Le cycle pyrannique est du type 'bateau croisé'. En effet, C(2) et C(5) sont situés du même côté du plan moyen P(B) défini par C(1), C(3), C(4) et O(6). Le premier en est éloigné de 0,40 (1) Å, le second de 0,62 (1) Å. En outre, les diagonales du quadrilatère C(1)C(3)C(4)O(6) se trouvent de part et d'autre de P(B) et les distances à ce plan des atomes qu'elles joignent sont de 0,11 (1) ou de 0,120 (7) Å, c'est-à-dire pratiquement égales. Les valeurs de ΔC_s relatives à deux plans passant, l'un par C(2), l'autre par le milieu de C(3)—C(4), sont respectivement de 29,5 et de 29,7°. Elles traduisent l'écart entre la conformation observée et la conformation bateau idéale.

Dans le cycle C, les symétries dominantes sont la symétrie par rapport à un plan passant par C(14) $(\Delta C_s^{14} = 11,4^\circ)$, ou par O(12) $(\Delta C_s^{12} = 16,2^\circ)$, et la symétrie par rapport à un axe binaire issu de C(4) $(\Delta C_2^4 = 3,4^\circ)$. C(3), C(4), O(12) et O(13) sont situés approximativement dans un même plan $(\chi^2 = 92)$. La distance de C(14) au plan moyen P(C) défini par ces quatre atomes est de 0,47 (1) Å. Ainsi, la forme de C peut être considérée comme intermédiaire entre la forme enveloppe et la forme demi-chaise.

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Structure of Tetraaquahexadecakis(2-pyridinecarboxylato)tetraneodymiumdibarium 11.6-Hydrate

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Abstract. $[Ba_2Nd_4(C_6H_4NO_2)_{16}(H_2O)_4].11\cdot 6H_2O$, $M_r = 3086\cdot3$, monoclinic, $P2_1/n$, $a = 15\cdot 495$ (7), $b = 20\cdot 296$ (12), $c = 19\cdot 309$ (11) Å, $\beta = 110\cdot 75$ (3)°, V = 5679 (6) Å³, Z = 2, $D_m = 1\cdot 81$, $D_x = 1\cdot 805$ (2) Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 2\cdot 61 \text{ mm}^{-1}$, F(000) = 3032, T = 300 (1) K, final R = 0.039 for 6227 reflections. The title compound is a centrosymmetric aggregate, with four Nd and two Ba cations. There are two modes of Nd coordination. Each Nd ion is surrounded by four N atoms and either by five carboxylic O atoms or by one water and four carboxylic O atoms. The environment of the Ba cation consists of one water and eight carboxylic O atoms.

Introduction. This work is part of our study of the structures and properties of complexes with lanthanide–nitrogen bonds.

Experimental. The title compound was prepared by adding 2-pyridinecarboxylic (α -picolinic) acid to a warm aqueous suspension of Ba(OH)₂ and freshly precipitated neodymium carbonate. After two days parallelepiped pink-violet crystals were formed. A specimen $0.3 \times 0.3 \times 0.25$ mm was cut from a larger crystal. D_m by flotation in C₂H₄Br₂/CHCl₃. Oscillation and Weissenberg photographs showed that the crystals belong to the monoclinic system, space group $P2_1/n$. Syntex $P2_1$ diffractometer, Mo K α radiation for lattice parameters (15 reflections, 21 < $2\theta < 26^{\circ}$), variable $\omega/2\theta$ scan, $4 < 2\theta < 50^{\circ}$, two standards every 50 reflections, slight decay (10% every ca 180 h of exposure) was detected, mean relative e.s.d. of the control reflections (after correcting for the decay) 2.5%, 7045 intensities measured, of which 6227 were unique with $I \ge 3\sigma(I)$, $R_{int} =$ 0.016, index range $h \to 18$, $k \to 24$, $l \to 22 \to 22$, no

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Table	1.	Final	atomic	coordi	nates	and	equivalent	iso-
tropic thermal U factors								

