Ring-methyl activation in pentamethylcyclopentadienyl complexes 7 [1]
Reactions of $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2]^+BF_4^-$ with nucleophiles [2]

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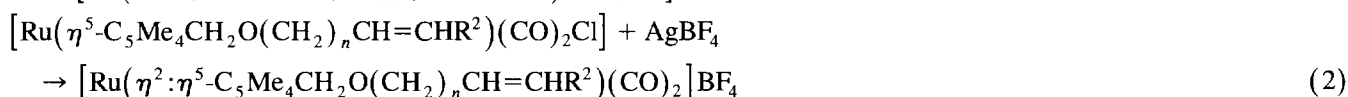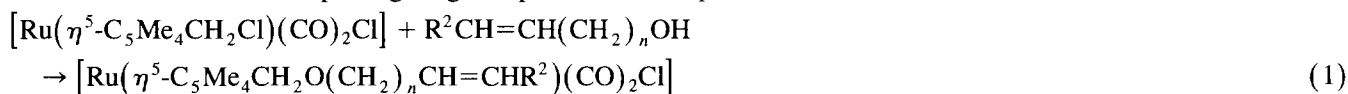[c] Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK

Abstract

The ruthenium chelates containing tethered olefinic side chains $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2]^+BF_4^-$ (**1a**, $R^2 = H$, $n = 1$; **1b**, $R^2 = Me$, $n = 1$; **1c**, $R^2 = H$, $n = 2$) react with $NaBH_4$ in MeOH or in water to give the non-chelated olefin hydride complexes $[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2(H)]$ (**2a–c**). By contrast, alkoxide attacked at a carbonyl ligand in **1a** giving the chelated olefin alkoxycarbonyl complexes $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(\eta^1\text{-}COOR^3)(CO)]$ (**3a,a'**, $R^3 = Me$; **4a,a'**, $R^3 = Et$), which form a separable mixture of diastereomers. There was no evidence for attack at the coordinated olefin in complex **1**. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Olefin chelate; Nucleophilic attack; Cyclopentadienyl; Crystal structure

1. Introduction

We have, over the last few years, described some very simple syntheses of substituted tetramethylcyclopentadienyl complexes of ruthenium(II), of the type $[Ru(C_5Me_4CH_2X)(CO)_2Cl]$. The C–H activation of the $\eta^5\text{-}C_5Me_5$ on Ru(II) is significantly easier than on rhodium or iridium [2], and the parent complex, $[Ru(C_5Me_4CH_2Cl)(CO_2Cl]$ [3], is readily made in a two-step, one pot, reaction from $[\{Ru(C_5Me_5)Cl_2\}_2]$ [4,5]. The CH_2Cl in $[Ru(C_5Me_4CH_2Cl)(CO)_2Cl]$ can be substituted by a variety of nucleophiles, including alcohols (R^1OH) which give $[Ru(C_5Me_4CH_2OR^1)(CO)_2Cl]$. We have also described the synthesis and structures of such complexes when R^1OH is an unsaturated alcohol $CH_2=CH(CH_2)_nOH$ ($n = 1$, 2; Eq. (1)); on reaction with $AgBF_4$, chloride is lost from the metal and the olefin chelates to the metal in its place giving complexes **1a–c**, Eq. (2)

$$[Ru(\eta^5\text{-}C_5Me_4CH_2Cl)(CO)_2Cl] + R^2CH=CH(CH_2)_nOH$$

$$\rightarrow [Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2Cl] \qquad (1)$$

$$[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2Cl] + AgBF_4$$

$$\rightarrow [Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2]BF_4 \qquad (2)$$

$$\text{**1a**, } n = 1, R^2 = H$$
$$\text{**1b**, } n = 1, R^2 = Me$$
$$\text{**1c**, } n = 2, R^2 = H$$

The structures of the cationic olefin chelates **1a–c** have been discussed [1]; we report here some of their reactions with nucleophiles.

