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Unsaturated ether chelate complexes of ruthenium(II)†

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The complexes $[Ru\{\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2Cl]$ (**2a** $R^1 = R^2 = H, n = 1$; **2b** $R^1 = R^2 = H, n = 2$; **2c** $R^1 = H, R^2 = Me, n = 1$; **2d** $R^1 = Me, R^2 = H, n = 1$) were prepared by heating $[Ru(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2Cl]$ **1** with the appropriate unsaturated alcohol. Reaction of complexes **2** with $AgBF_4$ led to loss of the chloride ligand and the formation of the cationic chelate complexes $[Ru\{\eta^5:\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2]BF_4$, with the double bond co-ordinated to the metal centre. Single-crystal X-ray structures determined for the complexes $[Ru\{\eta^5:\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2\}(CO)_2]BPh_4$ and $[Ru\{\eta^5:\eta^2\text{-}C_5Me_4CH_2O(CH_2)_2CH{=}CH_2\}(CO)_2]BF_4$ confirmed that the double bond was co-ordinated to the metal. The neutral chelate complex $[Ru\{\eta^5:\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2\}(CO)Cl]$ was formed on addition of trimethylamine *N*-oxide to a solution of **2a** by the replacement of one of the carbonyl ligands with the alkene on the pendant arm.

The aims of this work, to make complexes having 'hands' attached to substituted cyclopentadienyl rings which can grasp reactants and so effect stereoselective catalysis, have been described in previous papers of this series.[1–4] Thus, for example, we have made a variety of ether complexes of the type $[Ru(\eta^5\text{-}C_5Me_4CH_2OR)(CO)_2Cl]$ by reacting the chloride $[Ru(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2Cl]$ with the appropriate alcohol.[2] We here describe the extension of those reactions in which unsaturated alcohols are used to build up the side chains, which are then chelated to the metal centre.

Results and Discussion

Unsaturated ether complexes $[Ru\{(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2Cl]$

Heating $[Ru(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2Cl]$ **1** in prop-2-en-1-ol, or in but-3-en-1-ol, followed by chromatography led to the formation of the unsaturated ether complexes $[Ru\{\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2Cl]$, **2a** and **2b**, in 70–90% yield. Using a mixture of *trans*- and *cis*-crotyl alcohols (but-2-en-1-ol) gave an inseparable mixture of the corresponding complexes **2c** and **2d** (ratio 7 : 1), where the substituents on the double bond were *E* and *Z* respectively [$R^1 = R^2 = H, n = 1$ **2a**; $R^1 = R^2 = H, n = 2$ **2b**; $R^1 = H, R^2 = Me, n = 1$ **2c**; $R^1 = Me, R^2 = H, n = 1$ **2d**; equation (1)]. Increasing the temperature did not lead to a decrease in reaction times; instead, increased decomposition of the complexes was observed, however, the reaction was accelerated by addition of NEt_3.

$$\underset{\mathbf{1}}{[Ru(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2Cl]} + HO(CH_2)_nCH{=}CR^1R^2 \longrightarrow \underset{\mathbf{2a\text{–}2d}}{[Ru\{\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2Cl]} \quad (1)$$

The complexes **2a**–**2d** showed the expected IR spectra, with two carbonyl bands [ν(CO) *ca.* 1983 and 2036 cm^{-1}, Table 1] close to those found for the chloride **1** [ν(CO) 1989 and 2041 cm^{-1}]. The ^1H NMR spectra showed two singlets at *ca.* δ 1.9 and one further singlet at *ca.* δ 4.05, in the ratio 6 : 6 : 2, arising from two pairs of two equivalent methyls and one CH_2; this confirms that the $\eta^5\text{-}C_5Me_4CH_2$ is still present. Other signals arising from the allylic fragment, $O(CH_2)_nCH{=}CHR$, having the expected chemical shifts and coupling patterns, are also seen (Table 2). The ^{13}C NMR spectra (Table 3) show two methyls (at δ 9–10) and three resonances due to the ring carbons (at δ 90–106), arising from the C_5Me_4, as well as the ring CH_2 (at δ 72). Complexes **2a**–**2c** showed CH_2 resonances in the region *ca.* δ 62, while complex **2b** has an additional CH_2 signal at δ 33.9. Complexes **2a** and **2b** showed the alkenyl resonances at δ 115–120 (=CH_2) and 130–140 (–CH=), similar to those reported for $[Ir(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(CO)Ph(Me)]$[4] and for $[Co(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(CO)_2]$[5] where the alkenyl groups are *not* co-ordinated to the metal, while the carbonyl groups in **2a**–**2c** gave one singlet at δ 198, as has been found for related complexes $[Ru(\eta^5\text{-}C_5Me_4CH_2X)(CO)_2Cl]$.[2]

Cationic chelates $[Ru\{\eta^5:\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2]^+BF_4^-$

The ruthenium-bonded chloride in complexes **2a**–**2d** was removed by reaction with silver tetrafluoroborate in CH_2Cl_2, silver chloride was precipitated and the side chain double bond co-ordinated at the ruthenium vacant site to give the η^2-internally chelated cations $[\mathbf{3a}]^+$–$[\mathbf{3c}]^-$ in 70–80% yield {$R^1 = R^2 = H, n = 1$ $[\mathbf{3a}]^+$; $R^1 = R^2 = H, n = 2$ $[\mathbf{3b}]^+$; $R^1 = H, R^2 = Me, n = 1$ $[\mathbf{3c}]^+$; equation (2)}. The chelate complex derived from **2d** could not be detected in the mixture. An alternative route involved treatment of complex **1** with 2

$$\underset{\mathbf{2a\text{–}2c}}{[Ru\{\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CHR^1R^2\}(CO)_2Cl]} \xrightarrow{AgBF_4} \underset{[\mathbf{3a}]BF_4\text{–}[\mathbf{3b}]BF_4}{[Ru\{\eta^5:\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CR^1R^2\}(CO)_2]^+BF_4^-} + AgCl \quad (2)$$

