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Synthesis, characterization and reactivity of iron–olefin complexes of the type $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{X}^-$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{R} = \text{CH}_3$ to $n\text{-C}_{14}\text{H}_{29}$; $\text{X} = \text{PF}_6$ or BF_4)

Hadley S. Clayton^a, John R. Moss^{b,*}, Mark E. Dry^c^a Department of Chemistry, University of South Africa, Pretoria 0003, South Africa^b Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa^c Department of Chemical Engineering, University of Cape Town, Rondebosch 7701, South Africa

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Abstract

A series of iron–olefin complexes of the type $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ($\text{R} = \text{CH}_3$ to $n\text{-C}_{14}\text{H}_{29}$) have been prepared using various synthesis methods. In addition, the complexes $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$; $\text{R} = \text{CH}_3$, $n\text{-C}_3\text{H}_7$ and $n\text{-C}_{14}\text{H}_{29}$) and $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ($\text{R} = \text{CH}_3$, $n\text{-C}_3\text{H}_7$ and $n\text{-C}_{14}\text{H}_{29}$) have been synthesized by reacting the iron–alkyl complexes $\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CH}_2\text{CH}_2\text{R})$ or ruthenium–alkyl complexes $\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CH}_2\text{R})$ with Ph_3CPF_6 . A number of these complexes are new and have been fully characterized by analytical and spectroscopic methods. The reaction of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ with the isopropoxide ion gave the new ether derivatives $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{R})]$ ($\text{R} = \text{CH}_3$, $n\text{-C}_2\text{H}_5$, $n\text{-C}_4\text{H}_9$ and $n\text{-C}_{13}\text{H}_{27}$).

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Keywords: Iron; Olefin; Cyclopentadienyl; Pentamethylcyclopentadienyl; Ruthenium

1. Introduction

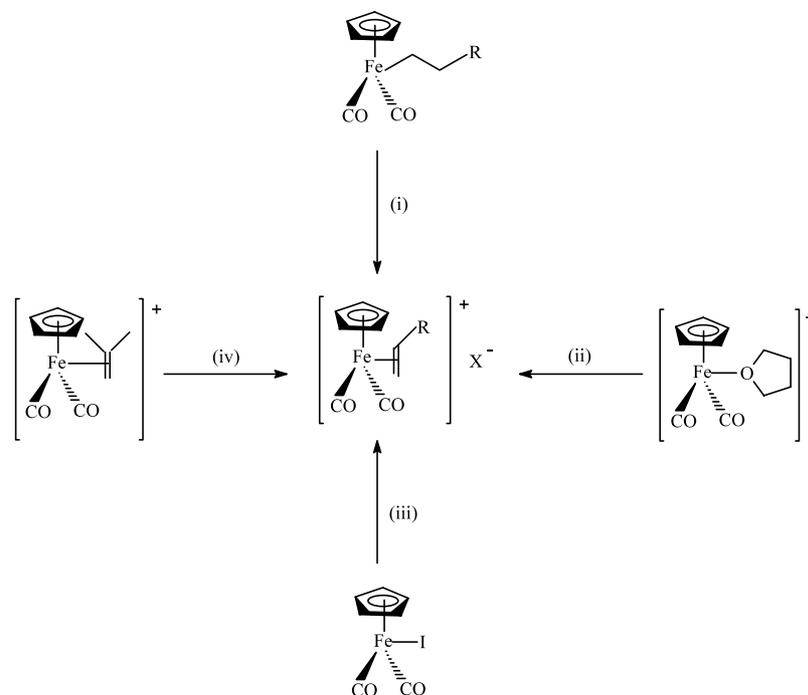
While transition metal–olefin complexes of the type $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ($\text{R} = \text{H}$, CH_3) are well known and the properties and reactivity of these complexes have been extensively investigated [1], comparatively little work has been carried out on the analogous long chain α -olefin complexes ($\text{R} \geq n\text{-C}_4\text{H}_9$). These iron–olefin complexes are important because of their significance as model compounds for transition metal–olefin intermediates in a wide range of catalytic reactions and their applications in stoichiometric organic synthesis [2].

We have investigated the synthesis of the iron–olefin complexes using a number of different methods (Scheme 1). The complexes $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{PF}_6^-$ ($\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_5$, $n\text{-C}_{11}\text{H}_{23}$ to $n\text{-C}_{14}\text{H}_{29}$ and $n\text{-C}_{16}\text{H}_{33}$) were prepared by reacting the appropriate iron–alkyl complex with Ph_3CPF_6 . The complexes $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{BF}_4^-$ ($\text{R} = n\text{-C}_4\text{H}_9$ and $n\text{-C}_6\text{H}_{13}$) were prepared by reacting $[\text{CpFe}(\text{CO})_2(\text{THF})]^+ \text{BF}_4^-$ with the corresponding α -olefin. The complexes $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{BF}_4^-$ ($\text{R} = n\text{-C}_5\text{H}_{11}$, $n\text{-C}_7\text{H}_{15}$ and $n\text{-C}_8\text{H}_{17}$) were prepared by reacting $\text{CpFe}(\text{CO})_2\text{I}$ with the corresponding α -olefin, while the complexes $\text{R} = n\text{-C}_9\text{H}_{19}$ and $n\text{-C}_{10}\text{H}_{21}$ were prepared by reacting the isobutene–iron complex $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=C}(\text{CH}_3)_2)]^+ \text{BF}_4^-$ with 1-undecene and 1-dodecene respectively.

Here we report the synthesis and full characterization of an extensive series of iron–olefin complexes

* Corresponding author. Tel.: +27-21-650-2535; fax: +27-21-689-7499.

E-mail address: jrm@science.uct.ac.za (J.R. Moss).



Scheme 1. (i) $\text{Ph}_3\text{CPF}_6/\text{CH}_2\text{Cl}_2$; (ii) α -olefin/ CH_2Cl_2 ; (iii) AgBF_4/α -olefin/ CH_2Cl_2 ; (iv) α -olefin/ CH_2Cl_2 .

$[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+\text{X}^-$ ($\text{R} = \text{CH}_3$ to $n\text{-C}_{14}\text{H}_{29}$; $\text{X} = \text{PF}_6^-$ or BF_4^-). Furthermore, the reactivity of a few of these complexes with isopropanol, leading to the elaboration of the olefin is also reported.

2. Results and discussions

2.1. Synthesis of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$

The olefin complexes **1–3** and **11–14** were synthesized by the reaction of the corresponding alkyl complex $[\text{CpFe}(\text{CO})_2\text{R}]$ with the trityl salt, Ph_3CPF_6 , in CH_2Cl_2 according to the method reported by Baird and co-workers [3]. It is found that the reaction of $[\text{CpFe}(\text{CO})_2\text{R}]$ with Ph_3CPF_6 at room temperature is chain-length dependent. Abstraction of a β -hydride ion from the short-chain iron-alkyls $[\text{CpFe}(\text{CO})_2\text{R}]$ ($\text{R} = n\text{-C}_3\text{H}_7$ to $n\text{-C}_5\text{H}_{11}$) proceeds rapidly at room temperature and the reaction is complete within 30 min. For the long-chain iron-alkyls ($\text{R} = n\text{-C}_{13}\text{H}_{27}$ to $n\text{-C}_{16}\text{H}_{33}$) however, the reaction rate is much slower and the reaction does not go to completion; the longer the polymethylene chain the longer the reaction time required. The large steric demand of the Ph_3C^+ cation could account for the decrease in the rate of the reaction with the increase in alkyl chain-length as Slack and Baird [4] have shown that the reaction proceeds by preferential elimination of the β -hydride.

