

Synthesis and X-ray crystal structures of the cyclic oxacarbene complexes $[\text{Ru}\{\overline{\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O}}\}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ ($n = 1$ or 2): boat conformation of the 2-oxacyclohexylidene ligand

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Abstract

The cyclic oxacarbene complexes $[\text{Ru}\{\overline{\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O}}\}(\text{dppe})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; $n = 1, 1$ or $2, 2$) have been synthesised by reaction of hydroxyalk-1-yne, $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{CH}_2\text{OH}$ with $[\text{RuCl}(\text{dppe})(\eta\text{-C}_5\text{H}_5)]/\text{NH}_4[\text{PF}_6]$ in refluxing methanol. The X-ray crystal structures of **1** and **2** reveal essentially vertically orientated carbene ligands with the oxygen directed 'down' away from the cyclopentadienyl ring. Both carbene rings exhibit folded conformations; the five-membered ring of **1** adopts an envelope configuration whilst the six-membered ring of **2** has a boat conformation.

Keywords: Carbene; Ruthenium; Cyclopentadienyl; Crystal structure

1. Introduction

The potential of the $\text{RuL}_2(\eta\text{-C}_5\text{H}_5)$ system ($L = \text{P}$ -donor ligand) to act as an organometallic auxiliary in the regio- and stereoselective elaboration of bound organic fragments has been the focus of much recent investigation [1]. A prominent area of this work involves the synthesis, structure and reactions of cationic carbene (CR_2), vinylidene ($\text{C}=\text{CR}_2$) and allenylidene ($\text{C}=\text{C}=\text{CR}_2$) derivatives [2]. Structural studies reveal that in complexes of symmetrical auxiliaries $\text{RuL}_2(\eta\text{-C}_5\text{H}_5)$ (both L identical), carbene and allenylidene ligands adopt a vertical orientation in which the ligand R substituents lie approximately in the pseudo mirror plane of the $\text{RuL}_2(\eta\text{-C}_5\text{H}_5)$ moiety whilst vinylidene ligand substituents are directed orthogonal to this plane in a horizontal orientation [2]. This successive twisting through 90° (carbene (vertical) \rightarrow vinylidene (horizontal) \rightarrow allenylidene (vertical)) observed experimentally, is consistent with theoretical investigations [3] and required to provide optimal interaction between the vacant p orbital on C_α of the ligand and orbitals of a' or a'' symmetry on the $\text{RuL}_2(\eta\text{-C}_5\text{H}_5)$ fragment.

We have recently reported a series of synthetic and structural investigations on vinylidene complexes of the cycloheptatrienylmolybdenum auxiliary $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ which establish [4] that, in this system, the vinylidene ligand adopts a preferred vertical orientation leading to the conjecture that the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ auxiliary might promote electronically preferred ligand orientations which are the converse of those supported by the $\text{RuL}_2(\eta\text{-C}_5\text{H}_5)$ auxiliary. Further to establish this hypothesis, we have prepared the cyclic oxacarbene derivatives $[\text{Mo}\{\overline{\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O}}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ ($n = 1$ or 2) and crystallographically confirmed a horizontal orientation of the cyclic oxacarbene ligand in the 2-oxacyclopentylidene derivative ($n = 1$) [5]. Although a number of X-ray crystal structures of carbene derivatives of the $\text{RuL}_2(\eta\text{-C}_5\text{H}_5)$ auxiliary [6–9] have been reported, none are direct analogues of $[\text{Mo}\{\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ and in fact the only example of a cyclic oxacarbene derivative is that of $[\text{Ru}\{\overline{\text{CCH}(\text{Ph})\text{CH}_2\text{CH}_2\text{O}}\}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ [9] in which, consistent with theoretical studies on complexes of unsymmetrical auxiliaries $\text{MLL}'(\eta\text{-C}_5\text{H}_5)$ [10], the plane of the oxacarbene ligand is aligned orthogonal to the $\text{Ru}-\text{P}$ vector. Therefore, to provide a more appropriate and direct comparison with the structure of $[\text{Mo}\{\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$, and so demonstrate conclusively the con-

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trasting orientational preferences of carbene ligands attached to $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ and $\text{Ru}(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ auxiliaries, we set out to synthesise and crystallographically characterise the complexes $[\text{Ru}(\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O})(\text{dppe})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ ($n = 1, 1; n = 2, 2$).