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† Ring-methyl activation in pentamethylcyclopentadienyl complexes. Part 6.[1]

Table 1 Microanalytical[a] and IR data

Complex	Yield (%)	$\tilde{\nu}$(CO)/cm^{-1}	Microanalysis (%) C	H	X
2a	70	1984; 2037	46.8 (46.9)	5.1 (5.0)	
2b	88	1983; 2037	48.8 (48.3)	5.5 (5.3)	
2c + **2d**	85	1984; 2036	48.7 (48.3)	5.5 (5.3)	
[**3a**]BF_4	78	2033; 2075	41.1 (41.4)	4.5 (4.4)	
[**3b**]BF_4	73	2026; 2070	42.4 (42.8)	4.7 (4.7)	
[**3c**]BF_4	79	2027; 2070	42.3 (42.8)	4.8 (4.7)	
4a	85	1973	48.0 (47.3)	5.2 (5.4)	10.0 (10.0)[b]
5a	76	1973	42.1 (42.0)	5.0 (4.8)	
6a	78	1972	38.2 (37.6)	4.5 (4.3)	27.4 (28.4)[c]
[**7a**]BF_4	71	2003	41.9 (42.9)	4.7 (5.0)	

[a] Calculated values in parentheses. [b] X = Cl. [c] X = I.

equivalents of $AgBF_4$ in the presence of allyl alcohol giving [Ru(η^5-$C_5Me_4CH_2Cl$)(CO)$_2$(η^2-$H_2C{=}CHCH_2OH$)]$^+BF_4^-$, which formed [**3a**]BF_4 upon heating.

The BF_4^- salts of complexes [**3a**]$^+$–[**3c**]$^+$ were characterised spectroscopically; complexes[**3a**]BPh_4 and [**3b**]BF_4 had their structures confirmed by single-crystal X-ray methods. All three complexes exhibited two ν(CO) bands in the regions 2026–2033 and 2070–2075 cm^{-1}; these were at higher frequencies than in **2a**–**2d** due to the positive charge on the ruthenium centre. The ^{1}H and ^{13}C NMR spectra clearly reveal the co-ordination of the olefinic double bond; thus in the ^{1}H NMR spectra of the $n = 1$ complexes [**3a**]$^+$ and [**3c**]$^+$, none of the methyl groups in C_5Me_4 is equivalent and four separate signals are observed; however in the $n = 2$ complex [**3b**]$^+$ three methyl resonances (1:2:1) were observed at ambient temperatures, and this may indicate a dynamic process. The protons in the ring CH_2 groups are also non-equivalent [dd, *J*(H-H) 17 Hz], and the alkenyl signals H_{cis} (R^1), H_{trans} (R^2) and $H_{central}$ (H^c) are at higher field (lower frequency), normally by > 1 ppm, by comparison with the resonances of the unco-ordinated alkene in complexes **2a**–**2d**. The ^{13}C NMR spectra (Table 3) show four resonances for the Me groups, and the signals of the co-ordinated alkenyls are shifted *ca.* 50 ppm by comparison with unco-ordinated alkenyl groups. Rather similar changes were seen in the iridium complexes [Ir(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)(CO)Ph(Me)] and [{Ir(η^5:η^2-$C_5Me_4CH_2CH_2CH{=}CH_2$)(Cl)(μ-Cl)}$_2$].[4]

The absence of a plane of symmetry in complexes [**3a**]$^+$–[**3c**]$^+$ was indicated by the ^{1}H and ^{13}C spectra which showed the ring methyls and the ring carbons all to be inequivalent. This arises because the co-ordinated alkenyl group is oriented parallel to the pentamethylcyclopentadienyl ring and the cations exist as racemic mixtures of enantiomers (Fig. 1). A similar situation has previously been observed for the chromium complexes [Cr{η^6:η^2-$C_6Me_5(CH_2)_nCH{=}CH_2$}(CO)$_2$].[6,7]

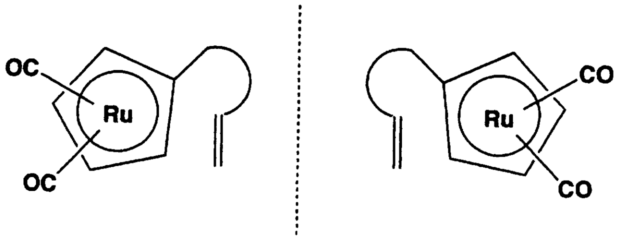


Fig. 1 Representation of the core of the cations [**3a**]$^+$–[**3c**]$^+$ showing the origin of the chirality

