Crystal structure of a pleochroic modification of dichlorotris(triphenylphospine)ruthenium, $C_{54}H_{45}Cl_2P_3Ru$, *at 200 K*

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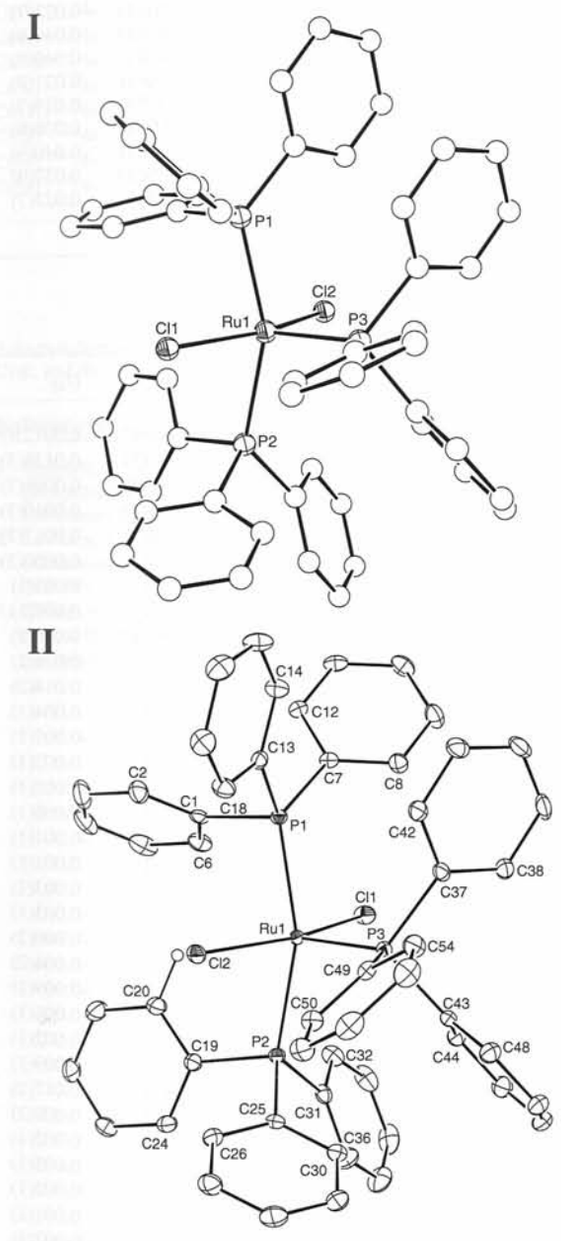

Abstract

$C_{54}H_{45}Cl_2P_3Ru$ (**II**), monoclinic, $P12_1/n1$ (No. 14), $a = 12.8928(2)$ Å, $b = 16.5190(2)$ Å, $c = 20.8714(3)$ Å, $\beta = 93.1955(7)°$, $V = 4438.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.040$, $wR_{ref}(F^2) = 0.080$, $T = 200$ K.

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Source of material

The compound was synthesized as described previously [1] and crystallized by slow diffusion of hexane into a concentrated methylene chloride solution.

Discussion

The structure of dichlorotris(triphenylphospine)ruthenium had originally been determined by La Placa and Ibers [2] at room temperature, revealing square-pyramidal primary coordination, with a hydrogen atom from a C-H bond occupying the remaining octahedral position (modification **I**, upper figure). As this species was one of the first two recognized examples of compounds having such a H—M interaction [3], it is of some historical significance. It was therefore of interest to obtain more accurate structural parameters, ideally including the location and refinement of the metal-proximate hydrogen atom position. However, a new, pleochroic (yellow, orange, pink, red, violet, green) modification (**II**, lower figure) was isolated, isomorphous with a previously reported osmium complex [4].