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

	X	V	Z	$U_{eq}(\mathbf{A}^{-})$
Ndl	0.46976 (4)	0.24155 (3)	0.93164 (3)	0.0288 (2)
Nd2	0.61001 (4)	0.47644 (3)	0.77314 (4)	0.0286 (2)
Po	0.61275 (4)	0.43402 (3)	0.08287 (3)	0.0268 (2)
Da	0.01273 (4)	0.43402 (3)	0.98287 (3)	0.0208 (2)
011	0.6167(5)	0.2982 (3)	0.9946 (3)	0.037(3)
O21	0.7502 (6)	0.3196 (4)	0.9813 (5)	0.063 (4)
012	0.4429 (5)	0.3559(3)	0.9584 (3)	0.036 (3)
022	0.3605 (6)	0.4358 (4)	0.9810 (4)	0.050 (4)
022	0.3003 (0)	0.4338 (4)	0.9810 (4)	0.039 (4)
013	0.7212 (5)	0.4781 (3)	0.9002 (3)	0.037(3)
O23	0.8634 (5)	0.4861 (5)	0.9848 (4)	0.065 (4)
014	0.4317(5)	0.1399 (3)	0.9811 (4)	0.047 (3)
014	0 40(1 (8)			0.097 (5)
024	0.4001 (8)	0.0771 (4)	1.0049 (3)	0.087 (2)
015	0.5822 (5)	0.5259 (3)	0.6522 (3)	0.036 (3)
025	0.5183 (6)	0.6106 (4)	0.5763 (4)	0.053 (3)
016	0.5346 (5)	0.5106 (3)	0.8576 (3)	0.030 (3)
010	0 5540 (5)	0 5500 (4)		0.057(3)
026	0.4213 (5)	0.5500 (4)	0.8906 (4)	0.020 (2)
017	0.4150 (5)	0.1632 (3)	0.8314 (4)	0.020 (3)
027	0.3663 (6)	0.1364 (4)	0.7120 (4)	0.059 (4)
018	0.5709 (5)	0.3802 (3)	0.8340 (3)	0.038 (3)
010		0 3734 (3)	0 0 0 0 0 (0)	0 0 4 2 (2)
028	0.2412 (2)	0.2734(3)	0.9391 (3)	0.043 (3)
OW1	0.7880 (5)	0.4448 (4)	1.0888 (4)	0.022 (3)
OW2	0.7260 (6)	0.3944(5)	0.7583 (5)	0.067 (4)
0113	0.1193 (7)	0.0339 (5)	0.0270 (5)	0.086 (5)
011/1		0 1077 (8)	0 1202 (7)	0 1 20 (9)
0#4	0.2040 (10)	0.1077 (8)	0.1292 (7)	0.130 (8)
0W5	0.1134 (13)	0.4402 (6)	0.8244 (7)	0.181 (10)
OW6	0.4461 (9)	0.0106 (6)	0.8063 (7)	0.133 (8)
0#7	0.3573 (11)	0.1612(7)	0.3896 (8)	0.075 (5)*+
01/2	0.0100 (17)	0.4112 (12)	0.0088 (13)	0.118 (0)++
000	0.0109 (17)	0.4113 (12)	0.9088 (13)	0.110 (3) 1
01/9	0.5572 (23)	0.0042 (16)	1.0587 (18)	0.086 (10)*†
OW10	0.9260 (24)	0.3821 (16)	0.8336 (18)	0.039 (9)*†
0#/11	0.9170 (24)	0.3457 (17)	0.9668 (18)	0.040 (9)*†
NI	0.6212 (6)	0.1722 (4)	0.0593 (4)	0.033 (3)
IN I	0.0212 (0)	01/22 (4)	0.9383 (4)	0.033 (3)
N2	0-3135 (6)	0.2666 (4)	0.9516 (4)	0.037(3)
N3	0.7754 (6)	0.5308 (5)	0.7957 (5)	0.045 (4)
N4	0.5085 (7)	0.2349(4)	1.0795 (5)	0.044(4)
NS	0.6062 (6)	0.6060 (4)	0.7608 (4)	0.030 (3)
	0.0002 (0)	0.0000 (4)	0 7098 (4)	0.035(3)
N6	0.4301 (6)	0.5072(4)	0.7151 (4)	0.035(3)
N7	0.3449 (6)	0.2864 (5)	0.8014 (4)	0.046 (4)
N8	0.5333 (6)	0.3733 (4)	0.6869 (4)	0.037 (3)
CU	0.6247 (9)	0.1078 (6)	0.9483 (6)	0.051 (5)
CII	0 7062 (10)	0.0755 (6)	0.0513 (6)	0.054 (5)
