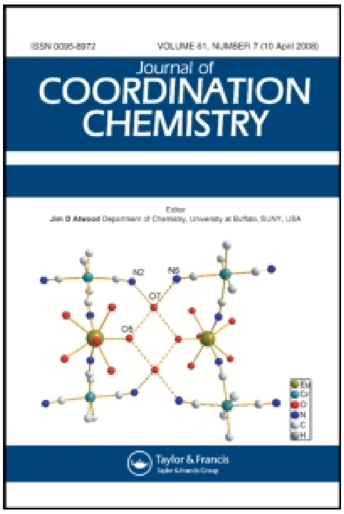

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Polam, Jayapal Reddy and Porter, Leigh Christopher(1993) 'LIGAND SUBSTITUTION REACTIONS IN PARAMAGNETIC RUTHENIUM(III) PHOSPHINE COMPLEXES. X-RAY CRYSTAL STRUCTURE OF [METHYLTRIPHENYLPHOSPHONIUM] [TETRACHLORO-BIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(III)]', Journal of Coordination Chemistry, 28: 3, 297 — 304

To link to this Article: DOI: 10.1080/00958979308037110

URL: http://dx.doi.org/10.1080/00958979308037110

J. Coord. Chem. 1993, Vol. 28, pp. 297–304
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LIGAND SUBSTITUTION REACTIONS IN PARAMAGNETIC RUTHENIUM(III) PHOSPHINE COMPLEXES. X-RAY CRYSTAL STRUCTURE OF [METHYLTRIPHENYLPHOSPHONIUM] [TETRACHLORO-BIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(III)]

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(Received 2 August 1992)

Reaction of the tetrachlorobis(triphenylphosphine)Ru(III) anion with either 1,2-bis(diphenylphosphino)ethane (diphos) or bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) in CH_2Cl_2 leads to the reduction of the Ru(III) centre with concomitant formation of dichlorobis(1,2-bis(diphenylphosphino)ethane)Ru(II) and dichloro(bis(2-diphenylphisphinoethyl)phenylphosphine)Ru(II), respectively. The products were characterized by ^{31}P NMR spectroscopy and the crystal structure of the anionic Ru(III) complex, $[MePPh_3][RuCl_4(PPh_3)_2]$, was determined and shown to possess *trans* octahedral geometry. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 10.744(3)$Å, $b = 20.875(5)$Å, $c = 21.637(6)$Å, and $V = 4832(2)$Å^3. Convergence to conventional R values of $R = 0.086$ and $R_w = 0.070$ was obtained for 186 variable parameters and 1466 reflections with $I > 2\sigma(I)$.

KEY WORDS: Ruthenium, paramagnetism, X-ray structure, NMR.

INTRODUCTION

Compared with their Ru(II) analogues, there exist relatively few reported examples of paramagnetic Ru(III) complexes containing tertiary phosphines. Neutral phosphine and arsine complexes of Ru(III) containing a coordinated solvent molecule can be obtained when $RuCl_3.3H_2O$ is reacted with a stoichiometric amount of ligand and refluxed in methanol for a short time.[1] On the basis of IR data, a *trans* configuration has been proposed for complexes of the type $[MX_4L_2]^-$, $X = Cl^-$ or Br^-; L = mono(tertiary) phosphine or arsine, and these systems are believed to be isomorphous with their Rh(III) analogues.[1] However, unlike Rh(III) systems, these Ru(III) complexes are paramagnetic with room temperature magnetic moments indicative of the presence of one unpaired electron.[1–3,6–8]

The reaction chemistry of several phosphine and arsine complexes of Ru(III) has also been explored.[1–5] In general, these reactions are characterized by either ligand displacement with retention of oxidation state, or substitution with concomitant

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reduction leading to the formation of octahedral Ru(II) complexes. Whether or not reduction of the transition metal occurs is highly dependent upon the nature of the solvent and the reaction conditions. Treatment of six-coordinate Ru(III) complexes containing a weakly coordinating solvent molecule with an excess of tertiary ammonium or arsonium halide in acetone, for example, leads to the formation of the corresponding anionic Ru(III) complex.[2-3] When the reaction is carried out in solvents such as methanol, however, reduction to Ru(II) occurs.[4,5] With chelating ligands more complicated forms of behaviour are frequently observed; products formulated as halogen-bridged dimers containing Ru(II) have been proposed, as well as monomeric complexes in which the oxidation state of the metal has been retained.[5]

