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# Chemistry of the podocarpaceae

# LXXI *. Preparation, structure, and reactions of some (arene)tricarbonylchromium(0) complexes. Crystal structure of α-tricarbonyl[(8,9,11,12,13,14-η)-methyl podocarpa-8,11,13-trien-19-oate]chromium(0)

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## Abstract

Tricarbonyl[(8,9,11,12,13,14-η)methyl podocarpa-8,11,13-trien-19-oate]chromium(0) (**7**), tricarbonyl[(4a,5,6,7,8,8a-η)-1,2,3,4-tetrahydronaphthalene]chromium(0) (**11**) and (benzene)tricarbonylchromium(0) (**10**) were prepared and examined. Complex **7** was obtained as a mixture of diastereomers, an X-ray structural determination showing that the α-isomer possesses a near eclipsed conformation, in agreement with the conformation in solution deduced from 400 MHz $^1$H NMR analysis.

Carbanions derived from 1,3-dithiane, 2-methyl-1,3-dithiane and 2-(2,2-dimethoxyethyl)-1,3-dithiane (**24**), and the dianion derived from 2,2′-methylenebis-1,3-dithiane (**27**) were prepared and brought into reaction with the complexes. Compounds **23** and **33** resulted from regioselective attack on **7** at the site predicted. Treatment with methyl electrophiles of the dithianyl $\eta^5$-intermediate leading to **22** did not give products of acetyl incorporation.

Arene lithiation-electrophilic quenching of **7** gave a mixture of compound **6** and its C(14) regioisomer along with the novel ketone **39** and its C(14) regioisomer.

## Introduction

Earlier we prepared a pentacarbonylcarbenechromium complex of the diterpenoid methyl 12-methoxypodocarpa-8,11,13-trien-19-oate (**1**) and investigated

* For part LXX see ref. 1.

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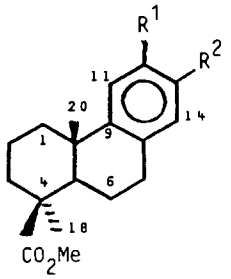
its reactions with some alkynes as a possible route to ring-C aromatic steroidal derivatives [1]. With the same aim we have now made the diastereomeric tricarbonylchromium(0) complexes (**7**) of methyl podocarpa-8,11,13-trien-19-oate (**2**) and investigated their structures and reactivity towards 2-lithio-1,3-dithianes.

## Results and discussion

Methyl podocarpa-8,11,13-trien-19-oate (**2**), prepared via a modification of the reported [2] hydrogenolysis of the tetrazolyl ether **8**, was converted into a mixture (7/3) of the $\alpha$- and $\beta$-diastereomers of the tricarbonylchromium(0) complex **7** by three procedures, viz. (i) by use of a Strohmeier apparatus [3,4], (ii) better, (with 90% yields) by Mahaffy and Pauson's method of 'THF-catalyzed' complexation [5], and (iii), (with very low yield (2%)) by Kündig's arene exchange method involving ($\eta^6$-naphthalene)tricarbonylchromium(0) (**9**) [6]. Also prepared as model compounds by Mahaffy and Pauson's method were (benzene)tricarbonylchromium(0) (**10**) and tricarbonyl[(4a,5,6,7,8,8a-$\eta$)-1,2,3,4-tetrahydronaphthalene]chromium(0) (**11**) [7,8].

The 400 MHz $^1$H NMR spectrum of the diterpenoid ligand **2** was examined to allow assignment of chemical shifts of individual aryl protons for comparison with the corresponding chemical shifts in the complexes **7**. The data enabled determination of the conformation of the tricarbonylchromium(0) moiety in solution thereby allowing prediction of the site of attack by a nucleophile. The aromatic region of the