Complexes **4** and **6** have been successfully synthesized in moderate yields by the reaction of $[\text{CpFe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$ with the corresponding ole-

fin. The preparation of **5**, **7** and **8** from the iodo complex $[\text{CpFe}(\text{CO})_2\text{I}]$ is a two step process: firstly the halide is eliminated to generate the coordinatively unsaturated intermediate $[\text{CpFe}(\text{CO})_2]^+$ which then reacts with the olefin to form the iron-olefin complex [5]. A side product of this reaction is the known iodine bridged complex $[\text{CpFe}(\text{CO})_2\text{I}]^+\text{BF}_4^-$ which is obtained in ca. 40% yield.

The olefin complexes **9** and **10** were prepared through a ligand exchange reaction using the thermodynamically unstable iron-isobutene complex. As this method is restricted to the preparation of olefin complexes more stable than the isobutene complex, and as stability generally decreases with olefin substitution, α -olefins are particularly well-suited as exchange partners.

The complexes $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+\text{PF}_6^-$ ($\text{R} = \text{CH}_3$, **15**; $n\text{-C}_3\text{H}_7$, **16**; $n\text{-C}_{14}\text{H}_{29}$, **17**) and $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+\text{PF}_6^-$ ($\text{R} = \text{CH}_3$, **18**; $n\text{-C}_3\text{H}_7$, **19**; $n\text{-C}_{14}\text{H}_{29}$, **20**) were synthesized by hydride abstraction from the β -carbon of the corresponding metal-alkyl complexes. These complexes cannot be synthesized by ligand exchange methods because of the stronger M–L bond ($\text{L} = \text{THF}$, halide, isobutene) in these systems due to the increased electron density on the metal.

The iron-olefin complexes were isolated as yellow crystalline solids and the ruthenium-olefin complexes as white crystalline solids after purification by recrystallization. The iron complexes are very stable at room temperature for periods of months both in solution and in the solid state. The ruthenium complexes however are less stable in solution and decompose after a few days at

–5 °C in solutions of acetone, dichloromethane and acetonitrile.

2.2. Characterization

The olefin complexes (**1–20**) have been fully characterized. The yields, melting points, IR spectral data as well as elemental analysis data for the compounds (**1–20**) are summarized in Tables 1–3. The complexes have been characterized by satisfactory C and H analysis. The ¹H- and ¹³C-NMR data are reported in Tables 4–9. The FAB mass spectral data for three of the cationic olefin complexes are summarized in Table 10.

2.2.1. IR spectroscopy

The IR spectral data for the complexes (**1–14**) are in good agreement with the data reported for some known compounds [6–8] and show two strong $\nu(\text{CO})$ bands in CH_2Cl_2 solution at ca. 2075 and 2035 cm^{-1} (Table 1). There is no significant shift in the $\nu(\text{CO})$ band positions upon changing the length of the polymethylene chain or as the counterion was varied.

The $\nu(\text{CO})$ values for the Cp* complexes are lower than that for the analogous Cp complexes by ca. 20 cm^{-1} (Table 2). This is consistent with the increase in electron density on the metal in the Cp* complexes which results in increased back-bonding to the carbonyl groups, and hence a lower $\nu(\text{CO})$ [9]. The ruthenium–olefin complexes exhibit carbonyl bands at 2085 and 2045 cm^{-1} (Table 3) indicating that the C–O bond is stronger in the $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ complexes than in the $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ complexes; conversely the Ru–CO bond is weaker than the Fe–CO bond.

2.2.2. ¹H-NMR spectroscopy

The ¹H-NMR data for complexes **1–14** are summarized in Table 4, **15–17** in Table 5, and **18–20** in Table 6. The ¹H-NMR spectra for the $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ complexes exhibit a sharp singlet at ca. 5.9 ppm (acetone-*d*₆) and 5.5 ppm (acetonitrile-*d*₃) for the five equivalent Cp protons, which is in good agreement with the data reported for the shorter chain complexes [8,10–12]. The Cp peak appears at ca. 6.1 (acetone-*d*₆) and 5.8 ppm (acetonitrile-*d*₃) for the analogous ruthenium complexes. The Cp* methyls for **15–17** give rise to a singlet at ca. 2.0 ppm (acetone-*d*₆) and 1.9 ppm (acetonitrile-*d*₃).

Upon coordination to the metal, the protons of the olefinic carbons become more shielded due to the effect of back-bonding from the metal, the partial change in hybridization of the olefinic carbon atoms towards *sp*³ and the magnetic anisotropy of the aromatic Cp ring. An upfield shift relative to the free olefin is observed for the geminal protons of about 1.3 ppm for the *trans* proton and 1 ppm for the *cis* proton in the $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ complexes. For the Cp* complexes the upfield shift for the *cis* proton increased to 1.8 ppm while the *trans* proton only shifted about 1.6 ppm relative to the free olefin. This could be an effect of a greater degree of *sp*³ character of the olefinic carbons in the Cp* complexes compared to the Cp complexes as a result of increased back-bonding from the metal. For the ruthenium complexes there is an upfield shift of about 0.9 ppm for the *cis* proton and 1.0 ppm for the *trans* proton relative to the free olefin. There is no evidence of geminal coupling in either the iron or ruthenium complexes. Separate resonances are observed for the two methylene protons α to the double bond. A distinct multiplet for one of the protons is observed at

Table 1
Data for $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$

| Compound | Yield | Dec. point (°C) | IR $\nu(\text{CO})$ (cm^{-1}) ^a | Elemental analysis (%) | |
|-----------|-------|-----------------|---|----------------------------|--------------------------|
| | | | | C found (calc.) | H found (calc.) |
| 1 | 66 | 146 | 2077, 2039 | 32.89 (33.00) | 3.04 (3.02) |
| 2 | 72 | 126 | 2078, 2039 | 35.16 (34.98) | 3.48 (3.44) |
| 3 | 72 | 121 | 2077, 2039 | 36.64 (36.78) | 3.88 (3.83) |
| 4 | 75 | 118 | 2074, 2032 | 45.01 (44.96) | 5.07 (4.98) |
| 5 | 38 | 104 | 2072, 2026 | 46.16 (46.48) | 5.18 (5.25) |
| 6 | 53 | 101 | 2075, 2037 | 47.55 (47.94) | 5.54 (5.59) |
| 7 | 47 | 96 | 2072, 2034 | 48.83 (49.30) | 5.70 (5.90) |
| 8 | 30 | 96 | 2073, 2036 | 50.48 (50.57) | 6.30 (6.19) |
| 9 | 52 | 97 | 2075, 2037 | 48.03 (48.27) ^b | 6.12 (6.08) ^b |
| 10 | 65 | 95 | 2074, 2035 | 53.13 (52.85) | 6.79 (6.72) |
| 11 | 76 | 103 | 2076, 2039 | 47.78 (47.66) | 6.29 (6.15) |
| 12 | 43 | 98 | 2077, 2039 | 48.78 (48.69) | 6.41 (6.37) |
| 13 | 81 | 101 | 2076, 2039 | 50.37 (49.66) | 6.51 (6.58) |
| 14 | 60 | 107 | 2075, 2037 | 50.05 (50.59) | 6.63 (6.78) |

^a Measured in CH_2Cl_2 .

