Preparation of Potential Macroligands for Alkali-metal lons using Open-chain Polyether Carboxylic Acids and Tricarbonylbis(triphenylphosphine)ruthenium. X-Ray Crystal Structure of Dicarbonylbis[1-(o-carboxymethoxyphenoxy)-2-(o-hydroxyphenoxy)ethanato(1-)]bis-(triphenylphosphine)ruthenium(II) †

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The preparation and X-ray crystal structure of the title compound is described. The compound crystallizes in the triclinic space group PT (no. 2) with unit-cell dimensions a = 9.677(2), b = 23.161(6), c = 15.432(5) Å, $\alpha = 92.91(2)$, $\beta = 91.29(4)$, $\gamma = 102.16(3)$, and Z = 2. The structure was refined to a final *R* factor of 0.094 for 4 681 reflections. The ruthenium ion is octahedrally co-ordinated by two mutually *cis* carbonyl ligands, two mutually *trans* phosphine ligands, and two mutually *cis* L ligands, [1-(o-carboxymethoxyphenoxy)-2-(o-hydroxyphenoxy)ethanato(1-)] each bound to ruthenium by one oxygen of the carboxylate group. The benzene rings of the phosphine ligands are staggered, and prevent close approach of the two L ligands required to form an oxygen cavity suitable for complexation with alkali metals.

We have recently reported the interaction of a polyether hydroxy-acid, 1-(o-carboxymethoxyphenoxy)-2-(o-hydroxyphenoxy)ethane (HL), with cobalt and potassium ions to $give <math>[Co(L_2K)_2]$, a neutral molecule which is freely soluble without dissociation in non-polar solvents such as methylene chloride. The cavities in the complex containing the potassium ions are highly discriminating for potassium over sodium, the corresponding sodium complex not being isolated.² This has potential for use in selective alkali-metal ion transport through membranes.

The alkali-metal ion binding in any cavity generated when a number of open-chain polyethers are 'anchored ' at one end to a transition metal is likely to depend on the size of the cavity. This, in turn, will vary according to the transition metal employed, its co-ordination number, and its oxidation state. We have therefore initiated the synthesis of a new range of potential ligands containing ruthenium using the methods of Robinson and Uttley,³ who noted that carboxylic acids, RCOOH, with $pK_a < 4.2$ react with tricarbonylbis(triphenylphosphine)ruthenium in boiling 2-methoxyethanol to give compounds of the general formula Ru(CO)₂(PPh₃)₂(OCOR)₂.³ In this manner, we have isolated several analogous compounds, and herein report the synthesis and X-ray crystal structure of the first member of the series using the strong acid, HL.

Experimental

The complex $[Ru(CO)_3(PPh_3)_2]^4$ (0.18 g) was suspended in 2-methoxyethanol (10 cm³) and HL (0.25 g) added. The mixture was refluxed for 30 min, during which time a clear yellow solution was obtained. Solvent was removed on a rotary evaporator, and the resulting green-yellow oil was dissolved in methylene chloride (5 cm³)-methanol (10 cm³) and allowed to stand overnight. The small pale yellow needles which were deposited were collected on a sinter, washed with a small amount of methanol, and dried *in vacuo*. Yield 0.21 g,

60%. Fine, clear, colourless needle crystals for X-ray analysis were obtained from a further recrystallisation from CH_2Cl_2 -MeOH, m.p. 96—99 °C, and showed two sharp carbonyl stretches at 2 059 and 1 991 cm⁻¹ (Nujol mull). Elemental analysis did not correspond with a simple formula, but rather suggested a solvate: the i.r. and n.m.r. spectra and the solvents used for recrystallisation supported the formula [Ru(CO)₂(PPh₃)₂L₂]·CH₂Cl₂·CH₃OH (Found: C, 60.7; H, 4.65; Cl, 4.4. C₇₂H₆₆Cl₂O₁₅P₂Ru requires C, 61.55; H, 4.75; Cl, 5.05%). A suitable crystal, dimensions 0.26 × 0.07 × 0.08 mm, was selected for X-ray analysis. Preliminary photographs showed that the crystals do not diffract too well, and have a triclinic space group.

