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trans-Dichlorobis[(*R,R*)-1,2-phenylenebis(methylphenylphosphine-*P*)]ruthenium(II)

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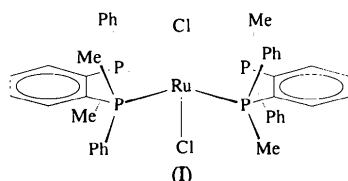
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Abstract

The title complex, $[\text{RuCl}_2(\text{C}_{20}\text{H}_{20}\text{P}_2)_2]$, is a convenient precursor for the synthesis of interesting symmetrical or unsymmetrical optically active ruthenium σ -acetylide complexes. The complex has *trans* geometry about the octahedral Ru atom, with Ru—P distances in the range 2.304 (1)–2.354 (1) Å and Ru—Cl distances of 2.426 (1) and 2.432 (1) Å.

Comment

We have been investigating the nonlinear optical properties of metal σ -acetylide complexes (Whittall, Humphrey, Hockless, Skelton & White, 1995; Whittall, Humphrey, Samoc, Swiatkiewicz & Luther-Davies, 1995). For these materials to exhibit second-order non-linearity in the bulk phase, a favourable molecular dipole alignment is required. The incorporation of a chiral ligand into a metal complex is one method of ensuring non-centrosymmetric packing for optimal molecular orientation in a crystal lattice. We have therefore commenced an investigation of complexes containing the optically active (*S,S*)-1,2-phenylenebis(methylphenylphosphine) (diphos) ligand. The title complex, *trans*-dichlorobis[(*R,R*)-1,2-phenylenebis(methylphenylphosphine)]ruthenium(II), (I), is a convenient precursor of ruthenium σ -acetylide complexes (McDonagh, 1995). The crystal and molecular structure of the complex has been determined for the following reasons: (i) the reactivity of terminal acetylenes with the *trans*-dichloro complex is significantly slower than with the corresponding *cis* compound, and (ii) accurate atomic positions are required for semi-empirical computational investigations.



The title complex is the second bis(diphos)-ruthenium(II) crystal structure to be determined, the other being that of the *trans*-carbonylhydridobis[(*S,S*)-1,2-phenylenebis(methylphenylphosphine)]ruthenium(II) cation, (II) (Grocott, Skelton & White, 1983). Both complexes have *trans* geometry about octahedral Ru atoms, but complex (I), unlike (II), does not contain a twofold rotation axis. Comparison of complex (I) with the three existing ruthenium mono or bis(diphos) structures, *i.e.* (II) (Grocott, Skelton & White, 1983), *trans*-dichloro[(*S,S*)-1,2-phenylenebis(methylphenylphosphine)]-[(*S,S*)-1,2-phenylenebis(methylphenylphosphine) oxide]-ruthenium(II), (III) (Hall, Skelton & White, 1983*a*), and *cis*-dichlorocarbonyl(dimethyl sulfoxide)[(*S,S*)-1,2-phenylenebis(methylphenylphosphine)]ruthenium(II), (IV) (Hall, Skelton & White, 1983*b*), shows very similar ruthenium–phosphorus geometries about the metal centre and comparable ruthenium–chlorine bond lengths.

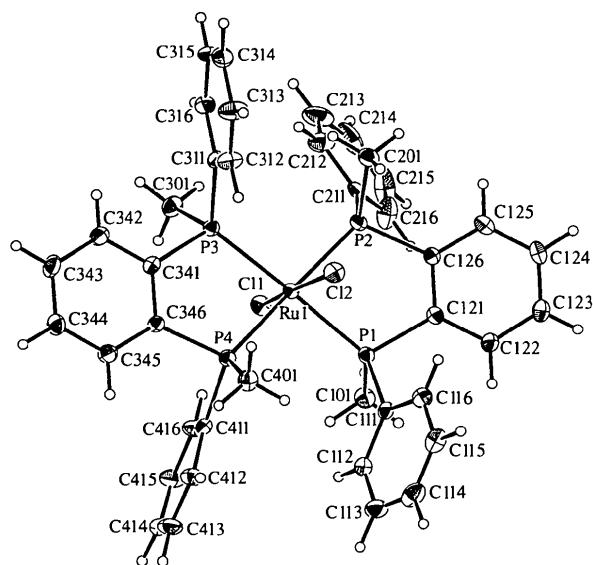


Fig. 1. The molecular structure of the title complex showing the labelling scheme for the non-H atoms. Displacement ellipsoids are shown at the 20% probability level and H atoms are drawn as circles of arbitrary radii.