(**1**: $R^1$ = OMe, $R^2$ = H

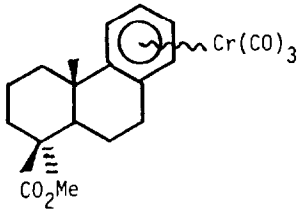
**2**: $R^1$ = $R^2$ = H

**3**: $R^1$ = H, $R^2$ = COMe

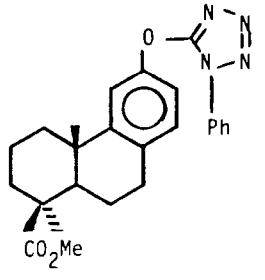
**4**: $R^1$ = H, $R^2$ = $CMe_3$

**5**: $R^1$ = H, $R^2$ = I

**6**: $R^1$ = H, $R^2$ = Me)




(**7**)

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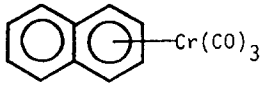


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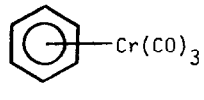


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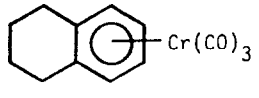


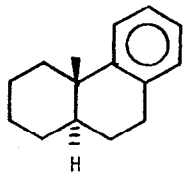

(**11**)

spectrum exhibited four distinct sets of signals, as expected for an *ortho*-disubstituted arene. Double irradiation experiments on these signals, and comparison of the extracted long-range benzylic coupling constants with those reported for toluene and substituted toluenes [9], indicated the following assignments; 7.27 (H(11)), 7.13 (H(12)), 7.08 (H(13)), and 7.04 ppm (H(14)). In order to confirm these assignments it was necessary to assign unequivocally the resonances due to the benzylic (H(7)) protons, and therefore also the resonances due to the H(6) protons. In turn, it was necessary to determine the conformation of ring B, which could exist either as a half-chair or as a half-boat. The signal for the C(10) methyl protons in **2** (1.04 ppm) is slightly upfield (−0.03 ppm) from that in the model hydrocarbon **12**, but considerably upfield (ca. −0.16 ppm) from that in a series of 4,4-disubstituted compounds for which a ring B half-boat conformation has been deduced [10]. This small shielding effect in **2** indicates that ring B has a half-chair conformation, since only then is the C(10) methyl group positioned as far above the aromatic ring as is possible within the constraints of the tricyclic system. Double irradiation experiments, coupling patterns, and the relationship of coupling constants to vicinal dihedral angles defined by the half-chair conformation of ring B allowed the following assignments; 2.18 (H(6$\alpha$)), 2.81 (H(7$\alpha$)), 2.91 (H(7$\beta$)), while H(6$\beta$) was part of the two-proton multiplet between 1.90–2.08 ppm. The relative magnitudes of the couplings between the various H(6) and H(7) protons were consistent with literature values [11]. Moreover, the relative chemical shifts are also consistent with the above assignments. Thus, in a ring B half-chair conformation the equatorial proton H(7$\beta$) is close to the plane of the aromatic ring while H(7$\alpha$) is nearly at 90° to the plane. Consequently, H(7$\beta$) is deshielded relative to H(7$\alpha$), and H(6$\alpha$) is deshielded relative to H(6$\beta$). Finally, double irradiation experiments involving the signals due to the benzylic protons and those due to the individual aromatic protons confirmed the assignments of the latter.

In the 100 MHz $^{13}$C NMR spectrum of **2**, non-aromatic resonances were assigned by comparison with those for the 12-methoxy analogue and other diterpenoids [12], and the aromatic signals were assigned by comparison with those for 1,4-dimethyl-1,2,3,4-tetrahydronaphthalene (**13**) [13].