2. Results

2.1. Reaction of $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2]^+BF_4^-$ (1a–c) with $NaBH_4$

Attack occurred at ruthenium when the cationic chelates **1a–c** were reacted with $NaBH_4$ (Scheme 1) in water or in MeOH, and the neutral hydride complexes **2a–c**, where the double bond was no longer coordinated, were obtained in high yields (Eq. (3)).

$$[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2]BF_4 + NaBH_4$$
$$\rightarrow [Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2H] \tag{3}$$

$$\text{2a}, n=1, R^2=H$$
$$\text{2b}, n=1, R^2=Me$$
$$\text{2c}, n=2, R^2=H$$
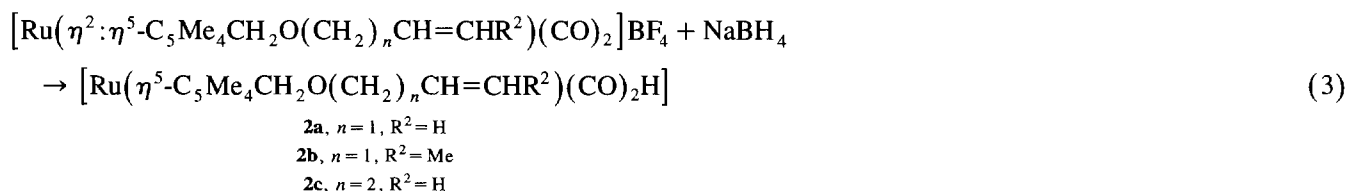
The complexes **2a–c** were relatively air stable and were characterised by microanalysis and spectroscopically. All three exhibited two terminal $\nu(CO)$ bands at rather lower frequencies than the chlorides $[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2Cl]$ [1]. This is expected since a ruthenium bonded to hydride should back-donate to the carbonyls better than one bonded to a chloride. The hydrides were observed as singlets close to $\delta-10$ ppm in the ^1H NMR spectra; the other features of the ^1H and the ^{13}C NMR spectra of **2a–c** were rather similar to those for $[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2Cl]$ [1]. Thus the two pairs of equivalent methyl groups of $\eta^5\text{-}C_5Me_4CH_2$ appeared as two singlets (δ 1.4–1.9 (^1H) and 10–11 (^{13}C)), and the CH_2 group resonated as a further singlet (δ 4.0–4.1 (^1H) and 62–64 (^{13}C)). The carbonyls were at δ 203 for all the complexes **2a–c**, and the other signals of the $O(CH_2)_nCH=CHR^2$ had chemical shifts and coupling patterns similar to those seen in the chloro-complexes.

2.2. Reaction of $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(CO)_2]^+BF_4^-$ (1a) with alkoxides

The reaction of **1a** with MeONa or EtONa in THF also led to unexpected products (Scheme 1), in this case the formation of the alkoxycarbonyl complexes $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(\eta^1\text{-}COOR^3)(CO)]$ (**3a,a'**, $R^3 =$ Me; **4a,a'**, $R^3 =$ Et), where attack had occurred at a carbonyl and the olefin remained chelated to the metal. The complexes were characterised spectroscopically and with the help of preliminary data from an X-ray structure determination.