^b Calculated with 0.5 mol of CH_2Cl_2 .

Table 2
Data for $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$

| Compound | Yield | M.p. (°C) | IR $\nu(\text{CO})$ (cm^{-1}) ^a | Elemental analysis (%) | |
|-----------|-------|-----------|---|------------------------|-----------------|
| | | | | C found (calc.) | H found (calc.) |
| 15 | 83 | 104 dec. | 2052, 2015 | 41.59 (41.52) | 4.88 (4.84) |
| 16 | 92 | 112 dec. | 2056, 2016 | 44.33 (44.20) | 5.47 (5.41) |
| 17 | 44 | 127–129 | 2056, 2015 | 54.46 (54.58) | 7.32 (7.63) |

^a A measured in CH_2Cl_2 solution.

about 0.7 ppm from the $-(\text{CH}_2)_x-$ resonance which obscures the signal from the other proton.

2.2.3. ^{13}C -NMR spectroscopy

The ^{13}C -NMR data for complexes **1–14** are summarized in Table 7, **15–17** in Table 8, and **18–20** in Table 9. The ^{13}C -NMR data for **4–6** and the tetrafluoroborate salts of **1–3** have been reported by Laycock and Baird [13] and our results agree well with their reported data. The $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ complexes give rise to a single peak at ca. 90 ppm for the five equivalent aromatic carbons of the Cp ligand. These signals were observed at ca. 93 ppm for the Cp* complexes and 103 ppm for the Ru complexes. This variation is due to the shielding of the carbon atoms by the methyl substituents on the aromatic ring in the Cp* complexes and the increased electron density on the metal in the Ru complexes. These resonances are not affected by the increase of the polymethylene chain length of the olefin.

The complexes are chiral and two diastereotopic carbonyl groups give rise to two distinct peaks; about 2 ppm apart for complexes **1–14**, 0.3 ppm apart for **15–17** and 1.5 ppm apart for **18–20**. The signals due to the carbonyl carbons are often weak and broad due to the long relaxation times of these carbon atoms and hence these peaks were not observed in a few of the spectra. The carbon atoms of the alkyl substituent exhibit resonances typical of normal organic hydrocarbons.

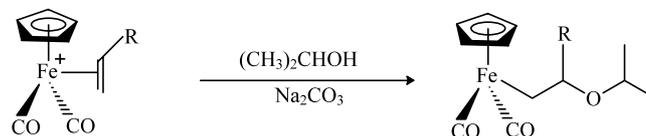
2.2.4. Mass spectra

The fast atom bombardment mass spectra for complexes **4**, **19** and **20** were recorded (Table 10). No mass spectral data for complexes of the type $[\text{CpM}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ($\text{M} = \text{Fe}, \text{Ru}$) have previously been

reported. The salts investigated exhibit peaks corresponding to the parent molecular ion (M^+) without its anionic counterion. All the complexes show similar fragmentation patterns. The two main fragmentation pathways are as follows: M^+ , M^+ – olefin, M^+ – olefin – CO, M^+ – olefin – 2CO (Path A) and M^+ , M^+ – CO, M^+ – 2CO, M^+ – 2CO – olefin (Path B). A peak of low intensity corresponding to the ion $[\text{CpM}(\text{CO})_2\text{H}]^+$ ($\text{M} = \text{Fe}, \text{Ru}$) was observed in each spectrum. The fragmentation pattern observed for these complexes is similar to that reported for the neutral $\text{CpMn}(\text{CO})_2(\eta^2\text{-olefin})$ complexes [14].

2.3. Reactivity of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ with isopropanol

The complexes $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ($\text{R} = \text{CH}_3, n\text{-C}_2\text{H}_5, n\text{-C}_4\text{H}_9$ and $n\text{-C}_{13}\text{H}_{27}$) react with $(\text{CH}_3)_2\text{CHOH}$ to form new σ -bonded ether complexes in low yield (Scheme 2). These complexes were isolated after vacuum sublimation as yellow, exceedingly air-sensitive oils. No increase in stability was observed as the length of the alkyl chain increased, however, the adducts of the longer chain olefins were more difficult to purify because of their reduced volatility. These new complexes were fully characterized by IR, ^1H -, ^{13}C -NMR, elemental analysis and mass spectroscopy.



Scheme 2.

Table 3
Data for $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$

| Compound | Yield | M.p. (°C) | IR $\nu(\text{CO})$ (cm^{-1}) ^a | Elemental analysis (%) | |
|-----------|-------|-----------|---|------------------------|-----------------|
| | | | | C found (calc.) | H found (calc.) |
| 18 | 90 | 187 dec. | 2086, 2040 | 29.76 (29.35) | 2.68 (2.69) |
| 19 | 57 | 134–136 | 2085, 2042 | 33.03 (32.98) | 3.56 (3.43) |
| 20 | 71 | 150–152 | 2085, 2042 | 47.17 (46.72) | 6.28 (6.26) |

^a A measured in CH_2Cl_2 solution.

Table 4

 $^1\text{H-NMR}$ data for $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ^a