An X-ray structure of the $\alpha$-diastereomer of the tricarbonylchromium(0) complex of **2** (see later) showed ring B to have a half-chair conformation in the solid state. The 400 MHz $^1$H NMR spectrum of this stereoisomer showed that coupling of H(6$\alpha$) to H(7$\alpha$) was comparable in both the free diterpenoid and its tricarbonylchromium(0) complex, and that there was no coupling between equatorial protons H(6$\alpha$) and H(7$\beta$) in either case, indicating that ring B in the $\alpha$-isomer of **7** was also a half-chair in solution. This was supported by the chemical shift (1.06 ppm) of the C(10) methyl proton signal in the spectrum of the $\alpha$-diastereomer of **7**. In contrast, the C(10) methyl proton signal of the $\beta$-diastereomer of **7** occurred at 1.14 ppm indicating [10] that this isomer may have a half-boat ring B conformation, although this case is more complicated because the C(10) methyl group is *cis* to the tricarbonylchromium(0) moiety and other effects may dominate.

Comparison of the aromatic proton chemical shifts of a complexed arene with those of the free ligand can be used to determine the preferred conformation of an ($\eta^6$-arene)tricarbonylchromium(0) complex in solution. Provided that protons eclipsed by CO ligands are deshielded relative to staggered protons [14], and that substituent effects do not vary between the free ligand and its complex [15], the



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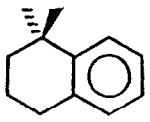

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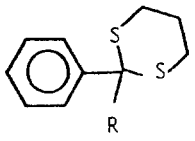
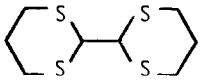


(14: R = H
15: R = Me)



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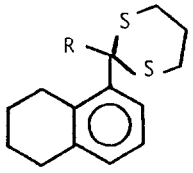
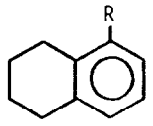


(17: R = H
18: R = Me)



(19: R = CHO
20: R = COMe
21: R = $CH_2CN$)

chemical shift difference ($\sigma\delta(H_x)$) of a proton ($x$) before and after complexation may be defined by relating the observed chemical shifts to those of benzene and its tricarbonylchromium(0) complex, i.e.

$$\sigma\delta(H_x) = \Delta\delta_x(\text{complex}) - \Delta\delta_x(\text{arene})$$

where $\Delta\delta(\text{arene}) = \delta(\text{arene}) - 7.35$ *

$\Delta\delta(\text{complex}) = \delta(\text{complex}) - 5.33$ **

The 400 MHz $^1$H NMR spectrum of the mixture of diastereomers of **7** indicated that the $\alpha$- and $\beta$-isomers were formed in a ratio of ca. 7/3. The aryl region of the spectrum of each isomer exhibited two doublets and two triplets. The doublets were readily assigned by comparison with those of the spectrum of **2**, but a conformational analysis of the $Cr(CO)_3$ tripod based on two possible assignments was necessary for unambiguous assignments of the triplets. Results for the $\alpha$-complex are given in Table 1. If the triplets due to H(12) and H(13) are assumed to maintain the same relative order of chemical shifts as in the uncomplexed diterpenoid (case 1), then H(11) and H(12) undergo downfield shifts relative to H(13) and H(14). This implies a tripod conformation where H(11) and H(12) are eclipsed while H(13) and H(14) are staggered, leading to an impossible structure. Alternatively, if the triplets due to H(12) and H(13) have reserved their chemical shifts relative to **2** (case 2), then H(11) and H(13) exhibit a substantial downfield shift relative to H(12) and H(14), implying a conformer in which H(11) and H(13) are eclipsed, a result in accord with the conformation in the solid state. Similar analysis of the $\beta$-complex indicated that it also possessed a structure in which H(11) and H(13) are eclipsed.

* Chemical shifts of free benzene (ppm) ($CDCl_3$).

