between non-hydrogen atoms up to 4·5 Å. The resulting plots were linear, with slopes near one and *y* intercepts near zero (Fig. 3*a*). These results indicate that the differences in the interatomic distances are normally distributed, and that there are no systematic differences in the ethyl sulfate ion geometry in any of the lanthanide ethyl sulfate structures studied. For this reason, the interatomic distances and angles for the ethyl sulfate ion listed in Table 5 are average values, determined from the results of all 14 structures. The standard deviations listed are those about the mean values. An analysis using distances for the ethyl sulfate ion at 171 K and at room temperature gave similar results (Fig. 3*b*), except that the slopes were near two, indicating a discrepancy in the standard deviations.

The distance and angle values given in Table 5 for the water molecules and the hydrogen bonds are average values determined from all 14 structures. Average values are reported here because (1) the H-atom parameters were the least well-determined parameters in the structures and (2) all individual values agreed with the corresponding mean values, according to the following distribution: 73% agreed with the mean value to within 1 standard deviation, 93% agreed within 2 standard deviations, and 98% agreed to within 3 standard deviations. A complete list of bond distances for all structures has been deposited along with the structure factors.

Although for the purposes of the present paper we have employed ionic radii of the lanthanides as given by Shannon (1976), the present data afford the possibility of an independent assignment of radii based on data from a single study of a series of salts of all the lanthanides (except Pm). An analysis of this matter is planned for a later paper.

The authors would like to thank Wilson H. De Camp for providing us with a copy of his probability-plot analysis program, on which ours was largely based, and Alan P. Lundstedt for the use of his plotting program *APLPLOT* II (Lundstedt, 1983). We would especially like to thank Dr Judith C. Gallucci, who gave us invaluable advice at every stage of this project. Computational facilities were provided by the Ohio State University IRCC.

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Structure of Tricarbonylbis(triphenylphosphine)ruthenium(0)–Tetrahydrofuran (2/1), $[Ru(CO)_3\{P(C_6H_5)_3\}_2].0{\cdot}5C_4H_8O$

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(*Received* 14 *October* 1983; *accepted* 27 *January* 1984)

Abstract. $M_r = 745$, monoclinic, $P2_1/c$, $a = 17{\cdot}845$ (2), $b = 12{\cdot}315$ (2), $c = 18{\cdot}351$ (3) Å, $\beta = 104{\cdot}55$ (1)°, $V = 3903{\cdot}5$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}27$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}51$ mm^{-1}, $F(000) = 1528$, $T = 293$ K. Final $R = 0{\cdot}045$ for 2894 observed reflections. Ru is fivefold coordinated, the three carbonyls being in the equatorial plane and the P atoms of the triphenylphosphines at the apices of a rather regular trigonal bipyramid, the preferred configuration for complexes in low oxidation states. The structure can be considered as $[Ru(CO)_3(PPh_3)_2]$ units with tetrahydrofuran molecules stabilizing the crystal packing.

0108-2701/84/050786-03$01.50

Introduction. During the course of our studies on the preparation of metal–metal bonded Mn–Ru complexes (Sabo, Chaudret & Gervais, 1984*a*), we investigated the reaction of [RuHCl(PPh$_3$)$_3$] on [NaMn(CO)$_5$]. A spectroscopic characterization of the reaction mixture showed it to be complicated (Sabo, Chaudret & Gervais, 1984*b*), but containing a significant amount of the Ru^0 complex [Ru(CO)$_3$(PPh$_3$)$_2$] (Collman & Roper, 1965) which could be separated by fractional crystallization. As the compound obtained was not isomorphous with [Os(CO)$_3$(PPh$_3$)$_2$] (Stalick & Ibers, 1969), the determination of its structure is reported here.