Crystal Data.—C₇₀H₆₀O₁₄P₂Ru·CH₂Cl₂·CH₄O, M = 1405.3, triclinic, space group $P\bar{I}$ (no. 2), a = 9.677(2), b = 23.161(6), c = 15.432(5) Å, $\alpha = 92.91(2)$, $\beta = 91.29(4)$, $\gamma = 102.16(3)^{\circ}$, U = 3375(1) Å³, F(000) = 1452, $D_c = 1.383$, Z = 2, $D_m = 1.36$ g cm⁻³, μ (Mo- K_a) = 4.2 cm⁻¹, λ (Mo- $K_{\bar{a}}$) = 0.710 69 Å.

Intensity data were measured on an Enraf-Nonius CAD4 diffractometer, with monochromated $Mo-K_{x}$ radiation. Lorentz and polarisation factors were applied; corrections for crystal deterioration and absorption were negligible and were not applied.

The principal parts of the structure were readily determined from Patterson and electron-density maps, and comprise a Ru complex $[Ru(CO)_2(PPh_3)_2L_2]$ and a dichloromethane solvate molecule. The other solvate molecules have not been identified with the same confidence but, currently, it is thought that the proposed formula is correct and that one methanol molecule is disordered over at least two sites. The oxygen atom, O(95), of one MeOH molecule is clear and occupies a site with an estimated 70% occupancy; the atom C(96) of this molecule is thought to occupy mainly one site but its high, refined thermal parameter suggests there may be alternative orientations in which the MeOH molecule pivots about the O atom. A second site for the MeOH molecule has been located, but refinement of the atoms, O(97) and C(98), given site occupancy factors of 0.3, was not totally satisfactory; also, some intermolecular contacts involving this molecule are

⁺ Supplementary data available (No. SUP 23803, 35 pp.): structure factors, thermal parameters, H-atom co-ordinates, additional molecular dimensions. See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1984, Issue 1, pp. xvii-xix.