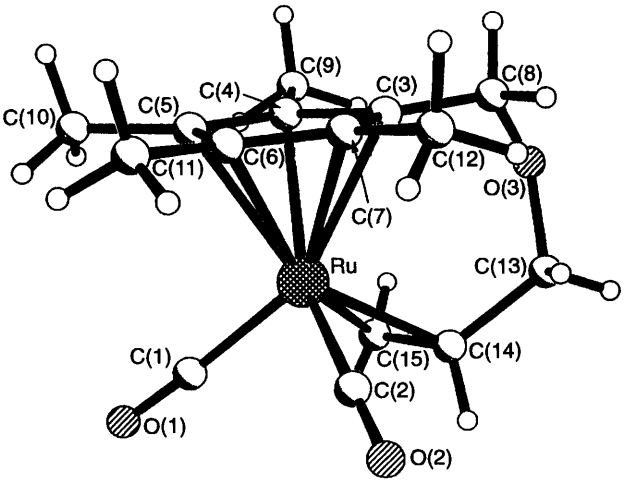


Fig. 2 Illustration of the structure of the cation [**3a**]$^+$

Crystal structures of the cationic chelates [Ru{η^5:η^2-$C_5Me_4CH_2O(CH_2)_nCH{=}CH_2$}(CO)$_2$]$^+$, [3a]$^+$ and [3b]$^+$

An X-ray determination was carried out on a crystal of [Ru(η^5:η^2-$C_5Me_4CH_2OCH_2CH{=}CH_2$)(CO)$_2$]$^+BPh_4^-$ (illustrated in Fig. 2), prepared by addition of $NaBPh_4$ to an aqueous solution of the BF_4 salt of [**3a**]$^+$; selected bond lengths and angles with estimated standard deviations are given in Table 4. A ruthenium(II) atom, slightly asymmetrically bonded (Ru–C 2.17–2.26 Å) to a (2-oxapent-4-enyl)tetramethylcyclopentadienyl ligand, is present in each molecular cation: root mean square (r.m.s.) deviation of C_5-ring 0.013 Å; perpendicular distance of the ruthenium atom from the mean plane 1.875 Å, displacements of the methyl carbons are between 0.099 and 0.159 Å away from the metal, whereas the carbon of the CH_2 group lies much more closely coplanar with the cyclopentadienyl ring at a distance of 0.046 Å from the metal. The ruthenium is also bonded to two carbonyl ligands, and to the terminal alkene residue of the pendant chain on the cyclopentadienyl ring (Ru–C 2.20 and 2.26 Å, with the longer distance to the terminal carbon). The alkene group lies almost parallel to the cyclopentadienyl ring at an angle to the normal of 89.4° and deviations from the ring plane of 3.03, 3.04 Å, thus the alkene is tilted, very slightly, in the opposite direction to the C_5 plane.

An X-ray determination was also carried out on a single crystal of [Ru{η^5-$C_5Me_4CH_2O(CH_2)_2CH{=}CH_2$}(CO)$_2$]$^+$-$BF_4^-$, [**3b**]$BF_4$, prepared by slow diffusion of diethyl ether into a chloroform solution of the complex. Each asymmetric unit contained two independent molecules of the chiral complex [**3b′**]$^+$, [**3b″**]$^+$ (Figs. 3 and 4) the enantiomer of [**3b′**]$^+$ is almost indistinguishable from [**3b″**]$^+$. Selected bond lengths and angles are given in Table 5. A ruthenium(II) atom, slightly asymmetrically bonded (Ru–C 2.20–2.28 Å) to a (2-oxahex-5-enyl)tetramethylcyclopentadienyl ligand is present in each molecular cation: r.m.s. deviations of the C_5-ring, 0.012 and

Table 2 Proton NMR spectra for the complexes (δ)[a]

Complex	C_5Me_4	CH_2	$(CH_2)_n$	H^c	R^1	R^2
2a	1.91, 1.96	4.08 (s)	4.04 (d, J = 6)	5.90 (ddd, J = 17, 10, 6)	5.23 (d, J = 10)	5.31 (d, J = 17)
2b	1.87, 1.93	4.05 (s)	2.33 (dt, J = 7, 7), 3.55 (t, J = 7)	5.76 (ddd, J = 17, 12, 7)	4.97 (d, J = 12)	5.11 (d, J = 17)
2c (*E*)	1.89, 1.96	4.03 (s)	3.94 (d, J = 7)	5.45–5.80 (m)	1.71 (d, J = 7)	5.45–5.80 (m)
2d (*Z*)	1.90, 1.98	4.05 (s)	4.08 (d, J = 7)	5.45–5.80 (m)	5.45–5.80 (m)	1.66 (d, J = 7)
[**3a**]BF_4	1.92, 2.20, 2.24, 2.26	3.68 (d, J = 14), 4.58 (d, J = 14)	3.28 (dd, J = 17, 2), 4.48 (dd, J = 17,2)	4.92 (dddd, J = 14, 8, 2, 2)	3.65 (d, J = 8)	2.74 (d, J = 14)
[**3b**]BF_4	2.03, 2.15, 2.25	3.96 (d, J = 14), 4.06 (d, J = 14)	3.7–3.8 (m)	4.6–4.8 (m)	4.6–4.8 (m)	1.74 (d, J = 6)
[**3c**]BF_4	1.96, 2.14, 2.16, 2.22	3.74 (d, J = 14), 4.43 (d, J = 14)	3.29 (dd, J = 16, 2); 4.23 (dd, J = 16, 2)	4.67 (ddd, J = 13, 2, 2)	1.98 (d, J = 6)	3.88 (dq, J = 13, 6)
4a	1.42, 1.70, 1.71, 1.77, 1.85, 1.91, 1.97, 2.01	3.21 (d, J = 14), 3.82 (d, J = 13), 4.16 (d, J = 13), 4.27 (d, J = 14)	3.01 (dd, J = 15, 2), 3.54 (dd, J = 15, 2), 3.96 (dd, J = 16, 3), 4.14 (dd, J = 16, 3)	4.16 (dddd, J = 13, 9, 3, 2), 4.28 (dddd, J = 13, 9, 3, 3)	3.18 (J = 9, 1), 3.51 (J = 9, 1)	2.60 (J = 13), 3.03 (J = 13)
5a	1.55, 1.78, 1.94, 1.94, 2.00, 2.01, 2.04, 2.05	3.29 (d, J = 13), 3.75 (d, J = 13), 4.26 (d, J = 13), 4.28 (d, J = 13)	3.10 (dd, J = 15, 2), 3.39 (dd, J = 15, 2), 4.14 (dd, J = 15, 2), 4.15 (dd, J = 15, 2)	4.30 (dddd, J = 13, 9, 2, 2), 4.42 (dddd, J = 13, 9, 2, 2)	3.36 (J = 9, 1), 2.80 (J = 9, 1)	2.44 (J = 13), 2.80 (J = 13)
6a	1.70, 1.71, 1.99, 2.05, 2.06, 2.09, 2.29, 2.39	3.44 (d, J = 13), 3.62 (d, J = 13), 4.29 (d, J = 13), 4.35 (d, J = 13)	3.20 (dd, J = 15, 2), 3.23 (dd, J = 15, 2), 4.15 (dd, J = 15, 2), 4.32 (dd, J = 15, 2)	4.10 (dddd, J = 13, 9, 2, 2), 4.57 (dddd, J = 13, 9, 2, 2)	3.11 (J = 9, 1), 3.58 (J = 9, 1)	2.22 (J = 13), 2.37 (J = 13)
[**7a**]BF_4	1.45, 1.90,[b] 1.91, 1.92, 1.95, 2.02, 2.08, 2.17, 2.50, 2.52	3.20 (d, J = 14), 3.87 (d, J = 14), 4.21 (d, J = 14), 4.30 (d, J = 14)	2.96 (dd, J = 16, 2), 3.69 (dd, J = 16, 2), 4.11 (dd, J = 16, 2), 4.27 (dd, J = 16, 2)	4.34 (dddd, J = 13, 9, 2, 2), 4.92 (dddd, J = 13, 9, 2, 2)	3.24 (J = 9, 1), 3.74 (J = 9, 1)	2.69 (J = 13), 3.32 (J = 13)

