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The Crystal and Molecular Structure of Tetra-μ-hydrido-decacarbonylbis(triphenylphosphine)-*tetrahedro*-tetraruthenium, $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$

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Abstract

Tetra-μ-hydrido-decacarbonylbis(triphenylphosphine)-*tetrahedro*-tetraruthenium, $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$, crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions a = 15·924 (3), b = 17·909 (3), c = 17·924 (6) Å and β = 112·07 (1)° The nucleus of the molecule is a tetrahedral ruthenium cluster with mean Ru—Ru bond lengths of 2·775 and 2·972 Å for two shorter and four longer Ru—Ru edges, respectively. The ten carbonyl and two triphenylphosphine groups are joined to the Ru atoms in groups of three ligands with mean bond lengths of Ru—P = 2·360 and Ru—C = 1·910 Å. The molecule possesses a non-crystallographic twofold axis crossing the midpoints of the two shorter Ru—Ru bonds which are opposite edges of the Ru tetrahedron. The four longer Ru—Ru bonds, due to μ_2-hydrogen bridging, are lengthened in accordance with other reported ruthenium hydridocarbonyls.

Introduction

Ruthenium hydrides of the type $H_4Ru_4(CO)_xL_y$ ($x + y = 12$, L = PPh_3; PBu_3) were found to be useful as hydrogenation and hydroformylation catalysts. The catalytic activity and thermal stability of these clusters varies with the number of triaryl- and trialkylphosphine substituents. For interpretation of the catalytic behaviour it seemed reasonable to determine the structure of the title compound, $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ (TDTTRU). The preparation of this material was reported earlier (Piacenti, Bianchi, Frediani & Benedetti, 1971).

Experimental

The crystals for X-ray diffraction were crystallized from a solution in a CH_2Cl_2/pentane mixture. Prior to crystallization purification was carried out by thin-layer chromatography. The deep-violet crystals are stubby in thinner or thicker plate form, very brittle and more or less twinned. For data collection the best crystal collected from a series of twinned crystals was used.

The crystal data are: a = 15·924 (3), b = 17·909 (3), c = 17·924 (6) Å and β = 112·07 (1)°, V = 4737·17 Å^3, $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$, M_r = 1213·0, $F(000)$ = 2384, D_m = 1·736, D_x = 1·700 Mg m^{-3}. $\lambda(\text{Mo } K\alpha_1)$ = 0·70926 Å, μ = 1·36 mm^{-1}, space group $P2_1/c$, Z = 4. The intensity data of 8959 independent reflections were collected on a Philips four-circle diffractometer with monochromatic Mo $K\alpha$ radiation. From the total 2851 reflections, those with $I < 2\sigma(I)$ were taken as unobserved. To save diffractometer time, the data collection was stopped at an early stage (maximum indices HM = 21, KM = 25 and LM = 12). The cell

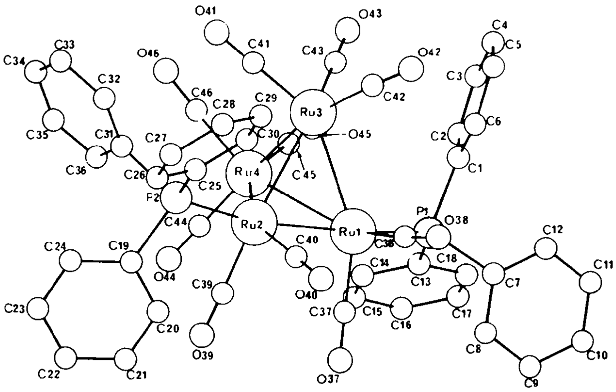

Fig. 1. Perspective view of the molecule with identification of the atoms.

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dimensions and their e.s.d.'s were calculated from diffractometer data of 30 reflections and refined by a least-squares method. The space group was determined from systematic absences. Though among the $h0l$ reflections there were a few with $l = 2n + 1$ for which the measured intensities were not definitely zero, the space group could later on be proved to be $P2_1/c$. After Lorentz–polarization correction the absolute scale and approximate isotropic temperature factor ($B = 3{\cdot}72$ Å^2) were determined by a Wilson plot using the complete reflection data set. No absorption correction was made.

