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Organoiron complexes of podocarpic acid derivatives

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Abstract

Treatment of the non-conjugated 1,4-dienes obtained by Birch reduction of podocarpa-8,11,13-trien-19-ol (**2**) and 12,19-dimethoxypodocarpa-8,11,13-triene (**4**) with $Fe_3(CO)_{12}$ leads (albeit in low yields) in each case to a mixture of η^4-1,3-diene iron complexes whose structures have been assigned by NMR spectroscopy. One of these complexes has been successfully converted into a cationic η^5-dienyl iron salt (**35**) by treatment with acid. Attempted complexation of the 1,4-dienol ethers by treatment with a variety of sources of $Fe(CO)_3$ under mild conditions has led to the conclusion that prior conversion of a 1,4-dienol ether into a 1,3-dienol ether is necessary for success. In model studies, treatment of 1-methoxy-3,4-dimethylcyclohexa-1,4-diene (**9**) with $Fe_3(CO)_{12}$ has given η^4-diene and subsequently η^5-dienyl iron complexes.

Introduction

Earlier we reported on the functionalisation of ring C of podocarpic acid (**1**) and its derivatives via organometal complexes, and in particular on nucleophilic additions to diterpenoid (η^6-arene)tricarbonylchromium(0) complexes [1] and the cyclopentaanulation of a diterpenoid chromium carbene complex [2]. Examination of the literature indicates that after Birch reduction podocarpic acid should be amenable to conversion into (η^4-diene)-$Fe(CO)_3$ complexes, and moreover that the derived cationic η^5-dienyl complexes should be readily functionalised by nucleophilic attack with high regioselectivity and stereoselectivity.

Nucleophilic addition to neutral (η^4-diene)tricarbonyliron(0) complexes and to cationic (η^5-dienyl)tricarbonyliron(II) complexes has been studied extensively [3–5], the positive charge on the η^5-dienyl salts making these complexes more reactive to nucleophilic attack than the neutral η^4-diene complexes. Conversion of the η^4-diene complexes into the η^5-salts can be achieved either by allylic hydride abstraction or, in the case of η^4-dienol methyl ether complexes, by acid catalyzed demethoxylation. We now report attempts to activate ring C in dienol ethers derived from **1** via tricarbonyliron complexation.

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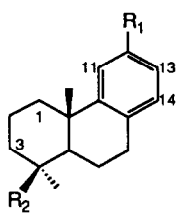
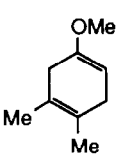
Results and discussion

In order to obtain ^{13}C and ^{1}H NMR data which would assist in the assignment of spectra of the diterpenoid complexes, model studies were carried out on 1-methoxy-4,5-dimethylcyclohexa-1,4-diene (**7**), the Birch reduction product of 1-methoxy-3,4-dimethylbenzene (**8**) [6]. A previous report [3] has shown that treatment of an equilibrium mixture (1 : 4) of the dienes **7** and **9** with $Fe(CO)_5$ in refluxing dibutyl ether gives tricarbonyl[(1,2,3,4-η)-1-methoxy-3,4-dimethylcyclohexa-1,3-diene]iron (0) (**10**) in 64% yield. Repetition of this work in the present study using **7** as the substrate gave a mixture (38%) of complexes consisting mainly (80%) of the η^4-dienol ether **10**. However, complexation of the non-conjugated dienol ether **7** under mild conditions using $Fe_3(CO)_{12}$ [7] in benzene as solvent afforded not only **10** (54%) but also three new complexes **11** (8%), **12** (10%), and **13** (5%) of which the latter two were obtained as a mixture.

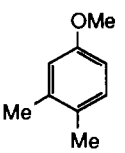
The regiochemistry of the stereoisomeric mixture of **12** and **13** was deduced from the ^{1}H NMR spectral data of the major component. Thus, the chemical shift (3.47 ppm) of the OMe signal indicated that this was a 1-methoxy substituted η^4-dienol ether complex, and the proposed general structure was supported by the presence of signals due to two inner protons (4.86 ppm, d, J 5 Hz, H(3); 5.10 ppm, d, J 5 Hz, H(2)) and the absence of signals due to outer protons [8]. The stereoisomers were



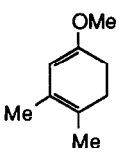
(**1** : R_1 = OH, R_2 = CO_2H
2 : R_1 = H, R_2 = CH_2OH
3 : R_1 = OH, R_2 = CO_2Me
4 : R_1 = OMe, R_2 = CH_2OMe
5 : R_1 = H, R_2 = CH_2OMe
6 : R_1 = OMe, R_2 = CO_2Me)



(**7**)



(**8**)



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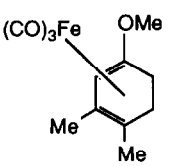
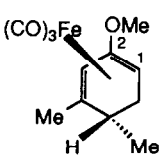
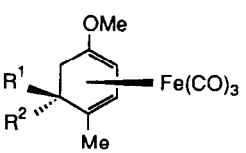


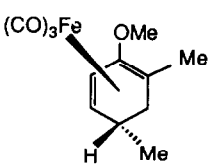
(**10**)



(**11**)



(**12** : R^1 = Me, R^2 = H
13 : R^1 = H, R^2 = Me)



(**14**)

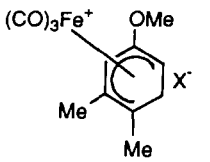
distinguished on the basis of the relative chemical shifts of the 5-CH_3 protons. Examples of closely related compounds in the literature [3,9,10] indicate that the chemical shift of an *endo* methyl group occurs downfield relative to that of an *exo* methyl group, from which the assignment of stereochemistry to the isomers **12** and **13** followed. Notwithstanding the fact that these isomers could not be separated, the ^{1}H- and ^{13}C-NMR spectra for the *exo* isomer **13** were fully assigned while those of the *endo* isomer were partially assigned.

The ratio of these stereoisomers in favour of the 5-*endo* isomer was unexpected, since the 5-*exo* isomer is presumably the thermodynamically more stable complex. However, any discussion of relative proportions of products based on the relative thermodynamic stabilities applies only if each step leading to each of the stereoisomeric tricarbonyliron complexes is reversible. This appears to be unlikely under the conditions of the experiment, since as CO departed from the iron coordination sphere it was deliberately displaced from the reaction medium by a continuous stream of argon. Unless the solvent molecule (benzene in this case) acts as a coordinating ligand to promote displacement of either the η^2-alkene intermediate or η^4-diene product (i.e. a sequence in direct opposition to the usual thermodynamically driven attachment of a diene ligand to form stable $Fe(CO)_3$-η^4-diene complexes) interconversion of the stereoisomeric complexes is unlikely. Although there are many reports [8] of the interconversion (thermally promoted or acid catalysed) of regioisometric tricarbonyl η^4-diene complexes, there does not appear to have been any study of the possibility of the interconversion of the stereoisomeric cyclohexadiene complexes by a sequence involving facial epimerisation by the detachment–reattachment of the metal centre. It would therefore appear that the 5-*endo*/5-*exo* ratio observed for the complexes **12** and **13** represents a kinetically controlled ratio. Birch et al. [11] have shown that polar substituents can result in the formation of *endo* stereoisomers in greater than expected yields (based on steric hindrance considerations) due to electronic interactions between such a substituent and the approaching iron fragment. However, this possibility is clearly not applicable in the case of **12** and **13** as the only polar substituent, the methoxyl group, is located on a planar coordinated double bond and therefore cannot exert a preferential stereocontrolling interaction. On the basis of steric hindrance to approach of the coordinatively unsaturated iron species the *exo* 5-methyl isomer **13** would have been expected to have been formed in greater relative yield, and thus the preponderance of the *endo* isomer **12** remains unexplained.

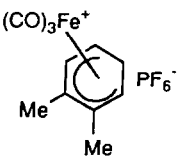
The structure of the tricarbonyl[(1,2,3,4-η)-2-methoxy-4,5-*exo*-dimethylcyclohexa-1,3-diene]iron(0) complex (**11**) was also assigned on the basis of its ^{1}H NMR spectral data. The chemical shift of the OMe group (3.63 ppm) was consistent with that expected for a 2-methoxyl substituted η^4-diene while the presence of signals for both an inner proton (5.07 ppm, d, J 1.7 Hz, H(3)) and an outer proton (3.16 ppm, dxt, J 3.3, 2.4 Hz H(1)) was taken as further evidence for the proposed structure. The stereochemistry was assigned tentatively as *exo* on the basis of the low chemical shift (0.91 ppm, d, J 6.8 Hz) for the 5-CH_3 group which was in agreement with that (0.89 ppm, d, J 6.5 Hz) [6] of the *exo* 5-CH_3 group in the isomeric complex **14**. The ^{13}C NMR data of **11** was assigned by comparison with the chemical shifts of the complex **14** [6].