C21	0.7062 (10)	0.0733 (0)	0.9313 (0)	0.034 (3)
C31	0.7828 (10)	0.1120 (6)	0.9600 (7)	0.057 (6)
C41	0.7773 (8)	0.1797 (6)	0.9677 (6)	0.049 (5)
C51	0.6952 (8)	0.2074 (5)	0.9670 (5)	0.036(4)
C41	0.6905 (9)	0.2806 (5)	0.0820 (5)	0.028 (4)
01	0.0093 (8)	0.2800 (3)	0.9830 (3)	0.038 (4)
C12	0-2464 (9)	0-2196 (7)	0.9460 (7)	0.028 (2)
C22	0.1641 (9)	0.2356 (7)	0.9501 (8)	0.059 (6)
C32	0.1459(10)	0.3003 (9)	0.9642 (8)	0.073 (7)
C42	0.2148 (0)	0.3491 (7)	0.0712 (7)	0.058 (5)
C42	0.2074(7)	0 2299 (6)	0 0 (45 (5)	0 0 0 0 (0)
C52	0.2974 (7)	0.3288 (5)	0.9645 (5)	0.037(4)
C62	0.3722 (8)	0.3780 (5)	0.9686 (5)	0.033 (4)
C13	0.8035 (9)	0.5584(7)	0.7430 (7)	0.062 (6)
C23	0.8918 (10)	0.5823 (7)	0.7583 (8)	0.062 (6)
C25		0 5323 (1)	0 0 0 0 0 0 0	0 002 (0)
033	0.9530 (9)	0.5777 (8)	0.8293 (8)	0.072 (0)
C43	0.9263 (9)	0.5498 (6)	0.8840 (7)	0.028 (2)
C53	0.8391 (8)	0.5286 (5)	0.8650 (5)	0.040 (4)
C63	0.8041 (8)	0.4930 (5)	0.9222 (6)	0.040 (4)
C05	0 5535 (0)	0 2702 (6)	1 1202 (6)	0 0 40 (5)
C14	0.3323 (9)	0.2793 (6)	1.1293 (0)	0.049 (3)
C24	0.5792 (10)	0.2691 (7)	1-2063 (6)	0.061 (6)
C34	0.5629 (11)	0.2118 (8)	1.2315 (6)	0.073 (6)
C44	0.5144 (10)	0.1622 (6)	1.1796 (6)	0.064 (6)
C54	0.4900 (9)	0.1772 (5)	1,1057 (6)	0.046 (5)
0.04	0.4899 (8)	0.1772 (3)		0.040 (5)
C04	0.4309 (9)	U·12/1 (3)	1.0421 (0)	0.024 (2)
C15	0.6370 (9)	0.6440 (6)	0.8312 (6)	0.022 (5)
C25	0.6603 (10)	0.7081 (6)	0.8281(7)	0.062 (6)
C35	0.6468 (12)	0.7370 (6)	0.7598 (9)	0.081 (7)
0.0	0 (000 (12)	0 7000 (0)		0.05((5)
C45	0.0093 (10)	0.7000 (6)	0.6934 (6)	0.020 (2)
C55	0.5924 (8)	U·6341 (5)	U·7035 (5)	0∙041 (4)
C65	0.5614 (7)	0.5875 (5)	0.6385 (5)	0.037 (4)
C16	0.3761 (8)	0.5100 (6)	0.6431 (5)	0.043 (4)
C26	0.2878 (8)	0.5343 (6)	0.6170 (6)	0.048 (5)
C20	0 20/0 (0)	0 5597 (0)		
C36	0.2007 (8)	0.224/ (0)	0.0001 (0)	0.022 (2)
C46	0.3037 (8)	0.5583 (5)	0.7411 (6)	0.042 (4)
C56	0.3909 (7)	0.5339 (5)	0.7628 (5)	0.032 (4)
C66	0.4534 (7)	0.5317 (5)	0.8441 (5)	0.032 (4)
C17	0.3007 (0)	0.3460 (6)	0.7854 (6)	0.056 (5)
017	0 3077 (7)	0 3407 (0)	0 70 74 (0)	0.000(0)
C27	U·2647 (9)	0.3097(7)	U·/148 (/)	0.002 (2)
C37	0.2539 (10)	0.3278 (7)	0.6576 (6)	0.069 (6)
C47	0.2881 (9)	0.2651 (7)	0.6705 (6)	0.057 (5)
C57	0.3360 (8)	0.2447 (5)	0.7449 (5)	0.041 (4)
	0 3300 (0)	0.17(0.(0)	0 7477 (3)	0.047 (4)
C6/	0.3/40 (8)	U·1/09 (0)	0.1072 (0)	0.04/(2)
C18	0-5193 (8)	0.3676 (6)	0.6149 (6)	0.046 (5)
C28	0.5148 (9)	0.3111 (6)	0.5791 (6)	0.054 (5)
	. /			