** Chemical shift of (benzene)tricarbonylchromium(0) ($CDCl_3$).

Table 1

$^1$H NMR analysis of aryl protons in α-isomer of **7**

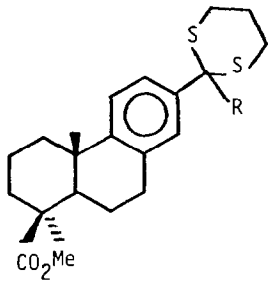
| Proton | Free ligand | | Complex (case 1) | | | Complex (case 2) | | |
|---|---|---|---|---|---|---|---|---|
| | δ | Δδ [a] | δ | Δδ [b] | σΔ | δ | Δδ [b] | Δδ |
| H(11) | 7.27 | −0.08 | 5.53 | +0.12 | +0.20 | 5.53 | +0.20 | +0.28 |
| H(12) | 7.13 | −0.22 | 5.51 | +0.04 | +0.32 | 5.00 | −0.33 | −0.11 |
| H(13) | 7.08 | −0.27 | 5.00 | −0.06 | −0.14 | 5.51 | +0.18 | +0.45 |
| H(14) | 7.04 | −0.31 | 5.05 | −0.03 | −0.05 | 5.05 | −0.28 | +0.03 |

[a] δ(benzene) 7.35 ppm. [b] δ((benzene)Cr(CO)$_3$) 5.33 ppm.

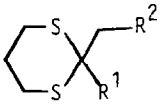
Consequently, for both diastereomers of **7**, C(11) and C(13) would be expected to bear a greater degree of positive charge than C(12) and C(14), and this would lead to the expectation of preferential kinetic attack by nucleophiles at C(11) and C(13). However, since C(11) is *ortho* to a bulky tertiary alkyl substituent, C(13) will be much less sterically hindered, and thus would be the favoured position for nucleophilic attack.

In order to ascertain the optimum conditions for the nucleophilic addition-electrophilic trapping reactions which were envisaged as leading eventually to the formation of steroidal derivatives, an investigation into the reactivity of **7** towards addition–oxidation of some dithiane anions was undertaken. Attack of these anions was expected to be irreversible [16]. Reactions with lithiodithianes gave rise to a range of colours, depending on the temperature and the time from when HMPT was added, changing from yellow through orange to brown. A maximum yield of aromatic product was obtained when the reaction was quenched with iodine at the point at which the mixture began to develop a faint orange tinge (cf. [17]). Compounds prepared in this manner by reaction of 2-lithio-1,3-dithiane [17] with complex **10** were 2-phenyl-1,3-dithiane (**14**) (60%) [18], and two reactions with complex **11** gave the adduct **17** and the derived aldehyde **19**, together with the 2,2′-bi-1,3-dithiane (**16**). Compound **16** was probably formed by initial reaction of 2-lithio-1,3-dithiane with iodine used in the quenching step to give 2-iodo-1,3-dithiane, which then reacted, probably via 2-methylene-1,3-dithiane, with another molecule of 2-lithio-1,3-dithiane. However, no addition–oxidation products were formed in reactions of either 2-lithio-1,3-dithiane or 2-lithio-1,3-dithiane-1-oxide [19] with complexes **7**.

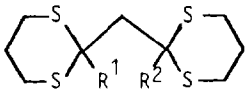
Compounds prepared from 2-lithio-2-methyl-1,3-dithiane were 2-methyl-2-phenyl-1,3-dithiane (**15**), 5-(2′-methyl-1′,3′-dithianyl)-1,2,3,4-tetrahydronaphthalene (**18**), and a mixture (2/1) of the dithianyl adducts **22** and its C(14) isomer derived from **7**. Unexpected products from the latter two reactions were identified as 5-acetyltetralin (**20**), and a mixture (2/1) of the known [20] methyl 13-acetylpodocarpa-8,11,13-trien-19-oate (**3**) and its 14-isomer, respectively. The $^1$H NMR spectrum of **20** was distinctly different from that of a sample of the 6-isomer, which was prepared by Friedel–Crafts acetylation of tetralin [21]. Compounds **20** and **3** were probably formed by dithiane cleavage by iodine acting as an electrophile during work up (cf. [22]). Thus, while the reaction of 2-lithio-2-methyl-1,3-dithiane with the tetralin complex **18** was highly regioselective, only moderate regioselection resulted from the diterpenoid complex although the C(13) substituted product predominated as anticipated.