[a] All spectra obtained in $CDCl_3$, J in Hz. [b] Two singlets arising from MeCN.

Table 3 Carbon-13 NMR spectra for the complexes (δ, $CDCl_3$ solution)

Complex	C_5Me_4	CH_2	$O(CH_2)_n$	-CH=	=CR^1H	CO
2a	9.7, 9.9, 92.3, 100.5, 105.7	72.1	62.1	134.0	118.0	198.0
2b	9.7, 9.9, 92.5, 100.5, 105.5	70.4	33.9, 62.9	134.8	118.3	198.0
2c	9.3, 9.9, 93.6, 100.8, 105.5	71.8	62.1	129.5	17.8 (Me), 127.3	199.5
[**3a**]BF_4	9.1, 10.0, 10.3, 10.5, 95.1, 97.2, 102.4, 110.5, 114.4	65.8	62.1	80.3	50.5	197.6, 198.4
[**3c**]BF_4	9.5, 10.1, 10.5, 10.6, 96.1, 97.7, 103.5, 110.6, 114.1	66.0	62.2	79.8	22.2 (Me), 75.1	198.5, 198.7
[**3b**]BF_4	10.2, 10.3, 10.4, 10.7, 98.2, 104.5, 105.3, 112.2, 114.1	67.9	34.5, 58.6	83.6	56.8	197.8, 200.4
4a	8.9, 8.9, 9.2, 9.5, 9.5, 9.6, 11.0, 89.9, 92.4, 94.4, 95.41, 97.6, 100.8, 118.1, 118.4	66.6, 67.3	62.0, 62.2	69.0, 76.6	48.5, 57.8	207.2, 207.9
5a	8.9, 9.3, 9.6, 9.6, 9.7, 10.5, 10.9, 84.6, 87.1, 89.5, 91.6, 93.1, 95.8, 97.5, 101.0	66.3, 66.6	62.1, 62.2	69.0, 76.7	46.3, 54.0	206.6, 207.1
6a	9.0, 9.5, 10.3, 10.7, 10.8, 10.9, 11.8, 12.6, 86.6, 89.2, 90.0, 91.0, 91.5, 96.7, 97.4, 101.5, 108.2, 114.9	66.1, 66.9	62.1, 62.6	65.5, 70.0	43.5, 47.5	205.8, 206.4
[**7a**]BF_4*	8.8, 9.0, 9.0, 9.6, 9.6, 10.4, 10.7, 82.4, 84.2, 86.7, 91.0, 93.0, 96.7, 97.4, 101.5, 108.2, 114.9	66.2, 66.6	61.5, 62.1	75.6, 77.2	51.7, 57.9	203.9, 204.7

* Signals of MeCN (from two diastereomers) were observed at δ 4.1, 129.6 and 131.0.

Table 4 Selected bond lengths (Å) and angles (°) in the complex $[Ru(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)_2]^+BPh_4^-$ [**3a**]BPh_4

Ru–C(15)	2.26(2)	C(8)–O(3)	1.33(2)
Ru–C(14)	2.20(2)	O(3)–C(13)	1.43(3)
Ru–C(3)	2.221(12)	C(13)–C(14)	1.5000(13)*
C(3)–C(8)	1.39(2)	C(14)–C(15)	1.3297(12)*
C(1)–Ru–C(2)	96.3(7)	C(8)–O(3)–C(13)	115(2)
C(15)–Ru–C(14)	34.7(2)	O(3)–C(13)–C(14)	120.3(13)
C(3)–C(8)–O(3)	119(2)	C(13)–C(14)–C(15)	119.84(14)*

* The positions of C(13), C(14) and C(15) were fixed to facilitate refinement of the structure.

