

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

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

	x	y	z	U_{eq}
Rh(1)	-0.0761 (1)	0	0	0.0224 (1)
Cl(1)	0	-0.0110 (2)	-1/4	0.0352 (1)
P(1)	-0.1847 (1)	0.0879 (1)	-0.0672 (1)	0.0275 (1)
P(2)	0.0306 (1)	0.1135 (1)	-0.0025 (2)	0.0276 (1)
C(1)	-0.1467 (5)	0.1577 (4)	-0.1589 (5)	0.0325 (2)
C(2)	-0.2569 (4)	0.1684 (4)	-0.0093 (7)	0.0359 (2)
C(3)	-0.3593 (5)	0.0213 (5)	-0.1152 (5)	0.0330 (2)
C(4)	-0.4151 (5)	-0.0371 (6)	-0.1635 (5)	0.0413 (2)
C(5)	-0.3797 (5)	-0.0988 (5)	-0.2200 (5)	0.0386 (2)
C(6)	-0.2858 (5)	-0.1030 (5)	-0.2309 (5)	0.0382 (2)
C(7)	-0.2291 (5)	-0.0441 (5)	-0.1850 (5)	0.0368 (2)
C(8)	-0.2647 (4)	0.0161 (5)	-0.1258 (5)	0.0309 (2)
C(9)	0.0905 (6)	0.1500 (5)	-0.1009 (5)	0.0387 (3)
C(10)	0.1254 (5)	0.0983 (5)	0.0733 (5)	0.0376 (2)
C(11)	-0.0290 (5)	0.2972 (4)	-0.0064 (8)	0.0455 (3)
C(12)	-0.0730 (7)	0.3707 (5)	0.0277 (7)	0.0623 (4)
C(13)	-0.1062 (6)	0.3689 (5)	0.1130 (7)	0.0547 (3)
C(14)	-0.0934 (6)	0.2919 (5)	0.1625 (6)	0.0522 (3)
C(15)	-0.0514 (5)	0.2158 (6)	0.1272 (5)	0.0420 (3)
C(16)	-0.0184 (5)	0.2176 (4)	0.0420 (5)	0.0301 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

Rh(1)—P(1)	2.306 (2)	C(3)—C(8)	1.408 (9)
Rh(1)—P(2)	2.302 (2)	C(4)—C(5)	1.362 (11)
Rh(1)—P(1) [†]	2.306 (2)	C(5)—C(6)	1.396 (10)
Rh(1)—P(2) [†]	2.302 (2)	C(6)—C(7)	1.396 (11)
P(1)—C(1)	1.829 (7)	C(7)—C(8)	1.375 (11)
P(1)—C(2)	1.827 (8)	C(11)—C(12)	1.371 (12)
P(1)—C(8)	1.824 (7)	C(11)—C(16)	1.401 (11)
P(2)—C(9)	1.826 (8)	C(12)—C(13)	1.392 (15)
P(2)—C(10)	1.829 (8)	C(13)—C(14)	1.382 (12)
P(2)—C(16)	1.833 (7)	C(14)—C(15)	1.395 (12)
C(3)—C(4)	1.403 (10)	C(15)—C(16)	1.389 (11)
P(1)—Rh(1)—P(2)	93.2 (1)	C(10)—P(2)—C(16)	99.8 (3)
P(1)—Rh(1)—P(1) [†]	92.0 (1)	C(4)—C(3)—C(8)	119.2 (6)
P(2)—Rh(1)—P(1) [†]	153.4 (1)	C(3)—C(4)—C(5)	121.4 (7)
P(1)—Rh(1)—P(2) [†]	153.4 (1)	C(4)—C(5)—C(6)	119.1 (7)
P(2)—Rh(1)—P(2) [†]	93.7 (1)	C(5)—C(6)—C(7)	120.5 (7)
P(1)—Rh(1)—P(2) [†]	93.2 (1)	C(6)—C(7)—C(8)	120.4 (7)
Rh(1)—P(1)—C(1)	116.6 (2)	P(1)—C(8)—C(3)	123.6 (5)
Rh(1)—P(1)—C(2)	123.9 (3)	P(1)—C(8)—C(7)	117.0 (5)
C(1)—P(1)—C(2)	100.4 (4)	C(3)—C(8)—C(7)	119.3 (6)
Rh(1)—P(1)—C(8)	109.8 (2)	C(12)—C(11)—C(16)	121.4 (9)
C(1)—P(1)—C(8)	98.7 (3)	C(11)—C(12)—C(13)	120.5 (9)
C(2)—P(1)—C(8)	103.9 (3)	C(12)—C(13)—C(14)	118.7 (8)
Rh(1)—P(2)—C(9)	124.1 (3)	C(13)—C(14)—C(15)	121.0 (9)
Rh(1)—P(2)—C(10)	115.0 (2)	C(14)—C(15)—C(16)	120.2 (7)
C(9)—P(2)—C(10)	100.8 (4)	P(2)—C(16)—C(11)	123.8 (7)
Rh(1)—P(2)—C(16)	109.7 (2)	P(2)—C(16)—C(15)	118.0 (5)
C(9)—P(2)—C(16)	104.3 (3)	C(11)—C(16)—C(15)	118.1 (7)