Experimental

The title complex can be prepared by the method of Grocott & Wild (1982), which involves the reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ by dihydrogen followed by the addition of two equivalents of diphos. It can also be prepared, together with the *cis* isomer, by adaptation of the preparation of $[\text{RuCl}_2(\text{dppm})_2]$ [dppm is bis(diphenylphosphino)methane] from $[\text{RuCl}_2(\text{dmsO})_4]$ (dmsO is dimethyl sulfoxide) (McDonagh, 1995). Suitable crystals were grown by diffusion of hexane into a dichloromethane solution of the complex at room temperature.

Crystal data

$[\text{RuCl}_2(\text{C}_{20}\text{H}_{20}\text{P}_2)_2]$
 $M_r = 816.63$

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$

Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	$\theta = 13.3\text{--}17.6^\circ$
$a = 11.641(6) \text{ \AA}$	$\mu = 0.745 \text{ mm}^{-1}$
$b = 12.245(8) \text{ \AA}$	$T = 296(1) \text{ K}$
$c = 26.446(5) \text{ \AA}$	Irregular
$V = 3769(2) \text{ \AA}^3$	$0.42 \times 0.40 \times 0.36 \text{ mm}$
$Z = 4$	Yellow
$D_x = 1.439 \text{ Mg m}^{-3}$	
D_m not measured	
Data collection	
Rigaku AFC-6S diffractometer	3310 observed reflections
$\omega/2\theta$ scans	$[I > 3\sigma(I)]$
Absorption correction: based on azimuthal (ψ) scan data (North, Phillips & Mathews, 1968)	$\theta_{\text{max}} = 25.08^\circ$
$T_{\text{min}} = 0.937$, $T_{\text{max}} = 1.000$	$h = 0 \rightarrow 13$
3784 measured reflections	$k = 0 \rightarrow 14$
3784 independent reflections	$l = 0 \rightarrow 31$
	3 standard reflections monitored every 150 reflections
	intensity decay: none
Refinement	
Refinement on F	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
$R = 0.0251$	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
$wR = 0.0190$	Extinction correction: Zachariasen (1967)
$S = 1.874$	Extinction coefficient: $5.64(6) \times 10^{-7}$
3310 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
425 parameters	
H-atom parameters not refined	
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.001F_o^2)^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.0028$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ru(1)	-0.16429(3)	-0.15190(3)	-0.14145(1)	0.02977(9)
Cl(1)	-0.3193(1)	-0.1371(1)	-0.08051(4)	0.0460(4)
Cl(2)	-0.0161(1)	-0.1403(1)	-0.20608(4)	0.0479(4)
P(1)	-0.2949(1)	-0.1132(1)	-0.20444(5)	0.0344(4)
P(2)	-0.1380(1)	0.03596(10)	-0.13933(5)	0.0370(4)
P(3)	-0.0409(1)	-0.1947(1)	-0.07457(5)	0.0348(4)
P(4)	-0.1695(1)	-0.3424(1)	-0.15305(4)	0.0348(3)
C(101)	-0.4466(4)	-0.1161(4)	-0.1878(2)	0.050(2)
C(111)	-0.2935(4)	-0.1877(4)	-0.2648(2)	0.037(1)
C(112)	-0.3647(5)	-0.2770(4)	-0.2720(2)	0.052(2)
C(113)	-0.3625(5)	-0.3355(5)	-0.3172(2)	0.069(2)
C(114)	-0.2920(5)	-0.3031(5)	-0.3551(2)	0.070(2)
C(115)	-0.2222(5)	-0.2167(4)	-0.3487(2)	0.056(2)
C(116)	-0.2210(4)	-0.1586(4)	-0.3043(2)	0.047(2)
C(121)	-0.2759(4)	0.0284(4)	-0.2245(2)	0.037(1)
C(122)	-0.3306(5)	0.0701(4)	-0.2672(2)	0.047(2)
C(123)	-0.3110(5)	0.1773(4)	-0.2819(2)	0.051(2)
C(124)	-0.2378(5)	0.2412(4)	-0.2553(2)	0.050(2)
C(125)	-0.1857(5)	0.2016(4)	-0.2122(2)	0.048(2)
C(126)	-0.2034(4)	0.0943(4)	-0.1964(2)	0.034(1)
C(201)	0.0075(4)	0.0894(4)	-0.1411(2)	0.054(2)
C(211)	-0.2016(5)	0.1199(4)	-0.0892(2)	0.044(2)
C(212)	-0.1440(5)	0.1339(5)	-0.0443(2)	0.071(2)
C(213)	-0.1881(7)	0.1966(6)	-0.0051(3)	0.098(3)