| Compound | Cp | =CH | =CH ₂ (<i>cis</i>) ³ J(HH) ^b | =CH ₂ (<i>trans</i>) ³ J(HH) ^b | =CHCH | -(CH ₂) _x - | -CH ₃ ³ J(HH) ^b |
|----------|--------------|--------------|---|---|--------------|------------------------------------|--|
| 1 | 5.88 (5H, s) | 5.20 (1H, m) | 4.06 (1H, d, 8.0) | 3.68 (1H, d, 14.4) | | | 1.91 (3H, t, 6.0) |
| 2 | 5.89 (5H, s) | 5.33 (1H, m) | 4.04 (1H, d, 8.3) | 3.63 (1H, d, 14.7) | 2.46 (1H, m) | 1.70 (1H, m) | 1.18 (3H, t, 7.3) |
| 3 | 5.89 (5H, s) | 5.28 (1H, m) | 4.08 (1H, d, 8.3) | 3.67 (1H, d, 14.4) | 2.50 (1H, m) | 1.60 (3H, m) | 0.96 (3H, t, 7.0) |
| 4 | 5.89 (5H, s) | 5.30 (1H, m) | 4.06 (1H, d, 8.2) | 3.61 (1H, d, 14.6) | 2.50 (1H, m) | 1.50 (5H, m) | 0.89 (3H, t, 6.9) |
| 5 | 5.90 (5H, s) | 5.31 (1H, m) | 4.06 (1H, d, 8.1) | 3.65 (1H, d, 14.5) | 2.52 (1H, m) | 1.50 (7H, m) | 0.87 (3H, t, 6.7) |
| 6 | 5.87 (5H, s) | 5.30 (1H, m) | 4.06 (1H, d, 8.3) | 3.60 (1H, d, 14.7) | 2.51 (1H, m) | 1.45 (9H, m) | 0.86 (3H, t, 6.3) |
| 7 | 5.88 (5H, s) | 5.31 (1H, m) | 4.06 (1H, d, 8.1) | 3.62 (1H, d, 14.7) | 2.52 (1H, m) | 1.45 (11H, m) | 0.86 (3H, t, 6.7) |
| 8 | 5.50 (5H, s) | 4.97 (1H, m) | 3.75 (1H, d, 8.2) | 3.35 (1H, d, 14.6) | 2.37 (1H, m) | 1.40 (13H, m) | 0.87 (3H, t, 6.7) |
| 9 | 5.52 (5H, s) | 4.98 (1H, m) | 3.76 (1H, d, 8.3) | 3.37 (1H, d, 14.7) | 2.37 (1H, m) | 1.45 (15H, m) | 0.89 (3H, t, 6.7) |
| 10 | 5.52 (5H, s) | 4.98 (1H, m) | 3.77 (1H, d, 8.1) | 3.37 (1H, d, 14.8) | 2.37 (1H, m) | 1.45 (17H, m) | 0.89 (3H, t, 6.7) |
| 11 | 5.50 (5H, s) | 4.95 (1H, m) | 3.75 (1H, d, 8.3) | 3.35 (1H, d, 14.7) | 2.35 (1H, m) | 1.45 (19H, m) | 0.87 (3H, t, 6.8) |
| 12 | 5.52 (5H, s) | 4.98 (1H, m) | 3.76 (1H, d, 8.3) | 3.37 (1H, d, 14.7) | 2.37 (1H, m) | 1.45 (21H, m) | 0.89 (3H, t, 6.7) |
| 13 | 5.50 (5H, s) | 4.96 (1H, m) | 3.75 (1H, d, 8.2) | 3.35 (1H, d, 14.7) | 2.36 (1H, m) | 1.45 (23H, m) | 0.87 (3H, t, 6.4) |
| 14 | 5.52 (5H, s) | 4.96 (1H, m) | 3.77 (1H, d, 8.3) | 3.36 (1H, d, 14.5) | 2.38 (1H, m) | 1.40 (25H, m) | 0.88 (3H, t, 6.2) |

^a **1–7** measured in acetone-*d*₆; **8–14** measured in acetonitrile-*d*₃.^b Coupling constants are given in Hz.

The regioselectivity of the reaction appears to be complete, with only the Markovnikov product being formed as indicated by the single Cp resonance in the $^1\text{H-NMR}$ spectrum. In the IR spectra a shift in the $\nu(\text{CO})$ bands is observed from that of a cationic complex at ca. 2075 and 2035 cm^{-1} to the expected 2000 and 1940 cm^{-1} for a neutral complex. A band at 1217 cm^{-1} was observed which is attributed to the C–O–C bond. The $^1\text{H-NMR}$ spectra of **21–24** all show a single peak at ca. 4.76 ppm. A multiplet at ca. 1.5 ppm for the diastereotopic FeCH₂ methylene group was obtained, characteristic of a σ -bonded alkyl group. Low resolution mass spectra were obtained for complexes **21–24**. Parent molecular ions were observed for all the iron–ether complexes. The characteristic organic R–OR' ether cleavage was observed in each spectrum, however no peak due to the disassociated ether ligand was observed.

3. Conclusion

We have extended the series of known iron–olefin complexes to include the new complexes $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{X}^-$ (R = *n*-C₉H₁₉ to *n*-C₁₄H₂₉). The analogous new complexes $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{PF}_6^-$ and

$[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{PF}_6^-$ (R = CH₃, *n*-C₃H₇ and *n*-C₁₄H₂₉) have also been synthesized. All these new complexes have been fully characterised. The most effective method for the synthesis of the iron–olefin complexes has been found to be via hydride abstraction from the iron–alkyl complexes. The reaction conditions are mild and the products can be prepared on a large scale and in high yield. No side reactions have been observed, even with the long chain iron–alkyl complexes.

The complexes $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ (R = CH₃, *n*-C₂H₅, *n*-C₄H₉ and *n*-C₁₃H₂₇) have been shown to react with isopropanol in the same way as the short-chain olefin complexes with methanol. The reactivity pattern displayed is independent of the length of the alkyl substituent but linked to the basicity and structure of the nucleophile.

4. Experimental

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk tube techniques. Reagent grade THF, hexane and Et₂O were distilled from sodium/benzophenone; acetone, CH₂Cl₂ and MeCN were distilled from anhydrous CaCl₂ and isopropanol was distilled from anhydrous K₂CO₃ before use. Col-

Table 5

 $^1\text{H-NMR}$ data for $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+ \text{PF}_6^-$ ^a

| Compound | C ₅ (CH ₃) ₅ | =CH | =CH ₂ (<i>cis</i>) ³ J(HH) ^b | =CH ₂ (<i>trans</i>) ³ J(HH) ^b | =CHCH | -(CH ₂) _x - | -CH ₃ ³ J(HH) ^b |
|----------|--|--------------|---|---|--------------|------------------------------------|--|
| 15 | 2.01 (15H, s) | 4.33 (1H, m) | 3.16 (1H, d, 8.2) | 3.43 (1H, d, 14.5) | | | 1.80 (3H, t, 6.1) |
| 16 | 2.01 (15H, s) | 4.21 (1H, m) | 3.35 (1H, d, 8.2) | 3.40 (1H, d, 14.4) | 2.41 (1H, m) | 1.45 (3H, m) | 0.95 (3H, t, 7.1) |
| 17 | 1.86 (15H, s) | 5.30 (1H, m) | 2.89 (1H, d, 8.3) | 3.19 (1H, d, 14.5) | 2.31 (1H, m) | 1.45 (25H, m) | 0.89 (3H, t, 6.8) |

^a **15, 16** measured in acetone-*d*₆; **17** measured in acetonitrile-*d*₃.^b Coupling constants are given in Hz.