Although the number of reported Ru(III) complexes containing tertiary phosphine or arsine ligands has continued to increase, detailed crystallographic data is lacking. In this paper we report the crystal structure of an anionic tetrachlorobis(triphenylphosphine)ruthenium(III) complex containing a methyltriphenylphisphonium counterion. In addition, we preset the results of investigations involving substitution of the triphenylphosphine ligands with the chelating phosphines 1,2-bis(diphenylphosphino)-ethane (diphos) and bis(2-diphenylphosphinoethyl)phenylphosphine (triphos).

EXPERIMENTAL

Materials and Methods

All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or argon. All solvents were freshly distilled prior to use, using appropriate drying agents. The ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ and references to an 85% solution of H_3PO_4 in D_2O.

Crystal Data

$C_{55}H_{48}Cl_4P_3Ru$, $m = 1044.7$, orthorhombic, space group $P2_12_12_1$, $a = 10.744(3)$, $b = 20.787(5)$, $c = 21.637(6)$Å, $V = 4832(2)$Å^3, $D_{(calc)} = 1.436$ Mg m^{-3}, $Z = 4$, $\mu = 0.675$ mm^{-1}, λ(MoKα) = 0.71073Å, $F(000) = 2140$, $T = 298$, K, $R = 0.086$ and $R_w = 0.070$ for 186 variable parameters and 1466 reflections with $I > 2\sigma(I)$.

Crystal Structure Solution and Refinement

A small, regularly shaped crystal displaying a prismatic habit with approximate dimensions 0.01 × 0.01 × 0.04 mm was mounted on the end of a glass fibre in a random orientation. Orthorhombic symmetry was suggested on the basis of the interaxial angles and confirmed by axial rotation photographs which all displayed *m* symmetry. Refined cell parameters were determmined from the setting angles of 25 reflections with $15° < 2\theta < 30°$. Data collection was carried out at ambient temperature using the ω-scanning technique in bisecting geometry on a Nicolet R3m/V diffractometer equipped with graphite-monochromated MoKα radiation. Scan rate was variable, 3–15° min^{-1}; scan range, 1.5° in ω. Three standards measured for every 100 data showed no significant variation over the period of data collection. A total of 4146 reflections ($+h, +k, +l$ $h_{max} = 11$, $k_{max} = 22$, $l_{max} = 23$) with $3.5° < 2\theta < 45°$ were obtained and corrected for Lorentz and polarization effects. This led to 3539 unique reflections

($R_{int}=0.27\%$). Owing to the small size of the crystal and its low linear absorption coefficient, no correction for absorption was included. Structure solution was carried out using the *shelxtl-pc* collection of crystallographic software.[9] Intensity statistics favoured a non-centrosymmetric cell which was assigned to the $P2_12_12_1$ space on the basis of the systematically absent reflections (h,0,0; $h=2n+1$; 0,k,0: $k=2n+1$; 0,0,l: $l=2n+1$). The location of the Ru atom was determined from a sharpened Patterson map and used as an initial phasing model. All remaining non-hydrogen atoms were located on difference Fourier maps and refined using scattering factors that included terms for anomalous dispersion.[10] Phenyl rings were refined as rigid idealized polygons (C-C = 1.395Å) with hydrogen atoms included in idealized positions with fixed isotropic $U=0.08\text{Å}^2$. Refinement was based on F using weights of the form $w^{-1}=[\sigma^2(F)+0.0002(F^2)]$. A test to establish the correct enantiomorph was carried out by comparing the R values associated with two structure factor calculations, one of which involved using coordinates that were inverted. The correct assignment was made by comparing the resulting R values ($R=0.087$ and $R_w=0.070$ versus $R=0.086$ and $R_w=0.070$). For the final cycle, maximum shift/$\sigma=0.000$ with minimum and maximum residual electron densities of $+0.69\ \text{eÅ}^{-3}$ and $-0.75\ \text{eÅ}^{-3}$. Pertinent bond distances and angles are given in Table 1. Lists of structure factors and anisotropic thermal parameters are available from LCP.

