Structure of Tris(4-diphenylphosphinoyl-3-methyl-1-phenylpyrazol-5-onato-*O,O'*)-iron(III)

BY DOMINIQUE MATT AND DOMINIQUE LAKKIS

Laboratoire de Chimie Minérale et Analytique, URA 405 CNRS, EHICS, 1 rue Blaise Pascal, BP 296, F-67008 Strasbourg CEDEX, France

DANIEL GRANDJEAN

Laboratoire de Cristallochimie, UA 254 CNRS, Université de Rennes I, Avenue du Général Leclerc, F-35042 Rennes CEDEX, France

AND FADILA BALEGROUNE AND ACHOURA LAIDOUDI

Laboratoire de Cristallographie Appliquée, Université des Sciences et de la Technologie, Houari Boumediene, BP No. 9, Alger, Algeria

Abstract. [Fe($C_{22}H_{18}N_2O_2P$)$_3$], $M_r = 1175.97$, triclinic, $P\bar{1}$, $a = 9.802$ (2), $b = 13.288$ (2), $c = 22.686$ (3) Å, $\alpha = 88.69$ (1), $\beta = 89.29$ (2), $\gamma = 82.40$ (2)°, $V = 2928.2$ Å^3, $Z = 2$, $D_x = 1.334$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.924$ cm^{-1}, $F(000) = 1222$, room temperature, final $R = 0.053$ for 3276 observed reflections with $I \geq 3\sigma(I)$. The octahedral Fe centre is surrounded by three unsymmetrical *O,O*-chelating ligands, the chemically equivalent O atoms being coordinated facially. Each of the six-membered chelate rings can be regarded as having a pseudo-envelope conformation, the Fe atom lying *ca* 0.68 Å above the least-squares plane constituted by the other five atoms.

Introduction. A number of ligands derived from pyrazolones, especially deprotonated 4-acylpyrazolones (1), have been successfully used as selective extractants for metals [see for example, Gauthier, Lecolier, Soriaux & Chevalier (1984) and Lakkis, Lakkis, Goetz-Grandmont & Brunette (1991) and references therein]. The availability of two dissimilar O-atom binding sites allows ligands like (1) to form chelate complexes from which the metal ions may easily be recovered. The related anion (2), which combines a pyrazolone moiety with a phosphinoyl fragment in the position β to the carbonyl group of the pyrazolone, has not previously been reported. Obviously, (2) could act as a chelating ligand and might be expected to display interesting properties in view of the extraction enhancement usually observed when phosphine oxides or phosphate esters are present in extraction phases. In this paper we present the structure of a paramagnetic iron(III) tris(chelate)

complex containing a ligand of type (2), namely the 4-diphenylphosphinoylpyrazolonate anion (3).
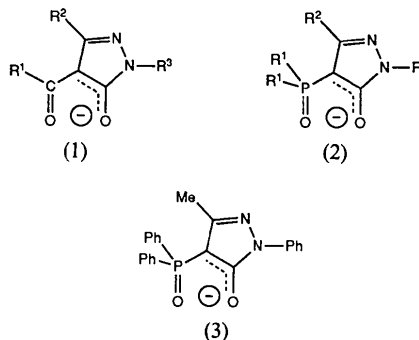
Experimental. The title compound was prepared by adding a solution of the conjugate acid of (3) in dichloromethane to an aqueous (pH 2) solution of Fe(NO$_3$)$_3$ and stirring vigorously. The Fe:pyrazolone ratio used was 10:1. After 0.5 h the two phases were separated and the red–brown dichloromethane solution evaporated under vacuum. The product was recrystallized from tetrahydrofuran (THF)–pentane. Black crystals suitable for X-ray analysis were obtained by slow diffusion at 258 K of pentane into a THF solution of the complex. IR(KBr): 1528 cm^{-1} $s(\nu_{C-O} + \nu_{C=C})$; 1122 cm^{-1} $s(\nu_{P=O}$, tentative assignment). An air-stable parallelepiped-shaped crystal (0.30 × 0.15 × 0.18 mm) was used for data collection at room temperature on an Enraf–Nonius CAD-4 four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters were calculated from the setting angles of 25