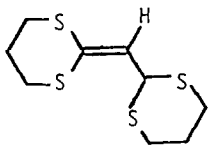
(**22**: R = Me
**23**: R = $CH_2CH(OMe)_2$)



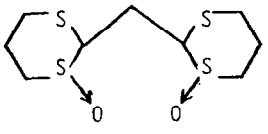
(**24**: $R^1$ = H, $R^2$ = $CH(OMe)_2$
**25**: $R^1$ = H, $R^2$ = CHO
**26**: $R^1$ = Ph, $R^2$ = $CH(OMe)_2$)



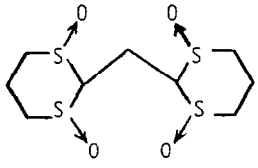
(**27**: $R^1$ = $R^2$ = H
**28**: $R^1$ = $R^2$ = $SiMe_3$
**29**: $R^1$ = Ph, $R^2$ = H)



(**30**)



(**31**)



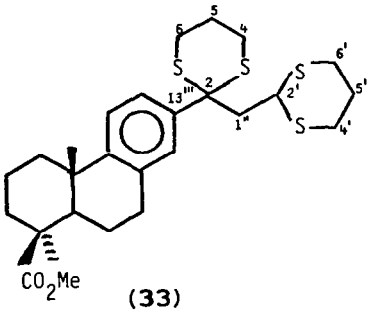
(**32**)

Some work was directed towards the preparation of a three-carbon dithiane, viz. 2-(2,2-dimethoxyethyl)-1,3-dithiane (**24**), since addition–oxidation of the derived anion to the complex **7** would be expected to yield an aromatic product susceptible to acid-catalysed ring closure. However, while repetition of Sher's method [18], involving treatment of 1,1,3,3-tetramethoxypropane (4 equiv.) with 1,3-propanedithiol (1 equiv.) catalyzed by $BF_3 \cdot Et_2O$/HOAc, resulted in a moderate conversion to the required monodithiane this could not be separated from the excess of starting material by either preparative PLC or vacuum distillation. Use of equivalent amounts of reactants gave two products viz. 2,2′-methylenebis-1,3-dithiane (**27**) [23] and 1,3-dithiane-2-acetaldehyde (**25**), the latter presumably arising by hydrolysis of the desired product **24**. Treatment of the aldehyde **25** with trimethyl orthoformate and cerium(III) chloride heptahydrate [24] gave the dithiane **24**, and the latter compound was also obtained by thionyl chloride-silica gel catalyzed thioacetalisation [25] of 1,1,3,3-tetramethoxypropane or by treatment of 2-chloro-1,1-dimethoxyethane with 2-lithio-1,3-dithiane (cf. [26]). The bis-1,3-dithiane **27** was itself prepared in high yield from 1,1,3,3-tetramethoxypropane (1 equiv.) and 1,3-propanedithiol (2 equiv.) in the presence of $BF_3 \cdot Et_2O$/HOAc.

Attempted reaction of either the lithio monoanion of 2,2′-methylenebis-1,3-dithiane (**27**) or of its derived cuprate [27] with complex **10** was unsuccessful, while reaction of the dianion of **27** (whose formation was demonstrated by quantitative formation of **28** on treatment with chlorotrimethylsilane) with complex **10** gave compounds **29** and **30**. In an attempt to improve the reactivity of an anion derived from **27** it was converted via the *meso*-bis-sulfoxide **31** into the tetrasulfoxide **32** by

oxidation with sodium metaperiodate. However, no product was obtained from the attempted reaction of the dianion of **32** with the complex **10**.

