*Journal of Organometallic Chemistry*, 409 (1991) 263–269
Elsevier Sequoia S.A., Lausanne
JOM 21717

# (Cyclopentadienyl)ruthenium(1 + ) complexes of aromatic diterpenoids

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(Received November 20th, 1990)

**Abstract**

Complexation of the $CpRu^+$ moiety to derivatives of three naturally occurring ring-C aromatic diterpenoids has been achieved in high yields under mild conditions. Assignment of stereochemistry in the resulting epimeric pairs of salts has been made by detailed analyses of their NMR spectra.

## Introduction

The temporary incorporation of organometallic addends to modify the chemistry of naturally occurring chiral molecules is of increasing interest. Work on the $\eta^6$ complexation of an arene ring in such compounds has been concerned mainly with the synthesis of neutral complexes by attachment of a $Cr(CO)_3$ fragment [1–3]. However, cationic complexes are more reactive towards nucleophilic attack [4] and the synthesis of such ($\eta^6$-arene) salts is therefore an attractive target. Both 17$\beta$-estradiol (**1**) and the dehydroabietylamine **2** have been reported [5] to complex to $CpFe^+$, although neither experimental details nor yields were disclosed. More recently [6] the $CpRu^+$ unit [7] has been complexed to estrone methyl ether (**3**). The mild conditions required for this latter complexation suggest that $\eta^6$-coordination to a $CpRu^+$ moiety should be applicable to a wide variety of relatively complicated arene ligands. We describe here attempts at synthesizing $CpFe^+$ complexes, and then successful syntheses of the $CpRu^+$ complexes of the diterpenoid compounds 12-methoxypodocarpa-8,11,13-trien-19-oate (**4**), 13-methoxytotara-8,11,13-triene (**7**), and 18-methoxyabieta-8,11,13-triene (**8**), together with assignment of the stereochemistry within each pair of salts based on NMR spectral analyses.

## Results and discussion

In view of the literature report [5] for 17$\beta$-estradiol and dehydroabietylamine, initial investigations were focussed on ($\eta^6$-arene)iron(1 + ) salts. However, neither **4**, its 12-demethoxy derivative **5**, nor the 12-hydroxy compound **6** complexed to

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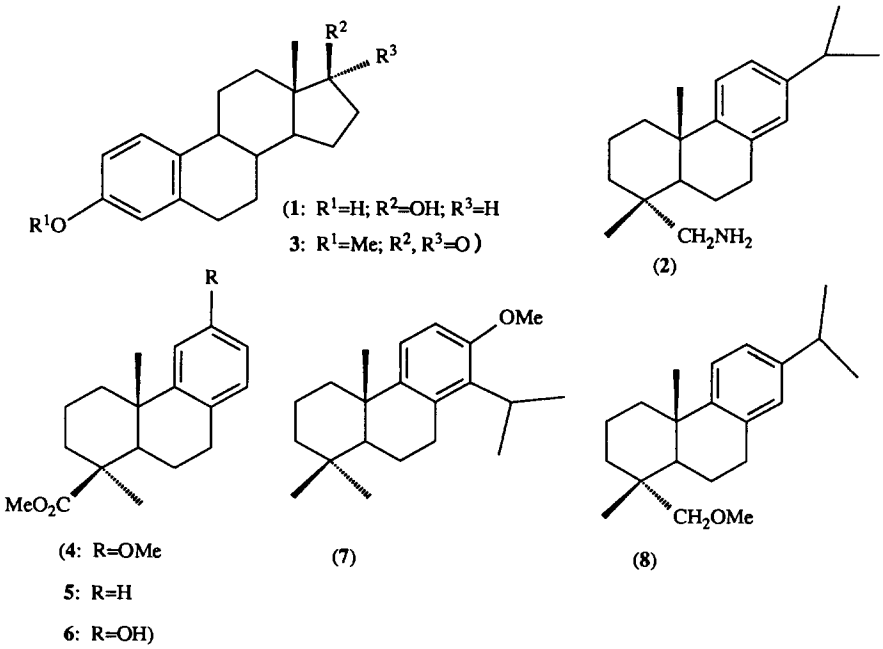