carefully centred reflections with $9 \le 2\theta \le 30°$. Data collection was by ω–2θ scan mode with scan width of $(1 + 0.35\tan\theta)°$, variable scan rate with maximum scan time 60 s per reflection, $2\theta_{max} = 50°$, collection range h 0→11, k – 15→15, l – 27→27. 10204 unique reflections were measured of which 3276 were considered as observed with $I \ge 3\sigma(I)$. The poor diffraction power of the crystals explains the low ratio of observed to measured intensities. Three orientation and three intensity control reflections checked every 400 reflections and every hour, respectively, showed no significant variation. Intensities were corrected for Lorentz–polarization effects but not for absorption. The crystal structure was solved by direct methods using *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses, and was refined by full-matrix least squares with anisotropic thermal parameters for all non-H atoms except for the C atoms of the phenyl groups which were refined isotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2[\sigma^2(F_o^2) + (0.05F_o^2)^2]^{-1}$. H atoms were included in structure factor calculations; their coordinates were chosen to give acceptable stereochemistry (C—H = 0.95 Å) and they were assigned isotropic thermal parameters of $B = 5.0$ Å^2. Atomic scattering factors and anomalous-dispersion corrections for all non-H atoms were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). For 469 parameters refined, final $R = 0.053$, $wR = 0.063$, $\Delta\rho_{max} = 0.41$, $\Delta\rho_{min} = -0.29$ e Å^{-3} in the final difference synthesis, $S = 1.539$, $(\Delta/\sigma) < 0.1$. For all computations the Enraf–Nonius *SDP* package was used (B. A. Frenz & Associates, Inc., 1985).
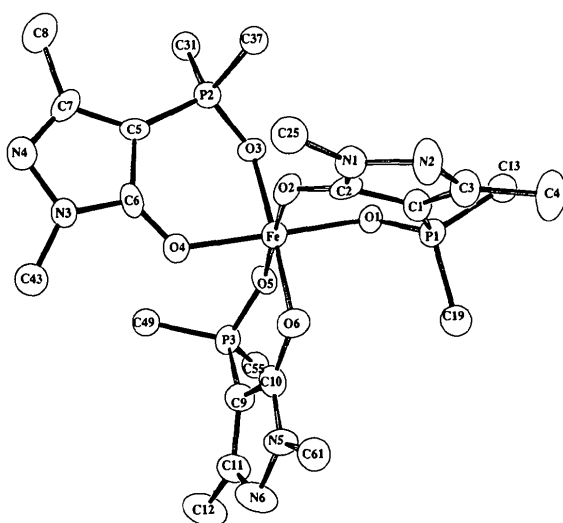

Fig. 1. Molecular configuration and atom-labelling scheme for the title complex (*ORTEP*; Johnson, 1965). For reasons of clarity only one C atom of each P-bound phenyl ring is represented.

Discussion. A perspective view of the molecule with atom labelling is shown in Fig. 1. Atom coordinates and equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1. Interatomic bond distances and angles are listed in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55027 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0279]

Table 1. *Positional parameters and isotropic or equivalent isotropic displacement parameters* (Å^2)

