

Synthesis, characterization and structure of the ethylene-bridged dimer $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ and comparison of its reactivity with that of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_3]$ and $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{Ru}(\text{CO})_2\text{Cp}]$: models for Fischer–Tropsch surface intermediates

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Abstract

The diruthenium ethylene-bridged complex $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) (**1**) has been prepared by two different synthetic routes. The complex has been fully characterized by IR, ^1H and ^{13}C NMR spectroscopy, mass spectrometry and X-ray crystallography. The complex crystallizes in the triclinic space group $P\bar{1}$ ($Z = 1$) with $a = 6.060(1)$, $b = 6.990(2)$ and $c = 10.097(1)$ Å and $\alpha = 85.30(1)$, $\beta = 76.86(1)$ and $\gamma = 74.46(2)^\circ$. The structure was refined to $R(F) = 0.029$ and shows that the $\text{CpRu}(\text{CO})_2$ units are centrosymmetrically bonded to each end of the ethylene fragment in a *trans* arrangement. The use of **1** as a model for ethylene on a metal catalyst surface is explored and some reactivity studies of **1** are described. Some reactions of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_3]$ (**2**) are also reported and compared with the reactions found for **1**. A reaction sequence of the pentamethylene-bridged compound $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{Ru}(\text{CO})_2\text{Cp}]$ (**3**) is found to give a high yield of 1-pentene.

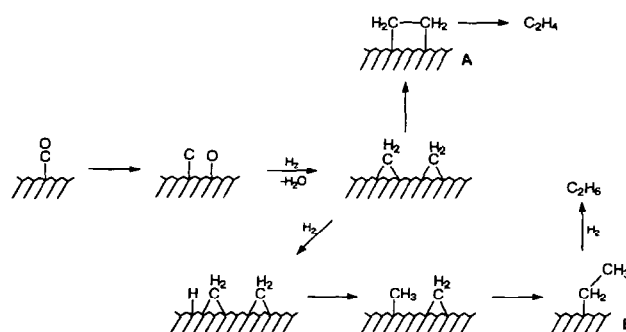
Keywords: Ruthenium; Cyclopentadienyl; Ethylene; Fischer–Tropsch; Crystal structure

1. Introduction

Compounds with hydrocarbon groups bridging two metals that are not joined by a metal–metal bond are now very numerous [1]. Such compounds can be used as models for hydrocarbons on a metal catalyst surface in important reactions including the Fischer–Tropsch reaction [2,3]. The mechanism of the Fischer–Tropsch reaction has been an area of much debate for many years [4–6]. The carbide mechanism, depicted in Scheme 1, has received fairly general acceptance [7]. Key intermediates in this scheme are the ethylene species **A** and the ethyl species **B**. We have prepared the compounds $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (**1**) and $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_3]$ (**2**) and now explore their use as models for the surface intermediates **A** and **B** respectively.

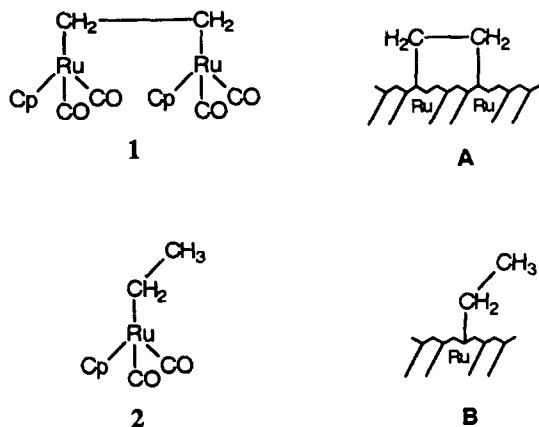
Even though a fairly large number of compounds of the type $\text{L}_n\text{MCH}_2\text{CH}_2\text{ML}_n$ has been prepared and well

characterized, their chemistry has not been studied in detail [1–3]. Since ruthenium is one of the most active Fischer–Tropsch catalysts [8], we believed that **1** and **2** might be particularly suitable models for Fischer–Tropsch intermediates. In this paper, we report the results of our studies on **1** and **2** and give a comparison of some reactions shown by the pentamethylene-bridged compound $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{Ru}(\text{CO})_2\text{Cp}]$ (**3**).



Scheme 1. The carbide mechanism for the Fischer–Tropsch reaction. Key intermediates are the ethylene species **A** and the ethyl species **B**.

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2. Experimental details

All reactions were carried out using Schlenk techniques under an atmosphere of nitrogen. Tetrahydrofuran (THF) was distilled from sodium. Methanol and CH_2Cl_2 were distilled from anhydrous CaCl_2 . Triphenylphosphine and AgBF_4 were purchased from Merck, $\text{ClCH}_2\text{CH}_2\text{OCH}_3$ and CF_3COOH were purchased from Aldrich, PPhMe_2 and $\text{Ru}_3(\text{CO})_{12}$ were obtained from Strem and $[\text{Ph}_3\text{C}][\text{PF}_6]$ was obtained from Alpha Products. $[\text{CpRu}(\text{CO})_2]_2$ [9], $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{Ru}(\text{CO})_2\text{Cp}]$ [10a] and $[\text{Cp}(\text{CO})_2\text{RuCH}_2=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}][\text{PF}_6]$ [10b] were prepared according to published procedures. ^1H and ^{13}C NMR spectra were recorded on a Varian XR200 spectrometer. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0.00$ ppm). IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer using solution cells with NaCl windows. Low resolution mass spectra were recorded on a VG Micromass 16F spectrometer operating at 70 eV ionizing voltage. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Melting points (m.p.s) were recorded on a Kofler hot-stage microscope (Reichert Thermovar) and are uncorrected.