Hydride abstraction from **10** using $Ph_3C^+PF_6^-$ in refluxing dichloromethane is reported [3] to give a quantitative yield of tricarbonyl[(1,2,3,4,5-η)-2-methoxy-4,5-di-

methylcyclohexadien-1-yl]iron(1 +) hexafluorophosphate(1 −) (**15a**). In the current study treatment of the η^4-dienol ether **10** with $Ph_3C^+BF_4^-$ in dichloromethane at room temperature gave the tetrafluoroborate salt **15b** (39%), while treatment of a mixture (ca. 2 : 1) of **10** and **12** with trifluoroacetic acid at −15 °C for 2 h and then at 2 °C for 11.5 h gave a mixture of **14** and **16**, in 85% yield. The ^{1}H NMR spectrum of the new salt **16** was assigned by the comparison with those of appropriate model compounds while the ^{13}C NMR data was assigned by comparison with the chemical shifts predicted on the basis of the substituent activity effects derived empirically by Birch et al. [12].



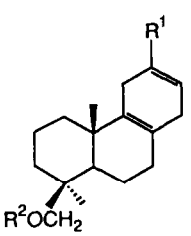
(15a : X = PF_6^-
15b : X = BF_4^-)



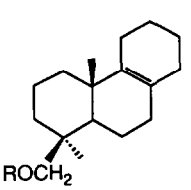
(16)

The aromatic diterpenoid alcohol **2** was synthesised from podocarpic acid (**1**) via methyl podocarpa-8,11,13-trien-19-oate (**3**) [1] by reduction with Redal, while the derived ether **4** was prepared by reduction of methyl 12-methoxypodocarpa-8,11,13-trien-19-oate with Redal and methylation as previously described [13]. Birch reductions of **2** and **4** using the procedure of Spencer et al. [14] gave the dienes **17** and **18** in yields of 70 and 65%, respectively. In addition to the non-conjugated dienes, over-reduction also afforded the mono-enes **20**, **22** (24%) and **21**, **23** (5%) respectively. Decreasing the reaction time did not increase the yields of the desired dienes and a decrease in the amount of mono-enes was offset by a corresponding increase in the amount of unreacted aromatic compound **2** or **4**.

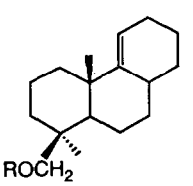
After extensive experimentation, optimum albeit low yielding complexation of the non-conjugated dienol ether **18** was accomplished by refluxing a degassed solution of the diterpenoid derivative with $Fe_3(CO)_{12}$ (1 mol. equiv.) in benzene in an inert atmosphere for 72 h. This procedure yielded a mixture of complexes which were purified by PLC to give **24** (8%), **25** (2%), and the demethoxylated aromatic derivative **5** (23%). Attempts to pre-conjugate the dienol ether **18** by acid catalysis (*p*-TsOH) [3], base catalysis ($NaNH_2$/liq NH_3) [6], or via rhodium complexes



(17 : R^1 = H, R^2 = H
18 : R^1 = OMe, R^2 = Me
19 : R^1 = H, R^2 = Me)

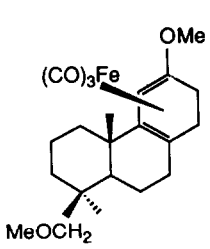


(20 : R = H
21 : R = Me)

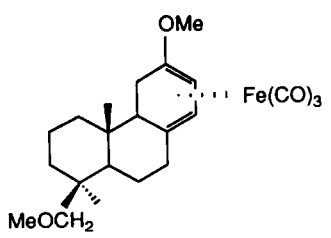


(22 : R = H
23 : R = Me)

$((PPh_3)_3RhCl)$ [15] were unsuccessful, leading to hydrolysis of the enol ether or to aromatization.



(24)



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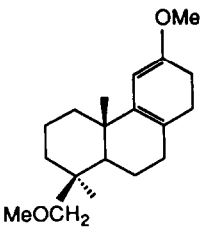
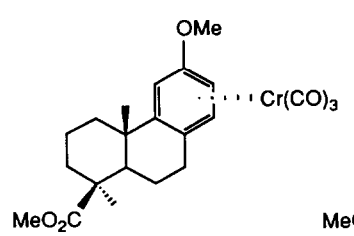


(26)

The structure of the 8,11-diene complex **24** was assigned from the presence of one inner proton H(11) as a singlet at 5.02 ppm in the ^1H NMR spectrum. The stereochemistry was assigned by analogy with the spectra of the monocyclic model complexes **11** and **14** where the chemical shift of a methyl group *endo* to the $Fe(CO)_3$ fragment (0.91 ppm) was further downfield relative to that (0.89 ppm) of the *exo* isomer. In the 8,11-diene complex **24** the chemical shift of $H(20)_3$ was observed at 1.40 ppm. Since the conjugated 8,11-diene ligand **26** was not isolated, the chemical shift of $H(20)_3$ in the uncomplexed diene was unknown. However, it is reasonable to assume that it would have a chemical shift between that of 12,19-dimethoxypodocarpa-8,11,13-triene (**4**) (1.24 ppm) and the non-conjugated 8,12-dienol ether (**18**) (0.99 ppm), and would probably be closer to that of the former since C(8), C(9), C(11) and C(12) are sp^2 hybridised in both **4** and **26** whereas C(11) is sp^3 hybridised in the non-conjugated 8,12-dienol ether **18**. With this assumption, it was concluded that in the 8,11-dienol ether complex **24** the chemical shift of $H(20)_3$ was substantially downfield from the predicted for the free 8,11-dienol ether **26** and was therefore indicative of the β stereoisomer. Further evidence for the greater deshielding of $H(20)_3$ in the β stereoisomer with respect to the free ligand arises from our earlier work [16] wherein both the α (**27**) and the β (**28**) stereoisomers of the tricarbonyl[(8,9,11,12,13,14-η)methyl 12-methoxypodocarpa-8,11,13-trien-19-oate] chromium(0) were characterized fully by ^1H- and ^{13}C-NMR spectra, and by X-ray crystallography. In the ^1H NMR spectrum of the β stereoisomer **28** $H(20)_3$ was deshielded by $\Delta\delta$ 0.21 ppm whereas in the α stereoisomer **27** $\Delta\delta$ was only 0.06 ppm. In the present work the isolation of only the β stereoisomer **24** of the 8,11-dienol ether complex was an unusual result since the α stereoisomer **29** would be expected to be the more stable isomer from thermodynamic considerations, and also to have been favoured kinetically since the axial C(10)-Me group would be expected to exert a significant retarding steric effect on the β face. However, similar observations of the kinetic preference for formation of the β stereoisomer over the α stereoisomer were made earlier [16] for the stereoisomeric η^6-arene complexes **27** and **28** of methyl 12-methoxypodocarpa-8,11,13-trien-19-oate (**6**) where the distribution of the α and β diastereoisomers was found to depend on the reaction time.



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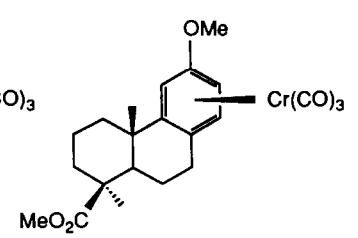

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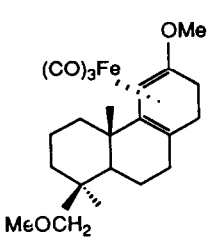
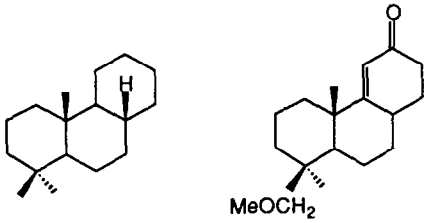


(29)

In the ^{1}H NMR spectrum of the α stereoisomer of tricarbonyl[(12,13,14,8-η)-12,19-dimethoxypodocarpa-12,14-diene]iron(0) (**25**) doublets at 4.96 (J 5 Hz) and 5.15 ppm (J 5 Hz) were indicative of the proposed regioisomer and were assigned to H(14) and H(13), respectively. The chemical shift of $H(20)_3$ at 0.63 ppm [17] (cf. 0.85 for **30** [18]) was taken as further evidence for this structure.