Phenyl C atoms C(13)—C(66) were refined isotropically. Equivalent isotropic displacement parameters are given for the remaining atoms; $B_{eq} = (4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{iso}/B_{eq}
Fe	– 0.0242 (1)	0.27921 (9)	0.74963 (5)	2.51 (3)
P(1)	0.0725 (2)	0.1401 (2)	0.6434 (1)	2.56 (5)
P(2)	0.0538 (2)	0.1849 (2)	0.8738 (1)	2.44 (5)
P(3)	– 0.0020 (3)	0.5110 (2)	0.7286 (1)	2.67 (5)
O(1)	0.1113 (6)	0.2031 (4)	0.6938 (2)	2.7 (1)
O(2)	– 0.1227 (6)	0.1584 (4)	0.7580 (2)	2.7 (1)
O(3)	0.0994 (5)	0.2331 (4)	0.8171 (2)	2.5 (1)
O(4)	– 0.1603 (5)	0.3495 (4)	0.8062 (2)	2.8 (1)
O(5)	0.0690 (6)	0.4030 (4)	0.7371 (2)	2.8 (1)
O(6)	– 0.1509 (6)	0.3275 (4)	0.6854 (2)	3.0 (1)
N(1)	– 0.2199 (7)	0.0202 (5)	0.7244 (3)	2.7 (2)
N(2)	– 0.2055 (8)	– 0.0472 (5)	0.6781 (3)	3.7 (2)
N(3)	– 0.2888 (7)	0.3643 (5)	0.8929 (3)	2.8 (2)
N(4)	– 0.2866 (7)	0.3269 (6)	0.9498 (3)	3.8 (2)
N(5)	– 0.2937 (7)	0.4436 (5)	0.6294 (3)	2.7 (2)
N(6)	– 0.3166 (7)	0.5460 (5)	0.6160 (3)	3.9 (2)
C(1)	– 0.0562 (9)	0.0706 (6)	0.6663 (4)	2.6 (2)
C(2)	– 0.1308 (8)	0.0915 (6)	0.7188 (3)	2.5 (2)
C(3)	– 0.1086 (9)	– 0.0169 (6)	0.6441 (4)	3.1 (2)
C(4)	– 0.066 (1)	– 0.0737 (7)	0.5894 (4)	4.8 (3)
C(5)	– 0.1001 (8)	0.2511 (6)	0.8978 (3)	2.4 (2)
C(6)	– 0.1779 (8)	0.3225 (6)	0.8600 (4)	2.6 (2)
C(7)	– 0.1767 (9)	0.2610 (6)	0.9519 (3)	3.1 (2)
C(8)	– 0.138 (1)	0.2024 (8)	1.0079 (4)	5.6 (3)
C(9)	– 0.1448 (8)	0.5111 (6)	0.6830 (4)	2.6 (2)
C(10)	– 0.1898 (8)	0.4199 (6)	0.6680 (4)	2.6 (2)
C(11)	– 0.2268 (9)	0.5846 (6)	0.6477 (4)	3.1 (2)
C(12)	– 0.222 (1)	0.6962 (7)	0.6447 (5)	5.1 (3)
C(13)	0.2208 (8)	0.0572 (6)	0.6212 (4)	2.6 (2)
C(14)	0.245 (1)	0.0284 (7)	0.5635 (4)	3.9 (2)
C(15)	0.361 (1)	– 0.0385 (7)	0.5478 (4)	4.9 (2)
C(16)	0.454 (1)	– 0.0704 (7)	0.5897 (4)	4.4 (2)
C(17)	0.436 (1)	– 0.0440 (7)	0.6482 (4)	4.4 (2)
C(18)	0.3205 (9)	0.0205 (7)	0.6639 (4)	3.6 (2)
C(19)	0.0245 (9)	0.2186 (6)	0.5797 (4)	3.0 (2)
C(20)	– 0.0902 (9)	0.2077 (7)	0.5468 (4)	3.9 (2)
C(21)	– 0.123 (1)	0.2703 (8)	0.4964 (5)	5.3 (3)
C(22)	– 0.038 (1)	0.3386 (8)	0.4815 (5)	5.7 (3)
C(23)	0.074 (1)	0.3535 (9)	0.5131 (5)	6.5 (3)
C(24)	0.107 (1)	0.2908 (7)	0.5639 (4)	4.9 (2)
C(25)	– 0.3180 (9)	0.0079 (6)	0.7699 (4)	3.3 (2)
C(26)	– 0.353 (1)	– 0.0881 (7)	0.7806 (4)	4.3 (2)
C(27)	– 0.452 (1)	– 0.0997 (8)	0.8255 (5)	5.3 (2)
C(28)	– 0.504 (1)	– 0.0224 (8)	0.8571 (5)	5.3 (3)
C(29)	– 0.469 (1)	0.0705 (8)	0.8475 (5)	5.8 (3)
C(30)	– 0.376 (1)	0.0893 (7)	0.8019 (4)	4.4 (2)
C(31)	0.1871 (9)	0.1892 (6)	0.9275 (4)	2.8 (2)
C(32)	0.222 (1)	0.1094 (7)	0.9663 (4)	3.9 (2)
C(33)	0.333 (1)	0.1138 (7)	1.0052 (4)	4.9 (2)
C(34)	0.404 (1)	0.1949 (7)	1.0031 (4)	4.9 (2)
C(35)	0.369 (1)	0.2744 (7)	0.9644 (5)	4.9 (2)
C(36)	0.2569 (9)	0.2720 (7)	0.9259 (4)	3.9 (2)
C(37)	0.0404 (8)	0.0528 (6)	0.8631 (3)	2.4 (2)
C(38)	0.142 (1)	0.0001 (7)	0.8308 (4)	4.1 (2)
C(39)	0.138 (1)	– 0.1040 (8)	0.8202 (5)	5.0 (2)
C(40)	0.029 (1)	– 0.1485 (7)	0.8421 (4)	4.6 (2)
C(41)	– 0.071 (1)	– 0.0966 (7)	0.8738 (4)	4.0 (2)