Preparation of Tetrachlorobis(Triphenylphosphine)Ru(III) Anion

To a six-fold excess of triphenylphosphine (1.2 g) in methanol was added 0.20 g of $RuCl_3.3H_2O$. The solution was refluxed for 2 hours, after which reddish brown crystals of dichlorotris(triphenylphosphine)Ru(II) separated from the green filtrate. The filtrate was then allowed to evaporate in an open breaker overnight. During this period it developed a reddish-brown colour and deposited numerous, well-formed, orange crystals. The crystals were isolated by filtration then recrystallized from a dichloromethane-acetone solution. ^{31}P NMR: 27.57 ppm (broad), 24.19 ppm (methyltriphenylphosphonium cation).

Reaction with 1,2-bis(Diphenylphosphino)Ethane (Diphos)

To 10 cm^3 of CH_2Cl_2 was added 30 mg of the tetrachlorobis(triphenylphosphine)Ru(III) anion and 20 mg of diphos. The reaction mixture was refluxed for six hours whereupon the solution colour changed from orange to yellow. The solvent was subsequently removed under reduced pressure and extracted with diethyl ether to remove any excess free phosphine. The resulting yellow solid was then redissolved in $CDCl_3$ and transferred to an NMR tube. ^{31}P NMR: 39.85 ppm.

Reaction with bis(2-Diphenylphosphinoethyl)Phenylphosphine (Triphos)

The same procedure as above was used in the preparation of the corresponding triphos derivative. However, owing the small quantity of product obtained, no special attempts were made to purify the product. Some 30 mg of the Ru(III) complex was reacted with 20 mg of triphos and refluxed in CH_2Cl_2 for approximately six hours. The solvent was removed under reduced pressure and the yellow-green product redissolved in $CDCl_3$ and transferred to an NMR tube. ^{31}P NMR: 45.26 (unresolved triplet), 39.09 ppm, 38.80 ppm (doublet).

RESULTS AND DISCUSSION

Description of the Structure

Our crystal structure determination confirms the stereochemistry proposed on the basis of IR data and is similar to the recently reported structure of another *trans* octahedral d^5 complex, tetrachlorobis(triethylphosphine)Os(III).[13] The Ru centre possesses a *trans* octahedral coordination geometry with the triphenylphosphine groups occupying axial sites at distances of 2.428(11) and 2.416(9)Å for Ru(1)-P(1) and Ru(1)-P(2), respectively. These bonds are longer, on average, by 0.054Å as compared with bonds to the equatorial Cl ligands. There is no crystallographically imposed symmetry in this structure and slight deviations from ideal octahedral geometry are evident in the coordination sphere of the Ru atom. Bonds in the Cl ligands range from 2.345(10) to 2.377(9)Å in length and interaxial bond angles vary from 84.7(3) to 95.5(4)°.

The triphenylphosphine ligands in this structure display no particularly unusual features; the P atoms possess tetrahedral geometries and form bonds to phenyl groups ranging from 1.80(2)Å to 1.86(3)Å. These values do not differ greatly from those typically observed in other transition metal complexes containing these ligands.

The methyltriphenylphosphonium counterion in this structure was obtained as a by-product during the synthesis of the Ru(III) complex in methanol. Structural features associated with this molecule are unexceptional and will not be discussed further, except to note that bonds to the phenyl groups are, on the average, slightly longer than the bond to C(1) of the methyl group (P(3)-C(1) = 1.766(34)Å).

Reaction of the Ru(III) Complex with Diphos and Triphos

The ^{31}P NMR spectrum of the cationic Ru(III) starting material displays two signals, both of which are singlets. The signal at 27.57 ppm is broad, owing to the proximity of the phosphorus atom to the paramagnetic Ru(III) centre. The other peak which is observed upfield at 24.19 ppm is sharp and corresponds to the phosphorous atom in the methyltriphenylphosphonium cation.