Table 1 (cont.)

	x	У	Z	$U_{\rm eq}({\rm \AA}^2)$
C38	0.5213 (10)	0.2507 (7)	0.6171 (6)	0.066 (6)
C48	0.5314 (10)	0.2559 (6)	0.6925 (6)	0.057 (5)
C58	0.5388 (7)	0.3179 (5)	0.7250 (5)	0.033 (4)
C68	0.5530 (7)	0.3249 (5)	0.8062 (5)	0.033 (4)

* Site occupancy factors: OW7 0.6; OW8 0.5; OW9 0.3; OW10 0.2; OW11 0.2.

† Refined isotropically, U_{iso} given.

correction for absorption or extinction. Structure was solved and refined with a locally modified version of SHELX76 (Sheldrick, 1976). Neutralatom scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV), real and imaginary components for anomalous dispersion included for all non-H atoms. The Nd atoms were located from a Patterson map; the remaining non-H atoms from subsequent difference syntheses; some hydrate molecules appeared to be disordered, their occupancy factors were chosen on the basis of the peak heights in a difference synthesis; C-bonded hydrogens placed geometrically, water hydrogens from difference syntheses, not all found. Final fullmatrix least-squares refinement based on F (non-H atoms anisotropic, disordered water oxygens isotropic, hydrogens isotropic with constrained positional parameters and common temperature factors, separately for C-bonded and water hydrogens, the constraints refined as additional parameters), R =0.0390, wR = 0.0378, the maximum shift/e.s.d. ratio 0.35, $\Delta \rho$ between -0.75 and 1.30 e Å⁻³, the highest peaks around Nd and Ba atoms, $w = 1/\sigma^2(F)$.

Discussion. Final atomic parameters are given in Table 1,* and the geometry of the coordination environment of the Nd and Ba ions is shown in Table 2, together with average bond lengths for the α -picolinate residues.

The complex molecule is an oligonuclear centrosymmetric aggregate built around four neodymium and two barium cations. The *ORTEP* view (Johnson, 1976) of the complex molecule is given in Fig. 1. All bond lengths are unexceptional (Sinha, 1976). The coordination figure of Nd1 may best be described as a tricapped trigonal prism with O12, N4, N2 and O28, N1, O17 forming the bases and O11, O14, N7 forming the caps. The Δ parameter is 0.067 Å² ($\Delta = \sum d_i^2/9$, d_i is the distance between the real position of the *i*th atom, and the relevant vertex in the ideal, least-squares-fitted polyhedron; Drew, 1977). The

^{*} Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bond details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53276 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (Å) and angles (°) for the Nd coordination spheres, the Ba—O and metal-metal distances and average bond lengths in the α -picolinate moieties