2. Results and discussion

The cyclic oxacarbene complexes $[\text{Ru}(\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O})(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ ($n = 1, \text{R} = \text{Me}$ or Ph ; $n = 2, \text{R} = \text{Ph}$), synthesised by reaction of hydroxyalk-1-yne with $[\text{RuCl}(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)]/\text{NH}_4[\text{PF}_6]$ in methanol, were first reported by Bruce et al. [11]. We adopted an identical procedure starting from $[\text{RuCl}(\text{dppe})(\eta\text{-C}_5\text{H}_5)]$ and $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{CH}_2\text{OH}$ ($n = 1$ or 2) to give the required complexes $[\text{Ru}(\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O})(\text{dppe})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ ($n = 1, 1; n = 2, 2$) which were isolated in good yield as white solids. Full details of the characterisation of **1** and **2** by microanalysis, mass spectroscopy, ^1H , ^{13}C and ^{31}P NMR spectroscopy are presented in Table 1. The identity of **1** and **2** as carbene complexes is confirmed by characteristic low field triplet resonances in the ^{13}C NMR spectra attributable to the carbene carbon C_α . The C_α resonance for the 2-oxacyclohexylidene derivative **2** is shifted to low field of that for **1** by approximately 8 ppm, a trend consistent with ^{13}C NMR data for $[\text{Mn}_2(\text{CO})_9(\text{CCH}_2(\text{CH}_2)_n\text{CH}_2\text{O})]$ ($n = 1$ or 2) [12,13].

The molecular geometries of both **1** and **2** were examined crystallographically to provide a direct comparison between 2-oxacyclopentylidene and 2-oxacyc-

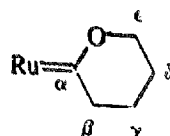
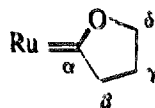
lohexylidene ligands in otherwise identical complexes. Our studies with the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ auxiliary reveal that the 2-oxacyclohexylidene complex $[\text{Mo}(\text{CCH}_2(\text{CH}_2)_2\text{CH}_2\text{O})(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ is formed with some difficulty from the isolable hydroxyvinylidene $[\text{Mo}(\text{C}=\text{C}(\text{H})(\text{CH}_2)_2\text{CH}_2\text{OH})(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$, whereas no corresponding intermediate was observed in the synthesis of the analogous 2-oxacyclopentylidene derivative. It was therefore of interest to establish whether, in these sterically congested systems, any structural constraints might be imposed on the formation of the larger six-membered ring. Moreover, a search of the Cambridge crystallographic database uncovered just three previous molecular structure determinations on complexes containing the 2-oxacyclohexylidene ligand [13,14].

The X-ray crystal structures of **1** and **2** (and the crystallographic numbering schemes adopted) are illustrated in Figs. 1 and 2 respectively, and details of important bond lengths and angles are presented in Table 2. The typical geometry of the $\text{Ru}(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ auxiliary is exhibited by both **1** and **2** with two phenyl groups of the dppe ligand flanking C_α of the oxacarbene ligands. The Ru–P distances (**1**, 2.267(3) and 2.273(3); **2**, 2.285(1), 2.280(1) Å) are intermediate between those of $[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)]$ (2.240(1), 2.250(1) Å) [8] and $[\text{Ru}(\text{C}=\text{CPh}(\text{C}_7\text{H}_7))(\text{dppe})(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ (2.298(2), 2.305(2) Å) [15] consistent with the relative π -acceptor capacities of alkynyl, carbene and vinylidene ligands [8]. The Ru– C_α distances (**1**, Ru–C(3) 1.92(1); **2**, Ru–C(3) 1.938(4) Å) are comparable with those of the methoxy-carbene complexes $[\text{Ru}(\text{C}(\text{OMe})\text{CH}_2\text{Ph})(\text{Ph}_2\text{PCHMeCH}_2\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)]$ -