Determination and refinement of the structure

The phase problem was solved by direct methods using the *MULTAN* 77 program (Main, Woolfson, Lessinger, Germain & Declercq, 1977). For the calculation of the normalized structure amplitudes the molecular scattering factors of different atomic groups with their expected geometry were used instead of the atomic scattering factors (Main, 1976). The K curve (Karle, Hauptman & Christ, 1958) was used for scaling structure factors to obtain E values. The first E map showed the four Ru atoms, the two P atoms and the C atoms in three of the phenyl rings. The remaining atoms were obtained from difference Fourier maps after least-squares refinement of the heavy atoms. The last atoms to appear belonged to the carbonyl groups associated with the Ru atoms.

The atomic parameters were refined by an anisotropic least-squares technique using the *SHELX* 76 program (Sheldrick, 1976). In this procedure the phenyl rings were treated as rigid groups with C—C bond lengths of 1·395 Å and bond angles of 120·0°. The H atoms belonging to the phenyl rings were geometrically generated at the end of the refinement of the non-hydrogen atoms. The probable locations of the four ligand H atoms belonging to the Ru atoms are discussed later. The final R was 0·084 for all reflections. The final atomic coordinates of the non-hydrogen atoms are given in Table 1.* The atomic scattering factors were calculated with the constants of Cromer & Mann (1968).

Discussion

The perspective view of the molecule with atomic numbering is given in Fig. 1. Bond lengths and angles of the molecule are summarized in Tables 2 and 3.

Table 1. *Final fractional coordinates* ($\times 10^4$) *for the non-hydrogen atoms*

Estimated standard deviations are in parentheses.

	x	y	z
Ru(1)	8949 (1)	7163 (1)	3064 (1)
Ru(2)	7073 (1)	7269 (1)	2424 (1)
Ru(3)	8150 (1)	8679 (1)	2828 (1)
Ru(4)	8066 (1)	7894 (1)	1467 (1)
P(1)	10538 (2)	7171 (2)	3453 (2)
P(2)	5519 (2)	7568 (2)	1971 (2)
C(37)	8839 (8)	6101 (7)	2965 (9)
O(37)	8787 (8)	5483 (6)	2930 (8)
C(38)	9055 (8)	7106 (9)	4178 (12)
O(38)	9148 (9)	7090 (10)	4819 (8)
C(39)	6880 (8)	6333 (8)	1874 (9)
O(39)	6761 (8)	5793 (6)	1525 (8)
C(40)	7074 (8)	6817 (8)	3391 (11)
O(40)	7058 (8)	6532 (8)	3943 (8)
C(41)	7146 (8)	9330 (8)	2295 (9)
O(41)	6542 (6)	9699 (6)	1989 (7)
C(42)	8452 (9)	9053 (8)	3929 (11)
O(42)	8668 (9)	9266 (7)	4541 (7)
C(43)	8966 (8)	9340 (7)	2620 (9)
O(43)	9432 (7)	9750 (6)	2479 (7)
C(44)	7791 (8)	7189 (9)	578 (9)
O(44)	7599 (8)	6786 (7)	65 (7)
C(45)	9170 (9)	8295 (8)	1415 (8)
O(45)	9814 (6)	8521 (7)	1394 (7)
C(46)	7385 (9)	8720 (9)	827 (9)
O(46)	7016 (8)	9208 (6)	452 (7)
C(1)	11018 (5)	8131 (4)	3669 (5)
C(2)	11518 (5)	8441 (4)	3252 (5)
C(3)	11803 (5)	9182 (4)	3386 (5)
C(4)	11588 (5)	9614 (4)	3938 (5)
C(5)	11089 (5)	9305 (4)	4355 (5)
C(6)	10804 (5)	8563 (4)	4221 (5)
C(7)	11108 (6)	6632 (5)	4392 (4)
C(8)	10954 (6)	5864 (5)	4359 (4)
C(9)	11317 (6)	5433 (5)	5056 (4)
C(10)	11835 (6)	5771 (5)	5785 (4)
C(11)	11990 (6)	6539 (5)	5818 (4)
C(12)	11626 (6)	6970 (5)	5122 (4)
C(13)	11040 (5)	6754 (5)	2765 (5)
C(14)	10500 (5)	6596 (5)	1965 (5)
C(15)	10891 (5)	6307 (5)	1449 (5)
C(16)	11822 (5)	6178 (5)	1731 (5)
C(17)	12362 (5)	6336 (5)	2530 (5)
C(18)	11971 (5)	6624 (5)	3047 (5)
C(19)	4758 (5)	6742 (4)	1594 (5)
C(20)	4941 (5)	6103 (4)	2073 (5)
C(21)	4392 (5)	5473 (4)	1816 (5)
C(22)	3661 (5)	5482 (4)	1079 (5)
C(23)	3478 (5)	6121 (4)	600 (5)
C(24)	4027 (5)	6751 (4)	857 (5)
C(25)	5116 (5)	7942 (5)	2741 (5)
C(26)	4214 (5)	7841 (5)	2651 (5)
C(27)	3900 (5)	8142 (5)	3215 (5)
C(28)	4487 (5)	8544 (5)	3870 (5)
C(29)	5389 (5)	8646 (5)	3960 (5)
C(30)	5703 (5)	8344 (5)	3395 (5)
C(31)	5060 (6)	8238 (5)	1124 (6)
C(32)	4539 (6)	8851 (5)	1168 (6)
C(33)	4174 (6)	9326 (5)	508 (6)
C(34)	4329 (6)	9189 (5)	−196 (6)
C(35)	4850 (6)	8576 (5)	−239 (6)
C(36)	5215 (6)	8101 (5)	420 (6)