$CpFe^+$ using several variations of the standard Fischer–Hafner conditions [5] involving attempted ligand exchange from ferrocene or the more reactive acetylferrocene in either heptane or decalin. In order to avoid the use of high temperature and a strong Lewis acid, photolytically-induced arene exchange [8–11] from [$\eta^6$-(1,4-dimethylbenzene)]$CpFe^+PF_6^-$ was also attempted. Thus, exposure of a degassed solution of **4** (a more basic arene than *p*-xylene) and the *p*-xylene salt in acetonitrile to bright sunlight resulted in a colour change from yellow to purple (2 min), and then yellow again (10 min). Although the purple colour is characteristic of $(MeCN)_3CpFe^+$ [9] which although relatively unstable is known to be a potent $CpFe^+$ donor, only decomplexation to ferrocene and *p*-xylene occurred, with no evidence ($^1$H NMR) for exchange-complexation of the diterpenoid. We therefore turned our attention to the ($\eta^6$-arene)ruthenium(1 + ) salts.

A solution of methyl 12-methoxypodocarpa-8,11,13-trien-19-oate (**4**) and $[(MeCN)_3CpRu]^+PF_6^-$ in 1,2-dichloroethane was warmed under nitrogen at 35 °C for 17 h [6]. Chromatography of the crude product on alumina afforded ($\eta^5$-2,4-cyclopentadien-1-yl)[methyl (8,9,11,12,13-$\eta$)-12-methoxypodocarpa-8,11,13-trien-19-oate]ruthenium(1 + ) hexafluorophosphate(1 − ) in 55% yield as a mixture (5 : 1) of the $\alpha$- and $\beta$-isomers **9** and **10**. The pure $\alpha$-isomer **9** was separated by fractional crystallization, and the $\beta$-isomer was obtained contaminated with only a trace of the $\alpha$-isomer. The IR spectrum of the mixture showed a distinctive broad P–F band at 835 $cm^{-1}$, and $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR assignments for each diastereomer were made by analogy with those for [(estrone methyl ether)$CpRu]^+PF_6^-$ [6] and the $Cr(CO)_3$ complexes [12] of methyl 12-methoxypodocarpa-8,11,13-trien-19-oate.

Table 1

Shifts observed in the $^1H$ NMR spectra upon complexation of the $CpRu^+$ moiety

| Proton | $\delta/CD_2Cl_2$ [12] | $\Delta\delta$/acetone-$d_6$ | |
|---|---|---|---|
| | (Ligand **4**) | (**9**−**4**) | (**10**−**4**) |
| 1ax | 1.41 | +0.16 | +0.09 |
| 1eq | 2.26 | 0.0 | −0.11 |
| 2ax | 2.03 | −0.04 | −0.09 |
| 2eq | 1.65 | +0.04 | −0.03 |
| 3ax | 1.13 | +0.19 | +0.02 |
| 3eq | 2.29 | +0.07 | −0.08 |
| 5 | 1.57 | +0.18 | −0.03 |
| 6ax | 1.98 | +0.12 | −0.16 |
| 6eq | 2.20 | −0.02 | +0.04 |
| 7ax | 2.76 | +0.13 | +0.14 |
| 7eq | 2.86 | +0.13 | −0.09 |
| 11 | 6.83 | −0.51 | −0.42 |
| 13 | 6.70 | −0.34 | −0.42 |
| 14 | 6.95 | −0.72 | −0.77 |
| 18 | 1.30 | −0.01 | −0.04 |
| 20 | 1.05 | +0.16 | +0.21 |
| $CO_2Me$ | 3.66 | 0.0 | +0.02 |
| OMe | 3.78 | +0.05 | +0.07 |

Table 1 presents the differential shifts of proton signals in the spectra of the respective complexes relative to those of the free diterpenoid ligand **4**. Although the NMR spectra of the salts were determined in acetone-$d_6$ while those of the free ligand were recorded in $CD_2Cl_2$ [12], the comparison is acceptable since the relative chemical shift differences are solvent-independent.

As expected, the signals of the aromatic protons are shifted upfield in the spectra of the complexes relative to those of the free ligand. Complexation of the $\alpha$-face causes a distinct downfield of signals due to H(1ax), H(3ax), and H(5), which all point directly downwards, whereas complexation on the $\beta$-face has an almost negligible effect on these signals. As in the case of the corresponding $Cr(CO)_3$ complexes, a larger downfield shift of the signal due to the axial methyl group $H(20)_3$ on the $\beta$-face is observed, thereby providing further evidence for the stereochemical assignment of the two diastereomers. Differential shifts of carbon signals in the $^{13}C$ NMR spectra of the respective complexes relative to those of **4** are given in Table 2. There is little diagnostic significance between the $\alpha$ and $\beta$ isomers except for the signal due to C(20). This methyl group is in the axial position on the $\beta$-face and hence coordination of the $CpRu^+$ unit on this face causes a characteristic downfield shift, whereas complexation to the $\alpha$-face causes virtually no change in the position of the resonance due to C(20).