While the overall geometric arrangement about the ruthenium center in **II** is similar to that observed earlier, there are differences in phenyl ring orientations, especially around P1, as can be seen from a comparison of upper (**I**) and lower (**II**) figures, and there are also differences in the locations of the hydrogen atom situated near the vacant octahedral site. In particular, in this case the apparent Ru···H distance is 2.82 Å, vs. ca. 2.59 Å in the original study. That there is still a Ru–H interaction, even at this longer distance, is suggested by the C20—H distance of 1.13(3) Å. All other C—H distances for this structure refined to values in the range of 0.86 Å – 0.99 Å. One other structural difference between the two polymorphs is that the new form exhibits a more regular square pyramidal coordination geometry; in the original polymorph, larger differences in the P3–Ru–Cl angles were observed (109.9(2)° vs. 92.9(2)° for **I** and 96.32(2)° vs. 101.10(2)° for **II**). The Ru—(Cl1, Cl2, P1, P2, and P3) distances in **II** are 2.3801(6) Å, 2.3948(6) Å, 2.3814(6) Å, 2.4435(6) Å, and 2.2331(7) Å, respectively.

Table 1. Data collection and handling.

Crystal:	pleochroic prism, size 0.28 × 0.30 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.20 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ/ω
$2\theta_{max}$:	55.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18387, 1056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7146
$N(param)_{refined}$:	722
Programs:	SIR97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.670(2)	0.241(2)	1.090(1)	0.040(9)
H(3)	4*e*	0.744(3)	0.155(2)	1.173(2)	0.08(1)
H(4)	4*e*	0.829(3)	0.038(2)	1.151(2)	0.06(1)
H(5)	4*e*	0.839(3)	0.001(2)	1.043(2)	0.05(1)
H(6)	4*e*	0.769(2)	0.080(2)	0.959(1)	0.027(8)
H(8)	4*e*	0.570(2)	0.208(2)	0.820(1)	0.024(7)
H(9)	4*e*	0.426(2)	0.134(2)	0.778(1)	0.044(9)
H(10)	4*e*	0.337(3)	0.048(2)	0.841(2)	0.06(1)
H(11)	4*e*	0.392(2)	0.031(2)	0.947(1)	0.029(8)
H(12)	4*e*	0.535(2)	0.099(2)	0.992(1)	0.017(7)
H(14)	4*e*	0.443(2)	0.251(2)	0.971(1)	0.033(8)
H(15)	4*e*	0.346(2)	0.342(2)	1.026(1)	0.041(9)
H(16)	4*e*	0.429(2)	0.453(2)	1.076(1)	0.042(9)
H(17)	4*e*	0.603(2)	0.471(2)	1.071(1)	0.043(9)
H(18)	4*e*	0.704(2)	0.375(2)	1.016(1)	0.022(7)
H(20)	4*e*	0.933(2)	0.163(2)	0.997(1)	0.043(8)
H(21)	4*e*	1.028(2)	0.099(2)	1.086(1)	0.042(9)
H(22)	4*e*	1.210(2)	0.102(2)	1.096(1)	0.032(8)
H(23)	4*e*	1.310(2)	0.157(2)	1.020(1)	0.034(8)