Experimental. Pale-yellow plate crystals obtained from a 2/1 tetrahydrofuran/hexane solution at 258 K; $0{\cdot}11 \times 0{\cdot}65 \times 0{\cdot}40$ mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, cell parameters from a least-squares fitting of the setting angles of 25 reflections with 2θ between 15 and 28°; a total of 3656 non-zero unique reflections measured using θ–2θ scans for 2θ from 3 to 45° ($h = 0$ to 19, $k = 0$ to 13, $l = -19$ to 19), scan range $0{\cdot}75° + 0{\cdot}35° \tan\theta$; intensities of three reflections (630, 152 and $20\bar{8}$) measured periodically during data collection varied less than 3% and thus indicated crystal stability; corrections for Lp but not for absorption; heavy-atom method followed by Fourier and least-squares techniques using 2894 reflections having $F_o > 20\sigma(F_o)$, $\sigma(F_o)$ based on counting statistics; full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, with anisotropic thermal parameters for Ru, P and CO atoms, isotropic rigid groups for phenyl rings (C–C = 1·395, C–H = 0·95 Å), $U_{\rm H} = 0{\cdot}075$ Å^2 kept fixed, THF (tetrahydrofuran) atoms refined isotropically with a multiplicity factor 0·5, THF H atoms not introduced; $R = 0{\cdot}045$, $R_w = 0{\cdot}058$; 174 variables; $w = 9{\cdot}88[\sigma^2(F_o) + 9{\cdot}2 \times 10^{-5}F_o^2]^{-1}$; $R = 0{\cdot}053$ for all data; mean and max. parameter shifts $0{\cdot}57\sigma$ and $1{\cdot}32\sigma$ respectively; max. and min. height in final ΔF map 0·90 and −0·39 e Å^{-3}; scattering factors including real and imaginary parts of anomalous dispersion from *International Tables for X-ray Crystallography* (1974) and from Stewart, Davidson & Simpson (1965) for H; DPS-8 computer; *SHELX76* (Sheldrick, 1976) and *ORFFE* (Busing, Martin & Levy, 1964) programs.

Discussion. The final positional and equivalent or isotropic thermal parameters are listed in Table 1.* The thermal ellipsoid plot of the [Ru(CO)$_3$(PPh$_3$)$_2$] molecule

Table 1. *Fractional atomic coordinates and isotropic or equivalent temperature factors* (Å^2 ×100) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\,\text{trace}\,\tilde{\mathbf{U}}.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Ru	0·21174 (3)	0·43958 (4)	0·50880 (3)	4·38 (4)
C(1)	0·3113 (5)	0·3900 (6)	0·5666 (5)	5·1 (5)
O(1)	0·3683 (4)	0·3645 (5)	0·5972 (4)	9·8 (5)
C(2)	0·1823 (6)	0·4762 (6)	0·4061 (6)	6·8 (6)
O(2)	0·1670 (5)	0·5010 (6)	0·3444 (4)	10·8 (5)
C(3)	0·1322 (5)	0·4539 (5)	0·5599 (4)	5·8 (5)
O(3)	0·0849 (4)	0·4618 (4)	0·5912 (4)	9·9 (5)
P(1)	0·17929 (10)	0·25933 (13)	0·47676 (10)	3·7 (1)
P(2)	0·24935 (9)	0·61970 (13)	0·53398 (9)	3·6 (1)
C(4)	0·1538 (2)	0·1743 (3)	0·5495 (1)	3·8 (2)
C(5)	0·1128 (2)	0·0778 (3)	0·5295 (1)	4·7 (2)
C(6)	0·0944 (2)	0·0129 (3)	0·5848 (1)	5·8 (2)
C(7)	0·1169 (2)	0·0445 (3)	0·6602 (1)	5·8 (2)
C(8)	0·1579 (2)	0·1409 (3)	0·6802 (1)	5·9 (2)
C(9)	0·1763 (2)	0·2058 (3)	0·6249 (1)	5·4 (2)
C(10)	0·2565 (3)	0·1815 (4)	0·4519 (2)	4·8 (2)
C(11)	0·2919 (3)	0·0933 (4)	0·4947 (2)	6·8 (2)
C(12)	0·3504 (3)	0·0361 (4)	0·4734 (2)	8·6 (3)
C(13)	0·3736 (3)	0·0670 (4)	0·4092 (2)	9·1 (3)
C(14)	0·3382 (3)	0·1551 (4)	0·3664 (2)	8·7 (3)
C(15)	0·2796 (3)	0·2124 (4)	0·3877 (2)	7·3 (2)
C(16)	0·0958 (2)	0·2395 (3)	0·3960 (2)	4·0 (2)
C(17)	0·0958 (2)	0·1650 (3)	0·3388 (2)	5·1 (2)
C(18)	0·0296 (2)	0·1512 (3)	0·2802 (2)	6·2 (2)
C(19)	−0·0367 (2)	0·2121 (3)	0·2787 (2)	6·2 (2)
C(20)	−0·0368 (2)	0·2866 (3)	0·3359 (2)	7·2 (2)
C(21)	0·0295 (2)	0·3004 (3)	0·3946 (2)	6·2 (2)
C(22)	0·2529 (3)	0·6714 (3)	0·6290 (3)	4·0 (2)
C(23)	0·2810 (3)	0·6038 (3)	0·6908 (3)	7·1 (2)
C(24)	0·2918 (3)	0·6446 (3)	0·7637 (3)	8·5 (3)
C(25)	0·2746 (3)	0·7529 (3)	0·7746 (3)	8·3 (3)
C(26)	0·2464 (3)	0·8205 (3)	0·7127 (3)	6·2 (2)
C(27)	0·2356 (3)	0·7797 (3)	0·6399 (3)	5·1 (2)
C(28)	0·3459 (3)	0·6553 (3)	0·5236 (2)	4·0 (2)
C(29)	0·3754 (3)	0·6011 (3)	0·4701 (2)	6·4 (2)
C(30)	0·4476 (3)	0·6298 (3)	0·4596 (2)	7·6 (3)
C(31)	0·4903 (3)	0·7128 (3)	0·5026 (2)	7·9 (2)
C(32)	0·4608 (3)	0·7670 (3)	0·5562 (2)	8·2 (3)
C(33)	0·3887 (3)	0·7383 (3)	0·5666 (2)	5·9 (2)
C(34)	0·1851 (1)	0·7181 (3)	0·4733 (2)	3·8 (2)
C(35)	0·2138 (1)	0·8035 (3)	0·4383 (2)	4·9 (2)
C(36)	0·1628 (1)	0·8768 (3)	0·3933 (2)	6·4 (2)
C(37)	0·0832 (1)	0·8646 (3)	0·3833 (2)	5·7 (2)
C(38)	0·0545 (1)	0·7792 (3)	0·4183 (2)	5·5 (2)
C(39)	0·1054 (1)	0·7059 (3)	0·4633 (2)	5·2 (2)
O(4)	0·4824 (8)	0·4952 (14)	0·1827 (9)	11·7 (5)
C(40)	0·4758 (14)	0·3866 (23)	0·1745 (14)	12·4 (8)
C(41)	0·4321 (14)	0·3523 (21)	0·2364 (15)	13·5 (9)
C(42)	0·4182 (14)	0·4473 (20)	0·2747 (14)	12·3 (8)
C(43)	0·4621 (15)	0·5363 (22)	0·2402 (17)	15·0 (9)