Upon reaction of the Ru(III) complex with chelating phosphine in CH_2Cl_2, complete substitution of the triphenylphosphine groups occurs with concomitant displacement of two of the four chloride ligands. At the same time, the Ru(III) centre becomes reduced to Ru(II). The ^{31}P spectra for the resulting Ru(II) complexes are sharp and the single resonance associated with the P atoms coordinated to the transition metal centre in the diphos complex is observed to be shifted downfield with respect to free diphos at 39.85 ppm. In this complex, the ^{31}P spectrum is identical to that of the product obtained using the reported literature procedure involving dichlorotris(triphenylphosphine)Ru(II) as starting material.[13,14] A crystal structure determination of the diphos complex confirms the proposed stoichiometry of this product. The structure possesses a *trans* stereochemistry with two chelating diphos ligands at equatorial sites and axial chloride ligands.[15]

For the reaction involving the triphos ligand, two distinct resonances are observed in the ^{31}P spectrum of the product. Both are observed to be shifted downfield with respect to free triphos indicating that coordination to the transition metal centre has occurred. The resonance centred at 45.26 ppm is observed as an incompletely resolved triplet and corresponds to the central P atom, whereas the doublet at 39.09 and

38.80 ppm arises from the two terminal P atoms. Since no attempts were made to purify the sample, a peak at 10.02 ppm was present due to free triphenylphosphine, as was another at 20.09 ppm which may indicate the presence of methyltriphenylphosphonium cation that was present initially in the reaction mixture. These same chemical shift values are also observed in the ^{31}P NMR spectrum of the Ru(II)-triphos product, formulated as Ru(Cl)$_2$(triphos), prepared using dichlorobis(triphenylphosphine)Ru(II).[14] This suggests that in both cases the products obtained are the same, although, interestingly, the spectrum of the Ru(II)-triphos product obtained using the reported literature procedure is considerably more complicated. Such behaviour may be indicative of the presence of two or more products, possibly isomers. Indeed, both *mer* and *fac* isomers have been observed in the preparation of Fe(II)-triphos complexes containing acetonitrile ligands.[16] Since it was not possible to obtain crystals of the Ru(II) triphos complex suitable for an X-ray crystal structure determination, information concerning possible stereochemistries of the Ru(II)-triphos complex is lacking and the structure of this complex remains uncertain.