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* Lists of structure factors, hydrogen-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33882 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The nucleus of the molecule is a tetrahedral Ru cluster. The ten carbonyl and two triphenylphosphine groups are joined to the Ru atoms in groups of three ligands. The tetrahedron is built up of two shorter Ru(1)–Ru(2) and Ru(3)–Ru(4) and four longer edges with mean Ru—Ru bond lengths of 2·775 and 2·965 Å and maximum deviations of 0·002 and 0·016 Å, respectively. These are in agreement with those published some years ago for other ruthenium hydridocarbonyls, *e.g.* $HRu_3(CO)_9(C_{12}H_{15})$ (Cox & Woodward, 1971) where the Ru atoms form a triangle with Ru—Ru bond lengths of 2·775, 2·779 and 2·929 Å, or $H_2FeRu_3(CO)_{13}$ (Gilmore & Woodward, 1971), where the Fe atom combines with the Ru triangle to form a tetrahedron in which Ru—Ru bond lengths are 2·777, 2·885 and 2·912 Å. The two shorter Ru—Ru bond lengths of the title molecule (2·776 and 2·773 Å) are the normal ones known from the literature but the other four are considerably lengthened (Table 2), and in accordance with the two cited cases there are as many lengthened Ru—Ru bonds as hydrido ligands.

The location of the hydrido ligands cannot be determined from the difference electron density. It can, however, be shown that in the molecule the criteria of μ_2-hydrido bridging of metal—metal bonds (Churchill, Bird, Kaesz, Bau & Fontal, 1968; Churchill, Wormald, Knight & Mays, 1970; Churchill, De Boer & Rotella, 1976) are satisfied, namely that to each lengthened Ru—Ru bond belongs one hydrido ligand and the angles bordering these lengthened bonds are significantly larger than 90° (Table 3). Thus similarly to the molecules cited above, the lengthened Ru—Ru bonds are μ_2-hydrido bridged, which lengthens the bond and pushes apart the ligands at the end of the same bond. In this way the expected orthogonality of the ligands is distorted.

Table 2. *Bond lengths* (Å) *with their estimated standard deviations in parentheses*

Bond lengths in phenyl rings are fixed at 1·395 Å.