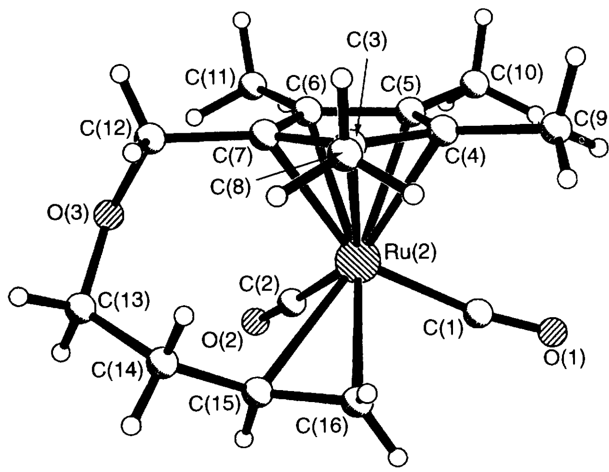


Fig. 3 Structure of one crystallographically independent cation [**3b′**]$^+$

0.013 Å respectively; perpendicular distance of the ruthenium from the mean plane, 1.875 and 1.881 Å, the methyl carbons are displaced between 0.091 and 0.223 Å away from the metal, the CH_2 group lies more closely coplanar with the C_5-ring at distances of 0.043 and 0.000 Å from the metal. The ruthenium is also bonded to two carbonyl ligands, and to the terminal alkene residue of the pendant chain on the cyclopentadienyl ring (Ru–C 2.26 and 2.33 Å, with the longer distance to the terminal carbon). The alkene group lies almost parallel to the cyclopentadienyl ring at angles to the normals of 89.3 and 87.6° and deviations from the ring plane of 3.26, 3.24 Å and 3.25, 3.30 Å; thus the alkenes are tilted, very slightly, in opposite directions relative to the cyclopentadienyl planes.

Table 5 Selected bond lengths (Å) and angles (°) in the complex $[Ru\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2O(CH_2)_2CH{=}CH_2\}(CO)_2]^+BF_4^-$ [**3b**]BF_4

[**3b′**]$^+$		[**3b″**]$^+$	
Ru(2)–C(16)	2.257(6)	Ru(1)–C(16a)	2.260(7)
Ru(2)–C(15)	2.333(6)	Ru(1)–C(15a)	2.331(7)
Ru(2)–C(7)	2.233(5)	Ru(1)–C(7a)	2.217(5)
C(7)–C(12)	1.509(8)	C(7a)–C(12a)	1.501(9)
C(12)–O(3)	1.421(7)	C(12a)–O(3a)	1.424(9)
O(3)–C(13)	1.405(7)	O(3a)–C(13a)	1.428(9)
C(13)–C(14)	1.474(9)	C(13a)–C(14a)	1.493(11)
C(14)–C(15)	1.425(9)	C(14a)–C(15a)	1.471(11)
C(15)–C(16)	1.342(9)	C(15a)–C(16a)	1.374(10)
C(1)–Ru(2)–C(2)	92.6(3)	C(1a)–Ru(1)–C(2a)	92.1(3)
C(15)–Ru(2)–C(16)	33.9(2)	C(15a)–Ru(1)–C(16a)	34.8(3)
C(7)–C(12)–O(3)	112.8(5)	C(7a)–C(12a)–O(3a)	111.3(5)
C(12)–O(3)–C(13)	115.1(5)	C(12a)–O(3a)–C(13a)	115.1(6)
O(3)–C(13)–C(14)	117.8(5)	O(3a)–C(13a)–C(14a)	116.7(6)
C(13)–C(14)–C(15)	122.8(6)	C(13a)–C(14a)–C(15a)	119.3(7)
C(14)–C(15)–C(16)	130.1(7)	C(14a)–C(15a)–C(16a)	124.4(8)

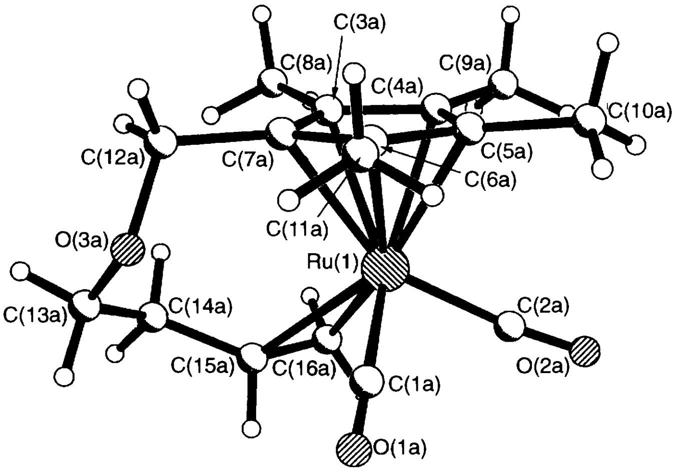


Fig. 4 Structure of the second crystallographically independent cation [**3b″**]$^+$ shown, as determined, as the enantiomer of [**3b′**]$^+$

The bond lengths and angles found for the two crystal structures [**3a**]$^+$, $n = 1$ and [**3b**]$^+$, $n = 2$ show few significant differences, indicating that the chelate rings in these complexes are not unduly strained. However, the bond angle subtended by the carbonyls at the ruthenium, C(1)–Ru–C(2), in [**3a**]$^+$ of 96.3(7)° is significantly larger than the corresponding angle C(1)–Ru(2)–C(2) of 92.6(3)° for [**3b′**]$^+$ and C(1a)–Ru(1)–C(2a) of 92.1(3)° for [**3b″**]$^+$. This suggests that the smaller chelate ring in $[\mathbf{3a}]^+$ does exert a tightening effect leading to a further opening of the OC–Ru–CO angle.