Table 1 (cont.)

	x	y	z	B_{iso}/B_{eq}
C(42)	−0.0673 (9)	0.0058 (6)	0.8849 (4)	3.3 (2)
C(43)	−0.3950 (9)	0.4434 (6)	0.8762 (4)	3.1 (2)
C(44)	−0.435 (1)	0.4568 (8)	0.8190 (4)	5.0 (2)
C(45)	−0.540 (1)	0.5383 (9)	0.8052 (5)	6.8 (3)
C(46)	−0.601 (1)	0.5993 (8)	0.8486 (5)	6.2 (3)
C(47)	−0.557 (1)	0.5841 (8)	0.9049 (5)	5.2 (3)
C(48)	−0.453 (1)	0.5057 (7)	0.9195 (4)	4.0 (2)
C(49)	−0.0496 (9)	0.5647 (6)	0.7992 (4)	2.8 (2)
C(50)	0.047 (1)	0.5420 (7)	0.8433 (5)	4.8 (2)
C(51)	0.012 (1)	0.5758 (8)	0.9014 (5)	5.9 (3)
C(52)	−0.114 (1)	0.6284 (8)	0.9125 (5)	5.4 (3)
C(53)	−0.203 (1)	0.6508 (7)	0.8703 (4)	4.6 (2)
C(54)	−0.1749 (9)	0.6197 (7)	0.8121 (4)	3.8 (2)
C(55)	0.1227 (8)	0.5834 (6)	0.6966 (4)	2.9 (2)
C(56)	0.116 (1)	0.6884 (7)	0.7028 (4)	4.5 (2)
C(57)	0.218 (1)	0.7393 (7)	0.6772 (4)	4.7 (2)
C(58)	0.321 (1)	0.6880 (8)	0.6469 (5)	5.4 (3)
C(59)	0.327 (1)	0.5879 (8)	0.6380 (5)	5.2 (2)
C(60)	0.229 (1)	0.5330 (7)	0.6645 (4)	4.2 (2)
C(61)	−0.3736 (9)	0.3771 (6)	0.6027 (4)	3.0 (2)
C(62)	−0.4202 (9)	0.3993 (7)	0.5460 (4)	3.7 (2)
C(63)	−0.501 (1)	0.3344 (7)	0.5189 (4)	4.7 (2)
C(64)	−0.527 (1)	0.2490 (8)	0.5475 (5)	5.2 (3)
C(65)	−0.482 (1)	0.2247 (8)	0.6019 (5)	5.5 (3)
C(66)	−0.404 (1)	0.2912 (7)	0.6316 (4)	4.6 (2)