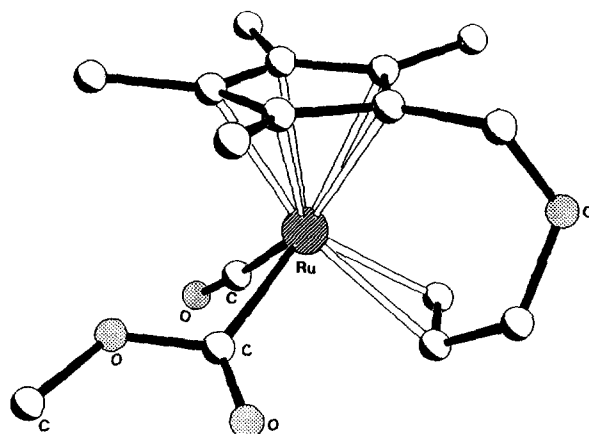a, $R^2 =$ H, n = 1; b, $R^2 =$ Me, n = 1; c, $R^2 =$ H, n = 2.
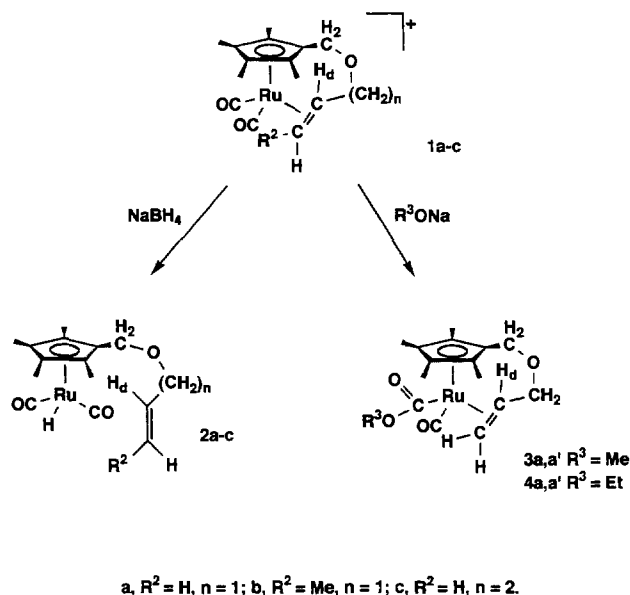
Scheme 1.

Fig. 1. The structure of $Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(\eta^1\text{-COOMe})(CO)]$, complex **3a**, derived from the preliminary results of the X-ray analysis (Ru–CO, 1.858; Ru–COOMe, 2.069; Ru–C(olefin terminal) 2.204; Ru–C(olefin internal) 2.206; Ru–C$_5$ ring (average), 2.250 Å).

The NMR spectra show that both **3a,a′** and **4a,a′** are 1:1 mixtures of diastereomers due to the presence of two chiral centres in the molecule; a parallel situation has been observed for $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)\text{-}(CO)Cl]$ [1] and for some other olefin chelates [6]. In contrast to the related diastereomers $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(CO)Cl]$, which interconverted in solution [1], the diastereomers **3a,a′** and **4a,a′** could be separated by fractional crystallisation from hexane. A single crystal of isomer **3a** was isolated from the less hexane-soluble fraction, and was submitted for an X-ray analysis; technical problems prevented collection of a full set of data, but the 1534 reflections measured allowed the structure, illustrated in Fig. 1, to be solved and refined (see Section 5). This showed the ruthenium atom in **3a** to be coordinated by the tetramethylcyclopentadienyl ligand, a carbonyl, a carbomethoxy, and the terminal alkene residue of the pendant chain of the substituted cyclopentadienyl ligand. The preliminary data indicate the bond lengths and angles in $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(\eta^1\text{-COOR}^3)(CO)]$ (**3a**) to be very similar to those recently found for $[Ru:\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CH_2)(CO)_2]^+BF_4^-$ ($n = 1$, or 2) [1].

The IR spectra of **3a,a′** and **4a,a′** showed bands at 1975–1976 cm^{-1} and 1640–1641 cm^{-1} characteristic of a terminal metal carbonyl and a COOR respectively. The ^{13}C NMR spectra showed one singlet for each CO in each diastereomer at δ 207–208 in **3a,a′** and **4a,a′**, while the COOMe groups in complexes **3a,a′** were observed at δ 3.69 (**3a**), 3.70 (**3a′**) (^{1}H NMR; OMe), and at δ 39.0 (**3a**), 38.9 (**3a′**) (OMe); 197.0 (**3a**), and 197.3 (**3a′**) (^{13}C NMR; COOMe). The ethyl groups in the COOEt substituents of **4a,a′** showed triplets at δ 1.21 (**4a,a′**), and quartets at 4.21 (**4a**), 4.23 (**4a′**) in the ^{1}H NMR spectrum, while the carboxy-carbons COOEt were observed at 196.5 (**4a**) and 195.2 ppm (**4a′**). The protons and carbon atoms of the $\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2$ ligands in **3a,a′** and **4a,a′** showed NMR chemical shifts and coupling patterns similar to those for $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(CO)_2Cl]$ [4].