2.1. Preparation of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (**1**)

2.1.1. Method (a)

A solution of $\text{Na}[\text{CpRu}(\text{CO})_2]$ (2.25 mmol) was prepared by stirring $[\text{CpRu}(\text{CO})_2]_2$ (0.497 g, 1.12 mmol) with sodium amalgam (2 ml of Hg; 0.3 g of Na) in THF (20 ml) for 3 h. This solution was added to a solution of dichloroethane (0.1 ml, 1.12 mmol) in THF (5 ml) over 5 min at -78°C in the dark. After 2 h the solvent was removed under reduced pressure. The orange–brown residue was extracted with hexane: CH_2Cl_2 (1 : 1; 3×50 ml), filtered and recrystallized from CH_2Cl_2 at -10°C to yield **1** as a pale-yellow crystalline solid (yield, 0.23 g (43%)); m.p., $130\text{--}131^\circ\text{C}$). IR (hexane): $\nu(\text{CO})$ 2007s,

1953s cm^{-1} . ^1H NMR (CDCl_3): δ 2.28 (s, 4H, CH_2CH_2), 5.22 (s, 10H, C_5H_5) ppm. ^{13}C NMR (CDCl_3): δ 203.25 (CO), 89.46 (C_5H_5), 13.13 (CH_2) ppm. The mass spectrum showed a molecular ion peak at m/z 472 ($M = 472.43$). Anal. Found: C, 40.6; H, 3.1. $\text{C}_{16}\text{H}_{14}\text{O}_4\text{Ru}_2$ Calc.: C, 40.7; H, 3.0%.

2.1.2. Method (b)

A solution of $\text{Na}[\text{CpRu}(\text{CO})_2]$ (0.39 mmol) in THF (5 ml) was added dropwise over 5 min to a solution of $[\text{CpRu}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{PF}_6$ (0.16 g, 0.39 mmol) in THF (10 ml) at 0°C . This solution was stirred for a further 3 h at room temperature. The solvent was then removed under reduced pressure, leaving an orange–brown residue which was extracted with hexane: CH_2Cl_2 (19 : 1; 3×40 ml). The extract was filtered and the solvent was removed under reduced pressure. The resulting solid was recrystallized from hexane at -78°C to give pale-yellow crystals of **1** (yield, 0.027 g (30%)).

2.2. Reaction of **1** with CO

A solution of **1** (0.05 g, 0.11 mmol) in THF (6 ml) was placed in an autoclave, which was then charged with CO (50 atm). The mixture was stirred at room temperature for 10 h and the gases were then vented. The resulting solid (0.045 g) was identified as **1** from its IR spectrum in the $\nu(\text{CO})$ region, thus indicating that no reaction had occurred.

2.3. Reaction of **1** with MeOH

Complex **1** (0.10 g, 0.21 mmol) in MeOH (10 ml) was boiled under reflux for 5 h. The solvent was removed under reduced pressure, leaving a yellow–orange residue which was extracted with hexane. The extract was filtered, concentrated and cooled to -78°C . The resulting solid was identified as $[\text{CpRu}(\text{CO})_2]_2$ (yield, 0.05 g (57%)) by its IR spectrum in the $\nu(\text{CO})$ region. The oil obtained from the mother liquor was identified as $[\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CH}_2\text{OCH}_3)]$ (yield, 29%), IR (CH_2Cl_2): $\nu(\text{CO})$ 2015s, 1952s cm^{-1} . IR (cyclohexane): $\nu(\text{CO})$ 2021s, 2017s, 1962s, 1958s,sh cm^{-1} . ^1H NMR (CDCl_3): δ 5.25 (s, 5H, C_5H_5), 3.44 (m, 2H, CH_2OCH_3), 3.33 (s, 3H, CH_3), 1.74 (m, 2H, $\text{Ru}-\text{CH}_2$) ppm. ^{13}C NMR (CDCl_3): δ 201.65 (CO), 88.05 (C_5H_5), 79.84 (CH_2OCH_3), 57.47 (CH_3), -6.49 ($\text{Ru}-\text{CH}_2$) ppm. The mass spectrum showed a molecular ion peak at m/z 281 ($M = 281.27$). Anal. Found: C, 42.4; H, 4.1. $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Ru}$ Calc.: C, 42.7; H, 4.3%.

2.4. Reaction of $\text{Na}[\text{CpRu}(\text{CO})_2]$ with $\text{ClCH}_2\text{CH}_2\text{OCH}_3$

A solution of $\text{Na}[\text{CpRu}(\text{CO})_2]$ (0.28 g, 1.13 mmol) in THF (12 ml) was added over 5 min to $\text{ClCH}_2\text{CH}_2\text{OCH}_3$ (0.11 g, 1.13 mmol) at -78°C with stirring. The solu-

tion was allowed to reach room temperature, and after 3 h the solvent was removed under reduced pressure. The orange–yellow residue was extracted with hexane, filtered, concentrated and recrystallized from hexane at -78°C . The precipitate was identified as $[\text{CpRu}(\text{CO})_2]_2$ (yield, 0.17 g (60%)) and the oil obtained from the mother liquor was identified as $[\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CH}_2\text{-OCH}_3)]$ (yield, 30%) by comparison of its IR and ^1H NMR spectra with those of an authentic sample and on the basis of elemental analysis. Anal. Found: C, 42.3; H, 4.1. $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Ru}$ Calc.: C, 42.7; H, 4.3%.

2.5. Reaction of **1** with PPh_3

No reaction occurred when **1** was boiled under reflux with PPh_3 in THF for 23 h or in toluene for 5 h. The reactions were monitored by IR spectroscopy of the $\nu(\text{CO})$ region.