	2 45 4 17	2110		
NaI-OII	2.434 (7)	Nd2-(213 2	. 448 (6)
	2.445 (6)		015 2	·436 (6)
014	2.432 (7)	_)16 2	420 (7)
-017	2.415 (7)		110	462 (6)
017	2 415 (7)	_	2	.403 (0)
-028	2.208 (7)	(JW2 2	.540 (10)
-NI	2.626 (9)	í í	√ 3 2	.680 (10)
—N2	2.633 (10	1 — ((JS 7	630 (8)
NA	2 000 (10	″ .		
-144	2.103 (9)	-1	NO 2	:084 (9)
— N 7	2.729 (8)	<u>۱</u> —۲	√8 2	.·677 (8)
Ba — 011	2.765 (6)	Ba — ()21 3	158 (9)
	2.064 1		1001 0	777 (9)
012	2 204 (7)			727 (8)
-013	2.841 (7)	-0	2016	-767 (6)
O26'	2.696 (8)	-0	2 2 2	.925 (6)
-01/1	2.769 (8)			.,
Nd1 Nd2	£ 444 (4)	D- 114		407 (2)
Nu1—Nu2	0.444 (4)	Da-INC	. 4	•427 (3)
BaNd2	4.126 (3)	BaBa	4	·632 (3)
O12-Nd1-011	69-4 (3)			
014-Nd1-011	121.0 (3)	014N	Id1—012 1	29.7 (3)
017-N41-011	125.0 (2)	017 1		20 2 (2)
	155.0 (5)	01/	ai—012 i	39.2 (3)
01/Nd1014	72-0 (3)			
O28-Nd1-011	70.4 (3)	O28—N	d1-012	93.4 (3)
028-Nd1-014	136.9 (3)	028N	Jd1-017	73.5 (3)
NI NAL OU	(20)	020 I		75.5 (5)
	03.0 (3)	NI-N	1-012 1	32.4 (3)
NI-NdI-014	78-0 (3)	NI-No	d1—017	80.8 (3)
N1-Nd1-028	71.7 (3)			
N2-Nd1-011	125.2 (3)	N2N	41-012	63.4 (2)
No NAL OIA	751(3)	N2 N	11 012	03.4 (3)
N2-N01-014	/3.1 (3)	N2N0		99·3 (3)
N2-Nd1-028	136-0 (3)	N2—No	d1—N1 1	51.5 (3)
N4-Nd1-011	71.4 (3)	N4—No	d1—012	79.3 (3)
N4-Nd1-014	62.4 (3)	N4-N	11-017 1	34.2 (3)
N4-Nd1 028	141.2 (2)	NA NI		95 2 (3)
N4Nu1-026	141.2 (3)	IN4-INC	11—141	82.2 (3)
N4N01N2	/4·1 (3)			
N7—Nd1—O11	122-1 (3)	N7—N6	d1—O12	76.1 (3)
N7-Nd1-014	117.0 (3)	N7N	11-017	63.1 (3)
N7 Nd1 029	66.7 (2)	N7 N		20 7 (3)
N/-Nu1-028	00.7 (3)	IN/—INC	11—NI I	30.7 (3)
N7—Nd1—N2	71.5 (3)			
N7—Nd1—N4	144-0 (3)			
015-Nd2-013	141.1 (3)			
016 Nd2 012	70.0 (2)	016		24.4.(2)
016-Na2-013	/0.0 (3)	010-1	102-015 1	24.4 (3)
O18Nd2O13	74.8 (3)	018—N	Id2—O15 1	42.6 (3)
O18-Nd2-O16	69-3 (3)			
OW2-Nd2-013	81.2 (3)	0#2-	Nd2-015	03.1 (3)
0.12 1.02 0.15	0.2(3)	0	1112 015)) I ())
OW2-Nd2-016	142.6 (3)	OW2-	Nd2018	80.7 (3)
N3-Nd2-013	62.5 (3)	N3_N/	12-015	70.7 (3)
N2_Nd2_016	115 9 (3)		12 015	7977 (3)
N3-Nu2-010	113.8 (3)	N3—N0	12-018 1	29.2 (3)
N3—Nd2—OW2	67-3 (3)			
N5-Nd2-013	90.7 (3)	N5-N0	12-015	64.5 (3)
N5-Nd2-016	73.6 (3)	NS_N	12-018 1	47.0 (3)
NS NH2 OVO	121 ((2)			42.5 (3)
N3Nd2	131.0 (3)	N3N0	12—N3	66·7 (3)
N6-Nd2-013	132-3 (3)	N6No	12-015	72.5 (3)
N6-Nd2-016	62.4 (3)	N6Na	i2—018	89.4 (3)
N6-Nd2-0#2	141.0 (3)	N6N6	12N2 1	20.9 (2)
NG NIJO NG	75 2 (2)	140-140	1 113	JF 0 (J)
IND-INDZ-IND	13.3 (3)			
N8Nd2013	129-3 (3)	N8No	12-015	80-6 (3)
N8-Nd2-016	115.4 (3)	N8Nc	i2—O18	63.0 (3)
N8-Nd2-0W2	66.0 (3)	N8	12N3 1	27.7 (2)
NO NAD NE	120 0 (3)	140-140	1 1 1 1	211 (3)
No-Na2-NS	139.9 (3)			
N8Nd2N6	75-9 (3)	· ·		
	n . A	v. dist.	Min. value	Max. value
0C	16 1.	251 (22)	1.224 (13)	1.295 (12)
N_C	16	244 (21)	1 210 (15)	1 207 (12)
N-0	10 1.	JTT (21)	1.510 (15)	1.201 (11)
u,-u,	32 1.	301 (28)	1.218 (51)	1.431 (19)
CC.	8 1-	523 (26)	1.488 (16)	1.569 (16)