H(24)	4*e*	1.222(2)	0.218(2)	0.929(1)	0.036(8)
H(26)	4*e*	1.119(2)	0.356(1)	0.971(1)	0.008(6)
H(27)	4*e*	1.185(2)	0.486(2)	0.972(1)	0.035(8)
H(28)	4*e*	1.192(2)	0.554(2)	0.874(1)	0.035(8)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
	4*e*	1.127(2)	0.490(2)	0.782(1)	0.031(8)
H(30)	4*e*	1.057(2)	0.364(2)	0.785(1)	0.014(6)
H(32)	4*e*	0.967(2)	0.093(2)	0.839(1)	0.035(8)
H(33)	4*e*	1.023(2)	0.008(2)	0.762(1)	0.05(1)
H(34)	4*e*	1.151(2)	0.045(2)	0.697(1)	0.047(9)
H(35)	4*e*	1.231(2)	0.173(2)	0.715(1)	0.047(9)
H(36)	4*e*	1.179(2)	0.257(2)	0.791(1)	0.029(8)
H(38)	4*e*	0.661(2)	0.304(2)	0.716(1)	0.031(8)
H(39)	4*e*	0.489(2)	0.296(2)	0.687(1)	0.038(9)
H(40)	4*e*	0.366(2)	0.334(2)	0.755(1)	0.039(9)
H(41)	4*e*	0.413(2)	0.384(2)	0.856(1)	0.039(9)
H(42)	4*e*	0.586(2)	0.398(2)	0.882(1)	0.019(7)
H(44)	4*e*	0.876(2)	0.236(2)	0.752(1)	0.030(8)
H(45)	4*e*	0.961(2)	0.238(2)	0.661(1)	0.023(7)
H(46)	4*e*	0.985(2)	0.358(2)	0.605(1)	0.044(9)
H(47)	4*e*	0.917(2)	0.479(2)	0.645(1)	0.040(9)
H(48)	4*e*	0.834(2)	0.475(2)	0.738(1)	0.021(7)
H(50)	4*e*	0.928(2)	0.448(2)	0.910(1)	0.019(7)
H(51)	4*e*	0.968(2)	0.582(2)	0.931(1)	0.038(8)
H(52)	4*e*	0.854(2)	0.678(2)	0.888(1)	0.040(9)
H(53)	4*e*	0.707(2)	0.640(2)	0.829(1)	0.037(9)
H(54)	4*e*	0.671(2)	0.506(2)	0.808(1)	0.023(7)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	4*e*	0.82518(1)	0.25557(1)	0.901420(8)	0.0147(1)	0.0157(1)	0.0142(1)	–0.00150(9)	0.00106(7)	–0.00123(9)
Cl(1)	4*e*	0.77855(5)	0.14650(4)	0.83107(3)	0.0268(4)	0.0258(4)	0.0290(3)	–0.0061(3)	0.0053(3)	–0.0128(3)
Cl(2)	4*e*	0.88215(5)	0.33190(4)	0.99438(3)	0.0222(3)	0.0298(4)	0.0221(3)	–0.0051(3)	0.0009(3)	–0.0098(3)
P(1)	4*e*	0.66429(5)	0.22938(4)	0.94825(3)	0.0156(3)	0.0179(4)	0.0175(3)	–0.0023(3)	0.0023(3)	–0.0010(3)
P(2)	4*e*	1.01123(5)	0.24831(4)	0.88532(3)	0.0159(3)	0.0192(3)	0.0180(3)	–0.0014(3)	0.0023(2)	–0.0017(3)
P(3)	4*e*	0.78008(5)	0.35462(4)	0.83258(3)	0.0173(3)	0.0181(3)	0.0156(3)	–0.0015(3)	–0.0003(3)	0.0000(3)
C(1)	4*e*	0.7145(2)	0.1671(2)	1.0156(1)	0.013(1)	0.022(1)	0.027(1)	–0.005(1)	0.001(1)	0.005(1)
C(2)	4*e*	0.7065(2)	0.1899(2)	1.0793(1)	0.031(2)	0.035(2)	0.030(2)	0.001(1)	–0.004(1)	0.007(1)
C(3)	4*e*	0.7483(3)	0.1412(2)	1.1283(2)	0.050(2)	0.058(2)	0.032(2)	–0.006(2)	–0.016(2)	0.009(2)
C(4)	4*e*	0.8002(2)	0.0708(2)	1.1149(2)	0.033(2)	0.044(2)	0.057(2)	–0.009(2)	–0.021(2)	0.024(2)
C(5)	4*e*	0.8081(2)	0.0476(2)	1.0525(2)	0.027(2)	0.022(2)	0.070(2)	–0.003(1)	–0.004(2)	0.014(2)