Table 6

¹H-NMR data for [CpRu(CO)₂(η²-CH₂=CHR)]⁺PF₆⁻ ^a

| Compound | Cp | =CH | =CH ₂ (<i>cis</i>) ³ J(HH) ^b | =CH ₂ (<i>trans</i>) ³ J(HH) ^b | =CHCH | -(CH ₂) _x - | -CH ₃ ³ J(HH) ^b |
|-----------|--------------|--------------|---|---|--------------|------------------------------------|--|
| 18 | 6.12 (5H, s) | 5.47 (1H, m) | 4.03 (1H, d, 8.2) | 3.97 (1H, d, 14.0) | | | 1.91 (3H, t, 6.0) |
| 19 | 6.14 (5H, s) | 4.21 (1H, m) | 4.01 (1H, d, 10.4) | 3.95 (1H, d, 14.2) | 2.45 (1H, m) | 1.65 (1H, m) | 1.18 (3H, t, 7.3) |
| 20 | 5.78 (5H, s) | 5.08 (1H, m) | 3.78 (1H, d, 8.3) | 3.69 (1H, d, 14.2) | 2.30 (1H, m) | 1.40 (25H, m) | 0.96 (3H, t, 7.0) |

^a **18**, **19** measured in acetone-*d*₆; **20** measured in acetonitrile-*d*₃.^b Coupling constants are given in Hz.

umn chromatography was carried out on Merck EM Reagent neutral “Alumina oxide 90” activity state I, deactivated by addition of water according to the manufacturer’s label directions and oven dried at 120 °C. The chemical reagents were obtained from the suppliers shown in parentheses: BF₃·Et₂O (Merck), HBF₄·Et₂O (Merck), Ph₃CPF₆ (Aldrich), AgBF₄ (Merck), [CpFe(CO)₂]₂ (Strem), [Cp*Fe(CO)₂]₂ (Strem). The α-olefins were obtained from Aldrich Chemical Co., purity shown in parentheses: 1-hexene (99%), 1-heptene (97%), 1-octene (98%), 1-nonene (98%), 1-decene (94%), and 1-undecene (95%). All other reagents were obtained commercially and used without purification unless otherwise stated.

Compounds of the type [LM(CO)₂(R)] (L = η⁵-C₅H₅, η⁵-C₅(CH₃)₅; R = *n*-C₃H₇ to *n*-C₆H₁₃ and *n*-C₁₃H₂₇ to *n*-C₁₆H₃₃) were prepared according to the literature

methods [15]. The complexes CpFe(CO)₂I [16] and [CpFe(CO)₂(THF)]⁺BF₄⁻ [17] were prepared and purified by published procedures.

Melting points were recorded on a Kofler hot-stage microscope (Riechert Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infra red spectra were recorded on a Perkin–Elmer 983 or a Paragon 1000 FTIR spectrophotometer in solution cells using NaCl windows. ¹H-NMR spectra were recorded on a Varian XR 200 (at 200 MHz) spectrometer or a Varian Unity 400 (at 400 MHz) spectrometer. ¹³C-NMR spectra were recorded on a Varian XR 200 (at 50 MHz) spectrometer or a Varian Unity 400 (at 100 MHz) spectrometer. Low resolution mass spectra were recorded with a VG Micromass 16F spectrometer operating at 70 eV ionizing voltage.

Table 7

¹³C-NMR data for [CpFe(CO)₂(η²-CH₂=CHR)]⁺ ^a

| Compound | CO | Cp | =CH | =CH ₂ | Other ^b |
|-----------|----------------|-------|-------|------------------|---|
| 1 | 211.41; 209.28 | 89.99 | 85.88 | 55.96 | 21.69 (CH ₃) |
| 2 | 211.41; 209.30 | 90.23 | 91.00 | 54.38 | ^c (C ₃); 17.08 (CH ₃) |
| 3 | ^c | 89.34 | 88.21 | 54.31 | 38.24(C ₃); 25.60(C ₄); 12.08 (CH ₃) |
| 4 | ^c | 90.94 | 90.20 | 55.83 | 37.59(C ₃); 36.14(C ₄); 23.46(C ₅); 14.67 (CH ₃) |
| 5 | ^c | 89.31 | 88.54 | 54.19 | 36.29(C ₃); 32.23(C ₄); 31.01(C ₅); 22.10(C ₆); 13.27 (CH ₃) |
| 6 | 212.19; 210.06 | 90.95 | 90.16 | 55.82 | 37.91(C ₃); 34.03(C ₄); 32.89(C ₅); ^c (C ₆); 23.81(C ₇); 14.91 (CH ₃) |
| 7 | 210.67; 208.52 | 89.44 | 88.50 | 54.24 | 36.36(C ₃); 32.56(C ₄); 31.55(C ₅); ^c (C ₆); ^c (C ₇); 22.34(C ₈); 13.42 (CH ₃) |
| 8 | 211.85; 209.15 | 89.95 | 89.79 | 54.93 | 37.19 (C ₃); 33.28(C ₄); 32.63(C ₅); 30.21(C ₆); 29.98(C ₇); 29.98(C ₈); 23.38(C ₉); 14.37 (CH ₃) |
| 9 | 211.17; 209.02 | 89.87 | 89.51 | 54.78 | 37.08 (C ₃); 33.22(C ₄); 32.51(C ₅); 30.09(C ₆); ^d (C ₇); 29.90(C ₈); 29.59(C ₉); 23.30(C ₁₀); 14.29 (CH ₃) |
| 10 | 211.22; 209.09 | 89.94 | 89.55 | 54.85 | 37.15 (C ₃); 33.27(C ₄); 32.61(C ₅); 30.26(C ₆); 30.19(C ₇); 30.01(C ₈); 29.96(C ₉); 29.66(C ₁₀); 23.37(C ₁₁); 14.36 (CH ₃) |
| 11 | 211.20; 209.06 | 89.94 | 89.74 | 54.90 | 37.18 (C ₃); 33.29(C ₄); 32.64(C ₅); 30.32(C ₆); ^d (C ₇); 30.20(C ₈); 30.05(C ₉); 29.98(C ₁₀); 29.68(C ₁₁); 23.39(C ₁₂); 14.29 (CH ₃) |
| 12 | 211.21; 209.06 | 89.91 | 89.57 | 54.84 | 37.15 (C ₃); 33.29(C ₄); 32.62(C ₅); 30.34(C ₆); 30.32(C ₇); 30.29(C ₈); 30.18(C ₉); 30.05(C ₁₀); 29.96(C ₁₁); 29.66(C ₁₂); 23.37(C ₁₃); 14.35 (CH ₃) |
| 13 | ^c | 89.93 | 89.68 | 54.88 | 37.17 (C ₃); 33.29(C ₄); 32.63(C ₅); 30.35(C ₆); 30.30(C ₇); ^d (C ₈); ^d (C ₉); 30.19(C ₁₀); 30.06(C ₁₁); 29.97(C ₁₂); 29.67(C ₁₃); 23.38(C ₁₄); 14.37 (CH ₃) |
| 14 | 211.19; 209.07 | 89.94 | 89.57 | 54.87 | 37.16 (C ₃); 34.44(C ₄); 33.29(C ₅); 32.63(C ₆); 30.35(C ₇); 30.19(C ₈); 30.06(C ₉); ^d (C ₁₀); ^d (C ₁₁); ^d (C ₁₂); 29.83(C ₁₃); 29.68(C ₁₄); 23.37(C ₁₅); 14.38 (CH ₃) |

^a **1–7** measured in acetone-*d*₆; **8–14** measured in acetonitrile-*d*₃.^b C₃ to C_n refer to the C atoms of the alkyl substituent on the alkene.^c Peak not observed.^d Peaks overlap.^e Peak obscured by solvent.