3. Discussion

The surprising feature of these reactions is that nucleophilic attack does not occur on the coordinated olefin in **1**. The products normally obtained from reactions of cationic π-olefin complexes with hydrides are σ-alkyl complexes [7], for example $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-CH}_2=CHC(=O)Et)(CO)_2]^+$ reacts with Na[BH$_3$CN] to give the σ-bonded complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^1\text{-CH(Me)C}(=O)Et)(CO)_2]$ [8]. We suggest that the presence of the rigid olefinic chelates in **1a–c** make the formation of the corresponding σ-complexes unfavourable, and hence the hydrides **2a–c** are obtained.

A further alternative direction for the reaction is the formation of σ-formyl complexes, as for example in the reaction of $[Ru(\eta^5\text{-}C_5Me_5)(CO)_2(L)]^+$ (L = CO, PMe$_2$Ph) with NaBH$_4$, where both the formyl $[Ru(\eta^5\text{-}C_5Me_5)(CO)(L)(CHO)]$ and the hydride $[Ru(\eta^5\text{-}C_5Me_5)(CO)(L)(H)]$ were obtained [9].

The formation of **2a–c** indicates that the replacement of olefins by hydride parallels the replacement of the chelated olefins in **1a** by chloride anion that was found to give $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(CO)_2Cl]$ [4].

Somewhat less surprising is the reaction of **1a** with alkoxide to give the esters **3** and **4** by attack at the carbonyl. This is reminiscent of the reaction of $[Ru(\eta^5\text{-}C_5Me_5)(CO)_3]^+$ with alkoxide anions which give $[Ru(\eta^5\text{-}C_5Me_5)(\eta^1\text{-COOR})(CO)_2]$ (R = H, Me, Et, ^{i}Pr, ^{t}Bu) [10].

4. Conclusion

The reactions of cationic chelates containing tethered side chains $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR)(CO)_2]^+BF_4^-$ (1a–c) with nucleophiles were investigated. It was found that the addition of the nucleophile can occur at ruthenium, or at the carbonyl. It does not seem to occur at the coordinated olefin. Reaction with BH_4^- gave the unchelated neutral hydride complexes $[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR)(CO)_2H]$ (2a–c), while the addition of alkoxide anion OR^- (R = Me, Et) gave the alkoxycarbonyl complexes $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(\eta^1\text{-}COOR)(CO)]$ (3a,a′; 4a,a′) as mixtures of diastereomers. The structure of $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(\eta^1\text{-}COOMe)(CO)]$ (3a) was confirmed by the preliminary X-ray analysis.

5. Experimental

All experiments were performed using standard Schlenk techniques under argon in solvents purified by standard methods. Complexes 1a–c were prepared as described in Ref. [4]. ^1H and ^{13}C NMR spectra were measured in C_6D_6 solution using Bruker-WP-200-SY and Varian VXR-400 spectrometers; chemical shifts are reported in parts per million (δ) with reference to TMS. IR spectra were measured in heptane with a Specord M-82. Microanalyses were performed by the Microanalysis Laboratory of the Institute of Organoelement Compounds.

5.1. General procedures for the conversion of $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2]^+BF_4^-$ (1a, $R^2 = H$, n = 1; 1b, $R^2 = Me$, n = 1; 1c, $R^2 = H$, n = 2) with $NaBH_4$ into $[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_nCH=CHR^2)(CO)_2(H)]$ (2a–c)