2.6. Reaction of **1** with PMe_2Ph

Complex **1** (0.10 g, 0.21 mol) and PMe_2Ph (0.90 g, 0.7 mmol) were boiled under reflux in THF (10 ml) for 55 h. The solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and chromatographed on an alumina column. A pale-yellow oil, believed to be $[\text{CpRu}(\text{CO})(\text{PMe}_2\text{Ph})_2][\mu\text{-CH}_2\text{CH}_2]$ (38%) was eluted with CH_2Cl_2 :hexane (1:1). IR (CH_2Cl_2): $\nu(\text{CO})$ 1951s cm^{-1} . ^1H NMR (CDCl_3): δ 7.55 (m, 10H, PPh), 4.86 (s, 10H, C_5H_5), 1.97 (d, 6H, PCH_3), 1.85 (d, 6H, PCH_3), 1.56 (s, 4H, C_2H_4) ppm. This product was not characterized further.

2.7. Reaction of **1** with $[\text{Ph}_3\text{C}][\text{PF}_6]$

Solid $[\text{Ph}_3\text{C}][\text{PF}_6]$ (0.12 g, 0.32 mmol) was added to a solution of **1** (0.10 g, 0.21 mmol) in CH_2Cl_2 (8 ml). The solution was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and the residue was dissolved in a minimum of acetone. After addition of diethyl ether, fine white microcrystals of $[\text{CpRu}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{PF}_6$ (yield, 0.05 g (60%)) were obtained. IR (CH_2Cl_2): $\nu(\text{CO})$ 2079s, 2038s cm^{-1} . ^1H NMR (CDCl_3): δ 6.18 (s, 5H, C_5H_5), 4.05 (s, 4H, CH_2CH_2). These data are in agreement with literature values [11]. The other complex formed in the reaction was identified by its IR spectrum in the $\nu(\text{CO})$ region as $[\text{CpRu}(\text{CO})_2]_2$.

2.8. Reaction of **1** with AgBF_4

AgBF_4 (0.06 g, 0.32 mmol) was added to a solution of **1** (0.11 g, 0.21 mmol) in CH_2Cl_2 (8 ml). The solution was stirred for 30 min at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in a minimum of acetone. After the addition of diethyl ether, a light-brown precip-

itate formed which was identified as $[\text{CpRu}(\text{CO})_2\text{-}(\text{C}_2\text{H}_4)]\text{BF}_4$. IR (CH_2Cl_2): $\nu(\text{CO})$ 2087s, 2045s cm^{-1} , agreeing with literature values [11].

2.9. Reaction of **1** with CF_3COOH

A solution of **1** (0.03 g, 0.08 mmol) in CH_2Cl_2 (8 ml) was added to CF_3COOH (0.09 g, 0.78 mmol) at room temperature. An immediate colour change occurred from yellow to violet–red. The solvent was removed under reduced pressure to give a violet–red oil. A methanol solution of the oil rapidly precipitated a white solid upon addition of a methanol solution of NaBPh_4 . This was filtered and dried to give white microcrystals of $[\text{CpRu}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{BPh}_4$ (yield, 0.02 g (51%)), identified by its IR spectrum. The fluoroacetato complex $[\text{CpRu}(\text{CO})_2(\text{O}_2\text{CCF}_3)]$ (IR (CH_2Cl_2): $\nu(\text{CO})$ 2061s, 2015s, 1688s cm^{-1}), containing traces of $[\text{CpRu}(\text{CO})_2]_2$, was obtained from the filtrate.

2.10. Reaction of **1** with HCl

A slight excess of an equimolar amount of HCl (dissolved in CDCl_3) was added to a solution of **1** (0.02 g, 0.04 mmol) in CDCl_3 (0.6 ml) in an NMR tube. ^1H NMR spectra were recorded before and after the addition of HCl . After addition of HCl , the ^1H NMR spectrum suggested that only two species were formed; thus, $\delta = 5.43$ (s, 5H, C_5H_5) ppm corresponds to $[\text{CpRu}(\text{CO})_2\text{Cl}]$ and $\delta = 6.1$ (s, 5H, C_5H_5), 4.1 (s, 4H, CH_2CH_2) ppm corresponds to $[\text{CpRu}(\text{CO})_2(\text{C}_2\text{H}_4)]^+$.

2.11. Reaction of **1** with NaBH_4

A slight excess of an equimolar amount of NaBH_4 was added to a solution of **1** (0.05 g, 0.11 mmol) in CH_2Cl_2 (5 ml). The reaction mixture was stirred at room temperature and after 24 h an IR spectrum revealed that no reaction had occurred.

2.12. Reaction of **1** with Br_2

A slight excess of an equimolar amount of Br_2 was added to a solution of **1** (0.02 g, 0.04 mmol) in CDCl_3 (0.6 ml) in an NMR tube. The ^1H NMR spectrum after the addition of Br_2 showed the following signals: $\delta = 5.43$ (s, 5H, C_5H_5) ppm, which corresponds to $[\text{CpRu}(\text{CO})_2\text{Br}]$; $\delta = 6.1$ (s, 5H, C_5H_5) and 4.1 (s, 4H, CH_2CH_2) ppm, corresponding to $[\text{CpRu}(\text{CO})_2\text{-}(\text{C}_2\text{H}_4)]^+$, and $\delta = 3.64$ (4H, CH_2CH_2) ppm, which corresponds to $\text{BrCH}_2\text{CH}_2\text{Br}$.

2.13. Thermal decomposition of **1**

2.13.1. In solution

A solution of **1** (0.02 g, 0.04 mmol) in C_6D_6 (0.6 ml) was transferred to a thick-walled NMR tube. The NMR

tube was connected to a vacuum line, evacuated at -196°C and sealed off after several freeze–thaw cycles. The sealed NMR tube was allowed to reach room temperature before it was heated in a silicone oil bath at 85°C . ^1H NMR spectra were recorded at $t = 0, 0.75, 3, 122$ and 312 h. Initially the spectra did not change, but after 122 h the intensities of the proton resonances of **1** decreased and a new resonance at $\delta = 5.27$ ppm appeared. This was assigned to free ethylene by comparison with an authentic ^1H NMR spectrum of ethylene in C_6D_6 . Complete decomposition of **1** occurred after about 312 h.