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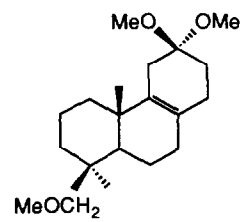
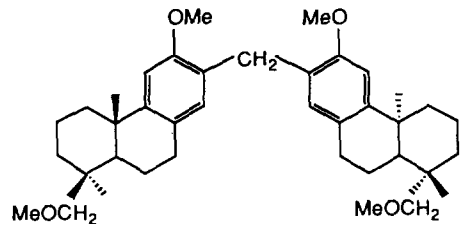
(31)



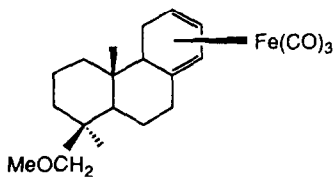
(32)

In an alternative approach the conjugated ketone (**31**), prepared from the crude Birch reduction product of **4** in 58% yield, was converted (71%) into the hemiacetal 12,12,19-trimethoxypodocarp-8-ene (**32**) by treatment with trimethyl orthoformate and oxalic acid in refluxing methanol and 1,2-dichloroethane. Attempts to effect controlled elimination of methanol from (**32**) to form the conjugated dienol ether (**26**) were unsuccessful and thus the trimethoxy derivative (**32**) was treated directly with dodecacarbonyltriiron(0) in refluxing benzene to give the β and α stereoisomers of tricarbonyl[(8,9,11,12-η)-12,19-dimethoxypodocarpa-8,11-diene]iron(0) (**24**) and (**29**) in 6 and 3% yields, respectively. In addition, the methoxylated aromatic derivative (**4**) (15%) and bis-[13,13′(12,19-dimethoxypodocarpa-8,11,13-triene)] methane (**33**) (9%) were formed, together with an unidentified complex (5%) which decomposed rapidly to **4** and **31**.



(33)

Treatment of the non-conjugated diene **19** with $Fe(CO)_5$ (3 mol. equiv.) in refluxing dibutyl ether afforded the ether **34** as the only isolable complex (2%), along with 85% of the fully aromatized diterpenoid **2**. When benzene was used as a solvent the amount of aromatization decreased but no increase in the amount of complexation was observed.



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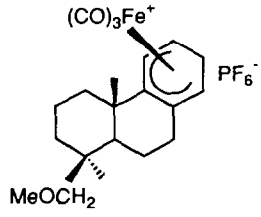

(35)

Treatment of a mixture (6 : 1) of the complexes **24** and **25** with trifluoroacetic acid at −15 °C for 3 h followed by the addition of NH_4PF_6 afforded the β-stereoisomer of tricarbonyl[14,8,9,11,12-η)-19-methoxypodocarpa-14(8),9-dien-12-yl]iron (1 +) hexafluorophosphate(1 −) (**35**) (15%). The structure of **35** was assigned by analogy with that of the monocyclic analogue **16**. The ^1H NMR chemical shift assignments of the ring C protons were supported by decoupling experiments, from which the following conclusions were drawn: (i) The sextet at 2.94 ppm was coupled (*J* 15 Hz) to the doublet at 1.83 ppm, providing a clear indication that the latter signal was due to H(13α) and that the former was due to H(13β). Because the α proton is displaced about the plane of ring C such that its angle relative to H(15) and H(12) is almost 90 °, its coupling to these protons is negligible. (ii) The doublet at 3.86 ppm was coupled (*J* 6 Hz) to the sextet at 2.94 ppm H(13β) and therefore was due to either H(12) or H(14). However, if it were due to H(12) there would have been an additional change elsewhere in the spectrum due to the loss of the significant coupling (*J* 8 Hz) of H(12) with H(11); since this was not observed, the proton at 3.86 ppm was assigned as H(14). (iii) The multiplet at 4.15 ppm was coupled weakly (*J* 1 Hz) to the doublet at 3.86 ppm (H(14)) as well as to the sextet at 2.94 ppm (H(13β)) (*J* 6 Hz) and to the doublet at 5.78 ppm (*J* 8 Hz). Since only H(13)β and H(12) can have three couplings, the signal at 4.15 ppm was assigned as H12. (iv) The doublet at 5.78 ppm was coupled only to the multiplet at 4.15 ppm (H(12)) and was therefore assigned to H(11). The ^{13}C NMR resonances for the ring C carbons were assigned by comparison with those of the monocyclic model η^5-dienyl complex **16**.

Attempted abstraction of hydride from **24** with $Ph_3C^+BF_4^-$ in refluxing dichloromethane gave only unreacted starting material.

The results of this study show that organoiron complexes derived from ring C aromatic diterpenoids can be prepared. However, use of η^5-dienyl complexes as substrates for functionalization of ring C by nucleophilic attack requires a higher yielding route to the salts. This in turn requires that the conjugated ring C diene be available in high yield so that the η^4-complex can be generated under mild conditions.

Experimental

For general experimental details see refs. 1 and 2. Except where indicated, ^1H NMR spectra were run at 400.13 MHz and ^{13}C NMR spectra at 100.62 MHz on a Brüker AM400 instrument operating at 9.2 Tesla.

η^4-(Diene)tricarbonyliron(0) complexation procedures

All complexations were carried out in a 25 mL flame-dried round bottom flask equipped with a single surface reflux condenser and a gas bubbler. Solutions were degassed with dry argon prior to heating, and the reactions were monitored by TLC and IR analysis of aliquots. After the appropriate reflux times the mixtures were filtered through alumina, washed with diethyl ether, and concentrated in vacuo. The crude mixtures were purified further either by PLC or by flash column chromatography on silica gel.

Complexation of 1-methoxy-4,5-dimethylcyclohexa-1,4-diene (7)

1-Methoxy-4,5-dimethylcyclohexa-1,4-diene (**7**) [6] (0.23 g, 1.7 mmol) and dodecacarbonyltriiron (0.85 g, 1.7 mmol) were heated under reflux in benzene (5 mL) for 69 h to give a mixture (0.30 g, 73%) of η^4-tricarbonyliron(0) complexes. The mixture was chromatographed on silica gel using hexanes/ether (17 : 1) as eluent to give (i) tricarbonyl[(1,2,3,4-η)-2-methoxy-4,5-*exo*-dimethylcyclohexa-1,3-diene]iron(0) (**11**) (24 mg, 8% of the mixture). ν_{max} (film) 2050, 1970br cm^{-1} (C≡O). δ(H) (ppm) 0.91, d, *J* 6.8 Hz, *exo* (5-Me); 1.10–1.16, m, *exo* H(6); 1.59, s, (4-Me); 1.99–2.07, m, *endo* H(5); 2.21, dxdxd, *J* 14.4, 10.6, 3.6 Hz, *endo* H(6); 3.16, dxt, *J* 3.3, 2.4 Hz, H(1); 3.63, s, (2-OMe); 5.07, d, *J* 1.7 Hz, H(3). δ(C) (ppm) 22.2, (5-Me); 24.3, (4-Me); 36.1, C(6); 36.5, C(5); 51.3, C(3); 54.2, (2-OMe); 71.0, C(1); 71.3, C(4); 137.0, C(2); 211.9, (CO). *m/z* 278 (3, M^+), 250 (35, M − CO), 222 (5, 250 − CO), 220 (30, 222 − 2H), 192 (100, 220 − CO); (ii) tricarbonyl[(1,2,3,4-η)-1-methoxy-4,5-dimethylcyclohexa-1,3-diene]iron(0) as a mixture (17 : 3) of 5-*exo* and *endo* stereoisomers (17 mg, 6%): 5-*exo* isomer (**13**), ν_{max} (film) 2048, 1953br cm^{-1} (C≡O). δ(H) (ppm) 0.97, d, *J* 6.8 Hz, *exo*(5-Me); 1.52, s, (4-Me); 1.44, dxd, *J* 14.6, 2.3 Hz, *exo* H(6); 2.18–2.27, m, *endo* H(5); 2.71, dxdxd, *J* 14.6, 10.7, 1.1 Hz, *endo* H(6); 3.41, s, (1-OMe); 4.94, d, *J* 4.5 Hz, H(3); 5.20, d, *J* 4.5 Hz, H(2). δ(C) (ppm) 22.4, (5-Me); 24.0, C(5); 36.1, (4-Me); 36.5, C(6); 56.6, (1-OMe); 75.6, 80.0, C(2,3); 76.6, C(4); 112.4, C(1); 213.1, (C≡O). *m/z* 278 (2, M^+), 250 (26, M − CO), 248 (3, 250 − 2H); 222 (8, 250 − CO), 220 (19, 248 − CO), 192 (100, 220 − CO). 5-*endo* isomer (**12**), δ(H) (ppm) 1.02, d, *J* 6.8 Hz, *endo* (5-Me); 1.49, s, (4-Me); 3.47, s, (1-OMe); 4.86, d, *J* 4.6 hz, H(3); 5.10, d, *J* 4.6 Hz, H(2). δ(C) (ppm) 20.5, (5-Me); 24.3, C(5); 31.7, (4-Me); 37.7, C96); 56.8, (1-OMe); 76.5, 79.8, C(2,3); 213.5, (C≡O); (iii) a mixture (80 mg, 27%, ca. 1 : 2) of (**12**) and (**10**); (iv) tricarbonyl[(1,2,3,4-η)-1-methoxy-3,4-dimethylcyclohexa-1,3-diene]iron(0) (**10**) (89 mg, 30%). ν_{max} (film) 2048, 1948br cm^{-1} (C≡O). δ(H) (ppm) 1.55, s, (4-Me); 2.07, s, (3-Me); 1.4–2.3, m, $H(6)_2$, $(5)_2$; 3.41, s, (1-OMe); 5.12, s, H(2). δ(C) (ppm) 18.0, (4-Me); 22.7, (3-Me); 26.0, C(6); 31.0, C(5); 56.7, (1-OMe); 73.7, C(4); 78.1, C(2); 95.3, C(3); 112.2, C(1), 213.0, (C≡O). *m/z* (< 1, M^+), 250 (12, M − CO), 220(9, M − 2CO − 2H), 192 (100, 220 − CO); and (v) a mixture (28 mg, 9%, ca. 3 : 2) of **10** and 3,4-dimethylphenol.