Symmetry code: (i) x, -y, -z.

A suitable crystal was chosen and mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in an N_2 cold stream. Inspection of axial photographs about each of the three axes confirmed axis length and Laue symmetry. ω scans of several intense reflections indicated acceptable crystal quality. The θ scan width was 1.2° with a scan rate variable between 2.0 and $14.6^\circ \text{ min}^{-1}$ in θ . The background was measured by the stationary crystal and stationary counter technique at the beginning and end of each reflection for half the total scan time. Intensities were corrected by a peak-profiling method (Diamond, 1969). Carbon-bound H atoms were placed in idealized positions [$C-H = 0.96 \text{ \AA}$, $U(H) = 0.08 \text{ \AA}^2$ (fixed)]. The H atom parameters were not refined. The absolute configuration was determined (Rogers, 1981). The structure of the title compound

and the numbering scheme used are shown in Fig. 1. The title compound was obtained from Dr C. Ovalles and S. Taboada (INTEVEP, SA, Venezuela).

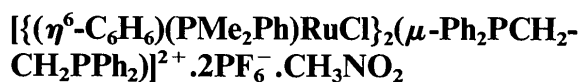
The X-ray diffraction and crystallographic computing system was purchased from funds provided by the National Science Foundation (USA) grant CHE-8513273.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55534 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1031]

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Acta Cryst. (1993). **C49**, 142–144



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(Received 30 January 1992; accepted 29 July 1992)

Abstract

In the title compound, [μ -ethylenebis(diphenylphosphine)-bis($(\eta^6$ -benzene)chloro(dimethylphenylphosphine)ruthenium(II))] bis(hexafluorophosphate) nitromethane solvate, the cation is crystallographically centrosymmetric about the midpoint of the $\text{CH}_2\text{—CH}_2$ bond. The diphosphine ligand adopts a bridging function between the two Ru^{II} centres.

Comment

Although we recently reported an analogous centrosymmetric dinuclear cation in which dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) links two $[(\text{C}_5\text{Me}_5)(\text{Et}_2\text{NCS}_2)\text{-Rh}]$ units (Blake, Fotheringham, Stephenson, Hambling & Sawyer, 1991), we are also interested in the structures of 1:1 complexes in which only one P donor is coordinated; the remaining P is 'dangling' and available for coordination to another metal centre, providing a route to mixed-metal species. Using dpmm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) in place of dppe with the same rhodium starting material yields a 1:1 complex with such a structure (Blake, Fotheringham & Stephenson, 1992).