n = number of bonds; C_r = ring carbon; C_{carb} = carboxyl carbon.

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

best alternative description of the coordination polyhedron is in terms of a monocapped square antiprism with O11 as the cap, and O14, O17, N7, N2 and N1, O28, O12, N4, as the noncapped and capped bases, respectively: $\Delta = 0.082 \text{ Å}^2$. In both

cases there is no particular symmetry around the central ion. The coordination polyhedron of Nd2 may be described as a tricapped trigonal prism (O15, N5, N6 and OW2, O13, O18 being the bases; N3, O16, N8 being the caps) with $\Delta = 0.072 \text{ Å}^2$ and approximate $C_s(m)$ point symmetry; the alternative description as a monocapped square antiprism (O13, O16, N5, N3 forming the noncapped base, O18, N6, O15, OW2 forming the capped base and N8 being the cap) gives $\Delta = 0.110 \text{ Å}^2$ and imposes no symmetry on the cation site. The Ba coordination polyhedron is rather irregular: the best fitted figure was a tricapped trigonal prism with $\Delta = 0.516 \text{ Å}^2$. There are five modes of α -picolinate-metal interaction. Each acid residue coordinates to one of the Nd ions via its nitrogen and one of its carboxyl oxygens. These may be the only bonds to metal ions [mole-



Fig. 1. Molecular diagram of the complex molecule. The numbering patterns of the ring atoms in the residues (1) through (8) follow that for the residue (1).



Fig. 2. View of the crystal structure. The dashed lines represent the hydrogen bonds.

cules (4), (5) and (7)]; however, the carboxyl oxygen involved in the chelate ring may also be bonded to the barium cation [molecule (3)]; both carboxyl oxygens may be bonded to the same barium [molecule (1)], to two different bariums [molecules (2) and (6)], or to the barium and the other neodymium ion [molecule (8)]. There is a pair of intramolecular hydrogen bonds in the complex molecule (represented by dashed lines in Fig. 1). The structure is held together by an elaborate network of intermolecular hydrogen bonds. The crystal packing is shown in Fig. 2 (the disordered waters OW8, OW9, OW10 and OW11 have been omitted for the sake of clarity). The author thanks Professors K. Bukietyńska and T. Głowiak for helpful discussions, and Dr T. Lis for advice and help in performing the measurements. This work was supported by the Polish Academy of Sciences (project CPBP 01.12).