C(6)	4*e*	0.7645(2)	0.0948(2)	1.0024(2)	0.023(2)	0.025(2)	0.045(2)	–0.003(1)	0.000(1)	0.004(1)
C(7)	4*e*	0.5649(2)	0.1621(2)	0.9112(1)	0.017(1)	0.019(1)	0.024(1)	–0.001(1)	0.004(1)	–0.002(1)
C(8)	4*e*	0.5324(2)	0.1706(2)	0.8471(1)	0.026(2)	0.022(2)	0.027(1)	–0.005(1)	–0.002(1)	0.002(1)
C(9)	4*e*	0.4480(2)	0.1278(2)	0.8213(2)	0.034(2)	0.035(2)	0.032(2)	–0.007(1)	–0.012(1)	0.002(1)
C(10)	4*e*	0.3944(2)	0.0754(2)	0.8591(2)	0.026(2)	0.029(2)	0.044(2)	–0.009(1)	–0.006(1)	–0.006(1)
C(11)	4*e*	0.4273(2)	0.0642(2)	0.9222(1)	0.023(2)	0.026(2)	0.040(2)	–0.005(1)	0.010(1)	–0.001(1)
C(12)	4*e*	0.5119(2)	0.1068(2)	0.9485(1)	0.022(1)	0.024(2)	0.023(1)	–0.001(1)	0.005(1)	0.001(1)
C(13)	4*e*	0.5833(2)	0.3041(2)	0.9878(1)	0.022(1)	0.021(1)	0.017(1)	0.001(1)	0.002(1)	0.003(1)
C(14)	4*e*	0.4765(2)	0.2945(2)	0.9904(1)	0.022(2)	0.027(2)	0.035(2)	–0.002(1)	0.004(1)	–0.003(1)
C(15)	4*e*	0.4187(2)	0.3501(2)	1.0233(2)	0.023(2)	0.034(2)	0.052(2)	0.004(1)	0.014(2)	–0.000(2)
C(16)	4*e*	0.4661(2)	0.4154(2)	1.0533(2)	0.041(2)	0.030(2)	0.042(2)	0.012(2)	0.013(2)	–0.004(2)
C(17)	4*e*	0.5715(2)	0.4264(2)	1.0499(1)	0.039(2)	0.029(2)	0.036(2)	0.004(2)	0.003(2)	–0.009(1)
C(18)	4*e*	0.6299(2)	0.3717(2)	1.0171(1)	0.022(2)	0.029(2)	0.034(2)	0.003(1)	0.002(1)	–0.006(1)
C(19)	4*e*	1.0773(2)	0.1993(2)	0.9557(1)	0.021(1)	0.023(1)	0.022(1)	–0.000(1)	0.002(1)	–0.002(1)
C(20)	4*e*	1.0208(2)	0.1632(2)	1.0024(1)	0.021(2)	0.040(2)	0.031(2)	–0.000(1)	0.001(1)	0.009(1)
C(21)	4*e*	1.0711(2)	0.1260(2)	1.0551(1)	0.031(2)	0.055(2)	0.033(2)	0.003(2)	0.006(1)	0.017(2)
C(22)	4*e*	1.1775(2)	0.1254(2)	1.0622(1)	0.035(2)	0.048(2)	0.028(2)	0.008(2)	–0.005(1)	0.009(2)
C(23)	4*e*	1.2348(2)	0.1604(2)	1.0158(1)	0.018(2)	0.044(2)	0.038(2)	0.006(1)	–0.002(1)	0.002(1)
C(24)	4*e*	1.1855(2)	0.1961(2)	0.9624(1)	0.021(1)	0.035(2)	0.029(2)	–0.000(1)	0.005(1)	0.005(1)
C(25)	4*e*	1.0814(2)	0.3445(2)	0.8802(1)	0.014(1)	0.020(1)	0.024(1)	–0.002(1)	0.003(1)	–0.002(1)
C(26)	4*e*	1.1228(2)	0.3818(2)	0.9357(1)	0.024(2)	0.026(2)	0.024(1)	–0.003(1)	0.003(1)	0.001(1)
C(27)	4*e*	1.1648(2)	0.4585(2)	0.9340(1)	0.031(2)	0.029(2)	0.035(2)	–0.009(1)	0.002(1)	–0.007(1)
C(28)	4*e*	1.1664(2)	0.4997(2)	0.8764(2)	0.035(2)	0.025(2)	0.046(2)	–0.012(1)	0.007(2)	0.001(1)
C(29)	4*e*	1.1277(2)	0.4630(2)	0.8207(1)	0.033(2)	0.032(2)	0.032(2)	–0.008(1)	0.004(1)	0.010(1)
C(30)	4*e*	1.0845(2)	0.3865(2)	0.8224(1)	0.020(1)	0.029(2)	0.025(1)	–0.004(1)	0.002(1)	–0.001(1)