Table 1
Microanalytical and spectroscopic data

	1	2
Analysis (%) ^a	C 53.9 (53.9) H 4.8 (4.5)	C 54.7 (54.5) H 4.7 (4.7)
Mass spectral data ^b	635 (M^+), 565 ($[M - \text{CCH}_2\text{CH}_2\text{CH}_2\text{O}]^+$)	649 (M^+), 565 ($[M - \text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}]^+$)
^1H NMR data (δ) ^c	7.56–7.17 (m, 20 H, Ph, dppe); 5.12 (s, 5H, C_5H_5); 3.30 (t, 2H, $\text{C}_\delta\text{H}_2$, $J[\text{H}_\delta\text{-H}_\gamma]$ 7); 3.09 (t, 2H, C_βH_2 , $J[\text{H}_\beta\text{-H}_\gamma]$ 8); 3.04, 2.65 (m, 4H, CH_2 , dppe); 1.29 (η , 2H, $\text{C}_\gamma\text{H}_2$) ^d	7.85–7.27 (m, 20 H, Ph, dppe); 5.18 (s, 5H, C_5H_5); 3.09 (t, 2H) and 3.00 (t, 2H) ($\text{C}_\delta\text{H}_2$ and C_βH_2); 3.09 and 2.77 (m, 4H, CH_2 , dppe); 1.16 (q, 2H) and 0.78 (q, 2H) ($\text{C}_\gamma\text{H}_2$ and $\text{C}_\delta\text{H}_2$)
^{13}C NMR data (δ) ^c	296.1 (t, C_α , $J[\text{C}_\alpha\text{-P}]$ 12.7); 139.9–129.4 (Ph, dppe); 90.4 (C_5H_5); 81.0 (C_δ); 59.0 (C_β); 29.0 (vt, CH_2 , dppe); 22.4 (C_γ) ^e	304.4 (t, C_α , $J[\text{C}_\alpha\text{-P}]$ 12.6); 141.1–129.0 (Ph, dppe); 91.2 (C_5H_5); 73.6 (C_δ); 54.0 (C_β); 29.3 (CH_2 , dppe); 21.2 and 17.4 (C_γ and C_δ)
^{31}P NMR data (δ) ^c	91.5, s	93.2, s

^a Calculated values in parentheses. ^b By FAB mass spectroscopy, m/z values based on ^{102}Ru . ^c s = singlet, t = triplet, vt = virtual triplet, q = quintet, m = multiplet; coupling constants J in hertz; in acetone- d_6 unless stated otherwise; ring lettering system as in diagrams below. ^d In CDCl_3 . ^e In CD_2Cl_2 .



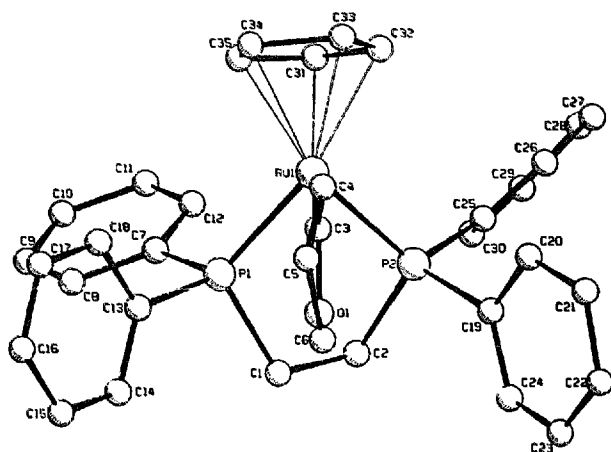


Fig. 1. Molecular structure of complex 1 showing the crystallographic numbering scheme (hydrogen atoms and PF_6 counter anion omitted for clarity).

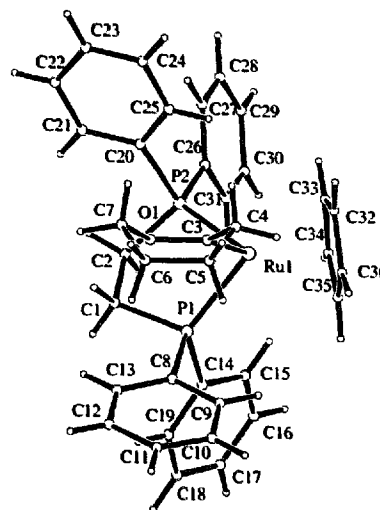


Fig. 2. Molecular structure of complex 2 showing the crystallographic numbering scheme (PF_6 counter anion omitted for clarity).