Table 8
 ^{13}C -NMR data for $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ^a

| Compound | CO | $\text{C}_5(\text{CH}_3)_5$ | =CH | =CH ₂ | $\text{C}_5(\text{CH}_3)_5$ | Other ^b |
|-----------|----------------|-----------------------------|--------|------------------|-----------------------------|---|
| 15 | ^c | 103.28 | 101.42 | 60.78 | 9.93 | 22.36 (CH ₃) |
| 16 | 214.20; 213.94 | 103.34 | 89.34 | 59.85 | 9.89 | 39.82(C ₃); 27.28(C ₄); 14.43(CH ₃) |
| 17 | 213.10; 213.40 | 102.52 | 88.93 | 58.88 | 9.41 | 37.05 (C ₃); 33.47(C ₄); 32.56(C ₅); 30.27(C ₆); ^d (C ₇); ^d (C ₈); ^d (C ₉); 30.22(C ₁₀); 30.12(C ₁₁); 29.99(C ₁₂); 29.92(C ₁₃); 29.68(C ₁₄); 23.31(C ₁₅); 14.31 (CH ₃) |

^a **15**, **16** measured in acetone-*d*₆; **17** measured in acetonitrile-*d*₃.

^b C₃ to C_n refer to the C atoms of the alkyl substituent on the alkene.

^c Peak not observed.

^d Peaks overlap.

Table 9
 ^{13}C -NMR data for $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+$ ^a

| Compound | CO | Cp | =CH | =CH ₂ | Other ^b |
|-----------|----------------|-------|-------|------------------|---|
| 18 | 197.35; 196.00 | 92.86 | 83.86 | 53.75 | 23.28 (CH ₃) |
| 19 | 197.47; 195.81 | 92.90 | 87.05 | 52.70 | 40.37(C ₃); 27.34(C ₄); 14.25 (CH ₃) |
| 20 | 196.72; 195.02 | 92.07 | 86.96 | 51.70 | 37.81 (C ₃); 33.54(C ₄); 32.63(C ₅); 30.39(C ₆); 30.37(C ₇); 30.35(C ₈); 30.31(C ₉); ^c (C ₁₀); ^c (C ₁₁); 30.06(C ₁₂); 29.99(C ₁₃); 29.59(C ₁₄); 23.39(C ₁₅); 14.37 (CH ₃) |

^a **18**, **19** measured in acetone-*d*₆; **20** measured in acetonitrile-*d*₃.

^b C₃ to C_n refer to the C atoms of the alkyl substituent on the alkene.

^c Peak obscured by solvent.

Table 10
 Mass spectral data for $[\text{CpM}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHR})]^+\text{X}^-$ (M = Fe, Ru; X = BF₄, PF₆)

| Possible assignments | Relative peak intensities (%) | | |
|----------------------|-------------------------------|-----------|-----------|
| | 4 | 19 | 20 |
| Parent, M | 100 | 100 | 100 |
| M – CO | 11 | 11 | 7 |
| M – 2CO | 5 | 10 | 2 |
| M – olefin | 92 | 51 | 54 |
| M – CO – olefin | 8 | 8 | 0 |
| M – 2CO – olefin | 10 | 7 | 0 |
| M – olefin + H | 15 | 30 | 15 |

4.1. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHCH}_3)]^+\text{PF}_6^-$ (**1**)

A solution of $\text{CpFe}(\text{CO})_2(n\text{-C}_3\text{H}_7)$ (0.19 g, 0.88 mmol) in CH_2Cl_2 (10 ml) was cooled to 0 °C and treated with a solution of Ph_3CPF_6 (0.39 g, 1.00 mmol) in CH_2Cl_2 (5 ml) over 5 min. The solution turned dark green. The solution was allowed to warm to room temperature (r.t.) and the reaction continued for a further 20 min. The solution was concentrated and ether added until precipitation of the salt was complete. The yellow precipitate was collected, washed with ether and recrystallized from acetone/ether to give pale yellow

microcrystals of **1** (0.21 g, 66%). Spectral data and analysis of **1** (and others **2–20**) are reported in Section 2.

4.2. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CHCH}_2\text{CH}_3)]^+\text{PF}_6^-$, **2**

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2(n\text{-C}_4\text{H}_9)$ (0.16 g, 0.69 mmol), Ph_3CPF_6 (0.30 g, 0.77 mmol), and a reaction time of 30 min at r.t. Work-up as described for **1** above gave **2** as pale yellow microcrystals (0.19 g, 72%).

4.3. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2\text{=CH}(\text{CH}_2)_2\text{CH}_3)]^+\text{PF}_6^-$ (**3**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2(n\text{-C}_5\text{H}_{11})$ (0.51 g, 2.05 mmol), Ph_3CPF_6 (0.97 g, 2.05 mmol), and a reaction time of 30 min at r.t. The solution was concentrated and ether added until precipitation of the salt was complete. The yellow precipitate was collected, washed with ether and recrystallized from acetone- CH_2Cl_2 /ether to give pale yellow microcrystals **3** (0.58 g, 72%).

4.4. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3)]^+\text{BF}_4^-$ (**4**)

To a solution of $[\text{CpFe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$ (0.78 g, 2.32 mmol) in CH_2Cl_2 was added 1-hexene (0.85 ml, 6.94 mmol). The reaction was allowed to proceed for 30 min and was then treated with $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.5 ml, 0.05 mmol) and stirred for a further 1 h at r.t. The solution was filtered, the solvent removed under reduced pressure and the residue dissolved in a minimum of CH_2Cl_2 . Addition of ether to the solution gave a yellow precipitate which was recrystallized from CH_2Cl_2 -ether to give fine, yellow microcrystals of **4** (0.60 g, 75%).

4.5. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}_3)]^+\text{BF}_4^-$ (**5**)

A solution of $\text{CpFe}(\text{CO})_2\text{I}$ (0.50 g, 1.64 mmol) in CH_2Cl_2 (10 ml) was treated with AgBF_4 (0.35 g, 1.80 mmol). After 1 h the solution was filtered under N_2 through Celite. To the filtrate was added 1-heptene (0.60 ml, 1.88 mmol) and the solution stirred for 30 min. The solvent was reduced under vacuum and ether added. This solution was cooled overnight at -15°C . The black precipitate that formed was collected, the filtrate concentrated and ether added to give a yellow precipitate. This product was recrystallized from CH_2Cl_2 -ether to yield yellow microcrystals of **5** (0.23 g, 38%). The black precipitate was identified as $[\text{CpFe}(\text{CO})_2\text{I}]^+\text{BF}_4^-$ (0.17 g, 37%) [**5**] m.p. $150\text{--}152^\circ\text{C}$ dec.; IR (CH_2Cl_2) $\nu(\text{CO})$ 2063, 2051, 2015 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 5.38 (10H, s, Cp); $^{13}\text{C}\{\text{H}\}\text{-NMR}$ (CDCl_3) δ (ppm) 85.63 (Cp).