Atom	x	у	Z	Atom	x	у	z
Ru(1)	2 831(1)	2 376.5(5)	3 374.5(7)	C(64a)	-2 135(23)	1 442(9)	1 009(13)
				C(65a)	-1 469(24)	985(11)	1 079(14)
O(1)	10 341(10)	4 102(4)	1 391(6)	C(66a)	8(20)	1 111(9)	1 366(12)
C(2)	10 032(13)	3 882(5)	563(8)	C(61b)	3 492(12)	2 325(5)	1 140(8)
C(3)	10 618(15)	3 470(6)	180(9)	C(62b)	2 908(15)	2 393(6)	336(9)
C(4)	10 323(15)	3 251(7)	- 664(9)	C(63b)	3 720(16)	2 739(6)	- 287(10)
C(5)	9 383(16)	3 477(7)	-1.148(11)	C(64b)	5 088(16)	3 009(7)	-75(10)
C(6)	8 765(15)	3 906(6)	-781(9)	C(65b)	5 653(16)	2 947(6)	714(9)
C(7)	9 048(13)	4 109(5)	54(8)	C(66b)	4 877(13)	2 600(6)	1 310(9)
O(8)	8 490(9)	4 527(4)	484(6)	C(61c)	3 134(14)	1 199(6)	1 774(8)
$\mathbf{C}(9)$	7 576(15)	4 794(6)	-42(9)	C(62c)	3391(17)	1013(7)	950(11)
C(10)	7 120(15)	5 256(6)	518(9)	C(63c)	3.881(20)	481(8)	783(13)
O(11)	6 033(9)	4 970(4)	1.078(6)	C(64c)	4 060(21)	150(9)	1 432(13)
C(12)	5 375(13)	5 320(5)	1 572(8)	C(65c)	3 769(22)	306(9)	22(13)
C(12)	5 811(15)	5 025(6)	1 771(0)	C(0)C)	3709(22)	SOU(9)	2 210(14)
C(13)	5 016(15)	5 723(0)	2 21(9)	C(00c)	5 516(19)	0.00(0)	2 423(12)
C(14)	3010(15)	5.044(7)	2 212(9)	D(7)	2 522(4)	2.020(2)	4 720(2)
	3 804(10)	5 944(7)	2 374(10)	$\mathbf{r}(7)$	5 522(4)	2 939(2)	4 / 30(2)
C(16)	3 331(16)	5 330(6)	2 418(9)	C(71a)	5 432(14)	3 041(6)	4 960(8)
C(17)	4 108(13)	5 025(6)	1 933(8)	C(72a)	6 314(15)	3 309(6)	4 363(10)
O(18)	3 561(9)	4 434(4)	1 741(6)	C(73a)	7 822(18)	3 393(7)	4 501(11)
C(19)	4 294(14)	4 059(6)	2 178(9)	C(74a)	8 276(19)	3 221(7)	5 247(11)
C(20)	3 223(13)	3 505(5)	2 404(8)	C(75a)	7 449(16)	2 957(7)	5 844(10)
O(21)	3 846(8)	3 160(3)	2 851(5)	C(76a)	5 986(15)	2 861(6)	5 700(9)
O(22)	1 987(8)	3 415(4)	2 200(6)	C(71b)	3 256(14)	3 694(6)	4 788(8)
				C(72b)	2 173(14)	3 850(6)	4 307(9)
O(31)	6 480(12)	- 973(6)	1 454(7)	C(73b)	1 901(17)	4 419(7)	4 413(10)
C(32)	5 178(16)	-1.302(7)	1 645(10)	C(74b)	2 620(18)	4 807(8)	5 045(11)
C(33)	4 365(20)	-1 649(8)	1 017(13)	C(75b)	3 687(19)	4 659(8)	5 537(12)
C(34)	3 034(21)	-1.981(9)	1 203(13)	C(76b)	3 995(16)	4 097(6)	5 390(10)
C(35)	2.568(21)	-1.955(8)	1 994(12)	C(71c)	2 707(13)	2 645(5)	5 718(8)
C(36)	3 389(18)	-1.602(8)	2 657(12)	C(72c)	2 814(14)	2 090(6)	5 946(9)
C(37)	4 689(16)	-1.282(6)	2 475(9)	C(73c)	2 326(15)	1.878(7)	6 740(9)
0(38)	5 598(10)	-925(4)	$\frac{2}{3}$ 085(7)	C(74c)	1.613(16)	2213(7)	7 245(10)
C(30)	5 139(16)	-861(7)	3 960(9)	C(75c)	1 427(15)	2 751(6)	7 022(9)
C(3)	6323(17)	-509(7)	$\frac{3}{4}\frac{3}{477}(10)$	C(76c)	1 965(14)	2 971(6)	6 249(8)
C(40)	6523(17)	-509(7)	4 179(6)	$C(i\omega)$	1 705(14)	2 7/1(0)	0 249(0)
C(41)	7502(12)	507(7)	4 120(0)	C(81)	2 040(12)	1 608(6)	2 002(8)
C(42)	/ 303(10)	307(7)	4 030(10)	O(81)	1 453(10)	1 050(0)	3 902(8)
C(43)	8 200(17)	434(7)	5 303(10)	C(82)	1 432(10)	7 525(5)	4 157(0)
C(44)	9 032(18)	927(7)	5 837(11)	C(83)	1028(13)	2555(5)	3 3 3 3 6 (8)
C(45)	8 996(17)	1 497(7)	5 587(10)	U(84)	-121(9)	2 394(4)	3 39/(6)
C(46)	8 240(15)	1 552(7)	4 840(9)				
C(47)	7 506(15)	1 081(6)	4 373(9)	CH_2Cl_2	solvent molecule		
O(48)	6 773(10)	1 081(4)	3 596(6)	C(90)	1.057(25)	4 926(10)	7 529(15)
C(49)	6 535(15)	1 626(6)	3 331(9)	Cl(91)	88(8)	4 388(4)	6 778(5)
C(50)	5 265(13)	1 808(6)	3 729(8)	Cl(92)	1 803(9)	5 558(4)	7.058(6)
O(51)	4 858(8)	2 202(3)	3 276(5)	01()2)	1 005(5)	5 550(1)	/ 050(0)
O(52)	4 687(9)	1 567(4)	4 338(5)	Manu	alvant malaaulaa		
				MeOH S			
P(6)	2 509(4)	1 884(1)	1 933(2)	O(95)	7 941(26)	- 28(9)	2 550(13)
C(61a)	682(14)	1 692(6)	1 537(9)	C(96)	9 152(55)	- 292(25)	2 391(39)
C(62a)	- 49(15)	2 119(7)	1 445(9)	O(97)	10 491(85)	- 803(34)	1 235(56)
C(63a)	-1504(20)	1 995(8)	1 153(12)	C(98)	9 573(71)	-1298(30)	967(43)

Table 1. Final fractional atomic co-ordinates (\times 10⁴) of [Ru(CO)₂(PPh₃)₂L₂] with estimated standard deviations (e.s.d.s) in parentheses

rather short. A final difference map did not show any alternative arrangements in this solvent region.