*Tricarbonyl[1,2,3,4,5-η)-2-methoxy-4,5-dimethylcyclohexadien-1-yl]iron(1 +) tetrafluoroborate(1 −) (**15b**)*

A mixture of triphenylmethyl tetrafluoroborate (93 mg, 0.34 mmol) in CH_2Cl_2 (0.5 mL) and the complex (**10**) (60 mg, 0.22 mmol) in CH_2Cl_2 (0.5 mL) was kept at room temperature under argon for 30 min and then diluted with ether and filtered. The residue was washed with ether and dried in vacuo to yield the tetrafluoroborate salt (**15b**) (31 mg, 39%) as a brown solid. ν_{max} (CH_3CN) 2110 (symm. C≡O), 2065 cm^{-1} (asymm. C≡O). δ(H) (ppm) (CD_3CN) (cf. ref. 3) 1.71, s, (5-Me); 2.15, s, (4-Me); 2.31, d, *J* 15.0 Hz, *exo* H(6); 3.00, dxd, *J* 15.0, 6.4 Hz, *endo* H(6); 3.76, s, (2-OMe); 3.89, dxd, *J* 6.3, 1.2 Hz, H(1); 6.83, d, *J* 2.3 Hz, H(3). δ(C) (ppm) (CD_3CN) 18.8, (5-Me); 21.2, (4-Me); 35.8, C(6); 43.2, C(1); 58.0, (2-OMe); 77.0, C(3); 84.2, C(5); 113.4, C(4); 149.2, C(2); 201.1, (C≡O).

*Treatment of the η^4-complexes **10** and **12** with trifluoroacetic acid*

Ice-cold trifluoroacetic acid (0.5 mL) was added to a chilled mixture (ca. 2 : 1) of complexes **10** and **12** (44 mg, 0.16 mmol) under argon and the solution was cooled

to −15 °C and left for 2 h. The temperature was then raised to 2 °C and maintained for 11.5 h, during which time the colour turned from orange brown to deep burgundy. The temperature was lowered to −15 °C, a solution of ammonium hexafluorophosphate (26 mg, 0.16 mmol) in water (1.0 mL) was added, and the mixture was warmed to room temperature (15 °C) and stirred for 15 min. Solvent was removed and the residue was washed with ether and dried by azeotropic distillation with benzene to give a mixture (42 mg) containing (i) tricarbonyl[(1,2,3,4,5-η)-2,3-dimethyl-2,4-cyclohexadien-1-yl]iron(1 +) hexafluorophosphate(1 −) (**16**) (ca. 70%). ν_{max} (CH_3CN) 2105, 2055 cm^{-1} (C≡O). δ(H) (ppm) (CD_3CN) 2.14, s, (2-Me); 2.70, s, (3-Me); 2.82-2.94, m, $H(6)_2$; 3.99, d, *J* 6.0 Hz, H(1); 4.18, br t, *J* 5.2 Hz, H(5); 5.80, d, *J* 5.2 Hz, H(4). δ(C) (ppm) (CD_3CN) 18.0, (3-Me); 19.5, (2-Me); 26.1, C(6); 62.0, C(5); 64.3, C(1); 101.8, C(4); 107.6, C(3), 203.7, (C≡O); C2 was not detected. δ(C) (ppm) (CF_3CO_2D) 18.0, (3-Me); 19.9, (2-Me); 30.8, C(6); 62.2, C(5); 64.4, C(1); 103.0, C(4); 108.3, C(3); 122.0, C(2); and (ii) tricarbonyl[(1,2,3,4,5-η)-2-methoxy-4,5-dimethylcyclohexadien-1-yl]iron(1 +) hexafluorophosphate(1 −) (**15a**). δ(H) (ppm) (CD_3CN) 1.71, s, (5-Me); 2.15, s, (4-Me); 3.75, s, (2-OMe); 3.89, br d, *J* 5.1 Hz, H(1); 6.83, d, *J* 2.1 Hz, H(3). δ(C) (ppm) (CD_3CN) 18.8, (5-Me); 21.2, (4-Me); 35.8, C(6); 43.2, C(1); 58.0, (2-OMe); 77.0, C(3); 84.3, C(5).

*12,19-Dimethoxypodocarpa-8,12-diene (**18**)*

Lithium (21.5 g, 3.12 mol) was added in portions to a stirred solution of 12,19-dimethoxypodocarpa-8,11,13-triene (**4**) (18.66 g, 64.8 mol) in redistilled liquid ammonia (950 mL) and freshly distilled THF (290 mL) over 11 min, and the reaction was then quenched by the addition of ethanol. The ammonia was evaporated overnight and the residue was partitioned between ether and water. The combined organic extracts were washed with water and brine, dried, and concentrated in vacuo to give a white solid (18.67 g). A portion (0.2 g) was purified by PLC (hexanes/ether, 9/1) to give (i) a mixture (58 mg, 29%) (3 : 1) of 19-methoxypodocarp-8-ene (**21**) and 12,19-dimethoxypodocarpa-8,12-diene (**18**) (0.13 g, 65%) which crystallized (hexanes) as needles, m.p. 64–67 °C (Found: C, 78.6; H, 10.3. $C_{19}H_{30}O_2$ calcd.: C, 78.5; H, 10.7%). ν_{max} (KBr) 1463, 1443 (C=C), 1104 cm^{-1} (COC). δ(H)(ppm) 0.93, txd, *J* 13.5, 4.4 Hz, H(3ax); 0.98, s, $H(18)_3$; 0.99, s, $H(20)_3$; 1.13, txd, *J* 12.9, 4.1 Hz, H(1ax); 1.28, dxd, *J* 12.9, 1.8 Hz, H(5); 1.44–1.58, m, 2H; 1.56, qxd, *J* 13.7, 3.2 Hz, H(2ax); 1.73, bd *J* 12.6 Hz, 1H; 1.78–1.83, m, 2H; 1.90–2.00, m, 2H; 2.53–2.72, m, 4H; 3.17, d, *J* 9.0 Hz, H(19); 3.30, s, (19-OMe); 3.48, d, *J* 9.0 Hz, H(19); 3.54, s, (12-OMe); 4.58, m, H(13). δ(C) (ppm) 18.8, C(2); 19.0, C(6); 19.9, C(20); 27.1, 32.3, C(11,14); 27.5, C(18); 31.6, C(7); 36.0, C(1); 37.1, C910); 37.9, C(4); 52.3, C(5); 53.8, (12-OMe); 59.4, (19-OMe); 76.0, C(19); 89.7, C(13); 124.1, C(9); 134.4, C(8); 153.6, C(12). *m/z* 290(50, M^+), 288(20, *M* − 2H), 161(27), 123(100), 122(80).