Ru(1)–Ru(2)	2·776 (1)	C(37)–O(37)	1·110 (17)
Ru(1)–Ru(3)	2·960 (1)	C(38)–O(38)	1·102 (26)
Ru(1)–Ru(4)	2·976 (1)	C(39)–O(39)	1·129 (19)
Ru(2)–Ru(3)	2·985 (1)	C(40)–O(40)	1·122 (24)
Ru(2)–Ru(4)	2·955 (2)	C(41)–O(41)	1·127 (15)
Ru(3)–Ru(4)	2·773 (2)	C(42)–O(42)	1·088 (22)
Ru(1)–P(1)	2·358 (3)	C(43)–O(43)	1·139 (19)
Ru(2)–P(2)	2·358 (3)	C(44)–O(44)	1·117 (20)
Ru(1)–C(37)	1·912 (13)	C(45)–O(45)	1·116 (19)
Ru(1)–C(38)	1·943 (22)	C(46)–O(46)	1·125 (18)
Ru(2)–C(39)	1·909 (15)	P(1)–C(1)	1·862 (9)
Ru(2)–C(40)	1·912 (19)	P(1)–C(7)	1·855 (9)
Ru(3)–C(41)	1·918 (12)	P(1)–C(13)	1·861 (9)
Ru(3)–C(42)	1·966 (18)	P(2)–C(19)	1·870 (9)
Ru(3)–C(43)	1·895 (15)	P(2)–C(25)	1·853 (9)
Ru(4)–C(44)	1·950 (15)	P(2)–C(31)	1·856 (10)
Ru(4)–C(45)	1·934 (15)		
Ru(4)–C(46)	1·935 (15)		

The ligands of the Ru atoms are distributed in such a way that the two shorter edges have identical ligands on their ends; namely Ru(1) and Ru(2) each possesses two carbonyls and one triphenylphosphine while at Ru(3) and Ru(4) the ligands are all carbonyls. With this arrangement the molecule approximately has a twofold axis of symmetry crossing the midpoints of the two shorter edges of the tetrahedron (Fig. 2). This symmetry is, however, a little distorted because intra- and intermolecular forces result in different inclination angles of the phenyl rings in the two triphenylphosphine groups. In each of these groups the P atom is coplanar with each phenyl ring with maximum deviations of 0·001, 0·019 and 0·021 Å, respectively. The dihedral angles of the phenyl rings are in the ranges of 61·0–79·1° and 74·4–84·5° for the two triphenylphosphine groups with P(1) and P(2), respectively.

Table 3. *Bond angles* (°), *with their estimated standard deviations in parentheses*

In rigid phenyl rings the bond angles are taken as 120·0°.

