176.0 (7)
P(3)-C(331)-C(334)	178.1 (7)	176.4 (7)

Table VI. Selected Intramolecular Contacts

Atoms	Distance, Å	
	Orange form	Red form
Rh-H(222)	2.84	
Rh-H(236)	2.94	
Rh-H(112)		2.77
Rh-H(216)		2.94
P(1)-P(2)	3.411 (5)	3.430 (5)
P(1)-Cl	3.190 (6)	3.208 (6)
P(2)-P(3)	3.404 (6)	3.485 (5)
P(3)-Cl	3.188 (6)	3.190 (6)

Table VII. Selected Intermolecular Contacts

Atoms	Symmetry operation on atom 2	Distance, Å	
		Orange form	Red form
H(112)-H(323)	$x, y + 1, z$	2.41	
H(113)-H(124)	$\bar{x}, \bar{y} + 1, 1/2 + z$	1.92	
H(212)-H(314)	$\bar{x}, \bar{y}, 1/2 + z - 1$	2.40	
H(213)-H(325)	$1/2 - x, 1/2 + y, 1/2 + z - 1$	2.41	
H(132)-H(335)	$\bar{x}, \bar{y}, 1/2 + z$		2.00
H(123)-H(213)	$1/2 - x, 1/2 + y - 1, 1/2 + z - 1$		2.38
H(124)-H(134)	$x, y, z - 1$		2.37
H(212)-H(225)	$1/2 - x, 1/2 + y - 1, 1/2 + z$		2.34

agreement and no significant deviations can be detected. For the red form the rhodium-phosphorus bond lengths to the chemically equivalent phosphorus atoms P(1) and P(3) are the same within experimental error in contrast to an apparently significant difference in the orange form. In all four structure determinations the chemically unique rhodium-phosphorus bond is substantially shorter than the other two. This pattern of bond lengths is consistent with the π acidity and thus the trans effect of phosphorus being greater than that of chlorine.^{22,23}

There appears to be a significant difference ($\Delta/\sigma \approx 4$) between the rhodium-chlorine bond lengths observed in the

Table VIII. Weighted Mean Molecular Planes^a

Atoms in Plane: Rh, Cl, P(1), P(2), P(3)		
Equations: Orange, $-0.1624x + 0.1708y + 0.9718z = 4.2984$		
Red, $-0.6629x - 0.2857y + 0.2690z = -4.8112$		
Deviations of Atoms from Plane		
Atom	Deviation, Å	
	Orange form	Red form
Rh	-0.014	0.010
Cl	-0.290	-0.489
P(1)	0.419	0.469
P(2)	-0.276	-0.436
P(3)	0.234	0.492

^a The orthogonal coordinate system (x, y, z) corresponds to the crystal a, b, c axes.

Table IX. Distances (Å) from Structures Containing the RhClP₃ Fragment

Atoms	RhClP ₃ ^a			RhLCl ^c
	Red	Red	Orange	
Rh-Cl	2.376 (4)	2.386	2.404 (4)	2.381 (2)
Rh-P (P trans to Cl)	2.214 (4)	2.210	2.225 (4)	2.201 (2)
	2.322 (4)	2.320	2.304 (4)	2.288 (2)
Rh-P (P trans to P)	2.334 (4)	2.331	2.338 (4)	2.288 (2) ^b
Σ Rh-ligand	9.246	9.44	9.271	9.158
Σ Rh-P	6.870	6.861	6.867	6.777
Ref	This work	3,4	This work	20

^a P' represents triphenylphosphine. ^b Related by symmetry to the value above. ^c L = (C₆H₅)₂P(C₃H₆)₂P(C₆H₅).

red (2.376 (4) Å) and the orange (2.404 (4) Å) forms. This difference persists even when the bond lengths are modified for the effects of thermal motion. This variation could be the result of the greater interligand repulsions which are present in the orange crystals and it is reasonable that such an effect should be noticeable in the weaker rhodium-chlorine bond rather than the rhodium-phosphorus bonds. Alternatively, the difference could result from the nonprimary valence interactions²¹ with the ortho hydrogens. However, given the disorder problem that is believed to exist for the red crystals, the difference may be the result of a systematic error and thus not significant.

A simple statistical analysis of the nine independent phosphorus-carbon distances in the red form (average 1.840 Å) suggests a standard deviation of 0.016 Å which should be compared with the typical values of approximately 0.009 Å obtained from ORFFE II. A similar analysis for the orange allotrope (average P-C = 1.844 Å) gives values of 0.014 Å (based on population analysis) and 0.010 Å as given by ORFFE II. Before assuming that the difference in these estimates of standard deviations was due to systematic errors present in both structures, the 18 phosphorus-carbon distances were regrouped on the basis of chemical environment.