Hydrolysis of Birch reduction mixture

A solution of the crude Birch reduction product of **4** (18.5 g) in methanol (150 mL) and dilute HCl (26 mL) was heated under reflux for 3 h, poured into water, and extracted into ether. The organic extracts were worked up to yield a brown oil (17.5 g) which was flash chromatographed on silica gel (hexanes/ether, 19/1) to give (i) a mixture (5.27 g, 30% of product mixture) (3 : 1) of 19-methoxypodocarp-8-

ene (**21**) and 19-methoxypodocarp-9(11)-ene (**23**); (ii) a mixture (1.39 g, 8%) (4 : 1 : 2) of the two enes **21** and **23** and a non-conjugated ketone. A portion (0.20 g) was further purified by PLC to yield 19-methoxypodocarpan-12-one (70 mg, 35%) as a clear oil. ν_{max} (film) 1700 (CO), 1100 cm^{-1} (COC). δ(H) (ppm) 0.82, s, $H(18)_3$; 0.84–0.94, m, 3H; 0.89, s, $H(20)_3$; 1.02–1.26, m, 3H; 1.31, dxd, *J* 13.1, 3.8 Hz, 1H; 1.35–1.46, m, 2H; 1.64–1.69,m, 1H; 1.72–1.76, m, 1H; 1.79–1.84, m, 1H; 1.88–1.92, m, 1H; 1.97, t, *J* 13.3 Hz, 1H; 2.21–2.32, m, 3H; 3.10, bd, *J* 9.0 Hz, H(19); 3.24, s, (19-OMe); 3.39, d, *J* 9.0 Hz, H(19). δ(C) (ppm) 14.5, C(20); 18.4, C(2); 21.4, C(6); 27.7, C(18); 34.0, 34.4, C(7,14); 35.3, C(8); 36.1, C(3); 37.0, C(4); 37.7, C(10); 38.6, C(1); 40.9, 41.0, C(11,13); 55.5, C(5); 56.0, C(9); 59.3, (19-OMe); 75.9, C(19); 213.2, C(12). *m/z* 278 (2, M^+), 233 (100, $M - CH_2OMe$); 232(37), 215(35); (iii) a mixture (1.91 g, 11%) (17 : 3) of 19-methoxypodocarp-9(11)-en-12-one (**31**) and 19-methoxypodocarp-8-en-12-one; and (iv) 19-methoxypodocarp-9(11)-en-12-one (**31**) (8.63 g, 49%). A portion of the mixture (0.20 g) was purified by PLC to give (a) 19-methoxypodocarp-8-en-12-one (32 mg) as rods (hexanes/ether), m.p. 104–107 °C (Found: C, 78.2; H, 10.2. $C_{18}H_{28}O_2$ calcd.: C, 78.3; H, 10.2%). ν_{max} (KBr) 1713 (CO), 1104 cm^{-1} (COC). δ(H) (ppm) 0.96, txd, *J* 13.5, 4.4 Hz, H(3ax); 0.96, s, $H(18)_3$; 0.99, s, $H(20)_3$; 1.09, txd, *J* 12.7, 4.3 Hz, H(1ax); 1.28, dxd, *J* 12.9, 1.7 Hz, H(5); 1.43–1.51, m, 2H; 1.53, qxt, *J* 13.4, 2.8 Hz, H(2ax); 1.64–1.68, m, 1H; 1.78–1.85, m, 2H; 2.02–2.04, m, 2H; 2.20–2.48, m, 4H; 2.72, dxd, *J* 20.2, 1.1 Hz, 1H; 2.86, bd, *J* 20.2 Hz, 1H; 3.18, bd, *J* 9.1 Hz, H(19); 3.30, s, (19-OMe); 3.43, d, *J* 9.1 Hz, H(19). δ(C) (ppm) 18.7, C(2); 19.0, C(6); 19.8, C(20); 27.6, C(18); 30.5, C(7); 32.2, C(14); 36.1, C(3); 36.6, C(1); 37.4, C(4), 37.8, C(10); 38.2, 38.5, C(11,13); 52.2, C(5); 59.3, (19-OMe); 76.0, C(19); 127.2, C(9); 135.7, C(8); 212.3, C(12); and (b) 19-methoxypodocarp-9(11)-en-12-one (**31**) (0.15 g), rods (hexane), m.p. 79–82 °C (Found: C, 78.3; H, 10.0. $C_{18}H_{28}O_2$ calcd.: C, 78.3; H, 10.2%). ν_{max} (KBr) 1667 (CO), 1598 (C=C), 1102 cm^{-1} (COC). δ(H) (ppm) 0.96, txd, *J* 13.1, 5.2 Hz, H(3ax); 0.97, s, $H(18)_3$; 1.13, s, $H(20)_3$; 1.12–1.28, m, 2H; 1.39, dxd, *J* 15.0, 5.5 Hz, 1H; 1.43, dxd, *J* 12.4, 4.7 Hz, H(5); 1.54–1.65, m, 3H; 1.67–1.74, m, 1H; 1.79–1.85, m, 2H; 1.98–2.13, m, 2H; 2.25, dxdxd, *J* 16.2, 12.5, 5.0 Hz, 1H; 2.38, dxt, *J* 16.2, 5.0 Hz, 1H; 2.51–2.58, m, 1H; 3.22, d, *J* 9.0 Hz, H(19); 3.32, s, (19-OMe); 3.45, d, *J* 9.0 Hz, H(19); 5.85, d, *J* 1.6 Hz, H(11). δ(C) (ppm) 18.5, C(2); 21.6, C(6); 21.9, C(20); 27.7, C(18); 29.3, C(7); 34.3, C(8); 35.5, C(14); 35.8, C(13); 36.0, C(3); 36.8, C(1); 38.5, C(4); 40.9, C(10); 53.7, C(5); 59.4, (19-OMe); 76.0, C(19); 119.7, C(11); 176.5, C(9); 201.5, C(12). *m/z* 276(15, M^+), 231(100, $M - CH_2OMe$), 213(11, $231 - H_2O$), 167(19), 149(58), 123(74), 110(57), 107(30).

Podocarpa-8,11,13-trien-19-ol (2)

Sodium bis(2-methoxyethoxy)aluminium hydride (2.16 mL, 3.4 molar, 1.84 mmol) was added to a cooled solution of methyl podocarpa-8,11,13-trien-19-oate (**6**) [1] (0.51 g, 1.9 mmol) in toluene (20 mL) and the solution was stirred at room temperature for 3.5 h. A saturated solution of sodium potassium tartrate (5 mL) was added dropwise and the mixture was poured into ice and extracted with ether. The organic extracts were worked up to give podocarpa-8,11,13-trien-19-ol (0.43 g, 94%) as needles (hexanes), m.p. 91–93.5 °C (Found: C, 83.7, H, 10.2. $C_{17}H_{24}O$ calcd.: C, 83.6; H, 9.9%). ν_{max} (KBr) 3360 (OH), 1027 cm^{-1} (CO). δ(H) (ppm) 1.03, txd, *J* 13.4, 4.0 Hz, H(3ax); 1.08, s, $H(18)_3$; 1.20, s, $H(20)_3$; 1.46, txd, *J* 13.0, 4.0 Hz, H(1ax); 1.53, dxd, *J* 12.8, 1.9 Hz, H(5); 1.62–1.82, m, H(2ax, 2eq, 6ax); 1.92, dm, *J*

13.6 Hz, H(3eq); 1.95, bs, (OH), D_2O exchangeable; 2.01, dxdxt, *J* 13.2, 7.1, 1.7 Hz, H(6eq); 2.35, dm, *J* 13.7 Hz, H(1eq); 2.86, dxdxd, *J* 17.3, 11.2, 7.1 Hz, H(7ax); 2.95, dxdxd, *J* 17.3, 6.7, 1.5 Hz, H(7eq); 3.58, d, *J* 10.9 Hz, H(19); 3.90, d, *J* 10.9 Hz, H(19); 7.05, dxd, *J* 7.5, 0.9 Hz, H(14); 7.09, txt, *J* 7.5, 1.4 Hz, H(13); 7.14, txt, *J* 7.5, 0.9 Hz, H(12); 7.28, dxd, *J* 7.5, 1.3 Hz, H(11). δ(C) (ppm) 19.0, C(2); 19.1, C(6); 25.8, C(20); 26.8, C(18); 30.9, C(7); 35.2, C(3); 37.7, C(10); 38.7, C(4); 38.9, C(1); 51.1, C(5); 65.3, C(19); 124.5, C(13); 125.3, C912); 125.7, C(11); 129.0, C(14); 134.8, C(8); 149.7, C(9). *m/z* 244(16, M^+), 229(61, M − Me), 211(51, 229 − H_2O), 131(100).