2.13.2. In the solid state

Crystals of **1** melt at 130 – 131°C , on a hot-stage microscope, to form an oily residue which crystallizes to afford $[\text{CpRu}(\text{CO})_2]_2$, as identified by IR spectroscopy.

2.14. Synthesis and characterization of $[\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CH}_3)]$ (**2**)

The method of Davison et al. [12] was used for the synthesis of $\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CH}_3)$. IR (hexane): $\nu(\text{CO})$ $2018\text{s}, 1959\text{s cm}^{-1}$. ^1H NMR (CDCl_3): δ 5.23 (s, 5H, Cp), 1.77 (q, $^3J_{\text{HH}} = 7.6$ Hz, 2H, CH_2), 1.37 (t, $^3J_{\text{HH}} = 7.6$ Hz, 3H, CH_3) ppm. ^{13}C NMR (CDCl_3): δ 202.4 (CO), 88.6 (Cp), 24.2 (CH_3), -10.0 (CH_2) ppm. The mass spectrum showed a molecular ion peak at m/z 251 ($M = 251.25$).

2.15. Reaction of **2** with CF_3COOH

A solution of **2** (0.02 g, 0.08 mmol) in CDCl_3 (0.6 ml) was treated with an excess of CF_3COOH (0.05 g, 0.48 mmol) at room temperature in an NMR tube. The complex $[\text{CpRu}(\text{CO})_2(\text{O}_2\text{CCF}_3)]$ and ethane were detected by ^1H NMR spectroscopy.

2.16. Reaction of **2** with MeOH

A solution of **2** (0.05 g, 0.20 mmol) in MeOH (10 ml) was heated under reflux for 14 days. The reaction was monitored by recording IR spectra periodically and these showed that no reaction occurred.

2.17. Reaction of **2** with $[\text{Ph}_3\text{C}][\text{PF}_6]$

Solid $[\text{Ph}_3\text{C}][\text{PF}_6]$ (0.15 g, 0.60 mmol) was added to a solution of **2** (0.16 g, 0.40 mmol) in CH_2Cl_2 (8 ml) and the solution was stirred at room temperature for 1 h. The solvent was removed and the residue was dissolved in a minimum of CH_2Cl_2 . Addition of hexane to the solution gave white microcrystals, which were filtered, washed with hexane and dried to give $[\text{CpRu}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{PF}_6$ (yield, 0.15 g (61%)) identified by its IR and ^1H NMR spectra.

2.18. Reaction of $[\text{Cp}(\text{CO})_2\text{RuCH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]\text{PF}_6$ with CF_3COOH

Trifluoroacetic acid (0.46 g, 4.02 mmol) was added to a solution of $[\text{Cp}(\text{CO})_2\text{RuCH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]\text{PF}_6$ (0.10 g, 0.16 mmol) in CH_2Cl_2 (5 ml) at room temperature. The reaction was monitored by IR spectroscopy. After 5 h the solvent was removed under reduced pressure to yield a red oil. This oil was taken up in a small volume of methanol, and a solution containing an excess of NaBPh_4 in methanol was added. A yellow precipitate formed immediately and this was filtered and dried. This product was identified as $[\text{CpRu}(\text{CO})_2(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3)]\text{BPh}_4$ (yield, 66% ; m.p., 112 – 114°C) by its IR, ^1H and ^{13}C NMR spectra. IR (CH_2Cl_2): $\nu(\text{CO})$ $2082\text{s}, 2039\text{s cm}^{-1}$. ^1H NMR (acetone- d_6): 5.95 (s, 5H, Cp), 5.25 (m, 1H, =CH), 3.90 (d, 1H, = CH_2 , $J_{\text{cis}} = 8.0$ Hz), 3.88 (d, 1H, = CH_2 , $J_{\text{trans}} = 14.0$ Hz), 2.38 – 1.60 (m, 4H, CH_2), 0.96 (t, 3H, CH_3) ppm. ^{13}C NMR (acetone- d_6): 137.0 (*m*-Ph), 126.0 (*o*-Ph), 122.3 (*p*-Ph), 92.1 (Cp), 86.5 (=CH), 51.9 (= CH_2), 39.7 (=CH CH_2), 26.7 (CH_2CH_3), 13.6 (CH_3). The trifluoroacetate complex $[\text{CpRu}(\text{CO})_2(\text{O}_2\text{CCF}_3)]$ was identified in the filtrate.

A similar reaction with $[\text{Cp}(\text{CO})_2\text{FeCH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}]\text{PF}_6$ gave $[\text{CpFe}(\text{CO})_2(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3)]\text{BPh}_4$ with a 90% yield and this was identified by IR and ^1H and ^{13}C NMR spectroscopy.

2.19. Reaction of $[\text{CpRu}(\text{CO})_2(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3)]\text{BPh}_4$ with NaI

The cationic complex $[\text{CpRu}(\text{CO})_2(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3)]\text{BPh}_4$ (0.03 g, 0.05 mmol) was dissolved in acetone- d_6 (0.60 ml) in an NMR tube and NaI (0.015 g, 0.10 mmol) was added. The ^1H NMR spectrum then showed the quantitative displacement of 1-pentene and the formation of $[\text{CpRu}(\text{CO})_2\text{I}]$.

2.20. X-ray crystallography

Pale yellow crystals of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (**1**) were obtained by slow crystallization from CH_2Cl_2 .