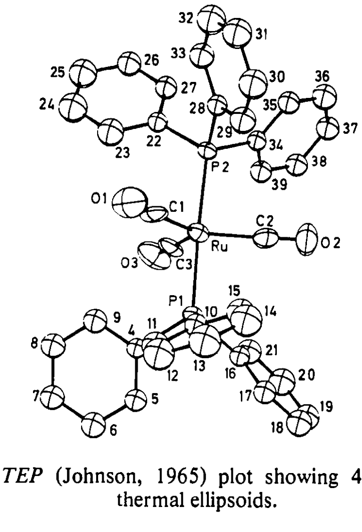

Fig. 1. *ORTEP* (Johnson, 1965) plot showing 40% probability thermal ellipsoids.

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, least-squares-planes' equations and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39226 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Johnson, 1965) is shown in Fig. 1 with the atomic numbering. The packing of the molecules in the unit cell is shown as a (100) projection in Fig. 2. Bond lengths and angles are listed in Table 2.

The $[Ru(CO)_3(PPh_3)_2]$ molecule has the trigonal-bipyramidal geometry with phosphine ligands at the apices. This configuration is preferred to tetragonal pyramidal or some intermediate form for complexes in low oxidation states (Raymond, Meek & Ibers, 1968; Favas & Kepert, 1980). The Ru—C distances are in the range of expected values (Churchill & De Boer, 1977) with Ru—C(1), 1·925 (8) Å, slightly longer than Ru—C(2), 1·880 (10) Å, and Ru—C(3), 1·895 (10) Å; and consequently C(1)—O(1), 1·079 (10) Å, is shorter than the other two C—O bonds, 1·138 (12) Å. Within the limits of error, Ru lies in the equatorial plane, —0·0012 (5) Å. The Ru environment can be compared to that of Os in $[Os(CO)_3(PPh_3)_2]$ (Stalick & Ibers, 1969) and to Fe in $[Fe(CO)_3\{P(OMe)_3\}_2]$ (Ginderow, 1974). The most noticeable difference is in the C—Ru—C angles. In the Os complex, the ideal 120° values are imposed by crystallographic symmetry and in the Fe complex the C—Fe—C angles are equal to 120° in the 3σ limits. In the Ru complex they have the significantly different values of 127·9 (4), 117·3 (4) and 114·7 (4)°.

The Ru—P distances, 2·332 (2) and 2·330 (2) Å do not differ and are similar to those generally found for second- and third-row transition-metal complexes containing phosphines. The P—C distances and C—P—C angles are within the ranges usually found for triphenylphosphine complexes. Phenyls are in nearly eclipsed positions. Along the P(1)—P(2) direction, the angles between phenyl pivots are 1·4° between C(4) and C(22), 2·2° between C(10) and C(22) and 2·4° between C(16) and C(34). Carbonyls are staggered from them with the respective values: 46·1° from C(10) and 48·3° from C(28) for C(1), 32·4° from C(16) and 34·6° from C(34) for C(2), 40·4° from C(4) and 41·8° from C(22) for C(3).