C(214)	-0.2911(8)	0.2464(6)	-0.0113(3)	0.102(3)
C(215)	-0.3528(8)	0.2323(5)	-0.0549(2)	0.107(3)
C(216)	-0.3074(6)	0.1682(5)	-0.0934(2)	0.079(2)
C(301)	-0.0972(4)	-0.1754(4)	-0.0107(2)	0.053(2)
C(311)	0.1050(4)	-0.1417(4)	-0.0700(2)	0.037(1)
C(312)	0.1824(4)	-0.1647(5)	-0.1072(2)	0.058(2)
C(313)	0.2938(5)	-0.1277(5)	-0.1049(2)	0.072(2)
C(314)	0.3311(5)	-0.0666(5)	-0.0656(2)	0.062(2)
C(315)	0.2556(5)	-0.0406(4)	-0.0275(2)	0.058(2)
C(316)	0.1439(4)	-0.0784(4)	-0.0300(2)	0.050(2)
C(341)	-0.0159(4)	-0.3414(4)	-0.0733(2)	0.038(1)
C(342)	0.0604(4)	-0.3890(4)	-0.0388(2)	0.049(2)
C(343)	0.0683(5)	-0.5006(4)	-0.0340(2)	0.057(2)
C(344)	0.0015(5)	-0.5664(4)	-0.0641(2)	0.055(2)
C(345)	-0.0724(5)	-0.5225(4)	-0.0995(2)	0.048(2)
C(346)	-0.0809(4)	-0.4088(4)	-0.1045(2)	0.035(1)
C(401)	-0.0986(4)	-0.3922(4)	-0.2101(2)	0.051(2)
C(411)	-0.3016(4)	-0.4248(4)	-0.1492(2)	0.038(1)
C(412)	-0.3177(5)	-0.5178(4)	-0.1781(2)	0.056(2)
C(413)	-0.4131(5)	-0.5835(4)	-0.1719(2)	0.065(2)
C(414)	-0.4941(5)	-0.5574(5)	-0.1370(2)	0.062(2)
C(415)	-0.4826(5)	-0.4631(5)	-0.1094(2)	0.068(2)
C(416)	-0.3861(5)	-0.3985(4)	-0.1153(2)	0.054(2)

Table 2. Comparison of important bond lengths (\AA) and angles ($^\circ$) with those of existing analogues

Complex (I) ^a	Ru—P	Ru—Cl	P—Ru—P
	2.304(1)	2.426(1)	84.29(5)
	2.321(1)	2.432(1)	83.82(4)
	2.338(1)		
	2.354(1)		
(II) ^b	2.320(2)		84.92(8)
	2.317(2)		
(III) ^c	2.310(3)	2.425(2)	83.09(9)
	2.219(2)	2.434(2)	
(IV) ^d	2.313(2)	2.469(2)	84.92(4)
	2.292(1)	2.446(2)	

References: (a) this work; (b) Grocott, Skelton & White (1983); (c) Hall, Skelton & White (1983a); (d) Hall, Skelton & White (1983b).