Table 2
Selected bond lengths (Å) and angles (deg) for complexes 1 and 2

1		2	
Ru–P(1)	2.267(3)	Ru–P(1)	2.285(1)
Ru–P(2)	2.273(3)	Ru–P(2)	2.280(1)
Ru–C(3)	1.92(1)	Ru–C(3)	1.938(4)
P(1)–C(1)	1.83(1)	P(1)–C(1)	1.839(4)
P(1)–C(7)	1.86(1)	P(1)–C(14)	1.829(4)
P(1)–C(13)	1.827(9)	P(1)–C(8)	1.816(4)
P(2)–C(2)	1.85(1)	P(2)–C(2)	1.833(4)
P(2)–C(19)	1.83(1)	P(2)–C(26)	1.829(4)
P(2)–C(25)	1.81(1)	P(2)–C(20)	1.816(4)
C(3)–O(1)	1.32(1)	C(3)–O(1)	1.314(5)
O(1)–C(6)	1.46(1)	O(1)–C(7)	1.463(6)
C(3)–C(4)	1.51(1)	C(3)–C(4)	1.497(6)
C(4)–C(5)	1.51(2)	C(4)–C(5)	1.515(8)
C(5)–C(6)	1.48(2)	C(5)–C(6)	1.477(9)
		C(6)–C(7)	1.457(8)
$\text{Cp}'\text{-Ru-C(3)}^a$	124	$\text{Cp}'\text{-Ru-C(3)}^a$	124
P(1)–Ru–P(2)	83.4(1)	P(1)–Ru–P(2)	82.99(4)
P(1)–Ru–C(3)	88.2(3)	P(1)–Ru–C(3)	86.7(1)
P(2)–Ru–C(3)	91.3(3)	P(2)–Ru–C(3)	92.4(1)
Ru–P(1)–C(1)	109.0(4)	Ru–P(1)–C(1)	109.5(1)
Ru–P(1)–C(7)	116.7(4)	Ru–P(1)–C(14)	119.5(1)
Ru–P(1)–C(13)	116.6(3)	Ru–P(1)–C(8)	117.2(1)
Ru–P(2)–C(2)	109.3(4)	Ru–P(2)–C(2)	110.3(1)
Ru–P(2)–C(19)	116.2(4)	Ru–P(2)–C(26)	117.1(1)
Ru–P(2)–C(25)	115.5(4)	Ru–P(2)–C(20)	117.5(1)
P(1)–C(1)–C(2)	111.2(9)	P(1)–C(1)–C(2)	107.0(3)
P(2)–C(2)–C(1)	110.8(9)	P(2)–C(2)–C(1)	109.3(3)
Ru–C(3)–O(1)	126.5(7)	Ru–C(3)–O(1)	123.1(3)
Ru–C(3)–C(4)	127.1(8)	Ru–C(3)–C(4)	125.1(3)
O(1)–C(3)–C(4)	106.3(9)	O(1)–C(3)–C(4)	111.7(4)
C(3)–C(4)–C(5)	105.0(10)	C(3)–C(4)–C(5)	113.4(5)
C(4)–C(5)–C(6)	106.0(10)	C(4)–C(5)–C(6)	113.2(5)
O(1)–C(6)–C(5)	104.0(10)	O(1)–C(7)–C(6)	111.5(5)
		C(5)–C(6)–C(7)	111.7(5)

^a Cp' represents the centroid of the cyclopentadienyl ring.

$[\text{PF}_6]_3$ [6] and $[\text{Ru}(\text{C}(\text{OMe})\text{R})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$ ($\text{R} = \text{Me}$, 4 [7], $\text{R} = \text{Et}$, 5 [8]), $(\text{Ru}-\text{C}_\alpha)$ (Å), 3, 1.93(2); 4, 1.931(9); 5, 1.959(6) with the $\text{Ru}-\text{C}_\alpha$ bond apparently longer for the six-membered ring complex 2 than for the five-membered analogue 1 (a trend consistent with $[\text{Mn}_2(\text{CO})_9(\overline{\text{C}}\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{O})]$ ($n = 1$ or 2) [12,13]), although e.s.d.s preclude a definitive conclusion on this point. However, the principal structural features of interest in 1 and 2 are associated with the orientation and conformation of the oxacarbene ligands.

In both 1 and 2 the cyclic oxacarbene ligands adopt an essentially vertical orientation with the oxygen directed 'down' away from the cyclopentadienyl ring; these features are in common with the methoxy-carbene derivatives 3–5. A more precise measure of carbene ligand orientation is provided by the dihedral angle θ between planes defined by $(\text{Cp}'-\text{Ru}-\text{C}_\alpha)$ and $(\text{O}-\text{C}_\alpha-\text{C}_\beta)$ (in 1 and 2, $(\text{Cp}'-\text{Ru}-\text{C}(3))$ and $(\text{O}-\text{C}(3)-\text{C}(4))$, $\text{Cp}' =$ centroid of the cyclopentadienyl ring). An increase in the magnitude of θ is generally accounted for