Data were collected with an Enraf–Nonius CAD-4 diffractometer using Mo K α radiation ($\lambda = 0.71069$ Å). Cell parameters were obtained by least-squares analysis of the setting angles of 24 reflections in the range $16^{\circ} \leq \theta \leq 17^{\circ}$. During the data collection the intensities of three standard reference reflections were monitored every hour, and recentring was checked every 100 measured reflections. Intensities were corrected for Lorentz–polarization effects and for absorption [13].

The structure was solved by location of the Ru atom in a Patterson map. All remaining atoms, including the hydrogen atoms, were located from subsequent differ-

Table 1

Crystal data and experimental details of data collection and structure refinement for [Cp(CO)₂RuCH₂CH₂Ru(CO)₂Cp] (**1**)

Molecular formula	C ₁₆ H ₁₄ O ₄ Ru ₂
<i>M_r</i> (g mol ⁻¹)	472.43
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	6.060(1)
<i>b</i> (Å)	6.990(2)
<i>c</i> (Å)	10.097(1)
α (°)	85.30(1)
β (°)	76.86(1)
γ (°)	74.46(2)
<i>V</i> (Å ³)	401(2)
<i>D_c</i> for <i>Z</i> = 1 (g cm ⁻³)	1.96
<i>F</i> (000)	230
μ (Mo K α) (cm ⁻¹)	18.13
Dimensions of crystal (mm)	0.23 × 0.23 × 0.30
Crystal decay (%)	2.9
Scan mode	ω -2 θ
Scan width (ω) (°)	1.00 + 0.35 tan θ
Aperture width (mm)	1.20 + 1.05 tan θ
θ range (°)	1–30
Transmission on absorption correction (%)	
minimum; maximum; average	97; 100; 98
Total number of reflections collected	2460
Number of reflections observed <i>N</i> (with <i>I</i> _{rel} > 2 σ <i>I</i> _{rel})	2223
Number <i>N_p</i> of parameters	102
$R(F) = \Sigma \Delta / \Sigma F_o $	0.029
$R_w(F) = \Sigma w^{1/2} \Delta / \Sigma w^{1/2} F_o $	0.034
Weighting scheme <i>w</i>	($\sigma^2 F_o + 0.0020 F_o^2$) ⁻¹
$S = (\Sigma \Delta ^2 / N - N_p)^{1/2}$	1.03

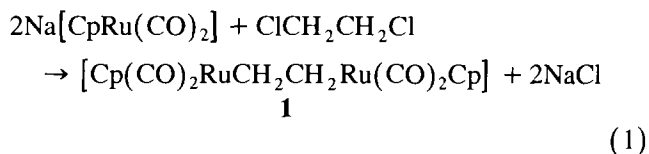
ence Fourier syntheses. In the final refinements, which were by the full-matrix least-squares method on *F*, all non-hydrogen atoms were treated anisotropically, while the hydrogen atoms were placed in calculated positions with separate isotropic temperature factors for the methylene and Cp hydrogen atoms. The maximum parameter-shift-to-estimated-standard-deviation ratio was 0.001 in the final run. In the difference map computed after the final cycle of refinement there was a residual electron density of 2.0 electron Å⁻³ at the origin. Refinement in the alternative space group *P*1 failed, and this superfluous peak may possibly be ascribed to residual absorption. Complex neutral-atom scattering factors for the non-hydrogen atoms were taken from Cromer and Mann [14] and for the hydrogen atoms from Stewart et al. [15]. Dispersion corrections were taken from Cromer and Liberman [16]. Structure solution and refinement were carried out using SHELX-76 [17] on a VAX 6000-330 computer, and drawings were obtained using PLUTO-89 [18].

Further details of the data collection, structure solution, and refinement are given in Table 1, while Table 2 lists the fractional coordinates of the non-hydrogen atoms. Tables of hydrogen atom coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

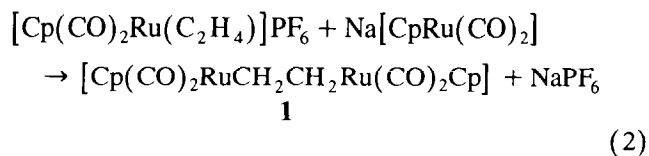
3. Results and discussion

3.1. Synthesis and characterization of the complexes

Complex **1** has been briefly mentioned before [19] but few details were given. We have prepared **1** by two routes, firstly by



This is the method used previously by Lin et al. [19]. Although this reaction is essentially quantitative by IR, the work-up and purification are difficult and isolated yields were typically only about 40%. We also show that **1** can be prepared from the ruthenium–ethylene cation according to



In the pure state, **1** is obtained as very-pale-yellow crystals (m.p., 130–131°C) and was characterized by

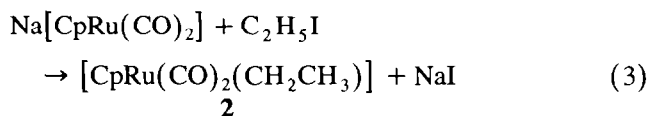
Table 2

Fractional coordinates of non-hydrogen atoms of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{-CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (**1**) with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ru	0.22691(3)	0.04690(2)	0.25815(2)
C(1)	0.4337(5)	-0.1802(5)	0.3099(3)
O(1)	0.5623(6)	-0.3173(4)	0.3426(4)
C(2)	0.1124(6)	-0.1056(4)	0.1603(3)
O(2)	0.0422(7)	-0.1936(4)	0.0980(3)
C(3)	-0.0328(5)	-0.0134(5)	0.4347(3)
C(4)	0.3130(7)	0.2796(6)	0.0995(3)
C(5)	0.0816(6)	0.3559(5)	0.1781(4)
C(6)	0.0988(6)	0.3751(5)	0.3120(3)
C(7)	0.3338(7)	0.3075(6)	0.3210(4)
C(8)	0.4697(6)	0.2497(6)	0.1872(4)