4.6. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_5\text{CH}_3)]^+\text{BF}_4^-$ (**6**)

This was prepared by the method described above for **4** with the following quantities of reagents: $[\text{CpFe}(\text{CO})_2(\text{THF})]^+\text{BF}_4^-$ (0.27 g, 0.81 mmol), $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.1 ml, 0.01 mmol), and a reaction time of 1.5 h at r.t. Work-up as described for **4** above gave **6** as pale yellow microcrystals (0.16 g, 53%).

4.7. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_6\text{CH}_3)]^+\text{BF}_4^-$ (**7**)

This was prepared by the method described above for **5** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2\text{I}$ (0.20 g, 0.64 mmol), 1-nonene (0.33 ml, 1.88 mmol), AgBF_4 (0.16 g, 0.82 mmol) and a reaction time of 1.5 h at r.t. Work-up as described for **5** above gave **7** as pale yellow needle-like crystals (0.12 g, 47%).

4.8. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}_3)]^+\text{BF}_4^-$ (**8**)

This was prepared by the method described above for **5** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2\text{I}$ (0.50 g, 1.64 mmol), 1-decene (0.30 ml, 1.58 mmol), AgBF_4 (0.36 g, 0.82 mmol) and a reaction time of 18 h at r.t. Work-up as described for **5** above gave **7** as pale yellow needle-like crystals (0.19 g, 30%).

4.9. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_8\text{CH}_3)]^+\text{BF}_4^-$ (**9**)

A solution of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_3)_2)]^+\text{BF}_4^-$ (0.25 g, 0.78 mmol) in CH_2Cl_2 (20 ml) was combined with 1-undecene (0.30 ml, 1.46 mmol) and stirred under reflux for 3.5 h. The solution was allowed to cool to r.t. and then filtered. The filtrate was concentrated under reduced pressure and cooled to -20°C . Ether was added to precipitate a waxy yellow-brown solid which was recrystallized from CH_2Cl_2 -ether at 4°C to give fine, yellow microcrystals of **9** (0.17 g, 52%).

4.10. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_9\text{CH}_3)]^+\text{BF}_4^-$ (**10**)

This was prepared by the method described above for **9** with the following quantities of reagents: $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_3)_2)]^+\text{BF}_4^-$ (0.17 g, 0.52 mmol), 1-dodecene (0.21 ml, 0.95 mmol), and a reaction time of 2 h under refluxing conditions. Work-up as described for **9** above gave **10** as pale yellow microcrystals (0.15 g, 65%).

4.11. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{10}\text{CH}_3)]^+\text{PF}_6^-$ (**11**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2(n\text{-C}_{13}\text{H}_{27})$ (0.33 g, 0.92 mmol), Ph_3CPF_6 (0.40 g, 1.02 mmol), and a reaction time of 1 h at r.t. Work-up as described for **1** above gave **11** as yellow microcrystals (0.35 g, 76%).

4.12. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{11}\text{CH}_3)]^+\text{PF}_6^-$ (**12**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2(n\text{-C}_{14}\text{H}_{29})$ (1.22 g, 3.35 mmol), Ph_3CPF_6 (1.33 g, 3.35 mmol), and a reaction time of 20 h at r.t. Work-up as described for **1** above gave **12** as yellow microcrystals (0.73 g, 43%).

4.13. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{12}\text{CH}_3)]^+ \text{PF}_6^-$ (**13**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2(n\text{-C}_{15}\text{H}_{31})$ (0.66 g, 1.71 mmol), Ph_3CPF_6 (0.71 g, 1.83 mmol), and a reaction time of 2 h at r.t. Work-up as described for **1** above gave **13** as yellow microcrystals (0.73 g, 81%).

4.14. Preparation of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{13}\text{CH}_3)]^+ \text{PF}_6^-$ (**14**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpFe}(\text{CO})_2(n\text{-C}_{16}\text{H}_{33})$ (0.50 g, 1.28 mmol), Ph_3CPF_6 (0.60 g, 1.54 mmol), and a reaction time of 2.5 h at r.t. Work-up as described for **1** above gave **14** as yellow microcrystals (0.41 g, 60%).

4.15. Preparation of $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_3)]^+ \text{PF}_6^-$ (**15**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{Cp}^*\text{Fe}(\text{CO})_2(n\text{-C}_3\text{H}_7)$ (0.13 g, 0.43 mmol), Ph_3CPF_6 (0.19 g, 0.51 mmol), and a reaction time of 10 min at r.t. Work-up as described for **1** above gave **15** as yellow microcrystals (0.16 g, 83%).

4.16. Preparation of $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3)]^+ \text{PF}_6^-$ (**16**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{Cp}^*\text{Fe}(\text{CO})_2(n\text{-C}_5\text{H}_{11})$ (0.47 g, 1.48 mmol), Ph_3CPF_6 (0.58 g, 1.50 mmol), and a reaction time of 30 min at r.t. Work-up as described for **1** above gave **16** as yellow microcrystals (0.63 g, 92%).

4.17. Preparation of $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{13}\text{CH}_3)]^+ \text{PF}_6^-$ (**17**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{Cp}^*\text{Fe}(\text{CO})_2(n\text{-C}_{16}\text{H}_{33})$ (0.32 g, 0.68 mmol), Ph_3CPF_6 (0.31 g, 0.80 mmol), and a reaction time of 1.5 h at r.t. Work-up as described for **1** above gave **17** as yellow microcrystals (0.18 g, 44%).

4.18. Preparation of $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_3)]^+ \text{PF}_6^-$ (**18**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpRu}(\text{CO})_2(n\text{-C}_3\text{H}_7)$ (0.13 g, 0.50 mmol), Ph_3CPF_6 (0.21 g, 0.55 mmol), and a reaction time of 2.8 h at r.t. Recrystallization from acetone–ether gave **18** as white microcrystals (0.18 g, 90%).

Table 11

Data for $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{R})]$

| Compound | Yield (%) | M.p. (°C) | IR $\nu(\text{CO})$ (cm^{-1}) ^a | Elemental analysis (%) | |
|-----------|-----------|-----------|---|------------------------|-----------------|
| | | | | C found (calc.) | H found (calc.) |
| 21 | 18 | Oil | 2002, 1942 | 56.5 (56.2) | 6.47 (6.47) |
| 22 | 15 | Oil | 2004, 1945 | | |
| 23 | 23 | Oil | 2004, 1944 | 59.8 (60.0) | 7.41 (7.50) |
| 24 | 7 | Oil | 2002, 1944 | | |

^a A measured in CH_2Cl_2 solution.