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Carbonyl(η^5 -cyclopentadienyl)bis(trimethyl phosphite)ruthenium(II) Tetrafluoroborate

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Abstract. [Ru(CO){P(OCH₃)₃}₂(C₅H₅)][BF₄], $M_r = 529 \cdot 13$, monoclinic, $P2_1/c$, $a = 11 \cdot 455$ (2), $b = 11 \cdot 648$ (4), $c = 15 \cdot 709$ (2) Å, $\beta = 99 \cdot 40$ (1)°, $V = 2067 \cdot 87$ Å³, Z = 4, $D_x = 1 \cdot 700$ g cm⁻³, Mo Ka radiation, $\lambda = 0 \cdot 7107$ Å, $\mu = 9 \cdot 577$ cm⁻¹, F(000) = 1064, T = 296 K, $R = 0 \cdot 039$ for 2941 observed reflections. The crystal structure of the title compound consists of discrete [Ru(CO){P(OMe)_3}₂(Cp)]⁺ cations and [BF₄]⁻ anions. The cation displays a typical 'three-legged piano stool' geometry about ruthenium with significant distances Ru—P1 2.258 (1), Ru—P2 2.260 (1), Ru—C1 1.880 (6), C1—O1 1.115 (6) Å, and angles Ru—C1—O1 176.9 (5), C1—Ru—P1 90.3 (2), C1—Ru—P2 89.8 (2) and P1—Ru—P2 92.2 (1)°.

Introduction. The $[\operatorname{Ru}(L)(\operatorname{PR}_3)_2(\operatorname{Cp})]$ system is extensively studied, particularly for $L = \operatorname{PPh}_3$ because the starting material $[\operatorname{RuCl}(\operatorname{PPh}_3)_2(\operatorname{Cp})]$ is easily synthesized and handled (Bruce, Hameister, Swincer, Wallis & Ittel, 1982) and both its chloride and phosphine ligands are substitutionally labile (Albers, Robinson & Singleton, 1987). We are interested in the chemistry of $[\operatorname{Ru}(L)(\operatorname{PR}_3)_2(\operatorname{Cp})]$ complexes with smaller ancillary phosphines such as trimethyl phosphite (Ashby, Bruce, Tomkins & Wallis, 1979; Bruce, Cifuentes, Snow & Tiekink, 1989; Treichel, Komar & Vincenti, 1984). We recently obtained single crystals of $[\operatorname{Ru}(\operatorname{CO})\{\operatorname{P}(\operatorname{OMe})_3\}_2(\operatorname{Cp})][\operatorname{BF4}]$

(I) during attempted slow recrystallization of $[Ru(C_2H_2){P(OMe)_3}_2(Cp)][BF_4]$, evidently via the oxidation of the C_2H_2 ligand by traces of air (Bruce, Swincer & Wallis, 1979). Compound (I) has not previously been reported.

Experimental. $[Ru(CO){P(OMe)_3}(Cp)][BF_4]$ (I) was prepared and crystallized by passing a stream of nitrogen gas saturated with diethyl ether over $[Ru(\eta^2-HC \equiv CH) \{P(OMe)_3\}_2(Cp)][BF_4]$ (Frank & Selegue, 1990) dissolved in a minimum of dichloromethane. A $0.42 \times 0.47 \times 0.53$ mm crystal suitable for X-ray diffraction was cut from one of the resulting large, pale vellow crystals. IR (CH₂Cl₂): ν (CO) 2022vs, $\nu(BF)$ 1094vs cm⁻¹. ¹H NMR (200 MHz, CDCl₃): $\delta_{\rm H} 4.43$ (t, ${}^{3}J_{\rm PH} = 1.0$ Hz, 5 H, Cp), 3.53 (virtual t, ${}^{3}J_{\rm PH} + {}^{5}J_{\rm PH} = 5.3$ Hz, 18 H, POCH₃). Data were measured with an Enraf-Nonius CAD-4 diffractometer controlled by a MicroVAX computer, graphite-monochromated Mo $K\alpha$ radiation; $\omega - 2\theta$ scan technique. Cell parameters were determined by least-squares refinement of 25 reflections ($6 < \theta <$ 16°). A total of 3989 reflections ($2 < \theta < 25^{\circ}$) were measured in the range $-13 \le h \le 13, 0 \le k \le 13, 0 \le$ $l \le 18$. Minor variation (max. 13%) was noted in the net intensities of three reference reflections $(13\overline{5}, 13\overline{7}, \overline{1}3\overline{3})$ measured every 5000 s. Of 3773 unique reflections, 2941 satisfied $I \ge 3\sigma(I)$. An empirical absorption correction was applied using

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