Method A: in water. A suspension of 1a (100 mg, 0.23 mmol) and $NaBH_4$ (87 mg, 2.3 mmol) in water (10 cm^3) and ether (10 cm^3) was stirred (1 h/20 °C), and then the two layers were separated. The ether layer was washed with water (3 × 5 cm^3), dried ($MgSO_4$), filtered and evaporated to leave a yellow oil, 2a (60 mg, 75%) after drying in vacuo. Anal. Found: C, 51.6; H, 5.8. $C_{15}H_{20}O_3Ru$. Calc.: C, 51.7; H, 5.8%. IR ν(CO) 1946; 2010 cm^{-1}. ^1H NMR δ: −10.2 (s, 1H, Ru–H); 1.46 (s, 6H, 2 × Me); 1.66 (s, 6H, 2 × Me); 3.80 (d, 2 × H, O–CH_2–CH=, J = 6 Hz); 4.11 (s, 2 × H, η^5-C$_5$Me$_4$–CH_2–O); 5.06 (d, H_{cis}, $J(H_d$–$H_{cis}) = 11$ Hz); 5.23 (d, H_{trans}, $J(H_d$–$H_{trans}) = 18$ Hz); 5.82 (m, H_d). ^{13}C NMR δ: 10.6 (2 × Me); 10.7 (2 × Me); 63.2 (CH$_2$); 71.4 (CH$_2$); 96.4 (C_5Me$_4$); 100.0 (C_5Me$_4$); 102.2 (C_5Me$_4$); 116.4 (CH$_2$); 135.2 (CH); 203.3 (CO).

Method B: in methanol. A suspension of 1a (100 mg, 0.23 mmol) and $NaBH_4$ (87 mg, 2.3 mmol) in MeOH (10 cm^3) was stirred (1 h/20 °C); the solvent was removed in vacuo and the solid residue was worked up as described above to give 2a (69 mg, 90%).

Complexes 2b and 2c were made by method A. Yield of $[Ru(\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CHMe)(CO)_2(H)]$ 2b (69 mg, 90%). Anal. Found: C, 52.9; H, 5.9. $C_{16}H_{22}O_3Ru$. Calc.: C, 52.9; H, 6.1%. IR ν(CO) 1945; 2010 cm^{-1}. ^1H NMR δ: −10.2 (s, 1H, Ru–H); 1.51 (d, 3H, MeCH=, J = 7 Hz); 1.63 (s, 6H, 2 × Me); 1.82 (s, 6H, 2 × Me); 3.57 (m, 2 × H, O–CH_2–CH=); 4.06 (s, 2 × H, η^5-C$_5$Me$_4$–CH_2–O); 5.4–5.6 (m, H_{cis}, $J(H_d$–$H_{cis}) = 11$ Hz); 5.4–5.6 (m, H_d). ^{13}C NMR δ: 10.6 (2 × Me); 10.7 (2 × Me); 17.7 (Me); 62.8 (CH$_2$); 71.3 (CH$_2$); 96.8 (C_5Me$_4$); 100.0 (C_5Me$_4$); 102.1 (C_5Me$_4$); 128.6 (CH); 128.7 (CH); 203.3 (CO).

Yield of $[Ru(\eta^5\text{-}C_5Me_4CH_2O(CH_2)_2CH=CH_2)(CO)_2(H)]$ (2c) (66 mg, 84%). Anal. Found: C, 52.8; H, 6.0. $C_{16}H_{22}O_3Ru$. Calc.: C, 52.9; H, 6.1%. IR ν(CO) 1947; 2010 cm^{-1}. ^1H NMR δ: −10.4 (s, 1H, Ru–H); 1.65 (s, 6H, 2 × Me); 1.85 (s, 6H, 2 × Me); 2.18 (m, 2 × H, OCH$_2$CH_2); 3.26 (t, 2H, OCH_2CH$_2$, J = 7 Hz); 4.01 (s, 2 × H, η^5-C$_5$Me$_4$–CH_2–O); 4.98 (d, H_{cis}, $J(H_d$–$H_{cis}) = 11$ Hz); 5.06 (d, H_{trans}, $J(H_d$–$H_{trans}) = 17$ Hz); 5.76 (m, H_d). ^{13}C NMR δ: 10.6 (2 × Me); 10.7 (2 × Me); 34.5 (CH$_2$); 63.8 (CH$_2$); 70.1 (CH$_2$); 96.5 (C_5Me$_4$); 99.9 (C_5Me$_4$); 102.1 (C_5Me$_4$); 116.3 (CH$_2$); 135.6 (CH); 203.3 (CO).