Complexation of 13-methoxytotara-8,11,13-triene (**7**) with $[(MeCN)_3CpRu]^+PF_6^-$ gave a mixture (2 : 1) of the $\alpha$ and $\beta$ stereoisomers **11** and **12** of ($\eta^5$-2,4-cyclopentadien-1-yl)[(8,9,11,12,13,14-$\eta$)-13-methoxytotara-8,11,13-triene]ruthenium(1 + ) hexafluorophosphate(1 − ) in 91% yield. The major diastereomer **11** was obtained pure by fractional recrystallization of the mixture from acetone-diethyl ether. Assignment of stereochemistry for the epimeric complexes was made from the relative chemical shifts of the signals due to H(5) in the $^1H$ NMR spectrum, and

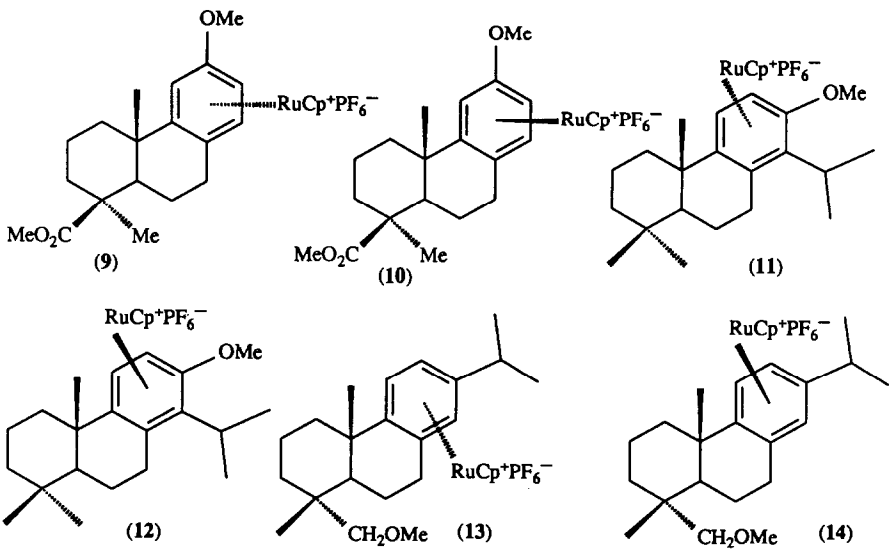
Table 2

Shifts observed in the $^{13}C$ NMR spectrum upon complexation of the $CpRu^+$ moiety

| Carbon | $\delta$/$CDCl_3$ | $\Delta\delta$/acetone-$d_6$ | |
|---|---|---|---|
| | (Ligand **4**) | (**9** − **4**) | (**10** − **4**) |
| 1 | 39.40 | −0.10 | +1.52 |
| 2 | 19.95 | +0.42 | +1.00 |
| 3 | 37.60 | +0.32 | −0.29 |
| 4 | 43.98 | +0.76 | +0.35 |
| 5 | 52.80 | −1.52 | −1.68 |
| 6 | 21.08 | −0.56 | +0.17 |
| 7 | 31.20 | −2.09 | +1.34 |
| 8 | 127.60 | −28.23 | −27.03 |
| 9 | 149.28 | −32.22 | −29.83 |
| 10 | 38.64 | −0.44 | −0.69 |
| 11 | 111.13 | −37.95 | −37.98 |
| 12 | 157.69 | −23.57 | −23.74 |
| 13 | 111.11 | −39.18 | −38.16 |
| 14 | 129.82 | −45.20 | −46.68 |
| 18 | 28.53 | +0.01 | −0.32 |
| 19 | 177.89 | −0.49 | −0.55 |
| 20 | 22.89 | +0.28 | +2.16 |
| $CO_2Me$ | 51.22 | +0.49 | +0.58 |
| OMe | 55.20 | +2.44 | +2.38 |