A slightly distorted octahedron around the Fe atom (see below) is formed by two inequivalent donor O atoms from each of the three identical chelate ligands; chemically equivalent O atoms are facial. This array of three unsymmetrical *O,O* chelates defines a so-called *cis* isomer (Cotton & Wilkinson, 1988). As expected for tris(chelate) complexes, the two enantiomeric configurations Λ and Δ are present in the unit cell. If one excludes the P-bound phenyl rings, the symmetry of the complex is approximately C_3. The *cis*-O—Fe—O angles [87.9 (2)–92.4 (2)°] and the Fe—O distances [1.966 (5)–2.013 (5) Å] indicate a quasi-octahedral coordination of the metal centre. As shown in Fig. 2, each chelate ring is puckered, having a pseudo-envelope conformation with the Fe atom displaced from the plane of the other five ring atoms. The Fe atom lies *ca* 0.68 Å (average) out of each chelate plane [*i.e.* the three planes O(1)—O(2)—P(1)—C(1)—C(2), O(3)—O(4)—P(2)—C(5)—C(6), O(5)—O(6)—P(3)—C(9)—C(10); see Table 2]. The pyrazole rings are planar within experimental error and make angles of *ca* 9° with the above defined chelate planes and of *ca* 30° with the aryl ring connected to each of them (see torsion angles, Table 2). The C(1)—C(2) and C(3)—N(2) bond lengths of respectively 1.404 (9) and 1.315 (9) Å are consistent with the aromaticity of the corresponding pyrazolone ring and are similar to those found in other pyrazolonato ligands [see, for example, Pettinari, Rafaiani, Lobbia, Lorenzotti & Bonati, (1991) and Okafor, Uzoukwu, Hitchcock & Smith (1990)]. This is also the case for the two other pyrazolone rings. The P atoms have the usual tetrahedral geometry, the angles around these atoms ranging from 105.2 (3) to 112.3 (3)° for P(1), 106.6 (3) to 112.0 (3)° for P(2) and 106.9 (3) to 111.8 (4)° for P(3). The lengths of

Table 2. Selected interatomic distances (Å), angles (°) and torsion angles (°) and Fe-atom distances from the chelate planes (Å)

Fe—O(1)	2.013 (5)	N(1)—N(2)	1.389 (7)
Fe—O(2)	1.984 (5)	N(1)—C(2)	1.374 (8)
Fe—O(3)	1.999 (4)	N(1)—C(25)	1.424 (9)
Fe—O(4)	1.995 (5)	N(2)—C(3)	1.315 (9)
Fe—O(5)	1.998 (4)	N(3)—N(4)	1.372 (8)
Fe—O(6)	1.966 (5)	N(3)—C(6)	1.374 (8)
P(1)—O(1)	1.513 (5)	N(3)—C(43)	1.428 (9)
P(1)—C(1)	1.728 (7)	N(4)—C(7)	1.296 (9)
P(1)—C(13)	1.779 (7)	N(5)—N(6)	1.378 (7)
P(1)—C(19)	1.794 (7)	N(5)—C(10)	1.352 (8)
P(2)—O(3)	1.513 (5)	N(6)—C(61)	1.408 (8)
P(2)—C(5)	1.731 (7)	N(6)—C(11)	1.307 (9)
P(2)—C(31)	1.804 (7)	C(1)—C(2)	1.404 (9)
P(2)—C(37)	1.798 (7)	C(1)—C(3)	1.434 (9)
P(3)—O(5)	1.519 (4)	C(3)—C(4)	1.49 (1)
P(3)—C(9)	1.751 (7)	C(5)—C(6)	1.416 (9)
P(3)—C(49)	1.799 (7)	C(5)—C(7)	1.432 (9)
P(3)—C(55)	1.789 (7)	C(7)—C(8)	1.50 (1)
O(2)—C(2)	1.283 (8)	C(9)—C(10)	1.393 (9)
O(4)—C(6)	1.281 (8)	C(9)—C(11)	1.419 (9)
O(6)—C(10)	1.292 (8)	C(11)—C(12)	1.49 (1)