Neutral chelates $[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)X]$

One CO group in **2a** was removed on reaction with trimethylamine *N*-oxide and this led to the formation of the neutral chelate complex $[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)Cl]$, **4a**, in high yield, equation (3). Attempts to

$$\underset{\mathbf{2a}}{[\mathrm{Ru}(\eta^5\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)_2Cl]} + \mathrm{Me_3NO} \longrightarrow$$

$$\underset{\mathbf{4a}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)Cl]} \quad (3)$$

prepare a similar chelate complex from complex **2c** gave an unstable product, characterised only by its IR spectrum.

Chelate **4a** reacted with KBr or KI in methanol giving the bromide **5a** and iodide **6a** respectively, equation (4). Although

$$\underset{\mathbf{4a}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)Cl]} + \mathrm{KX} \longrightarrow$$

$$\underset{\mathbf{5a,\ 6a}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)X]} \quad (4)$$

the IR spectra of complexes **4a**–**6a** showed only one band in the carbonyl region at 1972–1973 $\mathrm{cm^{-1}}$, both the ^{1}H and ^{13}C NMR spectra showed two sets of signals in a ratio close to 1 : 1 for each complex. The ratio was independent of the method of purification. The presence of two sets of signals is consistent with the presence of two pairs of diastereomers. These arise because there are now two sources of chirality in the molecules: one involves the co-ordinated alkene, as in complexes $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$ (Fig. 1), the other because the metal is now a chiral centre too, with four different ligands (C_5Me_4, alkene, CO and X).

At 60 °C the ^{1}H NMR spectrum showed slightly broadened signals, indicating the onset of a fluxional process; a broad singlet arising from four methyl groups was observed at 100 °C, but no coalescence of the other more widely spaced resonances was observed at this temperature. On cooling the sample back to room temperature the original spectrum was regenerated.

Reaction of the cationic chelate $[\mathbf{3a}]^+$ with LiCl in tetrahydrofuran (thf) also led to the reformation of the neutral complex **2a**, equation (5).

$$\underset{[\mathbf{3a}]\mathrm{BF_4}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)_2]^+BF_4^-} \xrightarrow{\mathrm{LiCl}}$$

$$\underset{\mathbf{2a}}{[\mathrm{Ru}(\eta^5\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)_2Cl]} \quad (5)$$

The cationic chelate $[\mathbf{3a}]^+$ was reformed by passing CO through a methanol solution of **4a** in the presence of $\mathrm{NH_4PF_6}$, equation (6).

$$\underset{\mathbf{4a}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)Cl]} \xrightarrow[\mathrm{NH_4PF_6}]{\mathrm{CO}}$$

$$\underset{[\mathbf{3a}]\mathrm{PF_6}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)_2]^+PF_6^-} \quad (6)$$

The reaction of **4a** with silver tetrafluoroborate in the presence of acetonitrile gave a mixture of stable cationic diastereomers $[\mathbf{7a}]\mathrm{BF_4}$ [equation (7)]. The ν(CO) stretching

$$\underset{\mathbf{4a}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)Cl]} \xrightarrow[\mathrm{AgBF_4}]{\mathrm{MeCN}}$$

$$\underset{[\mathbf{7a}]\mathrm{BF_4}}{[\mathrm{Ru}(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2)(CO)(NCMe)]^+} \quad (7)$$

frequency was at 2003 $\mathrm{cm^{-1}}$, rather higher than in **4a**–**6a**, due to the positive charge.

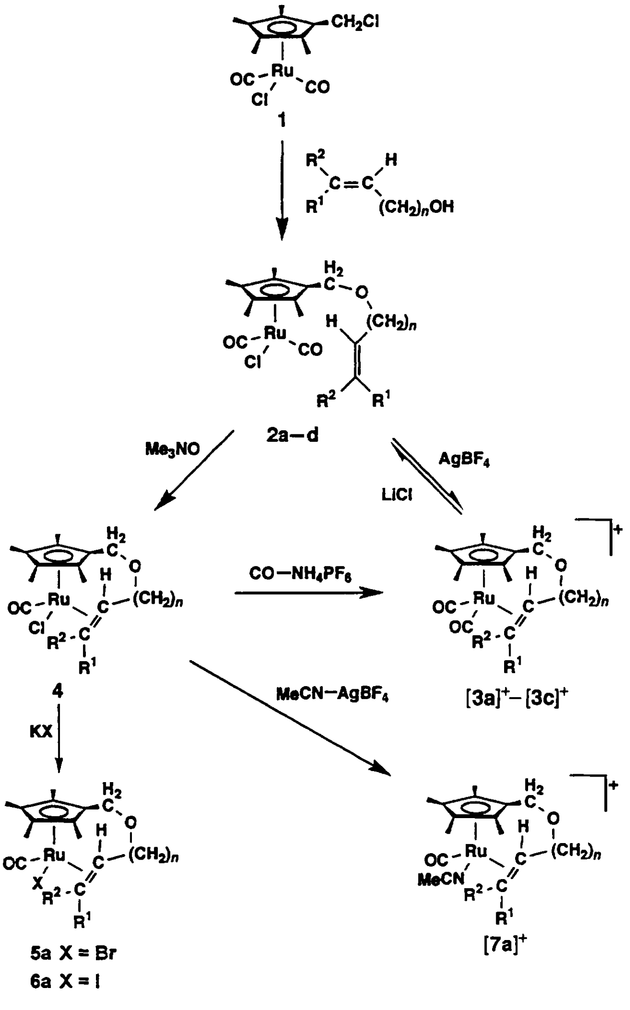
A summary of the syntheses of all of the complexes is shown in Scheme 1.