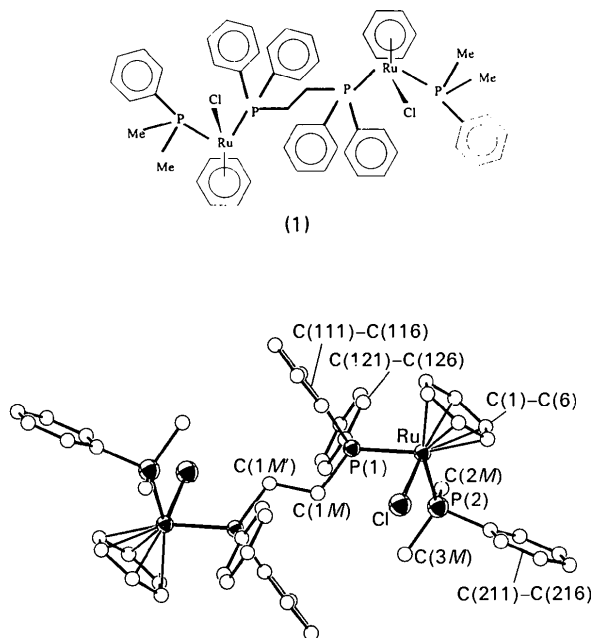


Fig. 1. View of the centrosymmetric dinuclear cation showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity.

Experimental

Crystal data

$[\text{Ru}_2\text{Cl}_2(\text{C}_6\text{H}_6)_2(\text{C}_8\text{H}_{11}\text{P})_2(\text{C}_{26}\text{H}_{24}\text{P}_2)][\text{PF}_6]_2 \cdot \text{CH}_3\text{NO}_2$

$M_r = 1454.8$

Monoclinic

$I2/c$

$a = 28.325$ (6) Å

$b = 9.790$ (5) Å

$c = 23.042$ (6) Å

$\beta = 105.999$ (6)°

$V = 6142$ Å³

$Z = 4$

$D_x = 1.573$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 15 reflections

$\theta = 3.5\text{--}17.5^\circ$

$\mu = 0.799$ mm⁻¹

$T = 293$ K

Needle

$0.64 \times 0.20 \times 0.14$ mm

Yellow

Data collection

Stoe Stadi-2 diffractometer

ω scans

Absorption correction:

none

5811 measured reflections

5313 independent reflections

4031 observed reflections

$[F > 6.0\sigma(F)]$

$R_{\text{int}} = 0.012$

$\theta_{\text{max}} = 25.0^\circ$

$h = -32 \rightarrow 33$

$k = 0 \rightarrow 11$

$l = 0 \rightarrow 27$

No standard reflections

Refinement

Refinement on F

Final $R = 0.0611$

$wR = 0.0753$

$S = 1.406$

4031 reflections

167 parameters

H atoms in calculated positions

$w = 1/[\sigma^2(F) + 0.000243F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.10$

$\Delta\rho_{\text{max}} = 0.98$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.64$ e Å⁻³