from those due to C(20) in the $^{13}C$ NMR spectrum. Thus, although the resonance due to H(5) was obscured by the signals due to $(H\text{-}18)_3$, $(H\text{-}19)_3$, and $(H\text{-}20)_3$ in the spectrum of the $\alpha$ isomer, in that of the $\beta$ isomer it was clearly visible further upfield at 1.21 ppm, in a position almost identical to that observed in the spectrum of the free ligand. In the $^{13}C$ NMR spectra, the signal due to C(20) showed a $\Delta\delta$ value of −0.35 ppm for the $\alpha$ isomer, and of +2.56 ppm for the $\beta$ isomer, as expected. A further consequence of complexation of the $CpRu^+$ moiety to **7** is that rotation of the 14-isopropyl group is hindered. In the free ligand the signal due to H(15) is a broadened signal, while the $(H\text{-}16)_3$ and $(H\text{-}17)_3$ signals are coincident. Complexation of the metal moiety hinders the magnetic site exchange and $(H\text{-}16)_3$ and $(H\text{-}17)_3$ then give rise to two doublets ($J$ 7 Hz) separated by 0.24 ppm, while the signal due to H(15) becomes extremely broadened. In the $^{13}C$ NMR spectrum of **7** rotation of the isopropyl group falls into the fast-exchange regime with respect to the NMR (100 MHz) time scale, and a signal corresponding to $\frac{1}{2}(\nu_{16} + \nu_{17})$ is observed at $\delta$ 20.4. However, when the bulky $CpRu^+$ group is introduced the rate of rotation is now in the slow exchange limit for each diastereomer and two signals are observed for C(16) and C(17).

Complexation of 18-methoxyabieta-8,11,13-triene (**8**) gave a mixture (6 : 1) of the $\alpha$ and $\beta$ stereoisomers **13** and **14** of ($\eta^4$-2,4-cyclopentadien-1-yl)[(8,9,11,12,13,14-$\eta$)-18-methoxyabieta-8,11,13-triene]ruthenium(1 + )hexafluorophosphate(1 − ) in 61% yield. In contrast to the isomeric pairs **9**/**10** and **11**/**12** which were obtained as separable white powders, the mixture of **13** and **14** was a yellow oil, from which the individual diastereomeric salts could not be separated. Because of the broadened nature of the signals in the $^1H$ NMR spectrum, assignments of those signals due to ring A and ring B protons were limited, and little comparison could be made




between the $\alpha$ and $\beta$ isomers. However, compelling evidence that the major product was the $\alpha$ diastereomer came from the $^{13}C$ NMR spectrum, since the signal due to C(20) was markedly deshielded for the minor isomer, as would be expected when the metal moiety is complexed to the same face.

## Experimental

For general experimental details see ref. 2. Assignments of NMR signals labelled *, ‡ or § may be interchanged.

*($\eta^5$-2,4-Cyclopentadien-1-yl)[methyl(8,9,11,12,13,14-$\eta$)-12-methoxypodocarpa-8,11,13-trien-19-oate]ruthenium(1 + ) hexafluorophosphates(1 − ) (9 and 10)*

A solution of methyl 12-methoxypodocarpa-8,11,13-trien-19-oate (**4**) (0.22 g, 0.71 mmol) in dry 1,2-dichloroethane (15 mL) was degassed with nitrogen for 10 min, tris(acetonitrile)($\eta^5$-2,4-cyclopentadien-1-yl)ruthenium(1 + ) hexafluorophosphate (1 − ) (0.25 g, 0.58 mmol) was added, and the solution was heated at 35 °C for 17 h. Solvent was removed *in vacuo* and the residue was washed with ether (3 × 10 mL) to give a fawn powder which was chromatographed on alumina (15 g). Elution with distilled acetone gave ($\eta^5$-2,4-cyclopentadien-1-yl)[methyl (8,9,11,12,13,14-$\eta$)-12-methoxypodocarpa-8,11,13-trien-19-oate]ruthenium(1 + ) hexafluorophosphate-(1 − ) (0.30 g, 85%) as a pale yellow powder containing a mixture (5 : 1) of $\alpha$- and $\beta$-stereoisomers **9** and **10**, m.p. 180–183 °C (Found: C, 47.2; H, 5.25. $C_{24}H_{31}F_6O_3PRu$ calcd.: C, 47.0; H, 5.1%). The $\alpha$-isomer **9** was separated by repeated recrystallization of the mixture from acetone–ether, m.p. 250–252 °C (Found: C, 47.0; H, 5.0. $C_{24}H_{31}F_6O_3PRu$ calc.: C, 47.0; H, 5.1%). $\nu_{max}$ (KBr): 1720 (strong, C=O), 835 $cm^{-1}$ (strong, broad, P–F). $\delta_H$ (ppm) ($CD_3COCD_3$): 1.21 (s, $H(20)_3$); 1.29 (s, $H(18)_3$); 1.32 (td, *J* 13.5, 4.1 Hz, H(3ax)); 1.57 (td, *J* 13.2, 4.1 Hz, H(1ax)); 1.69 (dm, *J* 14.2 Hz, H(2eq)); 1.75 (dd, *J* 12.1, 2.8 Hz, H(5)); 1.99 (qt, *J*