Conclusion

We have synthesised and structurally characterised the unsaturated ether complexes $[\mathrm{Ru}\{\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CH_2\}(CO)_2Cl]$ (**2a** $n = 1$ and **2b** $n = 2$) in which the double bond is not co-ordinated as well as in the cationic and neutral chelate complexes $[\mathrm{Ru}\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CH_2\}(CO)_2]^+$ ($[\mathbf{3a}]^+$ $n = 1$, and $[\mathbf{3b}]^+$ $n = 2$) and $[\mathrm{Ru}\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2OCH_2CH{=}CH_2\}(CO)Cl]$, **4a** in which the double bonds are co-ordinated. The presence of the (intramolecularly) co-ordinated double bonds in $[\mathrm{Ru}\{\eta^5{:}\eta^2\text{-}C_5Me_4CH_2O(CH_2)_nCH{=}CH_2\}(CO)_2]^+$ ($[\mathbf{3a}]^+$ $n = 1$, and $[\mathbf{3b}]^+$ $n = 2$) was confirmed by crystal-structure determinations. Some interconversions of the complexes are also reported. These results show that an 'arm' can be attached quite easily to a pentamethylcyclopentadienyl ring on ruthenium, that a pendant 'hand' can grasp the metal, and that such chelates seem to be essentially strain-free.

Experimental

Reactions were carried out using standard Schlenk-line techniques; solvents and reagents were purified and dried by standard methods. Microanalyses were performed by the Sheffield University Microanalysis Service and are listed,



Scheme 1 Transformations described in the text: **a** $R^1 = R^2 = H$, $n = 1$; **b** $R^1 = R^2 = H$, $n = 2$; **c** $R^1 = H$, $R^2 = Me$, $n = 1$; **d** $R^1 = Me$, $R^2 = H$, $n = 1$

together with yields and IR spectra, in Table 1. Infrared spectra were recorded as KBr discs on a Perkin-Elmer PE1710 FTIR spectrometer, ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM250 or AC250 instruments using the solvent or tetramethylsilane as internal standard and are collected in Tables 2 and 3.

[Ru{η^5-$C_5Me_4CH_2O(CH_2)_nCH=CR^1R^2$}(CO)$_2$Cl], 2a–2d

A solution of [Ru(η^5-$C_5Me_4CH_2Cl$)(CO)$_2$Cl] **1** (100 mg, 0.28 mmol) in prop-2-en-1-ol (3 cm^3) was heated (70 °C, 36 h). It was then cooled to room temperature, the alcohol was removed under reduced pressure and the residue chromatographed on an alumina column. A yellow band was eluted with 3:1 light petroleum (b.p. 40–60 °C)–diethyl ether as solvent. Removal of the solvent gave **2a** (75 mg, 70%). Complex **2b** was prepared similarly from but-3-en-1-ol, and crotyl alcohol gave a mixture of **2c** and **2d** (ratio, 1:7 by NMR) which could not be separated.

[Ru{η^5:η^2-$C_5Me_4CH_2O(CH_2)_nCH=CR^1R^2$}(CO)$_2$]BF$_4$, [3a]BF$_4$–[3c]BF$_4$

Silver tetrafluoroborate (47 mg, 0.24 mmol) was added to a solution of [Ru{η^5-$C_5Me_4CH_2O(CH_2)_nCH=CH_2$}(CO)$_2$Cl] (100 mg, 0.24 mmol) in CH_2Cl_2 (10 cm^3) at −78 °C. The mixture was stirred (10 min) and then allowed to warm to room temperature and stirred (30 min more). The solution was filtered and the solvent removed under reduced pressure. The residue was crystallised from a mixture of CH_2Cl_2–Et_2O, giving [**3a**]BF$_4$ (82 mg, 78%). Complexes [**3b**]BF$_4$ and [**3c**]BF$_4$ were prepared similarly.

[Ru(η^5:η^2-$C_5Me_4CH_2OCH_2CH=CH_2$)(CO)Cl], 4a

A solution of trimethylamine *N*-oxide dihydrate (70 mg, 0.63 mmol) in MeOH (10 cm^3) was added dropwise to a solution of [**3a**]BF$_4$ (96 mg, 0.25 mmol) dissolved in MeOH (10 cm^3). The solution was then stirred (2 h, 20 °C), and the solvent removed under reduced pressure. The residue was crystallised from a mixture of diethyl ether–light petroleum giving **4a** (76 mg, 85%).

[Ru(η^5:η^2-$C_5Me_4CH_2OCH_2CH=CH_2$)(CO)X], 5a, 6a

A mixture of the chloro complex **4a** (71 mg, 0.20 mmol) and KBr (48 mg, 0.40 mmol) in methanol (10 cm^3) was stirred (2 h, 20 °C). The solvent was then removed under reduced pressure. The hexane-soluble portion of the residue was crystallised from hot hexane giving **5a** (63 mg, 76%). Complex **6a** (70 mg, 78%) was prepared similarly from **4a** and KI.