Refinement of the structure was started with the program SHELX,⁵ but introduction of the hydrogen atoms (in idealised positions, riding on their bonded C atoms) necessitated the use of our block-diagonal least-squares program BLOKLS.⁶ Scattering factors were taken from ref. 7. In the final cycles of refinement, the Ru, P, O [except for O(97)], and Cl atoms were allowed anisotropic thermal parameters, and the C atoms were refined isotropically; the C-O bond lengths of the two MeOH part-molecules were constrained to 1.41 Å ($\sigma = 0.05$ Å). The phenolic H atoms and those of the MeOH molecules were not included in any calculations. Final *R* and *R'* values were 0.094 and 0.090 for 4 681 reflections having

 $I > \sigma(I)$; the data were weighted according to $w = k(\sigma_F^2 + 0.002 F^2)^{-1}$.

Final parameters for the non-hydrogen atoms are given in Table 1. Table 2 contains the Ru co-ordination distances and the bond lengths and angles in the L ligands. Torsion angles in the L ligands are in Table 3.

Results

The Ru ion is octahedrally co-ordinated by two carbonyl ligands (mutually *cis*), two phosphine ligands (mutually *trans*) and two L ligands bound as planned in a *cis* arrangement, each through one O atom of the carboxylate group, Figure 1. The two L ligands do not align themselves in parallel planes

Table 2. Geometry about the Ru ion and in the L ligands; e.s.d.s are given in parentheses