14, 3.6 Hz, H(2ax)); 2.1 (ddt, *J* 15, 12.4, 6.4 Hz, H(6ax)); 2.18 (ddt, *J* 15, 7.2, 2.5 Hz, H(6eq)); 2.26 (dm, *J* 13, 4 Hz, H(1eq)); 2.36 (dm, *J* 12.7 Hz, H(3eq)); 2.89 (ddd, *J* 17.4, 12.1, 7.1 Hz, H(7ax)); 2.99 (ddd, *J* 17.4, 6.4, 2.0 Hz, H(7eq)); 3.66 (s, $CH_3O_2C$); 3.83 (s, $OCH_3$); 5.51 (s, $C_5H_5$); 6.23 (d, *J* 6.3 Hz, H(14)); 6.32 (d, *J* 1.6 Hz, H(11)); 6.36 (dd, *J* 6.3, 1.7 Hz, H(13)). $\delta_C$ (ppm) ($CD_3COCD_3$): 20.37 (C(2)*); 20.52 (C(6)*); 23.17 (C(20)); 28.54 (C(18)); 29.11 (C(7)); 37.92 (C(3)); 38.20 (C(10)); 39.30 (C1)); 44.74 (C(4)); 51.28 (C(5)); 51.71 ($CH_3O_2C$); 57.64 ($OCH_3$); 71.93 (C(13)); 73.18 (C(11)); 81.52 ($C_5H_5$); 84.62 (C(14)); 99.37 (C(8)); 117.06 (C(9)); 134.12 (C(12)); 177.40 (C(19)). *β*-isomer **10**: (ppm) $\delta_H$ ($CD_3COCD_3$): 1.15 (td, *J* 13.6, 4.5 Hz, H(3ax)); 1.26 (s, $H(20)_3$ and $H(18)_3$); 1.50 (td, *J* 13,4.1 Hz, H(1ax)); 1.54 (dd, *J* 12, 4 Hz, H(5)); 1.62 (dm, *J* 14 Hz, H(2eq)); 1.82 (qd, *J* 13, 4.5 Hz, H(6ax)); 1.94 (qt, *J* 13.8, 3.9 Hz, H(2ax)); 2.15 (dm, *J* 13 Hz, H(1eq)*); 2.21 (dm, *J* 13 Hz, H(3eq)*); 2.24 (dd, *J* 14, 5 Hz, H(6eq)); 2.77 (ddd, *J* 16.8, 4.5, 1.6 Hz, H(7eq)); 2.90 (ddd, *J* 16.7, 12.2, 5.5 Hz, H(7ax)); 3.68 (s, $CH_3O_2C$); 3.85 (s, $OCH_3$); 5.49 (s, $C_5H_5$); 6.18 (d, *J* 6.3 Hz, H(14)); 6.28 (dd, *J* 6.3, 1.6 Hz, H(13)); 6.41 (d, *J* 1.5 Hz, H(11)). $\delta_C$ (ppm) ($CD_3COCD_3$): 20.95 (C(2)*); 21.25 (C(6)*); 25.23 (C(20)); 28.24 (C(18)); 32.54 (C(7)); 37.31 (C(3)); 37.95 (C(10)); 40.92 (C(1)); 44.33 (C(4)); 51.12 (C(5)); 53.38 ($CH_3O_2C$); 57.58 ($OCH_3$); 72.95 (C(13)$^{\#}$); 73.15 (C(11)$^{\#}$); 81.18 ($C_5H_5$); 83.14 (C(14)); 100.57 (C(8)); 119.45 (C(9)); 133.95 (C(12)); 177.34 (C(19)).