Podocarpa-8,12-dien-19-ol (17)

Podocarpa-8,11,13-trien-19-ol (**2**) (0.20 g, 0.82 mmol) in THF (5.0 mL), t-BuOH (5.0 mL), and liquid ammonia (20 mL) was reduced with lithium (0.25 g, 36.1 mmol) as for **4**. Work up gave a solid (0.20 g) which was flash chromatographed on silica gel and eluted with hexanes/ether (19/1) to give (i) a mixture (1 : 3 : 9, 24% of product) of podocarp-9(11)-en-19-ol (**22**), podocarp-8-en-19-ol (**20**) and podocarpa-8,12-dien-19-ol. Podocarp-9(11)-en-19-ol (**22**): δ(H) (ppm) 0.94, s, $H(18)_3$; 1.00, s, $H(20)_3$; 3.38, d, *J* 10.9 Hz, H(19); 3.74, d, *J* 10.9 Hz, H(19); 5.29, t, *J* 2.5 Hz, H(11); δ(C) (ppm) 18.7, C(2); 21.1, C(6); 21.9, C(13); 22.1 C(20); 25.9, C(14); 26.8, C(18); 31(8), C(7), 33.4, C(8); 35.5, C(3); 36.6, C(1); 37.5, C(12); 38.9, 39.4, C94,10); 54.6, C(5); 65.2, C(19); 114.5, C(11); 151.1, C(9). Podocarp-8-en-19-ol (**20**): δ(H) (ppm) 0.93, s, $H(18)_3$; 0.99, s, $H(20)_3$; 3.40, d, *J* 10.9 Hz, H(19); 3.73, d, *J* 10.9 Hz, H(19). δ(C) (ppm) 18.7, C(2); 19.1, C(6); 19.8, C(20); 22.9, 23.6, C(12,13); 23.7, C(11); 26.7, C(18); 30.6, C(7); 32.9, C(14); 35.4, C(3); 36.4, C(1); 37.6, 38.6, C(4,10); 52.5, C(5); 65.6, C(19), 125.9, C(8); 138.1, C(9); and podocarpa-8,12-dien-19-ol (70% of product), m.p. (hexanes/ether) 100–102°C (Found: $M^{+\cdot}$ 246.1977. $C_{17}H_{26}O$ calcd.: $M^{+\cdot}$ 246.1984). ν_{max} (KBr) 3360 (OH), 1016 cm^{-1} (CO). δ(H) (ppm) 0.92–0.97, m, H(3ax); 0.97, s, $H(18)_3$; 1.00, s, $H(20)_3$; 1.15 txd, *J* 12.8, 4.2 Hz, H(1ax); 1.25, bs, OH, D_2O exchangeable; 1.37, dxd, *J* 13.0, 1.6 Hz, H(5); 1.43–1.51, m, 2H; 1.57, qxt, *J* 13.6, 3.1 Hz, H(2ax); 1.73–1.83, m, 3H; 1.91, txd, *J* 17.1, 6.3 Hz, 1H; 1.96–2.03, 1H; 2.41–2.63, m, 4H; 3.48, d, *J* 10.9 Hz, H(19) and 3.80, d, *J* 10.9 Hz, H(19); 5.65–5.69, dm, *J* 10.7 Hz and 5.72–5.76, dm, *J* 10.7 Hz, H(12,13). δ(C) (ppm) 18.6, C(2); 18.9, C(6); 20.0, C(20); 24.4, C(11); 26.7, C(18); 32.0, 32.2, C(7,14); 35.2, C(3), 36.7, C(1); 37.2, C(10); 38.6, C(4); 52.2, C(5); 65.4, C(19); 123.7, 124.9, C(12,13); 123.9, C(8); 135.1, C(9). *m/z* 246(46, M^+), 244(2, M − 2H), 231(16, M − Me), 215(49, M − CH_2OH), 213(13), 91(100).

19-Methoxypodocarpa-8,12-diene (19)

A solution of the crude Birch reduction product of podocarpa-8,11,13-trien-19-ol (**2**) (9.73 g, 39.6 mmol) and imidazole (55 mg, 0.81 mmol) in THF (50 mL) was added dropwise to a stirred suspension of pre-washed (hexanes) sodium hydride (5.5 g, 50% w/w dispersion, 114 mmol) in freshly distilled THF (50 mL), and the mixture was heated under reflux for 1 h. Iodomethane (16.3 mL, 260 mmol) was added dropwise to the cooled mixture which was stirred at room temperature for 30 min and then heated under reflux for 3 h. The cooled mixture was treated with methanol and extracted with ether to give an oil (10.81 g) which was flash chromatographed on silica gel (hexanes) to give a solid (9.98 g). A portion was purified by PLC to give (i) a mixture (ca. 5 : 1, 5%) of 19-methoxypodocarp-9(11)-ene

(**23**) and 19-methoxypodocarp-8-ene (**21**) (Found: $M^{+\cdot}$ 262.2275. $C_{18}H_{30}O$ calcd.: $M^{+\cdot}$ 262.2297). 8-Ene (**21**): δ(H) (ppm) 0.94, s, $H(18)_3$; 0.97, s, $H(20)_3$; 1.24, dxd, *J* 12.9, 1.8 Hz, H(5); 3.15, dxd, *J* 9.1, 1.1 Hz, H(19); 3.31 s, (19-OMe); 3.48, d, *J* 9.1 Hz, H(19). δ(C) (ppm) 18.8, C(2); 19.2, C(6); 19.7, C(20); 22.9, 23.6, 23.7, C(11,12,13); 27.5, C(18); 30.6, C(7); 32.9, C(14); 36.1, C(3); 36.4, C(1); 37.6, C(10); 37.9, C(4); 52.7, C(5); 59.4, (19-OMe); 76.0, C(19); 125.9, C(9); 138.1, C(8). *m/z* 262(48, M^+), 247(24, M − Me); 217(100, $M - CH_2OMe$). 9(11)-Ene (**23**): δ(H) (ppm) 0.92, s, $H(18)_3$; 1.01, s, $H(20)_3$; 3.14, dxd, *J* 9.0, 1.2 Hz, H(19); 3.31, s, (19-OMe); 3.49, d, *J* 9.0 Hz, H(19); 5.36, m, H(11). δ(C) (ppm) 18.9, C(2); 21.1, C(6); 21.9, C(20); 22.1, 25.9, C(12,13); 27.6, C(18); 31.8, C(7); 33.4 C(8); 36.3, 36.6, 37.5, C(1,3,14); 38.3, C(10); 39.4, C(4); 54.6, C(5); 59.4, (19-OMe); 75.8, C(19); 114.4, C(11); 151.3, C(9); (ii) 19-methoxypodocarpa-8,12-diene (77%), needles (MeOH), m.p. 51–53°C (Found: C, 83.0; H, 10.7. $C_{18}H_{28}O$ calcd.: C, 83.1; H, 10.8%). ν_{max} (KBr) 1459 (C=C), 1098 cm^{-1} (COC). δ(H) (ppm) 0.94, txd, *J* 12.9, 4.4 Hz, H(3ax); 0.98(2), s, $H(18)_3$; 0.98(5), s, $H(20)_3$; 1.25, txd, *J* 12.9, 1.9 Hz, H(5); 1.45 − 1.56, m 2H; 1.57, qxt, *J* 13.7, 3.3 Hz, H(2ax); 1.74, dm, 2H; 1.91, txd, *J* 17.2, 6.5 Hz, 1H; 1.94–1.98, m 1H; 2.45–2.64, m, 4H; 3.17, dxd, *J* 9.1, 0.8 Hz, H(19); 3.31, s, (19-OMe); 3.49, d, *J* 9.1 Hz, H(19); 5.67, dm, *J* 10.8 Hz and 5.75, dm, *J* 10.8 Hz, H(12,13). δ(C) (ppm) 18.8, C(2); 19.0, C(6); 20.0, C(20); 24.4, C(11); 27.5, C(18); 32.1, 32.3, C(7,14); 36.0, C(3); 36.7, C(1); 37.2, C(10); 37.9, C(4); 52.4, C(5); 59.4, (19-OMe); 75.9, C(19); 123.7, 125.0, C(12,13); 123.9, C(8); 135.2, C(9). *m/z* 260(69, M^+), 245(12, M − Me), 228(18, M − MeOH), 215(64, $M - CH_2OMe$), 145(44), 131(66), 117(58), 105(81), 91(100); and (iii) 19-methoxypodocarpa-8,11,13-triene (**5**) (17%) as rods (MeOH), m.p. 66–69°C (Found: C, 83.7; H, 10.1. $C_{18}H_{26}O$ calcd.: C, 83.8, H, 10.1%). ν_{max} (KBr) 1485, 1465, 1450 (aryl C=C), 1095 cm^{-1} (COC). δ(H) (ppm) 1.01, txd, *J* 14.3, 4.3 Hz, H(3ax); 1.04, s, $H(18)_3$; 1.20, s, $H(20)_3$; 1.42, txd, *J* 13.2, 3.4 Hz, H(1ax); 1.44, dxd, *J* 12.5, 2.0 Hz, H(5); 1.61, dxpentet, *J* 14.1, 3.3 Hz, H(2eq); 1.67–1.78, m. H(2ax, 6ax); 1.88, dm, *J* 13.5 Hz, H(3eq); 1.98, dxdxt, *J* 13.4, 7.3, 1.6 Hz, H(6eq); 2.32, dm, *J* 12.8 Hz, H(1eq); 2.84, dxdxd, *J* 17.5, 11.5, 7.1 Hz, H(7ax); 2.93, dxdxd, *J* 17.5, 6.9, 1.9 Hz, H(7eq); 3.25, dxd, *J* 9.1, 1.1 Hz, H(19; 3.34, s, (19-OMe); 3.55, d, *J* 9.1 Hz, H(19); 7.03, bd, *J* 7.5 Hz, H(14); 7.07, txd, *J* 7.5, 1.4 Hz, H(13); 7.12, txq, *J* 7.4, 0.8 Hz, H(12); 7.26, dxd, *J* 8.2, 1.4 Hz, H(11). δ(C) (ppm) 19.1, C(2), 19.2, C(6); 25.6, C(20); 27.6, C(18); 30.9, C(7); 35.9, C(3); 37.7, C(10); 38.0, C(4); 38.9, C(1); 51.2, C(5); 59.4, (19-OMe); 75.8, C(19); 124.5, C(13); 125.2, C(12); 125.7, C(11); 129.0, C(14); 135.0, C(8); 149.9 C(9). *m/z* 258(37, M^+), 243(37, M − Me), 226(3, M − MeOH), 210(29, 243 − Me − H_2O), 143(18), 131(100).