by steric factors which lead to a twisting of the carbene ligand away from the electronically preferred vertical orientation. In fact, the calculated values of θ (1, 4°; 2, 6°) are small by comparison with those of 3, (16°, reported) and 5, (17.5°, calculated from atomic coordinates) suggesting that both oxacarbene ligands are relatively sterically undemanding with no significant difference between five- and six-membered rings. Both carbene rings exhibit folded conformations. The five-membered ring of 1 adopts an envelope configuration [16] with a dihedral angle of 18.6° between planes defined by $(\text{C}(6)-\text{O}(1)-\text{C}(3)-\text{C}(4))$ and $(\text{C}(4)-\text{C}(5)-\text{C}(6))$. The unexpected boat conformation of the six-membered ring of 2 is clear from an inspection of Fig. 2, with the atoms $\text{C}(4)$ and $\text{C}(7)$ (C_β and C_ϵ) occupying the flagpole positions; deviations from the ideal boat conformation are small, as evidenced by torsion angles $(\text{C}(4)-\text{C}(3)-\text{O}(1)-\text{C}(7))$ 2.6(6)°, $(\text{C}(4)-\text{C}(5)-\text{C}(6)-\text{C}(7))$ -3.1(8)° and the co-planarity of $\text{O}(1)$, $\text{C}(3)$, $\text{C}(5)$ and $\text{C}(6)$ (mean deviation from plane 0.007 Å). The

Table 3
Crystal and data collection parameters for complexes 1 and 2

	1	2
<i>Crystal data</i>		
Formula	$\text{C}_{35}\text{H}_{35}\text{F}_6\text{O}_3\text{P}_3\text{Ru}$	$\text{C}_{36}\text{H}_{37}\text{F}_6\text{O}_3\text{P}_3\text{Ru}$
Mass	779.64	793.67
Crystal system	monoclinic	monoclinic
Crystal colour, habit	colourless, prismatic	colourless, prismatic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	13.109(5)	9.747(2)
b (Å)	15.685(5)	14.646(4)
c (Å)	16.791(7)	24.026(3)
β (deg)	98.14(3)	98.36(1)
Volume V (Å ³)	3418(2)	3393(1)
Temperature T (°C)	25	21
No. of molecules in unit cell Z	4	4
Density D_{calc} (g cm ⁻³)	1.515	1.553
$F(000)$	1584	1616
μ (cm ⁻¹)	6.46 (Mo K α)	6.52 (Mo K α)
Crystal dimensions (mm ³)	0.12 × 0.22 × 0.65	0.17 × 0.27 × 0.39
<i>Data collection/reduction</i>		
Diffractometer	Rigaku AFC6S	Rigaku AFC5R
Radiation, λ (Å)	Mo K α , 0.71069	Mo K α , 0.71069
2θ range (deg)	1.0–50.0	1.0–50.1
Scan type	$\omega-2\theta$	ω
Scan width (deg)	(1.00 + 0.30 tan θ)	(1.05 + 0.30 tan θ)
Total data	6357	6677
Unique data	6066	6284
'Observed' data ($I > 3\sigma(I)$), N_o	3285	4869
<i>Solution and refinement</i>		
Structure solution	Direct methods	Patterson methods
Refinement	Full-matrix least squares	Full-matrix least squares
Least squares variables, N_r	415	424
R^a	0.061	0.035
R_w^a	0.077	0.040
Goodness of fit S^a	2.62	2.26
Difference map features (e ⁻ Å ⁻³)	+0.80, -0.68	+0.56, -0.38

^a $R = \sum |\Delta| / \sum |F_o|$; $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$; $S = [\sum w\Delta^2 / (N_o - N_r)]^{1/2}$; $\Delta = F_o - F_c$.