*($\eta^5$-2,4-Cyclopentadien-1-yl)[(8,9,11,12,13,14-η)-13-methoxytotara-8,11,13-triene] ruthenium(1 + ) hexafluorophosphates(1 − ) (**11** and **12**)*

A solution of 13-methoxytotara-8,11,13-triene (**7**) (225 mg, 0.75 mmol) in dry 1,2-dichloroethane (15 mL) was degassed with nitrogen, $(MeCN)_3CpRu^+PF_6^-$ (0.25 g, 0.58 mmol) was added, and the brown solution was stirred at ca. 45 °C under a nitrogen atmosphere for 16 h. After removing the solvent the residue was washed with ether and chromatographed on alumina. Elution with distilled acetone afforded ($\eta^5$-2,4-cyclopentadien-1-yl)[(8,9,11,12,13,14-η)-13-methoxytotara-8,11,13-triene]ruthenium(1 + ) hexafluorophosphate(1 − ) (321 mg, 91%) as an off-white powder containing a mixture (2 : 1) of the *α*- and *β*-stereoisomers **11** and **12**, m.p. 244–246 °C (Found: C, 51.2; H, 5.8. $C_{26}H_{37}F_6OPRu$ calcd.: C, 51.1; H, 6.1%). $\nu_{max}$(KBr): 1258 (sharp, C–O), 830 $cm^{-1}$ (strong, broad, P–F). The *α*-isomer **11** was separated by repeated recrystallizations from acetone–ether, m.p. 289–291 °C (dec.). $\delta_H$ (ppm) ($CD_3COCD_3$): 0.92 (s, $H(19)_3^*$); 0.99 (s, $H(18)_3^*$); 1.31 (d, *J* 7 Hz, H(16)$^{\#}_3$); 1.33 (s, $H(20)_3$); 1.36 (dt, *J* 14, 4 Hz, H(3ax)); 1.40 (m, H(1ax)); 1.45 (d, *J* 7 Hz, H(17)$^{\#}_3$); 1.51 (dm, *J* 14 Hz H(3eq)); 1.64 (dm, *J* 14 Hz, H(2eq)); 1.75 (qt, *J* 14, 3 Hz, H(2ax)); 1.98 (m, H(6eq)); 2.22 (dm, *J* 12 Hz, H(1eq)); 2.83 (brs, H(15)); 3.21 (m, H(7ax)); 3.40 (m, H(7eq)); 3.87 (s, $OCH_3$); 5.45 (s, $C_5H_5$); 6.14 (d, *J* 7 Hz, H(12)$^{\S}$); 6.18 (d, *J* 7 Hz, 1H, H(11)$^{\S}$). $\delta_C$ (ppm) ($CD_3COCD_3$): 19.07 (C(6)*); 19.47 (C(2)*); 19.63 (br, C(16)$^{\#}$); 21.44 (C(19)); 23.41 (br, C(17)$^{\#}$); 24.84 (C(20)); 27.42 (C(7)); 28.40 (C(15)); 33.44 (C(18)); 33.87 (C(4)); 37.53 (C(10)); 39.12 (C(1)); 41.81 (C(3)); 49.03 (C(5)); 57.44 ($OCH_3$); 69.78 (C(12)); 78.98 (C(11)); 81.10 ($C_5H_5$); 101.05 (C(14)$^{\S}$); 101.91 (C(8)$^{\S}$); 115.55 (C(9)); 133.77 (C(13)). *β*-isomer **12**: $\delta_H$ (ppm) ($CD_3COCD_3$): 0.96 (s, $H(18)_3$ and $H(19)_3$); 1.21 (dm, *J* 11 Hz, H(5)); 1.38 (s, $H(20)_3$); 2.11 (dm, *J* 13 Hz, H(1eq)); 2.90 (ddd, *J* 17, 11, 7 Hz, H(7ax)); 3.10 (dd, *J* 17, 5 Hz, H(7eq)); 3.86 (s, $OCH_3$); 5.46 (s, $C_5H_5$); 6.20 (d, *J* 7 Hz, H(12)*); 6.30 (d, *J* 7 Hz, H(11)*). $\delta_C$ (ppm) ($CD_3COCD_3$): 8.88 (C(6)*); 19.63

(br, C(16)[#]); 20.79 (C(2)*); 21.85 (C(19)); 23.41 (br, C(17)[#]); 27.75 (C(20)); 28.06 (C(15)); 31.69 (C(7)); 33.23 (C(18)); 34.02 (C(4)); 37.73 (C(10)); 41.23 (C(1)[§]); 41.28 (C(3)[§]); 51.60 (C(5)); 57.37 ($OCH_3$); 69.00 (C(12)); 80.82 (C(11)); 81.07 ($C_5H_5$); 100.41 (C(14)); 102.00 (C(8)); 120.28 (C(9)); 133.27 (C(13)).