*Complexation of 12,19-dimethoxypodocarpa-8,12-diene (**18**) with dodecacarbonyltriiron(0)*

A mixture of crude 12,19-dimethoxypodocarpa-8,12-diene (**18**) (0.36 g, containing ca. 0.20 g, 0.68 mmol of **18** and 0.10 g of **4**, and dodecacarbonyltriiron(0) (0.12 g, 0.23 mmol) was heated in refluxing benzene (5 mL) for 71 h. Work up gave an oil (0.31 g), ν_{max} (film) 2042, 1953 cm^{-1} (C≡O), which was separated by PLC to give (i) 19-methoxypodocarpa-8,11,13-triene (**5**) (41 mg, 23% based on starting diene); (ii) a mixture (71 mg, ca. 9 : 3 : 1) of 12,19-dimethoxypodocarpa-8,11,13-triene (**4**), the β stereoisomer of tricarbonyl[(8,9,11,12-η)-12,19-dimethoxypodocarpa-8,11-diene]iron(0) (**24**), and 12,19-dimethoxypodocarpa-8,12-diene (**18**); and (iii) a mix-

ture (23 mg, 7%) containing **24** and the α stereoisomer of tricarbonyl[(12,13,14,8-η)-12,19-dimethoxypodocarpa-12,14-diene]iron(0) (**25**). δ(H) (ppm) 0.63, s, $H(20)_3$; 0.93, s, $H(18)_3$; 3.11, d, J 9 Hz, H(19); 3.28, s, (19-OMe); 3.40, s, (12-OMe); 3.54, d, J 9 Hz, H(19); 4.96, d, J 5 Hz, H(14); 5.15, d, J 5 Hz, H(13). δ(C) (ppm) 14.4, C(20); 18.8, C(2); 25.0, C(6); 27.5, C(11); 27.6, C(18); 36.4, C(3); 37.7, C(4); 39.5, 39.6, C(1,7); 40.7, C(10); 55.6, C(5); 55.7, (12-OMe); 56.8, C(9); 59.4, (19-OMe); 76.0, C(19); 79.0, C(8); 80.5, C(13); 110.3, C(14); 114.1, C(12); 213.4, (C≡O).

12,12,19-Trimethoxypodocarpa-8-ene (32)

A solution of 19-methoxypodocarp-9(11)-en-12-one (**31**) (0.20 g, 0.72 mmol), oxalic acid (0.10 g, 1.13 mmol), and trimethyl orthoformate (2.0 mL, 18.2 mmol) in methanol (2 mL) and 1,2-dichloroethane (2 mL) was heated under reflux for 6 h under argon. The mixture was cooled to room temperature, diluted with ether, and washed with a saturated solution of sodium hydrogencarbonate. The dried organic fractions were concentrated in vacuo to give a residue (0.21 g) which was purified by PLC to give 12,12,19-trimethoxypodocarp-8-ene (0.17 g, 71%) as a crystalline solid, m.p. 84–86 °C (Found: $M^{+\cdot}$ – MeOH, 290.2227. $C_{19}H_{30}O_2$ calcd.: M^+ – MeOH, 290.2246). ν_{max} (KBr) 1108 (COC, aralkyl), 1041 cm^{-1} (COC, dialkyl). δ(H) (ppm) 0.94, txd, J 13.5, 4.4 Hz, H(3ax); 0.96(9), s, $H(18)_3$; 0.97(3), s, $H(20)_3$; 1.08, txd, J 12.8, 1.4 Hz, H(1ax); 1.26, dxd, J 12.8, 1.4 Hz, H(5); 1.40–1.60, m, 4H; 1.70–1.82, m, 3H; 1.85–1.96, m, 5H; 2.07, bd, J 16.9 Hz, 1H; 2.24, bd, J 16.6 Hz, 1H; 3.16, bd, J 9.0 Hz, H(19); 3.19, s, (12-OMe); 3.24, s, (12-OMe); 3.30, s, (19-OMe); 3.47, d, J 9.0 Hz, H(19). δ(C) (ppm) 18.8, C(2); 19.0, C(6); 19.8, C(20); 27.5, C(18); 28.3, 28.8, C(11,13); 32.1, C(7); 32.2, C(14); 36.0, C(3); 36.7, C(1); 37.4, 37.9, C(4,10); 47.7, (ax12-OMe); 47.8, (eq12-OMe); 52.4, C(5); 59.3, (19-OMe); 76.0, C(19); 100.2, C(12); 125.6, C(9); 134.4, C(8). m/z 322(< 1, M^+), 290(100, M – MeOH), 275(23, 290 – OMe), 136(42), 123(61), 121(55).

Complexation of 12,12,19-trimethoxypodocarp-8-ene (32)

Triangulo-di-μ-carbonyltriiron(0) (0.36 g, 0.72 mmol) was added to a solution of 12,12,19-trimethoxypodocarp-8-ene (**32**) prepared as above, and the mixture was heated under reflux for 14 h under argon, filtered through alumina, and concentrated in vacuo to give an oil. Multiple PLC (hexanes, hexanes/ether, 19/1) gave (i) an unidentified complex (17 mg, 5%) δ(H) (ppm) 1.01, s, $H(18)_3$, $H(20)_3$; 3.36, s, (19-OMe); 3.56, s, (12-OMe); 4.97, s, 1H, inner proton, which decomposed rapidly to the triene (**4**) and 19-methoxypodocarpa-9(11)-en-12-one (**31**); (ii) a mixture (42 mg, 18%, 3 : 1) of 12,19-dimethoxypodocarpa-8,11,13-triene (**4**) [13] δ(C) (ppm) 19.1, C(2); 19.3, C(6); 25.6, C(20); 27.6, C(18); 30.1, C(7); 35.9, C(3); 37.9, C(10); 38.0, C(4); 38.9, C(1); 51.3, C(5); 55.2, (12-OMe); 59.4, (19-OMe); 75.8, C(19); 110.2, C(11); 110.8, C(13); 127.2, C(8); 129.7, C(14); 151.1, C(9); 157.6, C(12), and the α stereoisomer of tricarbonyl[(8,9,11,12-η)-12,19-dimethoxypodocarpa-8,11-diene]iron(0) (**29**), ν_{max} (film) 2007, 1947br cm^{-1}, (C≡O). δ(H) (ppm) 0.98, s, $H(18)_3$; 1.25, s, $H(20)_3$; 3.21, d, J 9.1 Hz, H(19); 3.29, s, (19-OMe); 3.36, d, J 9.1 Hz, H(19); 3.46, s, (12-OMe); 5.06, s, H(11). δ(C) (ppm) 19.0, C(2); 20.9, C(6); 24.6, C(13); 25.5, C(20); 27.6, C(18); 33.6, C(7); 36.2, C(3); 36.3, C(10); 38.1, C(4); 38.9, C(1); 43.7, C(14); 54.4, C(5); 56.7, (12-OMe); 59.3, (19-OMe); 74.1, C(11); 76.2, C(8); 76.3, C(19); 111.6, C(9); 115.0, C(12); 213.3, C(≡O); (iii) the β stereoisomer of tricarbonyl[(8,9,11,12-η)-12,19-dimethoxypodocarpa-8,11-diene]iron(0) (**24**)