Table 4
Atomic coordinates for complex I

Atom	x	y	z	Atom	x	y	z
Ru1	0.49117(6)	0.14551(5)	0.18843(5)	C14	0.4430(8)	0.4332(7)	0.2362(7)
P1	0.4245(2)	0.2754(2)	0.1521(2)	C15	0.499(1)	0.4971(8)	0.2808(7)
P2	0.3244(2)	0.1126(2)	0.1977(2)	C16	0.603(1)	0.4965(8)	0.2895(8)
P3	0.4316(3)	0.1998(2)	0.6608(2)	C17	0.652(1)	0.432(1)	0.255(1)
F1	0.5148(9)	0.194(1)	0.7327(7)	C18	0.5973(8)	0.3664(7)	0.2118(9)
F2	0.3466(8)	0.215(1)	0.7129(6)	C19	0.2955(9)	0.0861(7)	0.2984(7)
F3	0.449(1)	0.2918(6)	0.664(1)	C20	0.361(1)	0.0311(8)	0.3447(7)
F4	0.410(1)	0.1013(7)	0.658(1)	C21	0.346(1)	0.012(1)	0.424(1)
F5	0.512(1)	0.188(1)	0.6073(7)	C22	0.262(2)	0.092(2)	0.454(1)
F6	0.3463(9)	0.2069(7)	0.5865(6)	C23	0.201(2)	0.107(1)	0.407(2)
O1	0.4503(5)	0.2336(5)	0.3330(4)	C24	0.215(1)	0.1210(8)	0.331(1)
C1	0.2926(8)	0.2810(7)	0.1756(7)	C25	0.272(1)	0.023(1)	0.1375(8)
C2	0.241(1)	0.2030(8)	0.160(1)	C26	0.300(1)	-0.057(1)	0.157(1)
C3	0.5131(8)	0.1848(7)	0.2977(6)	C27	0.275(2)	-0.128(1)	0.109(1)
C4	0.605(1)	0.166(1)	0.3607(8)	C28	0.220(2)	-0.121(2)	0.038(2)
C5	0.595(1)	0.227(1)	0.4288(9)	C29	0.178(2)	-0.042(2)	0.017(1)
C6	0.487(1)	0.255(1)	0.4165(7)	C30	0.206(2)	0.031(1)	0.064(1)
C7	0.4129(8)	0.3033(7)	0.0437(6)	C31	0.529(1)	0.069(2)	0.084(1)
C8	0.422(1)	0.3869(8)	0.0193(8)	C32	0.544(1)	0.0190(8)	0.153(1)
C9	0.412(1)	0.404(1)	-0.064(1)	C33	0.622(1)	0.050(1)	0.200(1)
C10	0.394(1)	0.341(1)	-0.1177(8)	C34	0.656(1)	0.127(1)	0.106(1)
C11	0.383(1)	0.258(1)	-0.0944(7)	C35	0.595(2)	0.135(1)	0.096(1)
C12	0.390(1)	0.2402(8)	-0.0128(7)				
C13	0.4906(8)	0.3676(5)	0.2020(6)				

Table 5
Atomic coordinates for complex 2

Atom	x	y	z	Atom	x	y	z
Ru1	0.46686(3)	0.28268(2)	0.58807(1)	C14	0.1625(4)	0.4170(3)	0.5885(2)
P1	0.2498(1)	0.30934(8)	0.60974(4)	C15	0.2286(5)	0.4893(3)	0.5669(2)
P2	0.5336(1)	0.32757(8)	0.67881(5)	C16	0.1605(5)	0.5709(3)	0.5536(2)
P3	0.2064(2)	0.1477(1)	0.36374(6)	C17	0.0763(6)	0.5811(4)	0.5622(2)
F1	0.3593(4)	0.1782(3)	0.5594(2)	C18	0.0420(5)	0.5104(4)	0.5839(2)
F2	0.2586(4)	0.0974(2)	0.4210(1)	C19	0.0250(4)	0.4290(3)	0.5968(2)
F3	0.2304(5)	0.0580(2)	0.3305(2)	C20	0.6180(4)	0.2434(3)	0.7277(2)
F4	0.0552(4)	0.1160(3)	0.3679(2)	C21	0.6031(5)	0.2412(3)	0.7835(2)
F5	0.1574(5)	0.1981(3)	0.3068(1)	C22	0.6781(6)	0.1796(4)	0.8190(2)
F6	0.1855(4)	0.2369(2)	0.3971(1)	C23	0.7678(6)	0.1201(4)	0.7996(2)
O1	0.3940(3)	0.1344(2)	0.6566(1)	C24	0.7820(5)	0.1207(4)	0.7445(2)
C1	0.2569(4)	0.3145(3)	0.6866(2)	C25	0.7070(5)	0.1816(3)	0.7089(2)
C2	0.3840(4)	0.3701(3)	0.7093(2)	C26	0.6552(4)	0.4231(3)	0.6904(2)
C3	0.4419(4)	0.1572(3)	0.6101(2)	C27	0.7870(5)	0.4144(3)	0.7200(2)
C4	0.4786(6)	0.0750(4)	0.5784(2)	C28	0.8741(5)	0.4889(4)	0.7290(2)
C5	0.3693(8)	0.0007(4)	0.5738(3)	C29	0.8317(6)	0.5729(4)	0.7084(2)
C6	0.3161(7)	-0.0168(4)	0.6273(3)	C30	0.7004(6)	0.5836(3)	0.6788(2)
C7	0.3875(7)	0.0385(4)	0.6730(2)	C31	0.6141(5)	0.5089(3)	0.6701(2)
C8	0.1170(4)	0.2251(3)	0.5867(2)	C32	0.6223(5)	0.2508(4)	0.5302(2)
C9	0.0957(4)	0.2012(3)	0.5302(2)	C33	0.6567(5)	0.3343(4)	0.5568(2)
C10	-0.0005(5)	0.1358(3)	0.5099(2)	C34	0.5509(5)	0.3969(3)	0.5391(2)
C11	-0.0736(5)	0.0917(3)	0.5469(2)	C35	0.4492(5)	0.3498(3)	0.5025(2)
C12	-0.0541(5)	0.1143(3)	0.6027(2)	C36	0.4922(5)	0.2602(3)	0.4964(2)
C13	0.0403(5)	0.1810(3)	0.6223(2)				