[Ru(η^5:η^2-$C_5Me_4CH_2OCH_2CH=CH_2$)(CO)(NCMe)]BF$_4$ [7a]BF$_4$

Silver tetrafluoroborate (50 mg, 0.25 mmol) was added to a mixture of **4a** (88 mg, 0.25 mmol) and MeCN (1 cm^3) in CH_2Cl_2 (20 cm^3) at −78 °C. The mixture was allowed to warm to room temperature and stirred (0.5 h). The solvent was removed under reduced pressure and the solid residue was crystallised from CH_2Cl_2–Et_2O giving [**7a**]BF$_4$ (80 mg, 71%).

Reaction of [3a]$^+$ with LiCl

A mixture of [**3a**]BF$_4$ (66 mg, 0.15 mmol) and LiCl (21 mg, 0.5 mmol) in thf (10 cm^3) was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the residue was crystallised from diethyl ether–hexane giving **2a** (50 mg, 81%).

Reaction of 4a with CO

A slow current of CO was passed through a solution of **4a** (71 mg, 0.20 mmol) and NH_4PF_6 (117 mg, 0.5 mmol) in methanol (10 cm^3) for 1 h. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 and precipitated by addition of diethyl ether giving [Ru(η^5:η^2-$C_5Me_4CH_2OCH_2CH=CH_2$)(CO)$_2$]PF$_6$ (82 mg, 83%).

Crystal structure determinations

(i) **[Ru{η^5:η^2-$C_5Me_4CH_2OCH_2CH=CH_2$}(CO)$_2$]BPh$_4$, [3a]BPh$_4$$^+$.** *Crystal data.* $C_{39}H_{39}BO_3Ru$, M = 667.58, crystallised from chloroform–1,2-dimethoxyethane as yellow blocks, crystal dimensions 0.54 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no.14) a = 10.051(5), b = 22.876(14), c = 14.632(11) Å, β = 90.36(6)°, U = 3364(4) Å^3, Z = 4, D_c = 1.318 g cm^{-3}, Mo-Kα radiation ($\bar{\lambda}$ = 0.710 73 Å), μ(Mo-Kα) = 0.501 mm^{-1}, $F(000)$ = 1384.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω-scan method. The 3566 independent reflections (of 5826 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0919 ($wR2$ = 0.2593 for all 4379 reflections, 375 parameters, mean and maximum δ/σ 0.003, 0.040), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −1.013 and 2.141 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1986P)^2 + 1.49P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93[8] as implemented on the Viglen 486dx computer. Important bond lengths and angles are collected in Table 4 and the numbering scheme is shown in Fig. 2.

(ii) **[Ru{η^5:η^2-$C_5Me_4CH_2O(CH_2)_2CH=CH_2$}(CO)$_2$]BF$_4$ 3b.** *Crystal data.* $C_{16}H_{21}BF_4O_3Ru$, M = 449.21, crystallised from chloroform–diethyl ether as colourless blocks, crystal dimensions 0.7 × 0.45 × 0.40 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 15.226(2), b = 16.621(3), c = 14.776(2) Å, β = 103.770(10)°, U = 3631.9(9) Å^3, Z = 8, D_c = 1.643 g cm^{-3}, Mo-Kα radiation ($\bar{\lambda}$ = 0.710 73 Å), μ(Mo-Kα) = 0.914 mm^{-1}, $F(000)$ = 1808.

Three-dimensional room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω-scan method. The 4108 independent reflections (of 5812 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0411 ($wR2$ = 0.1132 for all 4725 reflections, 451 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.619 and 0.980 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 7.67P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93[8] as implemented on the Viglen 486dx computer. Important bond lengths and angles are collected in Table 5 and the numbering schemes are shown in Figs. 3 and 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors. *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/59.

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References

1 Part 5, L. Fan, C. Wei, F. I. Aigbirhio, M. L. Turner, O. V. Gusev, L. N. Morozova, D. R. T. Knowles and P. M. Maitlis, *Organometallics*, 1996, **15**, 98.

2 L. Fan, M. L. Turner, H. Adams, N. A. Bailey and P. M. Maitlis, *Organometallics*, 1995, **14**, 676.

3 L. Fan, M. L. Turner, M. B. Hursthouse, K. M. A. Malik, O. V. Gusev and P. M. Maitlis, *J. Am. Chem. Soc.*, 1994, **116**, 385; C. Wei, F. Aigbirhio, H. Adams, N. A. Bailey, P. D. Hempstead and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1991, 883.

4 J. A. Miguel-Garcia and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1990, 1472; O. V. Gusev, A. Z. Rubezhov, J. A. Miguel-Garcia and P. M. Maitlis, *Mendeleev Commun.*, 1991, 21; J. A. Miguel-Garcia, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Organomet. Chem.*, 1991, **413**, 427; J. A. Miguel-Garcia, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1992, 131.

5 J. Okuda and K. H. Zimmermann, *Chem. Ber.*, 1990, **123**, 1641.

6 A. N. Nesmeyanov, V. V. Krivykh, P. V. Petrovskii, V. S. Kaganovich and M. I. Rybinskaya, *J. Organomet. Chem.*, 1978, **162**, 323.

7 See also: J. Kopf, M. Morf, B. Hagen, M. Bischoff and P. Koll, *Carbohydr. Res.*, 1994, **262**, 9; Y. T. Osano, A. Uchida and Y. Ohashi, *Nature (London)*, 1992, **352**, 510.

8 G. M. Sheldrick, SHELXL 93, An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, 1993.

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