Atomic scattering factors

inlaid except for Ru

(Cromer & Mann, 1968)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Ru	-0.129620 (20)	0.08718 (5)	0.360200 (20)	0.0314 (3)
Cl	-0.06788 (7)	0.26041 (20)	0.37346 (9)	0.0559 (12)
P(1)	-0.07333 (6)	-0.04528 (17)	0.43236 (8)	0.0312 (9)
P(2)	-0.15877 (8)	0.19502 (22)	0.43426 (9)	0.0523 (13)
C(1)	-0.12595 (15)	-0.0110 (5)	0.27282 (23)	0.0507 (19)
C(2)	-0.15011 (15)	-0.0992 (5)	0.30266 (23)	0.0524 (19)
C(3)	-0.19136 (15)	-0.0543 (5)	0.31912 (23)	0.0547 (20)
C(4)	-0.20840 (15)	0.0789 (5)	0.30576 (23)	0.0517 (19)
C(5)	-0.18424 (15)	0.1671 (5)	0.27594 (23)	0.0529 (20)
C(6)	-0.14301 (15)	0.1222 (5)	0.25946 (23)	0.0522 (20)
C(1M)	-0.02146 (23)	0.0462 (7)	0.4826 (3)	0.0354 (15)
C(111)	-0.04055 (16)	-0.1669 (4)	0.39713 (21)	0.0358 (15)
C(112)	-0.01479 (16)	-0.1116 (4)	0.35911 (21)	0.0442 (17)
C(113)	0.01443 (16)	-0.1956 (4)	0.33436 (21)	0.0622 (22)
C(114)	0.01786 (16)	-0.3349 (4)	0.34765 (21)	0.078 (3)
C(115)	-0.00790 (16)	-0.3902 (4)	0.38567 (21)	0.077 (3)
C(116)	-0.03712 (16)	-0.3062 (4)	0.41042 (21)	0.0561 (21)
C(121)	-0.10027 (17)	-0.1487 (5)	0.48165 (20)	0.0375 (16)
C(122)	-0.13601 (17)	-0.2446 (5)	0.45461 (20)	0.0495 (19)
C(123)	-0.15869 (17)	-0.3222 (5)	0.49004 (20)	0.0597 (22)
C(124)	-0.14559 (17)	-0.3041 (5)	0.55250 (20)	0.074 (3)
C(125)	-0.10983 (17)	-0.2083 (5)	0.57954 (20)	0.072 (3)
C(126)	-0.08716 (17)	-0.1306 (5)	0.54411 (20)	0.0542 (20)
C(2M)	-0.1966 (4)	0.0850 (10)	0.4676 (4)	0.076 (3)
C(3M)	-0.1175 (3)	0.2706 (10)	0.4996 (4)	0.077 (3)
C(211)	-0.19950 (16)	0.3378 (4)	0.40264 (22)	0.0438 (17)
C(212)	-0.18479 (16)	0.4327 (4)	0.36592 (22)	0.0522 (19)
C(213)	-0.21555 (16)	0.5414 (4)	0.34106 (22)	0.0579 (21)
C(214)	-0.26102 (16)	0.5554 (4)	0.35295 (22)	0.0651 (24)
C(215)	-0.27572 (16)	0.4606 (4)	0.38966 (22)	0.0651 (24)
C(216)	-0.24496 (16)	0.3518 (4)	0.41451 (22)	0.0568 (21)
P(3)	-0.34688 (8)	-0.07148 (24)	0.30998 (12)	0.0627 (15)
F(1)	-0.30538 (21)	-0.1508 (6)	0.2902 (3)	0.101 (5)
F(2)*	-0.3613 (4)	-0.2199 (12)	0.3310 (6)	0.089 (3)
F(3)	-0.3183 (5)	-0.0862 (13)	0.3745 (4)	0.238 (12)
F(4)*	-0.3141 (4)	0.0667 (11)	0.3294 (6)	0.077 (3)
F(5)*	-0.3854 (6)	-0.1016 (18)	0.2482 (8)	0.132 (5)
F(6)*	-0.3913 (4)	0.0252 (10)	0.3160 (5)	0.058 (3)
F(2')*	-0.3823 (5)	-0.1966 (14)	0.2905 (7)	0.100 (4)
F(4')*	-0.3271 (5)	0.0658 (14)	0.2906 (7)	0.105 (4)
F(5')*	-0.3646 (6)	-0.0189 (17)	0.2391 (7)	0.121 (5)
F(6')*	-0.3842 (5)	-0.0115 (14)	0.3447 (6)	0.095 (4)
N(1)	0.0000	-0.1948 (11)	0.7500	0.065 (3)
O(1)	-0.0356 (3)	-0.1323 (8)	0.7217 (4)	0.0996 (23)
C(15)	0.0000	-0.3411 (17)	0.7500	0.099 (5)

*Site occupancy 0.5.

Table 2. Geometric parameters (Å, °)