(a) Ru co-ordination dimensions; distances (Å) and angles (°)						
Ru(1)=O(21)	2.084(8)	Ru(1) - P(7)	2.411(4)			
Ru(1)=O(51)	2.092(7)	Ru(1) - C(81)	1.832(13)			
Ru(1) - P(6)	2.430(4)	Ru(1)-C(83)	1.857(12)			
O(21) = Ru(1) = O(51)	80.9(3)	O(51) - Ru(1) - C(83)	175.1(4)			
O(21) = Ru(1) = P(6)	90.3(2)	P(6) = Ru(1) = P(7)	170.8(1)			
O(21) = Ru(1) = P(7)	82.7(2)	P(6) - Ru(1) - C(81)	92.9(4)			
O(21) = Ru(1) = C(81)	175.5(4)	P(6) = Ru(1) = C(83)	93.3(4)			
O(21) = Ru(1) = C(83)	96.7(4)	P(7) - Ru(1) - C(81)	93.7(4)			
O(51) = Ru(1) = P(6)	82.4(2)	P(7) - Ru(1) - C(83)	93.4(4)			
O(51) = Ru(1) = P(7)	90.6(2)	C(81) - Ru(1) - C(83)	86.3(5)			
O(51) = Ru(1) = C(81)	96.3(4)					
0,01,) 110(1) 2,011,	,					
(b) Bond lengths (Å)) in L					
O(1) = C(2)	.355(15)	O(31) - C(32)	1.375(19)			
C(2) = C(3)	1.329(19)	C(32) - C(33)	1.350(25)			
C(2) = C(7)	1.421(18)	C(32) - C(37)	1.377(21)			
C(3) = C(4)	1 375(20)	C(33) = C(34)	1.398(27)			
C(4) = C(5)	1 367(21)	C(34) = C(35)	1.314(27)			
C(5) = C(6)	1 369(21)	C(35) = C(36)	1.397(26)			
C(6) = C(7)	1 351(19)	C(36) - C(37)	1.363(23)			
C(7) = O(8)	1.355(15)	C(37) = O(38)	1.386(18)			
O(8) - C(9)	1 440(17)	O(38) = C(39)	1.441(18)			
C(9) = C(10)	1.485(20)	C(39) - C(40)	1.454(22)			
C(10) = O(11)	1.405(20)	C(40) = O(41)	1.12(18)			
O(11) = C(12)	1 349(15)	O(41) - C(42)	1 380(18)			
C(12) = C(12)	1 381(10)	C(42) - C(43)	1.300(10) 1.373(22)			
C(12) = C(13)	1.301(19)	C(42) = C(43)	1.375(22) 1.404(20)			
C(12) = C(17)	1.356(20)	C(42) = C(44)	1.387(23)			
C(13) = C(14)	1.330(20)	C(43) = C(45)	1.307(23) 1.400(23)			
C(14) = C(15)	1.301(21)	C(45) = C(46)	1.700(23)			
C(15) C(10)	1.403(21)	C(45) = C(47)	1.377(22)			
C(10) C(17)	1.330(19)	C(40) = C(47)	1.330(20)			
O(18) = O(10)	1.373(13)	O(48) = O(48)	1.300(17)			
C(10) = C(10)	1.410(10)	C(40) = C(50)	1.409(10)			
C(19) C(20)	1.330(10)	C(49) = C(50)	1.313(19)			
C(20) = O(21)	1.311(14)	C(50) = O(51)	1.297(13) 1.205(15)			
C(20) = O(22)	1.202(13)	C(50) O(52)	1.203(13)			
(c) Valence angles (³) in L					
O(1)=C(2)=C(3)	124.0(12)	O(31) = C(32) = C(33)	120.1(15)			
O(1)=C(2)=C(7)	118.9(11)	O(31) = C(32) = C(37)	120.6(13)			
C(3) = C(2) = C(7)	117.0(12)	C(33) = C(32) = C(37)	119.3(15)			
C(2) = C(3) = C(4)	124 3(13)	C(32) = C(33) = C(34)	120 5(18)			
C(3) = C(4) = C(5)	118.1(14)	C(33) = C(34) = C(35)	119.8(19)			
C(4) = C(5) = C(6)	119 4(15)	C(34) = C(35) = C(36)	120 9(18)			
C(5)=C(6)=C(7)	121.7(14)	C(35) = C(36) = C(37)	119 1(16)			
C(2) = C(2) = C(6)	119 4(12)	C(32) = C(37) = C(36)	120 3(15)			
C(2) = C(7) = O(8)	114.0(11)	C(32) = C(37) = O(38)	115 8(13)			
C(6) = C(7) = O(8)	126.6(12)	C(36) = C(37) = O(38)	123.9(14)			
C(7) = O(8) = C(9)	114.6(10)	C(37) = O(38) = C(39)	119.2(11)			
O(8) = C(9) = C(10)	107.2(11)	O(38) - C(39) - C(40)	107.8(12)			
C(9) = C(10) = O(11)	108.7(11)	C(39) = C(40) = O(41)	107.3(13)			
C(10) = O(11) = C(12)	117.6(10)	C(40)=O(41)=C(42)	117 4(11)			
O(11) = C(12) = C(13)	125.8(12)	O(41) = C(42) = C(43)	124.9(14)			
O(11) = C(12) = C(17)	114.9(11)	O(41) - C(42) - C(47)	115.5(13)			

C(43) - C(42) - C(47)

C(42) - C(43) - C(44)

 $C(43)^{-}C(44)^{-}C(45)$

C(44)-C(45)-C(46)

C(45)-C(46)-C(47)

C(42) = C(47) = C(46)

C(42)⁻C(47)⁻O(48)

C(46) - C(47) - O(48)

C(47)⁻O(48)⁻C(49)

O(48)=C(49)=C(50)

C(49) = C(50) = O(51)

C(49)=C(50)=O(52)

O(51)=C(50)=O(52)

119.5(14)

119.6(15)

120.3(15)

118.3(15)

121.9(14)

120.3(13)

112.7(12)

126 9(13)

117.9(10)

114.1(11)

110.3(10)

122.0(12)

127.4(12)

C(13)=C(12)=C(17)=119.3(12)

C(12) = C(13) = C(14) = 119.4(13)

C(13) = C(14) = C(15) = 122.1(14)

C(15)=C(16)=C(17) 119.4(13)

C(12)=C(17)=C(16)=120.4(12)

C(16)=C(17)=O(18)=117.7(12)

C(17)=O(18)=C(19) 113.3(10)

O(18)-C(19)-C(20) 108.4(10)

C(19) - C(20) - O(21) - 110.4(10)

C(19)=C(20)=O(22) 123.5(11)

O(21)=C(20)=O(22) 126.1(11)

119.4(14)

121.6(11)

C(14)=C(15)=C(16)

C(12)-C(17)-O(18)

Table 3. Selected torsion angles (°) in the L ligands; e.s.d.s are given in parentheses