The 12 distances in the mutually trans phosphines average 1.837 Å with a standard deviation of 0.013 Å whereas the other six distances average 1.852 Å with a standard deviation of 0.012 Å. These standard deviations are still greater than the ORFFE II treatment of the least-squares data and it would still seem unwise to draw any firm conclusions on the difference between the chemically based groups. Nevertheless we note that the difference is present in both structures (orange form, P-C (P trans to P) = 1.838 Å, P-C (P trans to Cl) = 1.855 Å; red form, P-C (P trans to P) = 1.835 Å, P-C (P trans to Cl) = 1.850 Å; cf. 1.828 Å, uncomplexed ligand²⁴) and that some difference in phosphorus-carbon distances might be expected in view of the big difference in metal-phosphorus distances. In this instance we cannot claim to have a definite

case for such variations in phosphorus-carbon bond lengths but we wish to draw attention to the possibility.

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Registry No. RhCl(P(C₆H₅)₃), 14694-95-2.

Supplementary Material Available: Listings of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Alkali Metal Intercalates of Ta₂S₂C

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Alkali metals were intercalated in the layered structures of Ta₂S₂C. Only first-stage M_xTa₂S₂C phases have been obtained, in which the alkali metals occupy statistically all van der Waals gaps. In the case of potassium, rubidium, and cesium, the alkali metal has a trigonal prismatic coordination, whereas it is octahedrally surrounded for lithium derivatives. The Na-Ta₂S₂C system is a borderline case, with both coordinations for the sodium. The phases, limits, and variation of parameters are given and compared with the results obtained with the TS₂ intercalates. Structures of the M_xTa₂S₂C phases are proposed.

Introduction

The compound Ta₂S₂C prepared by Beckmann, Boller, and Nowotny¹ belongs to the class of the layer chalcogenides. The structure can be regarded as the result of stacking of two-dimensional slabs upon one another along the *c* axis. These slabs are made up of five-layer units, the stacking sequence being S-Ta-C-Ta-S; the heart of a slab consists of a carbon layer and the two external layers are sulfur layers. 1s and 3R forms are known, with octahedral voids in the van der Waals gap (Figure 1).

As in TaS₂ (Figure 1), very weak bonds exist between adjacent layers (van der Waals gap). Therefore, it is expected that various chemical intercalations can pull the layers apart. Boller and Sobczak² were able to prepare some ternary compounds Me_xTa₂S₂C (with Me = Ti, V, Cr, ...) whereas some molecular intercalate species were obtained by Schöllhorn and Weiss.³ In a short note,⁴ we have previously shown alkali metal intercalation to occur in Ta₂S₂C. In the present work, a complete survey of the experimental results and of the structures of the derivatives is given.

Experimental Section

Ta₂S₂C was prepared as previously reported by Beckmann et al.¹ Tantalum powder (99.7%), sulfur powder (≥99.99%), and graphite powder (99.999%) were from Koch Light Laboratories. The following sequences also lead to well-crystallized samples; the stoichiometric quantity corresponding to Ta₂S₂C is heated in a sealed silica tube under vacuum for 3 days at 550 °C, then, after returning to room temperature, the product is ground, pelleted, and heated under vacuum up to 1050 °C for 4 days.

The furnace is allowed to cool down again and the product is ground again, pelleted, and finally placed in a carbon tube itself put in a sealed

silica tube under vacuum. The sample is then fired at 1200 °C for 2 days and slowly cooled (40 °C/h).

Chunks of pure alkali metal were carefully weighed under nitrogen or argon atmosphere and sealed under vacuum in small breakable ampules. Alkali metals to be intercalated in Ta₂S₂C were dissolved in liquid ammonia. Very dry ammonia was obtained by vacuum distillation from sodium.

The intercalation was performed at room temperature in sealed Pyrex tubes (Figure 2). The tube has two branches, one to separate liquid ammonia from the intercalated powder, and the other containing a thin-walled Pyrex needle to prepare samples for x-ray powder spectra. These precautions had to be taken due to the extreme reactivity of the intercalates toward water and oxygen. Figure 2 helps in the understanding of the way intercalation was performed. A weighed amount of powdered Ta₂S₂C is placed in A, along with a small, breakable ampule containing a determined amount of alkali metal. Pure and dry ammonia is condensed frozen and the tube is sealed and brought slowly to room temperature. By shaking the Pyrex tube, the ampule breaks open and intercalation takes place within a minute, with instant decoloration for all M_xTa₂S₂C compositions (*x* ≤ 1). Liquid ammonia is then poured into C and frozen. While C is maintained at -180 °C, the intercalation product is heated for 12 h at 250 °C to remove ammonia. To get rid of it, a sealing is made at R₁ and the alkali metal present in it in very small amounts is analyzed to determine the exact amount of the intercalated metal.

The powder of the intercalated compound is stacked in the capillary contained in the remaining Pyrex branch which is sealed in R₂ and opened between R₂ and R₃, the capillary being finally sealed at R₃. Such a system allowed us to get better samples, free of any oxidation.

The intercalation products were carefully reacted with hydrochloric acid, then the aqueous solution was neutralized by NaOH and the Kjeldahl method was used to check that the sample did not contain ammonia. Alkali metal contained in liquid NH₃ was analyzed by flame absorption on a Unicam SP 1900 spectrophotometer.