O(1)—Fe—O(2)	89.9 (2)	Fe—O(6)—C(10)	128.2 (5)
O(1)—Fe—O(3)	89.9 (2)	N(2)—N(1)—C(2)	111.8 (6)
O(1)—Fe—O(4)	177.8 (2)	N(1)—N(2)—C(3)	104.9 (6)
O(1)—Fe—O(5)	89.8 (2)	N(4)—N(3)—C(6)	112.8 (6)
O(1)—Fe—O(6)	92.4 (2)	N(3)—N(4)—C(7)	104.2 (6)
O(2)—Fe—O(3)	92.2 (2)	N(6)—N(5)—C(10)	112.3 (6)
O(2)—Fe—O(4)	88.1 (2)	N(5)—N(6)—C(11)	104.1 (6)
O(2)—Fe—O(5)	176.8 (2)	P(1)—C(1)—C(2)	121.9 (5)
O(2)—Fe—O(6)	87.9 (2)	C(2)—C(1)—C(3)	104.1 (6)
O(3)—Fe—O(4)	89.4 (2)	O(2)—C(2)—C(1)	131.3 (7)
O(3)—Fe—O(5)	91.0 (2)	N(1)—C(2)—C(1)	106.5 (6)
O(3)—Fe—O(6)	177.7 (2)	N(2)—C(3)—C(1)	112.7 (7)
O(4)—Fe—O(5)	92.3 (2)	P(2)—C(5)—C(6)	120.6 (5)
O(4)—Fe—O(6)	88.3 (2)	C(6)—C(5)—C(7)	102.6 (6)
O(5)—Fe—O(6)	89.0 (2)	O(4)—C(6)—C(5)	132.2 (7)
O(1)—P(1)—C(1)	109.6 (3)	N(3)—C(6)—C(5)	105.9 (6)
O(3)—P(2)—C(5)	109.5 (3)	N(4)—C(7)—C(5)	114.4 (7)
O(5)—P(3)—C(9)	109.6 (3)	P(3)—C(9)—C(10)	120.3 (6)
Fe—O(1)—P(1)	124.6 (3)	C(10)—C(9)—C(11)	103.6 (6)
Fe—O(2)—C(2)	126.2 (4)	O(6)—C(10)—C(9)	131.4 (7)
Fe—O(3)—P(2)	124.8 (3)	N(5)—C(10)—C(9)	106.7 (6)
Fe—O(4)—C(6)	125.8 (4)	N(6)—C(11)—C(9)	113.3 (7)
Fe—O(5)—P(3)	126.0 (3)		

O(1)—P(1)—C(1)—C(2)	13.8 (8)	P(1)—C(1)—C(2)—O(2)	−0.4 (13)
O(5)—P(3)—C(9)—C(10)	9.7 (8)	P(3)—C(9)—C(10)—O(6)	6.1 (13)
O(3)—P(2)—C(5)—C(6)	13.0 (8)	P(2)—C(5)—C(6)—O(4)	2.7 (13)
O(5)—Fe—O(6)—C(10)	−27.7 (6)	C(6)—N(3)—C(43)—C(44)	30.3 (13)
O(1)—Fe—O(2)—C(2)	−29.9 (6)	C(2)—N(1)—C(25)—C(30)	27.4 (13)
O(3)—Fe—O(4)—C(6)	−29.5 (6)	C(10)—N(5)—C(61)—C(66)	32.8 (13)

Chelate plane*	Fe-atom distance
O(1)—P(1)—C(1)—C(2)—O(2)	0.669 (5)
O(3)—P(2)—C(5)—C(6)—O(4)	0.693 (5)
O(5)—P(3)—C(9)—C(10)—O(6)	0.660 (5)

* The maximum deviations of the defining atoms from these planes are respectively 0.09, 0.09 and 0.08 Å.
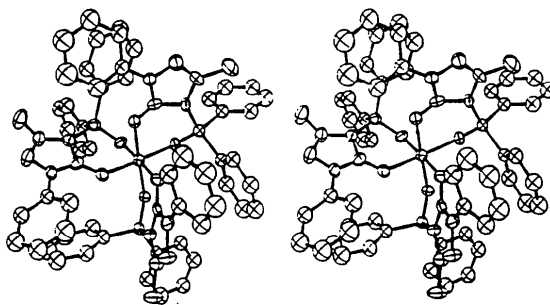

Fig. 2. Stereoview of the title complex.

the three P—O bonds [1.513 (5), 1.513 (5) and 1.519 (4) Å] lie between the values typical of single (1.75 Å) and double P—O (1.45 Å) bonds (see, for example, Zhang, Shao & Tang, 1990). To the best of our knowledge the ligand described in this study is the first example of a pyrazolone functionalized with a P-containing group.