C(31)	4*e*	1.0636(2)	0.1845(2)	0.8222(1)	0.021(1)	0.025(2)	0.021(1)	0.006(1)	–0.002(1)	–0.004(1)
C(32)	4*e*	1.0201(2)	0.1083(2)	0.8141(1)	0.026(2)	0.026(2)	0.038(2)	0.005(1)	–0.000(1)	–0.007(1)
C(33)	4*e*	1.0518(3)	0.0564(2)	0.7671(2)	0.037(2)	0.034(2)	0.049(2)	0.013(2)	–0.011(2)	–0.018(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(34)	4*e*	1.1307(3)	0.0792(2)	0.7290(2)	0.056(2)	0.052(2)	0.029(2)	0.028(2)	0.000(2)	–0.017(2)
C(35)	4*e*	1.1769(3)	0.1535(2)	0.7378(2)	0.046(2)	0.054(2)	0.035(2)	0.018(2)	0.017(2)	–0.002(2)
C(36)	4*e*	1.1443(2)	0.2062(2)	0.7847(1)	0.038(2)	0.034(2)	0.034(2)	0.002(2)	0.013(2)	–0.003(1)
C(37)	4*e*	0.6434(2)	0.3515(2)	0.8032(1)	0.020(1)	0.021(1)	0.023(1)	–0.003(1)	–0.004(1)	0.007(1)
C(38)	4*e*	0.6120(2)	0.3216(2)	0.7431(1)	0.027(2)	0.035(2)	0.022(1)	–0.008(1)	–0.002(1)	0.004(1)
C(39)	4*e*	0.5062(2)	0.3149(2)	0.7250(2)	0.037(2)	0.051(2)	0.026(2)	–0.015(2)	–0.017(2)	0.011(2)
C(40)	4*e*	0.4332(2)	0.3380(2)	0.7669(2)	0.019(2)	0.047(2)	0.048(2)	–0.006(2)	–0.010(2)	0.022(2)
C(41)	4*e*	0.4627(2)	0.3693(2)	0.8260(2)	0.022(2)	0.035(2)	0.040(2)	0.004(1)	0.000(1)	0.015(1)
C(42)	4*e*	0.5672(2)	0.3763(2)	0.8442(1)	0.025(2)	0.023(2)	0.025(2)	–0.001(1)	–0.001(1)	0.008(1)
C(43)	4*e*	0.8462(2)	0.3562(2)	0.7564(1)	0.017(1)	0.025(2)	0.018(1)	–0.006(1)	–0.001(1)	–0.000(1)
C(44)	4*e*	0.8846(2)	0.2851(2)	0.7315(1)	0.025(2)	0.031(2)	0.022(1)	–0.006(1)	–0.000(1)	–0.001(1)
C(45)	4*e*	0.9356(2)	0.2860(2)	0.6745(1)	0.030(2)	0.044(2)	0.024(2)	–0.002(2)	0.003(1)	–0.009(1)
C(46)	4*e*	0.9481(2)	0.3580(2)	0.6423(1)	0.029(2)	0.062(2)	0.020(1)	–0.010(2)	0.007(1)	–0.000(2)
C(47)	4*e*	0.9088(2)	0.4288(2)	0.6657(1)	0.032(2)	0.045(2)	0.025(2)	–0.013(2)	0.002(1)	0.009(2)
C(48)	4*e*	0.8584(2)	0.4283(2)	0.7228(1)	0.029(2)	0.030(2)	0.026(2)	–0.005(1)	0.003(1)	0.002(1)
C(49)	4*e*	0.7954(2)	0.4609(2)	0.8572(1)	0.024(1)	0.017(1)	0.017(1)	–0.000(1)	0.005(1)	0.000(1)
C(50)	4*e*	0.8836(2)	0.4847(2)	0.8933(1)	0.025(2)	0.020(2)	0.026(1)	0.001(1)	0.003(1)	–0.003(1)
C(51)	4*e*	0.9060(2)	0.5658(2)	0.9047(1)	0.032(2)	0.025(2)	0.030(2)	–0.008(1)	0.003(1)	–0.010(1)
C(52)	4*e*	0.8393(3)	0.6244(2)	0.8803(1)	0.049(2)	0.020(2)	0.035(2)	–0.004(2)	0.011(2)	–0.004(1)
C(53)	4*e*	0.7508(3)	0.6025(2)	0.8443(2)	0.044(2)	0.021(2)	0.038(2)	0.009(2)	0.005(2)	0.006(1)
C(54)	4*e*	0.7287(2)	0.5214(2)	0.8329(1)	0.028(2)	0.025(2)	0.031(2)	0.000(1)	0.000(1)	0.004(1)

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