5.2. Reaction of $[Ru(\eta^2:\eta^5\text{-}C_5Me_4CH_2OCH_2CH=CH_2)(CO)_2]^+BF_4^-$ 1a, with alkoxide

A solution of MeONa (0.25 mmol) in methanol was added to a suspension of 1a (88 mg, 0.2 mmol) in THF (5 cm^3) at −78 °C. The mixture was stirred 10 min, allowed to warm to ambient, and evaporated to dryness in vacuo, to leave a solid residue; this was extracted (Et$_2$O; 10 cm^3), the solution was filtered and hexane (10 cm^3) was added. That solution was concentrated to 2 cm^3 and cooled to −78 °C, to give a precipitate which was decanted and dried. Yield of 3a,3a′ (51 mg, 65%). Anal. Found: C, 51.1; H, 6.0. $C_{16}H_{22}O_4Ru$. Calc.: C, 50.65; H, 5.8%. IR ν(CO): 1975, 1641 cm^{-1}.

^{1}H NMR δ. **3a**: 1.41 (s, 3H, Me); 1.78 (s, 3H, Me); 1.80 (s, 3H, Me); 1.97 (s, 3H, Me); 2.01 (d, 1H, H$_{trans}$, J(H$_d$–H$_{trans}$) = 12 Hz); 2.87 (d, 1H, H$_{cis}$, J(H$_d$–H$_{cis}$) = 8 Hz); 3.26 (dd, 1H, O–CHH–CH, J = 15, 1 Hz); 3.31 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 3.69 (s, 3H, OMe); 3.80 (dddd, 1H, H$_d$, J = 12, 8, 1, 1 Hz); 4.08 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 4.24 (dd, 1H, O–CHH–CH, J = 15, 1 Hz). **3a'**: 1.48 (s, 3H, Me); 1.69 (s, 3H, Me); 1.91 (s, 3H, Me); 1.97 (s, 3H, Me); 2.13 (d, H$_{trans}$, J(H$_d$–H$_{trans}$) = 12 Hz); 2.93 (d, H$_{cis}$, J(H$_d$–H$_{cis}$) = 8 Hz); 3.01 (dd, 1H, O–CHH–CH, J = 14, 2 Hz); 3.22 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 3.63 (dd, 1H, O–CHH–CH, J = 14, 2 Hz); 3.70 (s, 3H, OMe); 3.76 (dddd, 1H, H$_d$, J = 12, 8, 2, 2 Hz); 3.85 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz).

^{13}C NMR δ. **3a**: 8.8 (Me); 9.5 (Me); 10.1 (Me); 10.3 (Me); 39.0 (OMe); 51.0 (CH$_2$); 63.1 (CH$_2$); 66.0 (CH$_2$); 67.6 (CH); 90.6 (C$_5$Me$_4$); 96.7 (C$_5$Me$_4$); 103.7 (C$_5$Me$_4$); 109.3 (C$_5$Me$_4$); 196.9 (COOMe); 207.7 (CO). **3a'**: 8.2 (Me); 9.1 (Me); 10.2 (Me); 10.6 (Me); 38.9 (OMe); 47.0 (CH$_2$); 61.5 (CH$_2$); 66.8 (CH$_2$); 71.7 (CH); 91.9 (C$_5$Me$_4$); 93.0 (C$_5$Me$_4$); 98.3 (C$_5$Me$_4$); 106.1 (C$_5$Me$_4$); 113.5 (C$_5$Me$_4$); 196.3 (COOMe); 207.5 (CO).

Complex **4a,a'** was prepared from **1a** and EtONa, yield (54 mg, 68%). Anal. Found: C, 51.4; H, 6.0. C$_{17}$H$_{24}$O$_4$Ru. Calc.: C, 51.9; H, 6.15%. IR ν(CO): 1975, 1641 cm^{-1}.