References

B. A. FRENZ & ASSOCIATES, INC. (1985). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.

COTTON, F. A. & WILKINSON, G. (1988). *Advanced Inorganic Chemistry*, 5th edition, p. 1323. New York: John Wiley.

GAUTHIER, J. C., LECOLIER, S., SORIAUX, C. & CHEVALIER, S. (1984). French patent application No. 2544745. *CA Selects*, **102**, 207120 J.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

LAKKIS, M., LAKKIS, Z., GOETZ-GRANDMONT, G. J. & BRUNETTE, J.-P. (1991). *Monatsh. Chem.* **122**, 9–15.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

OKAFOR, C. E., UZOUKWU, A. B., HITCHCOCK, P. B. & SMITH, J. D. (1990). *Inorg. Chim. Acta*, **172**, 97–103.

PETTINARI, C., RAFAIANI, G., LOBBIA, G. G., LORENZOTTI, A. & BONATI, F. (1991). *J. Organomet. Chem.* **405**, 75–92.

ZHANG, S.-W., SHAO, M.-C. & TANG, Y.-Q. (1990). *Acta Cryst.* A46, C-217–C-218.

Structure of *cis*-Dicarbonyl[2-carboxylato-1-methoxycarbonyl-2-(4-methylphenyl)vinyl]-*trans*-bis(dimethylphenylphosphine)ruthenium(II), a Complex Containing a Bidentate Vinyl Ligand

By ALEXANDER J. BLAKE

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

JOSEPH R. CROOK

Department of Chemistry, Western Washington University, Bellingham, WA 98225, USA

ROGER J. MAWBY

Department of Chemistry, University of York, York YO1 5DD, England

AND AMANDA J. REID AND COLIN D. REYNOLDS*

Structural Biophysics Unit, Physics Division, School of Information Science and Technology, Liverpool Polytechnic, Liverpool L3 3AF, England

Abstract. [Ru(CO)$_2${C(CO$_2$Me)=C(COO)(C$_6$H$_4$-Me)}(PMe$_2$Ph)$_2$]; [Ru(C$_{12}$H$_{10}$O$_4$)(C$_8$H$_{11}$P)$_2$(CO)$_2$], M_r = 651.6, orthorhombic, $P2_12_12_1$, a = 9.3667 (8), b = 13.6888 (20), c = 23.0421 (20) Å, V = 2954.4 Å^3, Z = 4, D_x = 1.465 Mg m^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, μ = 5.74 mm^{-1}, $F(000)$ = 1336, T = 298 K, R = 0.040 for 4794 observed reflections with $F_o > 3\sigma(F_o)$ and 372 parameters. The complex exists as discrete monomeric units in the crystal, and exhibits approximate octahedral geometry around the Ru atom. The five-membered metallacycle ring is essentially planar with Ru—C and Ru—O distances of 2.087 (5) and 2.071 (4) Å. The Ru—C(carbonyl) distances of 1.824 (6) and 1.913 (6) Å show a marked difference. The average Ru—P distance is 2.384 (2) Å.

Introduction. Reactions between ruthenium(II) aryl complexes [Ru(CO)$_2$(C$_6$H$_4$X-4)Cl(PMe$_2$Ph)$_2$] (X = H, Cl, Me or OMe) and the alkyne MeO$_2$CC≡CCO$_2$Me yield vinyl complexes [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)(C$_6$H$_4$X-4)}Cl(PMe$_2$Ph)$_2$], assigned structure (I), where L = PMe$_2$Ph, corresponding to *cis* addition of the ruthenium–aryl bond to the alkyne (Crook, Chamberlain & Mawby, 1989). Apparent confirmation of this stereochemistry was provided by the thermal decomposition of the vinyl complexes in

---

* To whom correspondence should be addressed.