relatively high energy boat conformation adopted by the 2-oxacyclohexylidene ligand of **2** may, at first, appear difficult to rationalise, but there is a clear precedent in the structure of six-membered lactone rings [17] where the requirement for a planar C–C(O)–O–C arrangement imposes a boat conformation. Drawing parallels between the lactone ring C–C(O)–O–C and oxacarbene C_{β} – C_{α} (Ru)–O– C_{ϵ} fragments suggests a requirement for co-planarity of the atoms C(4)–C(3)–O(1)–C(7) in **2** (mean deviation from plane 0.011 Å); similarly, in **1** the atoms C(4)–C(3)–O(1)–C(6) exhibit a mean deviation of just 0.006 Å from a plane. Re-examination of the structural data for $[Mn_2(CO)_9(\overline{CCH_2(CH_2)_2CH(R)O})]$ (R = H or Me) [13] suggests that, here as well, the atoms C_{β} – C_{α} –O– C_{ϵ} , (C(29)–C(25)–O(25)–C(26)) of the 2-oxacyclohexylidene ligand maintain co-planarity (torsion angles (C(29)–C(25)–O(25)–C(26)), R = H, 1.0(12)°; R = Me, –0.8(9)°) but the co-planarity of C_{β} – C_{γ} – C_{δ} – C_{ϵ} , (C(29)–C(28)–C(27)–C(26)) is less well controlled with torsion angles (C(29)–C(28)–C(27)–C(26)), R = H, 32.9(19)°; R = Me, 7.0(15)°. However, from the data currently available, it appears that severe limitations are placed upon the conformational flexibility of the 2-oxacyclohexylidene ligand which, in sterically congested environments, may indeed impose some interesting structural constraints.

3. Experimental

3.1. General procedures

The preparation and purification of the complexes described were carried out under dry nitrogen, and solvents were dried and purified by standard methods. The complex $[RuCl(dppe)(\eta-C_5H_5)]$ was prepared by the literature procedure [18] and the chemicals dppe and $HC\equiv C(CH_2)_nCH_2OH$ ($n = 1$ or 2) obtained from Lancaster Synthesis. 300 MHz 1H and 75 MHz ^{13}C NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers, 122 MHz ^{31}P NMR spectra on the Varian Associates XL 300 and mass spectra using a Kratos Concept IS. Microanalyses were by the Microanalytical Service of the Department of Chemistry, University of Manchester.

3.2. Preparations

$[Ru(CCH_2CH_2CH_2O)(dppe)(\eta-C_5H_5)]PF_6$ **1**. A mixture of $[RuCl(dppe)(\eta-C_5H_5)]$ (0.46 g, 0.77 mmol), $NH_4[PF_6]$ (0.15 g, 0.92 mmol) and 3-butyn-1-ol (0.41 g, 5.85 mmol) in methanol (50 cm³) was refluxed for 3 h to give a very pale yellow solution. After filtration, the volume was reduced and diethyl ether added to precipitate **1** as a white solid which was collected and recrystallised from CH_2Cl_2 –diethyl ether; yield 0.32 g (54%).

Complex **2** was prepared in 74% yield by an identical procedure starting from $[RuCl(dppe)(\eta-C_5H_5)]$ (0.360 g, 0.60 mmol), $NH_4[PF_6]$ (0.117 g, 0.72 mmol) and 4-pentyn-1-ol (0.384 g, 4.57 mmol).