*($\eta^5$-2,4-Cyclopentadien-1-yl)[(8,9,11,12,13,14-$\eta$)-18-methoxyabieta-8,11,13-triene] ruthenium(1 + ) hexafluorophosphates(1 − ) (**13** and **14**)*

18-Methoxyabieta-8,11,13-triene (**8**) (0.225 g, 0.75 mmol) was dissolved in dry 1,2-dichloroethane (15 mL) and nitrogen was passed through the solution for 10 min. The addition of $(MeCN)_3CpRu^+PF_6^-$ (250 mg, 0.58 mmol) gave a dark brown solution which was stirred at 45 °C for 17 h. Removal of the solvent gave a dark brown oil which was washed with ether and chromatographed on alumina using distilled acetone to afford a yellow oil (216 mg, 61%) which was a mixture (6 : 1) of the $\alpha$- and $\beta$-stereoisomers **13** and **14** of ($\eta^5$-2,4-cyclopentadien-1-yl)[(8,9,11,12,13,14-$\eta$)-18-methoxyabieta-8,11,13-triene]ruthenium(1 + ) hexafluorophosphate(1 − ) (Found: C, 52.2; H, 6.5. $C_{26}H_{13}F_6OPRu \cdot 1.2CH_3COCH_3$ calcd.: C, 52.2; H, 6.5%). $\nu_{max}$(film): 1095 (C–O), 830 $cm^{-1}$ (broad, P–F). $\alpha$-isomer **13**: $\delta_H$ (ppm) ($CD_3COCD_3$): 0.88 (s, $H(20)_3$); 1.28 (d, *J* 7.1 Hz, $H(16)_3^*$); 1.30 (d, *J* 7.1 Hz, $H(17)_3^*$); 1.34 (s, $H(19)_3$; 2.18 (dm, *J* 13 Hz, H(1eq)); 2.85 (m, H(15)); 2.85 (d, *J* 9 Hz, $H(18)_A$); 2.93 (dd, *J* 18, 9 Hz, H(7ax)); 3.08 (ddd, *J* 18, 8.9, 2.2 Hz, H(7eq)); 3.31 (d, *J* 9 Hz, $H(18)_B$); 3.34 (s, OMe); 5.43 (s, $C_5H_5$); 6.10 (d, *J* 6.2 Hz, H(12)); 6.24 (d, *J* 6.1 Hz, H(11)); 6.25 (s, H(14)). $\delta_C$ (ppm) ($CD_3COCD_3$): 17.64 (C(19)); 18.17 (C(2)*); 18.61 (C(6)*); 23.10 (C(17)[#]); 23.30 (C(16)[#]); 23.56 (C(20)); 26.87 (C(7)); 32.57 (C(15)); 36.47 (C(10)[§]); 36.20 (C(3)); 37.98 (C(1)); 38.04 (C(4)[§]); 42.49 (C(5)); 59.24 (OMe); 81.40 (C(18)); 81.71 ($C_5H_5$); 81.91 (C(12)); 83.38 (C(11)); 84.91 (C(14)); 101.75 (C(8)); 112.38 (C(13)); 119.51 (C(9)). $\beta$-isomer **14**: (ppm) $\delta_H$ ($CD_3COCD_3$): 0.86 (s, $H(20)_3$); 3.28 (s, OMe); 6.19 (d, *J* 6.4 Hz, H(12)); 6.22 (s, H(14)); 6.30 (d, *J* 6.1 Hz, H(11)). $\delta_C$ (ppm) ($CD_3COCD_3$): 18.35 (C(19)); 18.35 (C(2)*); 20.07 (C(6)*); 23.10 (C(16) or C(17)); 28.64 (C(20)); 32.15 (C(7)); 35.47 (C(3)); 40.30 (C(1)); 81.40 (C(18)); 81.51 ($C_5H_5$); 82.76 (C(12)); 83.22 (C(11)); 83.99 (C(14)).

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