O(1)-C(2)-C(7)-O(8)	- 2(2)
C(2)-C(7)-O(8)-C(9)	175(1)
C(7) - O(8) - C(9) - C(10)	-177(1)
O(8)-C(9)-C(10)-O(11)	-77(1)
C(9)-C(10)-O(11)-C(12)	-173(1)
$\hat{C}(10) = \hat{O}(11) = \hat{C}(12) = \hat{C}(17)$	165(1)
O(11) - C(12) - C(17) - O(18)	-4(2)
C(12) - C(17) - O(18) - C(19)	76(2)
C(17) = O(18) = C(19) = C(20)	145(1)
O(18) - C(19) - C(20) - O(21)	-177(1)
O(18) = C(19) = C(20) = O(22)	3(2)
0(10) 0(1)) 0(20) 0(22)	5(2)
O(31) = C(32) = C(37) = O(38)	-1(2)
C(32) - C(37) - O(38) - C(39)	177(1)
C(37) = O(38) = C(39) = C(40)	175(1)
O(38) - C(39) - C(40) - O(41)	63(2)
C(39) = C(40) = O(41) = C(42)	165(1)
C(40) = O(41) = C(42) = C(47)	-164(1)
O(41) = C(42) = C(42) = O(48)	-7(2)
C(47) = C(47) = O(48) = C(49)	171(1)
C(42) = C(42) = C(42) = C(42) = C(42)	.92(1)
O(48) = C(49) = C(50) = O(51)	= 65(1)
O(48) = C(49) = C(50) = O(51)	-101(1)
U(40) ~U(49) ~U(30)~U(32)	14(2)



Figure 1. The complex $[Ru(CO)_2(PPh_3)_2L_2]$ showing the Ru coordination pattern and the arrangement of the two L ligands. For clarity, the phenyl rings of the phosphine ligands have been omitted. The atoms of L are numbered n and (30 + n) as described in ref. 2; the phenolic O atoms of the two ligands are thus O(1) and O(31)

{as they do in $[Co(L_2K)_2]$ and $[Co(L_2Rb)_2]^{1,2}$ } but diverge and there are no interactions between them.

The torsion angles (Table 3) show very similar and unstrained conformations of the L ligands (once clear of the carboxylate groups). This contrasts with all the ligands in the two Co complexes where, in each ligand, there is at least one torsion angle considerably different from the normal *trans* (180°) or *gauche* ($\pm 60^{\circ}$) values. The O atoms in each of L in the Ru complex do not form any good plane. The absence of an alkali-metal cation releases the ligands from all the strains found in the Co complexes.

The phenolic groups of O(1) and O(31) both appear to be involved in hydrogen bonding, but of quite different types. O(1) is 2.80 Å from the carboxylate O(22) atom of the next molecule along the *a* axis, and the angle $C(2)^{-}O(1)^{+} \cdots$ O(22') is suitable for the formation of a hydrogen bond; the complex molecules are thus linked in chains parallel to the *a* axis, the needle axis of the crystal. The atom O(31) is hydrogen bonded to a solvent methanol molecule in its **Table 4.** Dimensions in potential hydrogen-bonding contacts. Proposed principal hydrogen bonds are marked with asterisks; e.s.d.s are given in parentheses

	$0 \cdots 0/Å$	$C - O \cdots O/2$	5		
$C(2) = O(1) = H \cdots O(18^{1})$	3.077(13)	110.7(7)			
$C(2) = O(1) = H \cdots O(22^{1})$	2.795(13)	108.6(8) *			
$C(32) - O(31) - H \cdots O(95)$	2.80(2)	122.5(10) *			
$C(96) - O(95) - H \cdots O(31)$	2.80(2)	84(2)			
$C(96) - O(95) - H \cdots O(38)$	2.90(3)	109(2) *			
C(96)-O(95)-H · · · O(41)	2.78(2)	126(3) •			
	C · · · O/Å	H ··· O/Å C	-H · · · O/°		
$C(90)$ - $H(90b) \cdots O(1^{11})$	3.27(2)	2.47	138(1)		
Roman superscripts identify atoms of symmetry-related molecules to those of Table 1: molecule I is at $x + 1$, y , z and II at $1 - x$,					

principal occupancy site, and in turn the MeOH probably donates its hydroxide H atom in a hydrogen bond O(31)- $H \cdots O(41)$; when the MeOH is in the other site, there does not appear to be any hydrogen bonding of O(31) or the MeOH molecule. The atom H(90b) of the dichloromethane molecule is 2.47 Å from O(1) and we suggest the formation of a weak C-H \cdots O hydrogen-bonding contact. All potential hydrogenbonding dimensions are given in Table 4.