3.3. X-ray crystal structure analyses of complexes **1** and **2**

The majority of details of the structure analyses carried out on **1** and **2** are given in Table 3; non-hydrogen atom positional parameters for **1** and **2** are listed in Tables 4 and 5 respectively. Colourless crystals of **1** were obtained by slow diffusion of a diethyl ether layer into a CH_2Cl_2 solution of the complex, whilst colourless crystals of **2** were grown by vapour diffusion of diethyl ether into an acetone solution of **2**. Cell dimensions for **1** were determined from the setting angles of 25 carefully centred reflections in the range $14.47 < 2\theta < 22.23^\circ$ and for **2** from 24 carefully centred reflections in the range $30.35 < 2\theta < 38.34^\circ$. Empirical absorption corrections based on azimuthal scans were applied to the data for **1** and **2** (resulting in transmission factors of 0.90 to 1.00 for **1** and 0.97 to 1.00 for **2**) and in each case the data were also corrected for Lorentz and polarisation effects. Linear decay corrections were applied to the data for **1** and **2**, based in each case on the intensities of three representative reflections which were measured after every 150 reflections and declined by –0.8% for **1** and –0.6% for **2**. Non-hydrogen atoms were refined anisotropically. For **1**, hydrogen atoms were included in the structure factor calculation in idealised positions ($C-H = 0.95 \text{ \AA}$) and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded; for **2**, hydrogen atoms were included but not refined. For **1**, $w = 4F_o^2/\sigma^2(F_o^2)$ with a p -factor of 0.03 to downweight strong reflections, whilst for **2**, $w = 1/[\sigma_c^2(F_o) + (p^2/4)(F_o^2)]$ with a p -factor of 0.0070. Neutral atom scattering factors were taken from Ref. [19] and all calculations were performed using the TEXSAN crystallographic software packages of Molecular Structure Corporation [20]. Crystallographic data for this work has been deposited at the Cambridge Crystallographic Data Centre.

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References

- [1] S.G. Davies, J.P. McNally and A.J. Smallridge, *Adv. Organomet. Chem.*, **30** (1990) 1.

- [2] M.I. Bruce, *Chem. Rev.*, 91 (1991) 197.
- [3] N.M. Kostic and R.F. Fenske, *Organometallics*, 1 (1982) 974.
- [4] R.L. Beddoes, C. Bitcon, R.W. Grime, A. Ricalton and M.W. Whiteley, *J. Chem. Soc. Dalton Trans.*, (1995) 2873.
- [5] R.L. Beddoes, R.W. Grime, Z.I. Hussain and M.W. Whiteley, *J. Chem. Soc., Dalton Trans.*, (1996) 3893.
- [6] G. Consiglio, F. Morandini, G.F. Ciani and A. Sironi, *Organometallics*, 5 (1986) 1976.
- [7] M.I. Bruce, G.A. Koutsantonis and E.R.T. Tiekink, *Acta Crystallogr. Sect. C*, 44 (1988) 1130.
- [8] M.I. Bruce, M.G. Humphrey, M.R. Snow and E.R.T. Tiekink, *J. Organomet. Chem.*, 314 (1986) 213.
- [9] P. Nombel, N. Lugan and R. Mathieu, *J. Organomet. Chem.*, 503 (1995) C22.
- [10] B.E.R. Schilling, R. Hoffmann and J.W. Faller, *J. Am. Chem. Soc.*, 101 (1979) 592.
- [11] M.I. Bruce, A.G. Swincer, B.J. Thomson and R.C. Wallis, *Aust. J. Chem.*, 33 (1980) 2605.
- [12] J.-A.M. Garner, A. Irving and J.R. Moss, *Organometallics*, 9 (1990) 2836.
- [13] J.-A.M. Andersen, S.J. Archer, J.R. Moss and M.L. Niven, *Inorg. Chim. Acta*, 206 (1993) 187.
- [14] C. Kelley, N. Lugan, M.R. Terry, G.L. Geoffroy, B.S. Haggerty and A.L. Rheingold, *J. Am. Chem. Soc.*, 114 (1992) 6735.
- [15] M.I. Bruce, C. Dean, D.N. Duffy, M.G. Humphrey and G.A. Koutsantonis, *J. Organomet. Chem.*, 295 (1985) C40.
- [16] H. Adams, N.A. Bailey, M. Grayson, C. Ridgway, A.J. Smith, P. Taylor and M.J. Winter, *Organometallics*, 9 (1990) 2621.
- [17] J.F. McConnell, A.McL. Mathieson and B.P. Schoenborn, *Tetrahedron Lett.*, (1962) 445.
- [18] G.S. Ashby, M.I. Bruce, I.B. Tomkins and R.C. Wallis, *Aust. J. Chem.*, 32 (1979) 1003.
- [19] D.T. Cromer and J.T. Waber, *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.
- [20] TEXSAN-TEXRAY, *Structure analysis package*, 1985 (Molecular Structure Corporation, The Woodlands, TX).