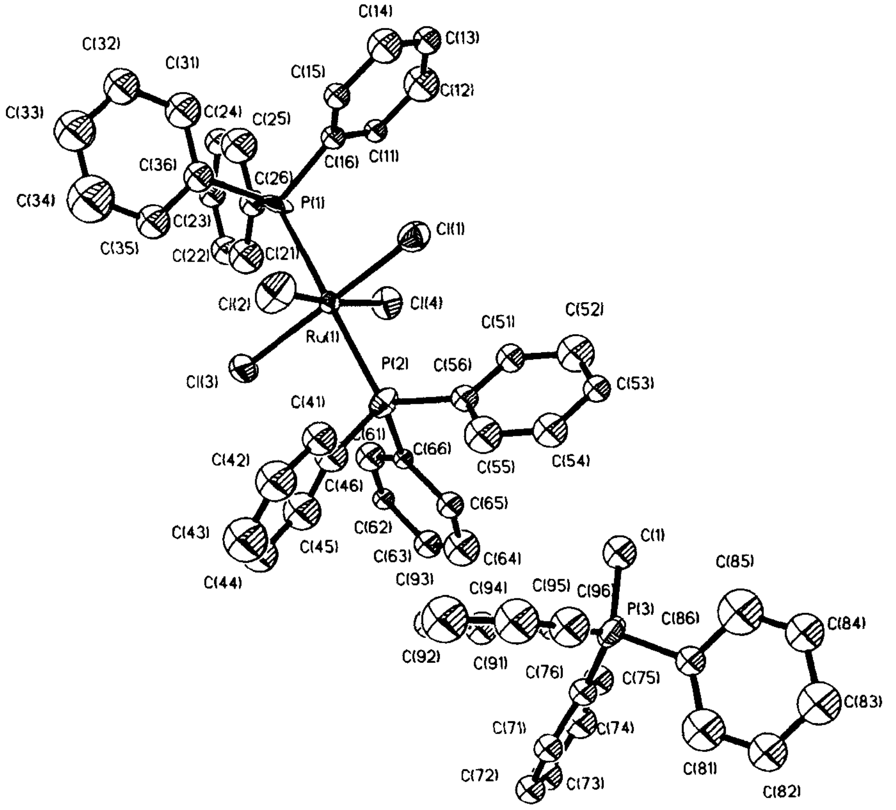

Figure 1 A perspective view of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x/a	*y/b*	*z/c*	*U*(eq)*
Ru(1)	8830(3)	9714(2)	916(1)	21(1)
Cl(1)	9262(9)	9506(4)	−143(4)	42(4)
Cl(2)	11000(8)	9753(5)	1024(5)	57(4)
Cl(3)	8571(10)	9901(4)	1992(4)	48(4)
Cl(4)	6670(7)	9679(5)	686(4)	43(3)
P(1)	8776(12)	10855(5)	679(4)	37(4)
P(2)	8848(10)	8576(4)	1144(4)	32(4)
P(3)	8052(9)	5444(4)	1014(5)	39(4)
C(1)	7343(30)	6019(15)	528(15)	47(11)
C(11)	7429(15)	10963(10)	−413(9)	24(9)
C(12)	7321	10998	−1054	58(13)
C(13)	8385	11054	−1420	34(10)
C(14)	9557	11075	−1144	51(12)
C(15)	9666	11040	−502	28(10)
C(16)	8601	10984	−137	25(9)
C(21)	6687(23)	11133(9)	1457(12)	58(14)
C(22)	5755	11541	1677	42(12)
C(23)	5596	12149	1415	36(11)
C(24)	6370	12349	935	37(9)
C(25)	7302	11941	715	62(14)
C(26)	7460	11333	976	31(10)
C(31)	10374(23)	11918(12)	634(10)	56(13)
C(32)	11317	12326	842	54(11)
C(33)	11975	12176	1378	71(15)
C(34)	11690	11618	1708	92(18)
C(35)	10747	11211	1500	50(13)
C(36)	10089	11360	963	39(10)
C(41)	11288(24)	8353(9(	1561(8)	44(10)
C(42)	12189	8197	2000	62(13)
C(43)	11835	8046	2603	75(15)
C(44)	10579	8052	2767	52(12)
C(45)	9678	8207	2328	59(13)
C(46)	10032	8358	1725	44(11)
C(51)	8346(18)	8081(9)	−7(11)	34(10)
C(52)	8426	7653	−502	58(13)
C(53)	9264	7141	−480	29(10)
C(54)	10020	7056	38	46(11)
C(55)	9940	7484	535	55(12)
C(56)	9103	7996	511	30(10)
C(61)	6608(19)	8612(7)	1831(10)	40(11)
C(62)	5590	8334	2128	22(9)
C(63)	5406	7670	2099	36(10)
C(64)	6240	7285	1722	59(12)
C(65)	7259	7563	1474	31(10)
C(66)	7443	8227	1504	18(8)
C(71)	7619(15)	5064(11)	2247(10)	34(10)
C(72)	6842	4938	2749	37(12)
C(73)	5560	5029	2695	43(12)
C(74)	5055	5247	2139	51(10)
C(75)	5832	5374	1637	40(10)
C(76)	7114	5282	1691	32(9)
C(81)	8451(21)	4131(14)	935(8)	71(14)
C(82)	8723	3569	610	58(11)
C(83)	8811	3583	−34	71(12)
C(84)	8626	4159	−315	56(12)

Table 1 *Continued*

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)*
C(85)	8353	4721	−26	82(14)
C(86)	8266	4707	617	35(9)
C(91)	9525(16)	6184(10)	1759(9)	42(11)
C(92)	10657	6436	1961	33(10)
C(93)	11769	6229	1694	78(16)
C(94)	11748	5769	1225	71(15)
C(95)	10617	5516	1022	58(13)
C(96)	9505	5724	1289	12(9)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2 Geometrical data for the complex

Bond lengths (Å)