IR, ^1H NMR, ^{13}C NMR and elemental analysis (for details, see Section 2). A parent ion was also seen in the mass spectrum of **1** which further confirmed its composition. In the IR spectrum of **1**, the $\nu(\text{CO})$ bands are at lower frequencies than those for other members of the series $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_n\text{Ru}(\text{CO})_2\text{Cp}]$ ($n = 3-10$) [10a]. This may well be a result of electronic effects from the proximity of the two Ru centres and this may affect the chemistry of **1** (see later). In the ^1H NMR spectrum of **1**, the ethylene protons appeared as a singlet as expected; this remained unchanged even down to -60°C . The ^{13}C NMR spectrum of **1** is consistent with the proposed structure. It is interesting to note that for the series $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_n\text{Ru}(\text{CO})_2\text{Cp}]$, there are dramatic shifts in the α -carbon resonances of the polymethylene chain for the first four members of the series, after which the value is almost invariable: $n = 1$ ($\delta = -37.42$ ppm in CD_2Cl_2) [19], $n = 2$ ($\delta = 13.13$ ppm in CDCl_3), $n = 3$ ($\delta = 0.9$ ppm in CDCl_3) and $n = 4$ ($\delta = -3.3$ ppm in CDCl_3) [10a]. These results may suggest why the chemistries of the first two members of the series are significantly different from those of the remaining members of the series. The proton-coupled ^{13}C NMR spectrum of **1** was recorded in order to probe for any agostic interactions. The ethylene carbon atoms were seen as a triplet of triplets ($J(^{13}\text{C}-^1\text{H}) = 139$ and 6 Hz), suggesting that agostic interactions are not present. Additional fine structure was observed and attributed to second-order effects; this was confirmed by computer simulation of the spectra. A doublet of quintets for the Cp carbon atoms was also observed ($J(^{13}\text{C}-^1\text{H}) = 178$ and 7 Hz).

$[\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CH}_3)]$ (**2**) has been previously reported together with some characterization data [12,20–23]. We prepared this complex by the following reaction, i.e. by the method of Davison et al. [12]:



We isolated **2** as a volatile colourless oil and characterized it by IR, ^1H NMR and ^{13}C NMR. The mass spectrum shows a molecular ion peak at 251 amu. The IR spectrum shows two strong $\nu(\text{CO})$ bands at 2018 and 1959 cm^{-1} , frequencies which are the same as for other members of the homologous series $[\text{Cp}(\text{CO})_2\text{RuR}]$ [24]. The ^1H NMR spectrum of **2** showed the expected triplet and quartet resonances for the ethyl group but additional fine structure was also observed. This was shown by computer simulation to result from second-order effects. The proton-coupled ^{13}C NMR spectrum gave the following data: $\delta = -10.0$ (triplet, $J(^{13}\text{C}-^1\text{H}) = 132$ Hz), 24.2 (quartet, $J(^{13}\text{C}-^1\text{H}) = 123$ Hz) and 88.6 (doublet of quintets, $J(^{13}\text{C}-^1\text{H}) = 178$ and 7 Hz) ppm, suggesting that the ethyl group in **2** is not involved in agostic interactions.

3.2. Molecular structure of **1**

The molecular structure of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (**1**) was determined by X-ray crystallography and is shown in Fig. 1, together with the atom-labelling scheme. Selected interatomic distances and angles are given in Table 3. The structure confirms that the $\text{CpRu}(\text{CO})_2$ units are centrosymmetrically bonded to each end of the ethylene fragment and, as expected, there is no π interaction between the C_2H_4 group and the Ru atoms. There is, however, a shortening of the ethylene $\text{C}(3)-\text{C}(3')$ bond ($1.499(6)$ Å) compared with accepted $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}$ lengths, which tend to cluster around 1.53 Å [25]. Similar shortening was observed in the $\text{C}_\alpha-\text{C}_\beta$ bonds of the pentamethylene-linked compound $[\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2)_5\text{Ru}(\text{CO})_2\text{Cp}]$ (**3**) [10a], although this was not observed in the diiron compounds $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{Fe}(\text{CO})_2\text{Cp}]$ ($n = 3$ or 4) [26]. The $\text{Ru}-\text{C}(\text{alkyl})$ bond distance of $2.189(3)$ Å in **1** is close to that found in the μ -methylene complex $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (average, 2.18 Å) [19] and to that in **3** (average, $2.172(9)$ Å), although the chemistries of these three binuclear complexes are significantly different (see later). These $\text{Ru}-\text{CH}_2$ distances all correspond closely to accepted $\text{Ru}-\text{C}(\text{alkyl})$ single-bond lengths [27]. The $\text{Ru} \cdots \text{Ru}'$ distance of 5.12 Å confirms that the two ruthenium atoms in **1** are not bonded; comparison can

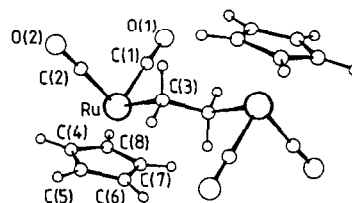


Fig. 1. Molecular structure of $[\text{Cp}(\text{CO})_2\text{RuCH}_2\text{CH}_2\text{Ru}(\text{CO})_2\text{Cp}]$ (**1**), showing the atom-numbering scheme. The unlabelled heavy atoms are related by the centre of inversion and are indicated by a prime in the text.