The carbonyl and phosphine ligands, Figure 2, have normal dimensions and are arranged about the Ru atom in pseudotwo-fold symmetry; the three phenyl rings on each P atom are arranged as the blades of a propeller about the Ru-P axis. The carboxylate groups of the L ligands also conform to the pseudo-two-fold symmetry, an arrangement probably imposed by the bulky phosphine ligands. The planes of the carboxylate groups are thus restricted from rotation and the two L ligands are not able to form the biplanar arrangement necessary for encapsulation of alkali-metal cations.^{1,2}

Discussion

1 - y, 1 - z.

In their initial paper on the general synthesis of platinum metal carboxylates, Robinson and Uttley ³ suggested that the stereochemistry of the compounds $[Ru(CO)_2(PPh_3)_2(OCOR)_2]$ was made up of two *cis* carbonyls, two *cis* phosphines, and two *trans* monodentate carboxylates. This stereochemistry had been postulated previously by Collman and Roper.⁸ In a later paper, Robinson and co-workers ⁹ suggested that the carboxylate ligands are *cis* and the phosphines *trans*. The Nujol mull i.r. spectrum of our complex exhibits two strong bands at 2 059 and 1 991 cm⁻¹, indicating *cis* carbonyls, and three medium strength bands in the region expected for $v(OCO)_{asym}$ of monodentate carboxylates (1 645, 1 625, and 1 605 cm⁻¹). A rather broad band is observed in the region 3 350–3 100 cm⁻¹ with sharper weak bands at 3 680 and 3 500 cm⁻¹.

The X-ray crystal structure (Figure 1) confirms the stereochemistry proposed in Robinson's later paper,⁹ showing two *cis* carbonyl groups, two *cis* monodentate carboxylates, and two *trans* phosphines. The two polyether ligands point away



Figure 2. The complex $[Ru(CO)_2(PPh_3)_2L_2]$ showing the pseudotwo-fold symmetry about the Ru atom and in the phosphine ligands; the pseudo-axis lies vertically in the plane of the paper. Most of the atoms of L have been omitted

from each other, and the space between them is partially filled by the staggered phenyl rings of the two triphenylphosphine groups. This suggests that this particular complex will not be suitable for encapsulating alkali-metal cations, since the two open-chain ligands cannot approach each other to form a cavity. We note, in particular, that the reaction of KCl (or KSCN) with $[Ru(CO)_2(PPh_3)_2L_2]$ leads to the displacement of one or both L ligands as KL and the formation of transition-metal complexes containing co-ordinated chloride (or thiocyanate).

The general method of preparation of potential flexible macroligands for alkali metals using carboxylic acid openchain ethers co-ordinated to ruthenium has, however, been established. Therefore, ruthenium complexes with other carboxylate ligands and smaller phosphine groups are being investigated. The preparation of complexes $[Ru(CO)(PPh_3)_2-(OCOR)_2]$ where the phosphines are *cis*^{3,9} is also being studied.

References

- 1 D. L. Hughes and J. N. Wingfield, J. Chem. Soc., Dalton Trans., 1982, 1239.
- 2 D. L. Hughes and J. N. Wingfield, J. Chem. Soc., Dalton Trans., 1983, 915.
- 3 S. D. Robinson and M. F. Uttley, J. Chem. Soc., Dalton Trans., 1973, 1912.
- 4 J. J. Levison and S. D. Robinson, J. Chem. Soc. A, 1970, 2947.
- 5 SHELX 76, program for crystal structure determination, G. M. Sheldrick, University of Cambridge, 1976.
- 6 BLOKLS, block-diagonal least-squares refinement program, part of J. D. Owen's program suite for the Prime computer, Rothamsted Experimental Station, 1982.
- 7 ' International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
- 8 J. P. Collman and W. R. Roper, J. Am. Chem. Soc., 1965, 87, 4008.
- 9 A. Dobson, S. D. Robinson, and M. F. Uttley, J. Chem. Soc., Dalton Trans., 1975, 370.

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