Ru(2)–Ru(1)–Ru(3)	62·6 (1)	Ru(3)–Ru(4)–C(46)	88·0 (5)
Ru(2)–Ru(1)–Ru(4)	61·7 (1)	Ru(1)–C(37)–O(37)	178·1 (13)
Ru(3)–Ru(1)–Ru(4)	55·7 (1)	Ru(1)–C(38)–O(38)	177·0 (14)
Ru(1)–Ru(2)–Ru(3)	61·7 (1)	Ru(2)–C(39)–O(39)	177·5 (15)
Ru(1)–Ru(2)–Ru(4)	62·5 (1)	Ru(2)–C(40)–O(40)	177·6 (13)
Ru(3)–Ru(2)–Ru(4)	55·7 (1)	Ru(3)–C(41)–O(41)	178·0 (14)
Ru(1)–Ru(3)–Ru(2)	55·7 (1)	Ru(3)–C(42)–O(42)	175·9 (16)
Ru(1)–Ru(3)–Ru(4)	62·5 (1)	Ru(3)–C(43)–O(43)	177·7 (10)
Ru(2)–Ru(3)–Ru(4)	61·6 (1)	Ru(4)–C(44)–O(44)	177·2 (12)
Ru(1)–Ru(4)–Ru(2)	55·8 (1)	Ru(4)–C(45)–O(45)	179·1 (12)
Ru(1)–Ru(4)–Ru(3)	61·8 (1)	Ru(4)–C(46)–O(46)	177·7 (15)
Ru(2)–Ru(4)–Ru(3)	62·7 (1)	Ru(1)–P(1)–C(1)	112·2 (4)
Ru(2)–Ru(1)–P(1)	172·1 (1)	Ru(1)–P(1)–C(7)	111·7 (3)
Ru(3)–Ru(1)–P(1)	113·1 (1)	Ru(1)–P(1)–C(13)	118·8 (3)
Ru(4)–Ru(1)–P(1)	110·4 (1)	Ru(2)–P(2)–C(19)	113·5 (4)
Ru(2)–Ru(1)–C(37)	89·0 (4)	Ru(2)–P(2)–C(25)	116·0 (3)
Ru(3)–Ru(1)–C(37)	151·6 (4)	Ru(2)–P(2)–C(31)	117·9 (3)
Ru(4)–Ru(1)–C(37)	110·8 (4)	P(1)–Ru(1)–C(37)	94·8 (4)
Ru(2)–Ru(1)–C(38)	95·3 (4)	P(1)–Ru(1)–C(38)	91·5 (4)
Ru(3)–Ru(1)–C(38)	93·6 (5)	C(37)–Ru(1)–C(38)	90·7 (7)
Ru(4)–Ru(1)–C(38)	147·0 (4)	P(2)–Ru(2)–C(39)	94·4 (4)
Ru(1)–Ru(2)–P(2)	170·2 (1)	P(2)–Ru(2)–C(40)	93·0 (4)
Ru(3)–Ru(2)–P(2)	108·9 (1)	C(39)–Ru(2)–C(40)	92·4 (7)
Ru(4)–Ru(2)–P(2)	115·8 (1)	C(41)–Ru(3)–C(42)	97·8 (6)
Ru(1)–Ru(2)–C(39)	95·3 (4)	C(41)–Ru(3)–C(43)	91·5 (6)
Ru(3)–Ru(2)–C(39)	146·5 (5)	C(42)–Ru(3)–C(43)	93·2 (7)
Ru(4)–Ru(2)–C(39)	92·9 (5)	C(44)–Ru(4)–C(45)	97·4 (6)
Ru(1)–Ru(2)–C(40)	87·8 (4)	C(44)–Ru(4)–C(46)	96·1 (6)
Ru(3)–Ru(2)–C(40)	109·5 (4)	C(45)–Ru(4)–C(46)	90·3 (6)
Ru(4)–Ru(2)–C(40)	150·2 (4)	C(1)–P(1)–C(7)	105·6 (6)
Ru(1)–Ru(3)–C(41)	149·5 (4)	C(1)–P(1)–C(13)	105·3 (6)
Ru(2)–Ru(3)–C(41)	95·6 (4)	C(7)–P(1)–C(13)	102·0 (6)
Ru(4)–Ru(3)–C(41)	96·5 (5)	C(19)–P(2)–C(25)	101·3 (7)
Ru(1)–Ru(3)–C(42)	103·9 (4)	C(19)–P(2)–C(31)	102·3 (6)
Ru(2)–Ru(3)–C(42)	115·7 (5)	C(25)–P(2)–C(31)	103·6 (7)
Ru(4)–Ru(3)–C(42)	165·6 (4)	P(1)–C(1)–C(2)	121·9 (6)
Ru(1)–Ru(3)–C(43)	108·2 (4)	P(1)–C(1)–C(6)	118·0 (6)
Ru(2)–Ru(3)–C(43)	148·8 (5)	P(1)–C(7)–C(8)	117·2 (6)
Ru(4)–Ru(3)–C(43)	87·4 (5)	P(1)–C(7)–C(12)	122·7 (6)
Ru(1)–Ru(4)–C(44)	112·4 (4)	P(1)–C(13)–C(14)	120·7 (6)
Ru(2)–Ru(4)–C(44)	103·0 (5)	P(1)–C(13)–C(18)	119·3 (6)
Ru(3)–Ru(4)–C(44)	165·6 (5)	P(2)–C(19)–C(20)	118·0 (6)
Ru(1)–Ru(4)–C(45)	95·7 (4)	P(2)–C(19)–C(24)	122·0 (6)
Ru(2)–Ru(4)–C(45)	149·7 (4)	P(2)–C(25)–C(26)	119·8 (6)
Ru(3)–Ru(4)–C(45)	96·3 (4)	P(2)–C(25)–C(30)	120·2 (6)
Ru(1)–Ru(4)–C(46)	149·7 (5)	P(2)–C(31)–C(32)	121·5 (6)
Ru(2)–Ru(4)–C(46)	109·3 (5)	P(2)–C(31)–C(36)	118·5 (6)

The lengthening of four Ru—Ru bonds causes deformation of the Ru tetrahedron and consequently the dihedral angles of the tetrahedron planes all differ from the ideal 70·5° and vary between 63·8 and 74·7°, but dihedral angles at opposite edges are equal within 0·2°.