Intermolecular distances do not indicate any interaction stronger than normal van der Waals forces. The structure can therefore be considered as $[Ru(CO)_3(PPh_3)_2]$ units with THF molecules stabilizing the crystal packing.

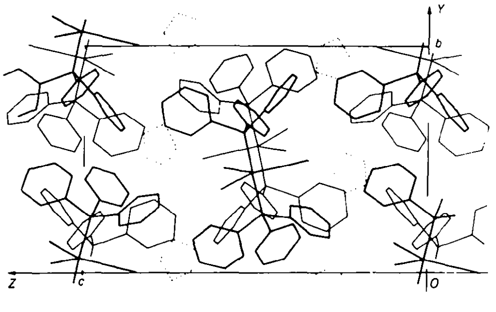

Fig. 2. A view of the unit-cell contents along the *x* axis. THF molecules are drawn with dotted lines.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ruthenium environment					
Ru–C(1)	1·925 (8)	C(1)–O(1)	1·079 (10)	Ru–C(1)–O(1)	177·3 (8)
Ru–C(2)	1·880 (10)	C(2)–O(2)	1·138 (12)	Ru–C(2)–O(2)	177·2 (8)
Ru–C(3)	1·895 (10)	C(3)–O(3)	1·138 (12)	Ru–C(3)–O(3)	179·3 (6)
		Ru–P(1)	2·332 (2)	Ru–P(2)	2·330 (2)
C(1)–Ru–C(2)	127·9 (4)	P(1)–Ru–C(3)	92·5 (2)		
C(1)–Ru–C(3)	117·3 (4)	P(2)–Ru–C(1)	90·7 (2)		
C(2)–Ru–C(3)	114·7 (4)	P(2)–Ru–C(2)	88·0 (2)		
P(1)–Ru–C(1)	88·5 (2)	P(2)–Ru–C(3)	91·6 (2)		
P(1)–Ru–C(2)	89·2 (2)	P(1)–Ru–P(2)	175·73 (7)		
Triphenylphosphines					
P(1)–C(4)	1·842 (4)	P(2)–C(22)	1·842 (5)		
P(1)–C(10)	1·829 (6)	P(2)–C(28)	1·834 (5)		
P(1)–C(16)	1·834 (4)	P(2)–C(34)	1·839 (4)		
Ru–P(1)–C(4)	116·7 (1)	Ru–P(2)–C(22)	117·1 (2)		
Ru–P(1)–C(10)	114·0 (2)	Ru–P(2)–C(28)	116·0 (2)		
Ru–P(1)–C(16)	115·5 (1)	Ru–P(2)–C(34)	113·7 (1)		
C(4)–P(1)–C(10)	102·8 (2)	C(22)–P(2)–C(28)	101·9 (2)		
C(4)–P(1)–C(16)	102·2 (2)	C(22)–P(2)–C(34)	102·3 (2)		
C(10)–P(1)–C(16)	103·8 (2)	C(28)–P(2)–C(34)	103·8 (2)		
P(1)–C(4)–C(5)	120·1 (2)	P(2)–C(22)–C(23)	119·0 (3)		
P(1)–C(4)–C(9)	119·9 (3)	P(2)–C(22)–C(27)	120·7 (3)		
P(1)–C(10)–C(11)	122·0 (4)	P(2)–C(28)–C(29)	119·3 (3)		
P(1)–C(10)–C(15)	118·0 (3)	P(2)–C(28)–C(33)	120·7 (4)		
P(1)–C(16)–C(17)	122·8 (3)	P(2)–C(34)–C(35)	122·0 (2)		
P(1)–C(16)–C(21)	117·2 (3)	P(2)–C(34)–C(39)	118·0 (3)		
THF molecule					
O(4)–C(40)	1·35 (3)	C(40)–O(4)–C(43)	116 (2)		
C(40)–C(41)	1·58 (4)	O(4)–C(40)–C(41)	103 (2)		
C(41)–C(42)	1·42 (4)	C(40)–C(41)–C(42)	108 (2)		
C(42)–C(43)	1·57 (4)	C(41)–C(42)–C(43)	102 (2)		
C(43)–O(4)	1·30 (4)	C(42)–C(43)–O(4)	109 (2)		

The authors gratefully thank Professor D. Gervais and Dr J. Galy for the interest they have taken in this problem. The CNRS, DESR and DGRST have financially supported this research.

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