(18 mg, 6%) (Found: C, 61.0; H, 7.5%; $M^{+\cdot}$ – CO, 402.1498. $C_{21}H_{30}FeO_4$ calcd.: C, 61.4; H, 7.0%; $M^{+\cdot}$ – CO, 402.1493). ν_{max} (film) 2025, 1948br cm^{-1} (C≡O). δ(H) (ppm) 0.97, s, $H(18)_3$; 1.06, txd, *J* 13, 5 Hz, H(3ax); 1.40, s, $H(20)_3$; 1.46, dxdxd, *J* 13, 5, 1.5 Hz, 1H; 1.52, txd, *J* 13, 5.5 Hz, H(1ax); 1.60–1.75, m, 6H; 1.80, dxd, *J* 12.5, 3.5 Hz, H(5); 1.93, dxd, *J* 6, 2 Hz, 1H; 2.01, dm, *J* 12 Hz, 1H; 2.12, dxdxd, *J* 15.5, 13, 6 Hz, 1H; 2.31, bt, *J* 11 Hz, 1H; 3.22, d, *J* 9 Hz, H(19); 3.30, s, (19-OMe); 3.41, d, *J* 9 Hz, H(19); 3.45, s, (12-OMe); 5.02, s, H(11). δ(C) (ppm) 18.7, C(2); 20.1, C(6); 25.2, C(13); 26.9, C(20); 27.9, C(18); 33.3, C(7); 34.9, C(14); 36.0, C(3); 36.2, C(1); 37.0, C(10); 37.8, C(4); 49.8, C(5); 56.7, (12-OMe); 59.3, (19-OMe); 70.8, C(11); 72.9, C(8); 76.0, C(19); 111.5, C(9); 112.9, C(12); 213.6, (C≡O). *m/z* 430(< 1, M^+), 402(28), *M* – CO), 372(97, *M* – 2CO – 2H), 344(100, 372 – CO), 296(35), 288(30), 121(20); and (iv) a mixture (63 mg) which was purified by PLC to give bis-[13,13′(12,19-dimethoxypodocarpa-8,11,13-triene)]methane (**33**) (37 mg, 9%) as a clear oil (Found: $M^{+\cdot}$ 588.4179. $C_{39}H_{56}O_4$ calcd.: $M^{+\cdot}$ 588.4156). ν_{max} (film) 1617, 1500, 1457 (aryl C=C), 1102 cm^{-1} (COC). δ(H) (ppm) 0.98–1.01, m, H(3ax, 3′ax); 1.00, s, $H(18)_3$,$(18')_3$; 1.19, s, $H(20)_3$, $(20')_3$; 1.40, dxd, *J* 12.6, 1.5 Hz, H(5, 5′); 1.43, txd, *J* 13.0, 3.6 Hz, H(1ax, 1′ax); 1.57–1.76, m, H(2ax, 2′ax, 2eq, 2′eq, 6ax, 6′ax); 1.86, bd, *J* 14.1 Hz, H(3eq, 3′eq); 1.91, dxd, *J* 14.4, 8.1 Hz, H(6eq, 6′eq); 2.27, bd, *J* 12.5 Hz, H(1eq, 1′eq); 2.66, dxdxd, *J* 10.8, 7.0, 6.3 Hz, H(7ax, 7′ax); 2.75, dxd, *J* 16.3, 6.5 Hz, H(7eq, 7′eq); 3.21, bd, *J* 9.1 Hz, H(19, 19′); 3.31, s, (19-OMe, 19-OMe′); 3.53, *J* 9.1 Hz, H(19, 19′); 3.77, s, (12-OMe, 12-OMe′); 3.79, s, bridging CH_2; 6.67, 6.72, 2s, H(11, 11′), H(14, 14′). δ(C) (ppm) 19.2, C(2, 2′); 19.4, C(6, 6′); 25.7, C(20, 20′); 27.6, C(18, 18′); 28.6, bridging CH_2; 30.2, C(7, 7′); 35.9, C(3, 3′); 37.8, C(10, 10′); 38.0, C(4, 4′); 39.1, C(1, 1′); 51.4, C(5, 5′); 55.6, C(12-OMe, 12-OMe′); 59.4, (19-OMe, 19-OMe′); 75.9, C(19, 19′); 106.6, C(11, 11′); 126.6, C(13, 13′); 126.7 C(8, 8′); 130.7, C(14, 14′); 148.2, C(9, 9′); 155.7, C(12, 12′). *m/z* 588(100, M^+), 573(10, *M* – Me), 577(18, *M* – OMe), 541(53), 301(35), 241(14), 149(48).

*Complexation of 19-methoxypodocarpa-8,12-diene (**19**) with pentacarbonyliron(0)*

A solution of crude 19-methoxypodocarpa-8,12-diene (**19**) 0.32 g, containing ca. 0.26 g, 1.0 mmol of **19** and 60 mg of **5**) and pentacarbonyliron(0) (0.53 mL, 3.98 mmol) in dibutyl ether (10 mL) was heated under reflux for 29 h. Work up gave a solid which was separated by PLC (hexanes/ether, 100/0, then 97/3) to give (i) a mixture 0.12 g, 3 : 1 : 1) of **5** and two unidentified iron complexes, ν_{max} (film) 2025, 1940–1975 cm^{-1}. *m/z* 400(1, M^+), 372(13, *M* – CO), 342(42, 372 – 2H – CO), 314(59, 342 – CO), 296(17), 281(10), 266(17); (ii) 19-methoxypodocarpa-8,11,13-triene (**5**) (0.17 g); and (iii) a mixture (18 mg, 2 : 3) of **5** and the β stereoisomer of tricarbonyl[(12,13,14,8-η)-19-methoxypodocarpa-12,14-diene]iron(0) (**34**) (2%, based on initial diene) (Found: $M^{+\cdot}$ 372.1382. $C_{20}H_{28}FeO_3$ calcd.: $M^{+\cdot}$ 372.1388). ν_{max} 2040, 1960br cm^{-1} (C≡O). δ(H) (ppm) 0.59, s, $H(20)_3$; 0.93, s, $H(18)_3$; 1.08, dxd, *J* 12.8, 2.5 Hz, 1H; 3.11, dxd, *J* 9.0, 0.8 Hz, H(19), 3.28, s, (19-OMe); 3.35, d, *J* 9.0 Hz, H(19); 5.11, dxdxd, *J* 6.4, 2.5, 0.5 Hz, H(13); 5.24, dxd, *J* 4.2, 1.2 Hz, H(14). δ(C) (ppm) 14.4, C(20); 18.8, C(2); 25.1, C(6); 26.3, C(11); 27.6, C(18); 36.4, C(3); 37.6, C(4); 39.5, 39.8, C91,7); 40.6, C(10); 55.7, C(5); 56.0, 58.9, C(9,12); 59.4, (19-OMe); 76.0, C(19); 80.2 C(13); 82.7, C(8); 87.9, C(14); 213.0, (C≡O). *m/z* 400(1, M^+), 372 (15, *M* – CO), 342(47, 372 – CO – 2H), 314(100, 342 – CO), 266(21), 131(16), 91(24).

*Treatment of the η^4-complexes **24** and **25** with trifluoroacetic acid.*

Cold trifluoroacetic acid (0.16 mL) was added to a chilled mixture (6 : 1, 23 mg, 0.05 mmol) of tricarbonyl[(8,9,11,12-η)-12,19-dimethoxypodocarpa-8,11-diene]iron(0) (**24**) and tricarbonyl[(12,13,14,8-η)12,19-dimethoxypodocarpa-12,14-diene]iron(0) (**25**) under argon at $-15\,^{\circ}$C, and left for 3 h. A solution of ammonium hexafluorophosphate (8.7 g, 0.05 mmol) in water (0.4 mL) was added dropwise and the mixture was stirred at $-15\,^{\circ}$C for 15 min and then at room temperature for 15 min. The solvent was removed and the residue was washed with ether. A solution of the solid in acetonitrile was evaporated in vacuo to give the β stereoisomer of tricarbonyl[(14,8,9,11,12-η)-19-methoxypodocarpa-14, (8) 9-dien-12-yl]iron(1 +) hexafluorophosphate(1 −) (**35**) (42 mg, 15%). ν_{max} (MeCN) 2072, 2143 cm^{-1} (C≡O). δ(H) (ppm) 1.04, s, $H(18)_3$; 1.22, txd, *J* 12.9, 3.8 Hz, H(3ax); 1.51, txd, *J* 12.8, 3.6 Hz, H(1ax); 1.66, s, $H(20)_3$; 1.83, d, *J* 15.5 Hz, *exo* H(13α); 2.37, bd, *J* 12.2 Hz, 1H; 2.79, dxd, *J* 18.0, 7.6 Hz, H(7β); 2.94, dxdxd, *J* 15.3, 6.0, 6.0 Hz, *endo* H(13β); 3.32, s, (19-OMe); 3.39, d, *J* 9.1 Hz, H(19); 3.55, d, *J* 9.1 Hz, H(19); 3.86, bd, *J* 5.8 Hz, H(14); 4.15, m, H(12); 5.78, d, *J* 7.5 Hz, H(11). δ(C) (ppm) 18.4, C(2); 19.3 C(6); 25.2, C(20); 25.8, 26.8, C(7,13); 28.0, C(18); 36.6, C(3); 38.4, C(10); 38.6, C(1); 39.1, C(4); 52.1, C(5); 59.1, C(12); 59.6, (19-OMe); 64.4, C(14); 76.1, C(19); 95.0, C(11); 120.7, 124.5, C(8,9). *m/z* (FAB) 441(8, $M^+ + H$), 357(24, $M + H - 3CO$), 111(100).

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