Table 3
Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses for [Cp(CO)₂RuCH₂CH₂-Ru(CO)₂Cp] (**1**)

Distances			
Ru–C(3)	2.189(3)	Ru–C(6)	2.285(3)
C(3)–C(3')	1.499(6)	Ru–C(7)	2.269(3)
Ru···C(3')	3.07(1)	Ru–C(8)	2.271(4)
Ru–C(1)	1.860(3)	C(4)–C(5)	1.429(5)
Ru–C(2)	1.864(3)	C(5)–C(6)	1.398(5)
C(1)–O(1)	1.140(4)	C(6)–C(7)	1.396(5)
C(2)–O(2)	1.131(4)	C(7)–C(8)	1.440(6)
Ru–C(4)	2.265(3)	C(8)–C(4)	1.405(6)
Ru–C(5)	2.261(3)		
Angles			
Ru–C(3)–C(3')	111.3(1)		
Ru–C(1)–O(1)	178.8(3)	C(5)–C(4)–C(8)	107.7(3)
Ru–C(2)–O(2)	177.9(3)	C(4)–C(5)–C(6)	108.0(3)
C(1)–Ru–C(3)	86.8(1)	C(5)–C(6)–C(7)	108.9(3)
C(2)–Ru–C(3)	86.4(1)	C(6)–C(7)–C(8)	107.7(3)
C(1)–Ru–C(2)	90.6(1)	C(4)–C(8)–C(7)	107.6(3)

be made with the non-bonded Ru···Ru' distance of 3.8 Å in [Cp(CO)₂RuCH₂Ru(CO)₂Cp] [19]. The Ru–C(3)–C(3') angle of 111.3(1)° is close enough to the sp³ tetrahedral angle to discount any serious steric crowding in the molecule; it has been suggested that the large Ru–C–Ru bond angle of 123° in [Cp-(CO)₂RuCH₂Ru(CO)₂Cp] reflects steric crowding around the μ-methylene group, which might be responsible for the unusual reactivity of this complex [19].

Interestingly, both **1** and [Cp(CO)₂RuCH₂Ru(CO)₂-Cp] crystallize with the two Cp rings on opposite sides of the Ru···Ru' axis in a *trans* arrangement (dihedral angle Ru–C(3)–C(3')–Ru', 180°), whereas the pentamethylene-bridged compound [Cp(CO)₂Ru(CH₂)₅Ru(CO)₂Cp] crystallizes with the Cp rings on the same side of the Ru···Ru axis in a *cis* arrangement, presumably because of an absence of any steric constraints in the latter molecule. In solution, rotation about the C–C bond in **1** is expected and would give rise to a slightly higher energy form, with the CpRu(CO)₂ groups on the same side of the CH₂CH₂ group, as depicted earlier when comparing **1** with surface intermediate **A**. There are no notable intermolecular contacts or unusual features about the packing of the molecules of **1** in the crystal structure.

3.3. Reactivity studies on **1** and **2**

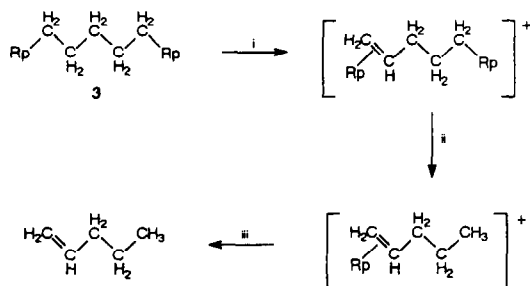
We have studied the reactivity of **1** and **2**, particularly to explore their usefulness as models for the Fischer–Tropsch intermediates **A** and **B** in Scheme 1. We find that **1** does not react with CO or PPh₃ under the conditions used. This contrasts with [Cp(CO)₂RuCH₂Ru(CO)₂Cp], which is reported to react readily with CO [19]. Even with the more basic PMe₂Ph, alkyl migration–CO insertion does not occur and only CO

substitution of **1** is observed. These results show that, in **1**, the Ru–CH₂– bond is not susceptible to migratory insertion reactions, at least not with CO. Similarly, for a combination of electronic and steric reasons, the M–CH₂– bond in intermediate **A** may also not be susceptible to insertion reactions, e.g. with methylene (CH₂), and thus might not be involved in chain growth processes. This lends support to the findings of Brady and Pettit [28] that CH₂N₂ alone on a catalytic surface will not give chain growth. The reaction of **1** with acids (HCl or CF₃COOH) yielded [Cp(CO)₂Ru(C₂H₄)]⁺ and [Cp(CO)₂RuX] (X = Cl or CF₃COO respectively), but none of the ethyl complex **2** could be detected. Thus, in the Fischer–Tropsch reaction, the conversion of surface ethylene (intermediate **A**) to surface ethyl (intermediate **B**) might also be difficult. It is particularly note worthy that [Cp(CO)₂Ru(C₂H₄)]⁺ is also a product of several other reactions of **1**, namely the reactions with Ag⁺, [Ph₃C][PF₆] and even Br₂. The complex [Cp(CO)₂Ru(C₂H₄)]⁺ could then readily decompose to give ethylene. We also show that the thermal decomposition of **1** in solution gives ethylene and, in the solid state, ethylene is the most likely organic product. Thus **1** readily gives ethylene and this may suggest that the easy decomposition pathway for intermediate **A** is also formation of ethylene.