At the shorter Ru(1)—Ru(2) bond of the tetrahedron the P(1)—Ru(1)—Ru(2) and Ru(1)—Ru(2)—P(2) angles are 172·1 and 170·2°, respectively, with a torsion angle of −77·7°. All other Ru—Ru—P angles vary between 109·0 and 115·9°. At the Ru(3)—Ru(4) short edge the C(42)—Ru(3)—Ru(4) and Ru(3)—Ru(4)—C(43) angles are both 165·6° with a torsion angle of 88·9°. The other Ru—Ru—C angles are either between 87·3 and 96·5° or alternatively between 109·5 and 151·8° (Table 3).

The mean length of the Ru—C bonds is 1·927 Å with a maximum deviation of 0·039 Å. This is in the range of bond lengths reported for the two compounds cited above (HRu_3 and H_2FeRu_3 complexes) for which the Ru—C bond lengths range between 1·79–2·00 Å and 1·71–1·99 Å, respectively. The two Ru—P bonds were found to be equal and their magnitude of 2·358 Å fits well in the range of reported values. The nearest to the present Ru—P bond length are those (2·337 and 2·353 Å) found in $Ru(NO)_2P(C_6H_5)_3.\frac{1}{2}C_6H_6$ (Gaughan, Corden, Eisenberg & Ibers, 1974).

The mean C=O bond length in the carbonyl groups is 1·118 Å with a maximum deviation of 0·030 Å. This is considerably shorter than in the cited HRu_3 and H_2FeRu_3 complexes (1·17 and 1·18 Å, respectively).

The P—C bonds with mean length of 1·860 Å and maximum deviation of 0·010 Å are somewhat longer than those reported for $Ru(NO)_2(PPh_3)_2.\frac{1}{2}C_6H_6$ (Gaughan *et al.*, 1974) with a mean value of 1·829 Å.

The mean Ru—P—C angles involved with P(1) and P(2) are 114·2 and 115·8°, respectively, *i.e.* significantly larger than the tetrahedral angle. Correspondingly, the mean C—P—C angles are smaller (104·3 and 102·4°, respectively) and are in agreement with those reported for the two phenylphosphine groups in $Ru(NO)_2(PPh_3)_2.\frac{1}{2}C_6H_6$ (Gaughan *et al.*, 1974) with mean values of 104·4 and 103·3°, respectively. The same agreement also holds for the Ru—P—C angles.

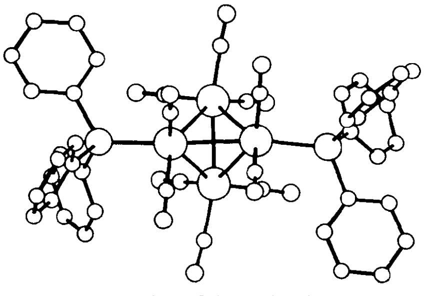

Fig. 2. Orthogonal projection of the molecule down the direction of the pseudo-twofold axis of the molecule crossing the midpoints of the two shorter edges of the Ru tetrahedron.

The mean value of the Ru—C—O angles is 177·5° with a maximum deviation of 1·6° and agrees with those Ru—C—O angles reported for the two independent molecules in the crystal structure of $HRu_3(CO)_{10}$-$(C{=}CH_3)_2$ which vary between 175·1 and 179·6° (Churchill, De Boer & Rotella, 1976).

The spatial packing of the molecules in the crystal structure conforms to the molecular close packing. The shortest intermolecular atomic distances, four for H—H, five for H—O and six for H—C, compare with the normal van der Waals distances.

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