The θ scan width used was $(1.00 + 0.3\text{tan}\theta)^\circ$ at a speed of $4.0^\circ \text{ min}^{-1}$ (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection, with a 2:1 ratio of peak to background counting time. H atoms were located from a difference map and fixed at ideal positions with C—H = 0.95 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The structure was solved by heavy-atom methods and expanded using Fourier techniques (*PATY* in *DIRDIF*; Beurskens *et al.*, 1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1995). Data collection and cell refinement used *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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***trans*-Dichloro(2-*n*-propylsulfinylpyridine-*N*)(triethylphosphine-*P*)palladium(II)**

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Abstract

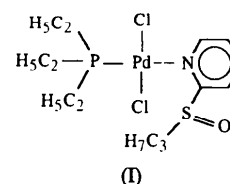
The structure determination of the title compound, [PdCl₂(C₆H₁₅P)(C₈H₁₁NOS)], revealed the occurrence of discrete molecules, in which the Pd atom has square-planar coordination geometry, with distances Pd—P 2.232 (1), Pd—N 2.128 (3) and Pd—Cl 2.293 (2) and 2.294 (2) Å. The sulfoxide derivative acts as a monodentate ligand.

Comment

Investigations of the coordination chemistry of some transition and post-transition metals, namely Ni, Pd, Pt, Sn and Sb, with ambidentate S-, N- and O-donor ligands have revealed a variety of structural features,

with sulfoxide behaving as a mono- or bidentate ligand, or bridging two metal cations (Zhu, Shao, Yao, Wang & Wang, 1990; de Sousa & Filgueiras, 1990*a,b*; de Sousa, Filgueiras, Darensbourg & Reibenspies, 1992; Adedapo *et al.*, 1993; Francisco, Gambardella, Rodrigues, de Sousa & Filgueiras, 1995).

In the title compound, (I), the N-bonded 2-*n*-propylsulfinylpyridine group is monodentate. The coordination around the metal atom is completed by a P atom and two chloride anions, the four atoms arranged with *trans* square-planar geometry. Distances between each of these five atoms and their least-squares plane are in the range –0.0289 (3) to 0.032 (4) Å. The pyridine ring is almost perpendicular [dihedral angle 81.9 (1)°] to the plane containing the metal and its ligands. The displacement parameters are larger for the C atoms of the alkyl groups than for those of the ring. A view of one molecule is shown in Fig. 1.



The proton-decoupled ³¹P NMR spectrum showed a chemical shift at 39.86 p.p.m. (relative to H₃PO₄) which agrees with a *trans*-Cl—Pd—Cl arrangement (Kunz & Pregosin, 1979). The IR spectra (CsI pellets) showed SO absorptions at 1055 and 1050 cm⁻¹, which were attributed to the stretching frequencies of the free ligand and the complex, respectively, suggesting little or no change of frequency upon complexation.

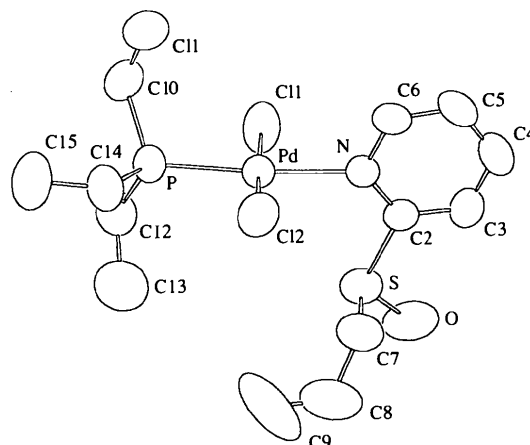


Fig. 1. ORTEP (Johnson, 1965) view of (I) showing the labelling of the non-H atoms and ellipsoids plotted at the 50% probability level.

Experimental

Orange single crystals of (I) were grown by slow evaporation of a warm 1:1 mixture of *n*-hexane and dichloromethane containing [PdCl(μ-Cl){P(C₂H₅)₃}]₂ (0.20 g, 0.34 mmol) and (NC₅H₅)SOC₃H₇ (0.115 g, 0.68 mmol).