Ru—Cl	2.3944 (21)	Ru—P(2)	2.3421 (22)
Ru—C(1)	2.259 (5)	P(1)—C(1M)	1.834 (7)
Ru—C(2)	2.236 (5)	P(1)—C(111)	1.832 (5)
Ru—C(3)	2.227 (5)	P(1)—C(121)	1.837 (5)
Ru—C(4)	2.240 (5)	P(2)—C(2M)	1.831 (10)
Ru—C(5)	2.263 (5)	P(2)—C(3M)	1.792 (10)
Ru—C(6)	2.273 (5)	P(2)—C(211)	1.831 (5)
Ru—P(1)	2.3509 (18)		
Cl—Ru—P(1)	88.36 (7)	P(1)—C(111)—C(116)	123.5 (3)
Cl—Ru—P(2)	88.83 (7)	P(1)—C(121)—C(122)	117.9 (4)
P(1)—Ru—P(2)	92.29 (7)	P(1)—C(121)—C(126)	122.0 (4)
Ru—P(1)—C(1M)	116.49 (22)	Ru—P(2)—C(2M)	113.9 (3)
Ru—P(1)—C(111)	111.90 (16)	Ru—P(2)—C(3M)	121.3 (3)
Ru—P(1)—C(121)	115.15 (17)	Ru—P(2)—C(211)	111.36 (18)
C(1M)—P(1)—C(111)	100.4 (3)	C(2M)—P(2)—C(3M)	102.3 (5)
C(1M)—P(1)—C(121)	106.0 (3)	C(2M)—P(2)—C(211)	103.8 (4)
C(111)—P(1)—C(121)	105.27 (22)	C(3M)—P(2)—C(211)	102.3 (4)
P(1)—C(1M)—C(1M')	114.8(5)	P(2)—C(211)—C(212)	119.3 (4)
P(1)—C(111)—C(112)	116.3 (3)	P(2)—C(211)—C(216)	120.7 (4)

C(1M') is related to C(1M) by inversion through (0, 0, $\frac{1}{2}$).

The title compound was prepared by mixing [(C₆H₆)(Me₂PPh)-RuCl₂] and dppe (2:1 molar ratio) in CH₂Cl₂/MeOH (5:1 v/v) in the presence of NH₄PF₆; crystals were grown from MeNO₂/MeOH. The crystal was pre-aligned using oscillation and Weissenberg photography and mounted with the *b* axis parallel to the spindle of the two-circle instrument. The ω -scan width was [1.0 + 0.5(sin μ /tan θ)]°. The structure was solved and refined using *SHELX76* (Sheldrick, 1976). The metal position was deduced from a Patterson synthesis and the remaining non-H atoms located by subsequent refinement and ΔF synthesis. Refinement was by full-matrix least squares. Disorder in the PF₆⁻ anion was modelled by allowing split occupancies for four of the F atoms.

Fig. 1 was produced using an interactive version of *ORTEPII* (Mallinson & Muir, 1985) and molecular-geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

We thank the SERC for support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55372 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1003]

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Acta Cryst. (1993). **C49**, 144–147

Dimeric Copper(II) 2,2-Dimethylpropanoate Adducts with 3- or 4-Picoline

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(Received 9 June 1992; accepted 24 August 1992)

Abstract

The structures of tetrakis(μ -2,2-dimethylpropanoate-*O,O'*)-bis(3- or 4-picoline)dicopper(II) benzene solvate, [Cu{(CH₃)₂CCOO}₂C₆H₇N]₂·C₆H₆, have been determined by single-crystal X-ray diffraction. The binuclear Cu^{II} complexes have a cage structure with a square-pyramidal coordination geometry around the Cu atoms. The Cu...Cu distances are 2.657 (3) and 2.648 (5) Å for 3- and 4-picoline adducts, respectively. In the crystal, benzene molecules are accommodated statistically in a hollow running along the *c* axis. The magneto-structural correlation could not be determined because of the easy removal of the benzene molecules from the crystals under the reduced pressure conditions at which the magnetic susceptibility measurements were made.

Comment

The magnetic properties of dimeric copper(II) 2,2-dimethylpropanoate complexes were reported by Muto, Hirashima, Tokii, Kato & Suzuki (1986), and some of them were remeasured later by one of the authors (TT). An unexpectedly small $-2J$ value (325 cm⁻¹) was observed for the 4-picoline adduct compared with related compounds (pyridine 368 cm⁻¹, 2- and 3-picoline adducts 372 and 363 cm⁻¹ respectively). The smaller $-2J$ value of the 4-picoline adduct was tentatively attributed to the higher basicity of the 4-picoline compared with other similar ligands (Muto *et al.*, 1986). However, the $-2J$ values of the 2-, 3- and 4-picoline adducts of