Table 12

¹H NMR data for $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{R})]^+$ in CDCl_3 relative to TMS

| Compound | Cp | FeCH ₂ | CH ₂ –CH | OCH | CH(CH ₃) ₂ | –(CH ₂) _x – | –CH ₃ |
|-----------|--------------|-------------------|---------------------|--------------|-----------------------------------|------------------------------------|------------------|
| 21 | 4.75 (5H, s) | 1.41 (2H, m) | 3.41 (1H, m) | 3.64 (1H, m) | 1.17 (3H, d); 1.13 (3H, d) | | 1.14 (3H, d) |
| 22 | 4.76 (5H, s) | 1.47 (2H, m) | 3.18 (1H, m) | 3.63 (1H, m) | 1.14 (3H, d); 1.12 (3H, d) | 1.58 (2H, m) | 0.89 (3H, t) |
| 23 | 4.76 (5H, s) | 1.51 (2H, m) | 3.23 (1H, m) | 3.64 (1H, m) | 1.15 (3H, d); 1.12 (3H, d) | 1.31 (6H, m) | 0.89 (3H, t) |
| 24 | 4.76 (5H, s) | 1.52 (2H, m) | 3.23 (1H, m) | 3.63 (1H, m) | 1.15 (3H, d); 1.12 (3H, d) | 1.25 (24H, bs) | 0.88 (3H, t) |

Table 13
 $^{13}\text{C}\{\text{H}\}$ -NMR data for $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{R})]$ in CDCl_3 relative to TMS

| Compound | CO | Cp | FeCH ₂ | CH ₂ -CH | OCH | CH(CH ₃) ₂ | -(CH ₂) _x - | -CH ₃ |
|-----------|-------|------|-------------------|---------------------|------|-----------------------------------|------------------------------------|------------------|
| 21 | 217.6 | 85.3 | 9.1 | 77.9 | 68.1 | 23.3; 23.5 | | 22.4 |
| 22 | 217.6 | 85.3 | 5.9 | 83.4 | 68.3 | 22.7; 23.1 | 29.1 | 9.9 |
| 23 | 217.6 | 85.3 | 6.5 | 82.3 | 68.2 | 22.8; 23.1 | 36.4; 28.8; 23.0 | 14.2 |
| 24 | 217.6 | 85.3 | 6.5 | 82.3 | 68.2 | 22.8; 23.1 | 25.8–36.7 | 14.1 |

Table 14
 Mass spectral data for $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{R})]$

| Possible assignments | Relative peak intensities (%) | | | |
|--|-------------------------------|---|---|---|
| | 21 R = CH ₃ | 22 R = C ₂ H ₅ | 23 R = <i>n</i> -C ₄ H ₉ | 24 R = <i>n</i> -C ₁₃ H ₂₇ |
| Parent, M | 9 | 5 | 32 | 28 |
| M – CO | 6 | 4 | 8 | 0 |
| M – 2CO | 71 | 19 | 100 | 100 |
| M – 2CO – CH(CH ₃) ₂ | 100 | 6 | 43 | 41 |
| CpFeCH ₂ R | 52 | 100 | 26 | 0 |
| CpFe(CO) ₂ OCH(CH ₃) ₂ | 0 | 19 | 2 | 14 |

4.19. Preparation of $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3)]^+\text{PF}_6^-$ (**19**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpRu}(\text{CO})_2(\text{n-C}_5\text{H}_{11})$ (0.65 g, 2.52 mmol), Ph_3CPF_6 (1.00 g, 2.57 mmol), and a reaction time of 14 h at r.t. Recrystallization from acetone–dichloromethane (1:4, v/v)/ether gave **19** as white microcrystals (0.63 g, 92%).

4.20. Preparation of $[\text{CpRu}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{13}\text{CH}_3)]^+\text{PF}_6^-$ (**20**)

This was prepared by the method described above for **1** with the following quantities of reagents: $\text{CpRu}(\text{CO})_2(\text{n-C}_{16}\text{H}_{33})$ (0.15 g, 0.33 mmol), Ph_3CPF_6 (0.18 g, 0.46 mmol), and a reaction time of 2 h at r.t. Recrystallization from CH_2Cl_2 /ether gave **20** as white microcrystals (0.14 g, 71%).

4.21. Reaction of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_3)]^+\text{PF}_6^-$ with isopropanol, to give **21**

A suspension of **1** (0.10 g, 0.28 mmol) in isopropanol (10 ml) was treated with Na_2CO_3 (0.04 g, 0.34 mmol). The solution was stirred for 2 days at r.t. The reaction was monitored by IR. A colour change from yellow to orange–brown was observed. The solvent was removed under reduced pressure to give a red–brown gum. Sublimation of the residue at 40 °C/0.1 mmHg gave $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{CH}_3)$ (**21**), (0.014 g, 18%) as a bright yellow oil. Spectral data and analysis of **21–24** are reported in Tables 11–14.

4.22. Reaction of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CH}_3)]^+\text{PF}_6^-$ with isopropanol (**22**)

A suspension of **2** (0.38 g, 1.00 mmol) in CH_3CN (10 ml) and isopropanol (10 ml) was treated with Na_2CO_3 (0.12 g, 1.12 mmol). The solution was stirred for 16 h at r.t. and monitored by IR. The solvent was removed under reduced pressure to give a red–brown gum. Sublimation of the residue at 40 °C/0.05 mmHg gave $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}\text{CH}_2\text{CH}_3)$ (**22**), (0.044 g, 15%) as a bright yellow oil.

4.23. Reaction of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3)]^+\text{PF}_6^-$ with isopropanol (**23**)

A suspension of **4** (0.15 g, 0.37 mmol) in CH_3CN (5 ml) and isopropanol (10 ml) was treated with Na_2CO_3 (0.04 g, 0.41 mmol). The solution was stirred for 22 h at r.t. and monitored by IR. The solvent was removed under reduced pressure to give a red–brown gum. Sublimation of the residue at 25 °C/0.05 mmHg gave $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}(\text{CH}_2)_3\text{CH}_3)$ (**23**), (0.027 g, 23%) as a bright yellow oil.

4.24. Reaction of $[\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}(\text{CH}_2)_{12}\text{CH}_3)]^+\text{PF}_6^-$ with isopropanol (**24**)

A suspension of **13** (0.20 g, 0.38 mmol) in CH_2Cl_2 (10 ml) and isopropanol (10 ml) was treated with Na_2CO_3 (0.05 g, 0.50 mmol). The solution was stirred for 18 h at r.t. and monitored by IR. The solvent was removed under reduced pressure to give a orange–red oil. Sublimation of the residue at 30 °C/0.05 mmHg gave

$\text{CpFe(CO)}_2(\eta^1\text{-CH}_2\text{CH}\{\text{OCH}(\text{CH}_3)_2\}(\text{CH}_2)_{12}\text{CH}_3)$, **24**, (0.012 g, 7%) as a bright yellow oil.

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