An unexpected reaction of **1**, which is not typical of compounds containing a metal–CH₂– bond, is that with MeOH, yielding [Cp(CO)₂Ru(CH₂CH₂OMe)]. This new product was fully characterized by analytical and spectroscopic methods. Its formation was confirmed by independent synthesis from Na[CpRu(CO)₂] and ClCH₂CH₂OMe. Thus **1** shows a number of reactions that are not typical of metal–CH₂– compounds and it has a tendency to produce ethylene. Intermediate **A** may show similar behaviour and be a precursor for only ethylene in the Fischer–Tropsch reaction. In contrast, **2** shows reactions which either give or could lead to many of the primary Fischer–Tropsch products. It is also important to note that some of these reactions are also shown by higher alkyls of the type [Cp(CO)₂RuR] [24,29]. Thus reaction of **2** with CF₃COOH gives ethane, reaction with [Ph₃C][PF₆] gives [CpRu(CO)₂-(C₂H₄)]PF₆, and reaction with PPh₃ leads to the CO insertion product [Cp(CO)(PPh₃)Ru(COC₂H₅)] [22,30]. Insertion of CO has been proposed as the step prior to oxygenate formation [31]. Thus **2** shows all the required reactions of an alkyl intermediate in the Fischer–Tropsch reaction and indeed direct evidence of alkyl intermediates in the Fischer–Tropsch reaction has been obtained [32,33].

3.4. A reaction sequence for **3**

If intermediate **A** in Scheme 1 could insert methylene groups, then the hydrocarbon chains could grow along the surface of the catalyst (instead of perpendicular to it



Scheme 2. Rp = CpRu(CO)₂ for the following reagents and conditions: (i) [Ph₃C][PF₆]; (ii) CF₃COOH; (iii) NaI, acetone.

as an alkyl intermediate, M–R, may tend to). We were interested to see whether the complex [Cp(CO)₂Ru(CH₂)₅Ru(CO)₂Cp] (**3**) [10], which could be a model for the fragment –(CH₂)₅– coordinated to two active sites on a catalyst surface, would show chemistry leading to Fischer–Tropsch products. In particular, we wished to see whether binuclear complexes, such as **3**, could yield 1-alkenes on demetallation rather than dienes. In a sequence of reactions (Scheme 2) we show that high yields of 1-pentene can be obtained from **3**. The reaction of **3** with trityl salt is known to give the alkene–alkyl cation [10b]. This cation reacts with trifluoroacetic acid to cleave selectively the Ru–CH₂ (alkyl) bond, giving the alkene cation [Cp(CO)₂Ru(CH₂=CH–CH₂CH₂CH₃)⁺ and [CpRu(CO)₂(O₂CCF₃)]. In an NMR experiment, the reaction of [Cp(CO)₂Ru(CH₂=CHCH₂CH₂CH₃)⁺ with NaI in acetone-*d*₆ results in demetallation and gives quantitative formation of 1-pentene. We have also demonstrated a similar sequence of reactions with the analogous diiron compound [Cp(CO)₂Fe(CH₂)₅Fe(CO)₂Cp]. Thus **3** can yield some Fischer–Tropsch products; however, complexes or intermediates of this type could be expected to give rise to diols and diols, which are not important Fischer–Tropsch products. This would count against the involvement of this sort of intermediate, as of course would the difficulty that intermediate **A** may have in undergoing insertion reactions, as we have found for **2**.

Thus the results from our studies on metal complexes support the idea that it is the alkyl intermediates (M–R) that are the long-lived surface species and which give rise to the primary Fischer–Tropsch products (namely *n*-alkanes, 1-alkenes and oxygenates). We also find that the metal complexes [CpM(CO)₂R] are reluctant to undergo β elimination; this is also supported by calculations [34] and we believe that the termination step to give 1-alkenes in the Fischer–Tropsch reaction may be a β-hydride abstraction rather than a β elimination. The β-hydride abstraction for metal complexes of the type [CpM(CO)₂R] is a well-known reaction [11].

We are continuing our work on reactions of metal alkyl complexes which we believe will be of importance to catalytic reactions and we shall report on these results in forthcoming papers.

4. Conclusions

The complexes [Cp(CO)₂RuCH₂CH₂Ru(CO)₂Cp] (**1**) and [Cp(CO)₂RuCH₂CH₃] (**2**) have been prepared and fully characterized. All the compounds **1**, **2** and [Cp(CO)₂Ru(CH₂)₅Ru(CO)₂Cp] (**3**) can be models for surface intermediates in catalytic reactions such as the Fischer–Tropsch reaction. From reactivity studies on these and related compounds we find that there are significant differences in chemistry on going from **1** to **3** and, in particular, **1** shows less tendency to undergo alkyl migration–CO insertion than does [Cp(CO)₂Ru–CH₂Ru(CO)₂Cp].

In fact, we could not get **1** to undergo alkyl migration–CO insertion at all; higher temperatures caused decomposition to give ethylene. If the chemistry of organometallic complexes can be extrapolated to catalytic surface intermediates, then our studies on **1** and **2** may give some support for the mechanism shown in Scheme 1. The reluctance of **1** to undergo alkyl migration–CO insertion leads us to suggest that on the catalyst surface in the Fischer–Tropsch reaction intermediate **A** may also be reluctant to insert a methylene group, and thus the likelihood that the carbon chain grows along the catalyst surface, as envisaged, for example, by Craxford and Rideal [35], may be small. We say this in spite of our findings that a sequence of reactions of **3** can lead to a high yield of 1-pentene. Thus, if a pentamethylene species attached to two active sites on a catalyst surface were formed, we show that the chemistry is possible for this sort of intermediate to give 1-pentene selectively. Our experiments show that **1** readily decomposes to C₂H₄, as depicted for the surface ethylene species in Scheme 1, and this suggests that intermediate **A** does not show chain growth. This is also supported by the experiments of Brady and Pettit [28], who showed that CH₂N₂ on the surface alone does not give chain growth, but only when hydrogen is present. Our experiments reported in this paper lend support to the suggestions that it is the metal alkyl intermediates M–R (**B**) which are the long-lived intermediates that give rise to the primary products of the Fischer–Tropsch reaction, i.e. *n*-alkanes and 1-alkenes; oxygenates may be formed after an initial CO insertion step.

As has been said before [4], we can learn much about the mechanisms of heterogeneous catalytic reactions by studying metal complex chemistry.

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