Ru(1)-Cl(1)	2.377(9)	Ru(1)-Cl(2)	2.345(10)
Ru(1)-Cl(3)	2.377(9)	Ru(1)-Cl(4)	2.374(8)
Ru(1)-P(1)	2.428(11)	Ru(1)-P(2)	2.416(9)
P(1)-C(16)	1.796(21)	P(1)-C(26)	1.844(26)
P(1)-C(36)	1.863(27)	P(2)-C(46)	1.845(24)
P(2)-C(56)	1.845(24)	P(2)-C(66)	1.848(22)
P(3)-C(1)	1.766(34)	P(3)-C(76)	1.809(22)
P(3)-C(86)	1.771(27)	P(3)-C(96)	1.769(20)

Bond angles (°)

Cl(1)-Ru(1)-Cl(2)	84.7(3)	Cl(1)-Ru(1)-Cl(3)	175.3(4)
Cl(2)-Ru(1)-Cl(3)	90.7(4)	Cl(1)-Ru(1)-Cl(4)	89.1(3)
Cl(2)-Ru(1)-Cl(4)	173.6(4)	Cl(3)-Ru(1)-Cl(4)	95.5(4)
Cl(1)-Ru(1)-P(1)	88.8(3)	Cl(2)-Ru(1)-P(1)	90.6(4)
Cl(3)-Ru(1)-P(1)	92.5(3)	Cl(4)-Ru(1)-P(1)	87.9(4)
Cl(1)-Ru(1)-P(2)	91.0(3)	Cl(2)-Ru(1)-P(2)	90.3(4)
Cl(3)-Ru(1)-P(2)	87.8(3)	Cl(4)-Ru(1)-P(2)	91.2(4)
P(1)-Ru(1)-P(2)	179.0(4)	Ru(1)-P(1)-C(16)	110.8(8)
Ru(1)-P(1)-C(26)	118.1(8)	C(16)-P(1)- C(26)	100.5(11)
Ru(1)-P(1)-C(36)	117.6(9)	C(16)-P(1)-C(36)	108.6(10)
C(26)-P(1)-C(36)	99.3(11)	Ru(1)-P(2)-C(46)	112.7(8)
Ru(1)-P(2)-C(56)	119.3(8)	C(46)-P(2)-C(56)	104.0(10)
Ru(1)-P(2)-C(66)	117.7(7)	C(46)-P(2)-C(66)	100.3(10)
C(56)-P(2)-C(66)	100.2(9)	C(1)-P(3)-C(76)	111.6(13)
C(1)-P(3)-C(86)	110.6(13)	C(76)-P(3)-C(86)	107.8(11)
C(1)-P(3)-C(96)	111.0(13)	C(76)-P(3)-C(96)	106.3(10)
C(86)-P(3)-C(96)	109.5(11)	P(1)-C(16)-C(11)	120.7(7)
P(1)-C(16)-C(15)	118.9(7)	P(1)-C(26)-C(21)	123.8(7)
P(1)-C(26)-C(25)	116.1(7)	P(1)-C(36)-C(31)	117.8(8)
P(1)-C(36)-C(35)	122.2(8)	P(2)-C(46)-C(41)	119.7(8)
P(2)-C(46)-C(45)	120.3(8)	P(2)-C(56)-C(51)	115.3(7)
P(2)-C(56)-C(55)	124.7(7)	P(2)-C(66)-C(61)	120.9(6)
P(2)-C(66)-C(65)	119.0(6)	P(3)-C(76)-C(71)	122.8(6)
P(3)-C(76)-C(75)	117.2(6)	P(3)-C(86)-C(81)	121.4(7)
P(3)-C(86)-C(85)	118.4(7)	P(3)-C(96)-C(91)	119.0(7)
P(3)-C(96)-C(95)	120.9(7)		

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society and the Welch Foundation. We wish also to acknowledge support for this research with grants provided by the Exxon Educational Foundation, the University Research Institute, the Chancellors Research Council, and IM^3. We wish to especially thank the Engelhard Corporation for their gift of ruthenium trichloride, and F. Cervantes-Lee for collecting the intensity data.

Supplementary Data

Lists of structure factors, anisotropic thermal parameters, and hydrogen atom positions are available from the authors upon request.

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