^{1}H NMR δ. **4a**: 1.21 (t, 3H, OCH$_2$CH_3, J = 7 Hz); 1.44 (s, 3H, Me); 1.80 (s, 3H, Me); 1.81 (s, 3H, Me); 1.99 (s, 3H, Me); 2.00 (d, H$_{trans}$, J(H$_d$–H$_{trans}$) = 11 Hz); 2.87 (d, H$_{cis}$, J(H$_d$–H$_{cis}$) = 9 Hz); 3.27 (dd, 1H, O–CHH–CH, J = 15, 2 Hz); 3.36 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 3.76 (dddd, 1H, H$_d$, J = 11, 9, 2, 2 Hz); 4.11 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 4.24 (q, 2H, OCH_2CH$_3$, J = 7 Hz); 4.25 (dd, 1H, O–CHH–CH, J = 15, 2 Hz). **4a'**: 1.21 (t, 3H, OCH$_2$CH_3, J = 7 Hz); 1.49 (s, 3H, Me); 1.70 (s, 3H, Me); 1.94 (s, 3H, Me); 2.01 (s, 3H, Me); 2.16 (d, H$_{trans}$, J(H$_d$–H$_{trans}$) = 12 Hz); 2.94 (dd, 1H, O–CHH–CH, J = 14, 2 Hz); 3.01 (d, H$_{cis}$, J(H$_d$–H$_{cis}$) = 8 Hz); 3.24 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 3.64 (dd, 1H, O–CHH–CH, J = 14, 2 Hz); 3.75 (dddd, 1H, H$_d$, J = 12, 8, 2, 2 Hz); 3.86 (d, 1H, η^5-C$_5$Me$_4$–CHHO, J = 13 Hz); 4.21 (q, 2H, OCH_2CH$_3$, J = 7 Hz).

^{13}C NMR δ. **4a**: 8.9 (Me); 9.5 (Me); 10.1 (Me); 10.4 (Me); 15.2 (OCH$_2$$CH_3$); 39.0 (O$CH_2CH_3$); 58.9 (CH$_2$); 63.0 (CH$_2$); 66.0 (CH$_2$); 68.0 (CH); 90.6 (C$_5Me_4$); 91.8 (C$_5Me_4$); 96.9 (C$_5Me_4$); 103.9 (C$_5Me_4$); 109.0 (C$_5Me_4$); 196.5 (COOEt); 207.7 (CO). **4a'**: 8.3 (Me); 9.2 (Me); 10.2 (Me); 10.3 (Me); 15.2 (OCH$_2$$CH_3$); 39.6 (O$CH_2CH_3$); 47.7 (CH$_2$); 59.1 (CH$_2$); 66.9 (CH$_2$); 70.4 (CH); 93.0 (C$_5Me_4$); 94.6 (C$_5Me_4$); 95.7 (C$_5Me_4$); 98.6 (C$_5Me_4$); 113.6 (C$_5Me_4$); 195.2 (COOEt); 207.4 (CO).

5.3. The X-ray structure determination of complex 3a

A monoclinic, crystal of complex **3a** crystallised from hexane as yellow prisms ($0.2 \times 0.25 \times 0.3$ mm^3); crystal data, $a = 7.646(2)$ Å, $b = 15.896(3)$ Å, $c = 13.186(2)$ Å, $\beta = 98.56(2)°$, $V = 1584.8(6)$ Å^3, $Z = 4$, space group $P2_1/c$, $d_{calc} = 1.590$ g cm^{-3}, $F(000) = 776$, $\mu = 1.001$ mm^{-1}. Data were obtained at 295 K using a four circle Siemens P3/PC diffractometer (monochromatised Mo Kα radiation). During data collection severe technical problems were encountered and as a result only 1534 reflections could be measured. The structure was solved by direct methods and refined by a full-matrix least squares in the anisotropic–isotropic (H-atoms) approximation. The positions of the H-atoms were calculated geometrically and refined using a 'riding' model. The results of the refinement using 1355 independent reflections with $I > 2\sigma(I)$ are $R1 = 0.0271$, and $wR_2 = 0.0749$ and GOF = 1.246 for all 1534 measured reflections. All calculations were performed with a PC/AT computer using the SHELXTL programs package (version 5). The structure is illustrated in Fig. 1.

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