In contrast, reaction of the dianion of **27** with the diterpenoid complexes **7** gave the desired product 2-[13-(methyl podocarpa-8,11,13-trien-19-oate]-2,2′-methylene-bis-1,3-dithiane (**33**), and compound **2**. It was necessary to add trifluoroacetic acid (1 mol. equiv.) to the reaction mixture immediately before the introduction of iodine in order to avoid the formation of unstable 2-iodo-1,3-dithiane derivatives. The molecular formula of **33** was confirmed by elemental analysis and by the observation of a weak molecular ion at $m/z$ 522 in the mass spectrum. The IR spectrum showed bands due to the aromatic ring (1516 $cm^{-1}$), methoxycarbonyl group (1717 $cm^{-1}$), and the dithioacetal group (902 $cm^{-1}$), while the 400 MHz $^1H$ NMR spectrum displayed three three-proton singlets assigned to the C(10), C(4) and methoxycarbonyl methyl groups. The latter spectrum also showed a two-proton doublet at 2.42 ppm (H(1′)), a one-proton triplet at 4.14 ppm (H(2′)) and three aromatic signals, viz. doublets at 7.25 ppm (H(11), $J_{ortho}$ 8 Hz) and 7.56 ppm (H(14), $J_{meta}$ 2 Hz), and a doublet of doublets at 7.63 ppm (H(12), $J_{ortho}$ 8 Hz, $J_{meta}$ 2 Hz) which clearly indicated a 1,2,4-trisubstituted arene. Although the signal

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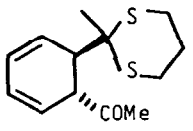


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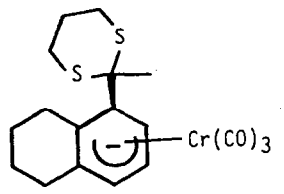


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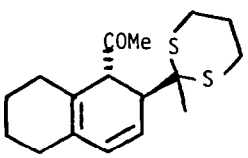
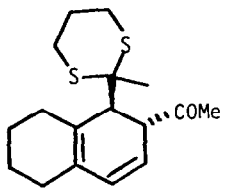
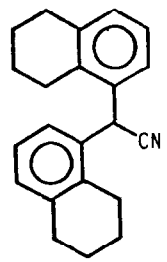


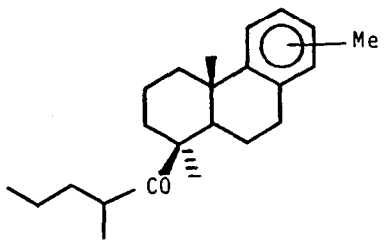

(37)




(36)




(38)




(39)

at 7.63 ppm showed no evidence of long-range benzylic coupling, the substituent could be placed at C(13) from a $^1$H NMR analysis similar to that carried out above for assignment of the preferred tripod conformations in the stereoisomers of **7**. Treatment of the monoanion of **24** with the diterpenoid complexes 7 gave product **23**, which possessed spectral parameters similar to those of **33**. The regiochemistry of attack on the complexes **7** by anions desired from **27** and **24** therefore agrees with that predicted from the $^1$H NMR studies.

Similarly, reaction of the anion of **24** with the complex **10** gave the 1,3-dithiane **26**, which was also formed by alkylation of 2-lithio-2-phenyl-1,3-dithiane with 2-chloro-1,1-dimethoxyethane.

A number of dithiane anion addition–electrophile trapping reactions were attempted but, although the recorded reaction [28] of **10** using 2-lithio-2-methyl-1,3-dithiane as nucleophile and methyl iodide as electrophile was repeated and gave the vicinal *trans*-2-methyl dithianylacetylcyclohexadiene adduct (**34**), no corresponding adducts were formed from the complexes **7** by use of either methyl iodide or methyl trifluoromethanesulfonate, or from **11** by use of methyl iodide. However, reaction of the dithianyl tetralin $\eta^5$-cyclohexadienyl intermediate (**35**) with three molar equivalents of the more reactive carbon electrophile methyl trifluoromethanesulfonate gave two acetylcyclohexadiene derivatives, which were assigned structures **36** and **37**.

Attempts to use t-butyllithium as a carbanion [16,29] and methyl triflate as the electrophile with complexes **7**, followed by decomplexation with triphenylphosphine, gave the 13-t-butyl derivative **4** but none of the desired t-butylacetyl adducts corresponding to the cyclohexadienes **36** or **37**.

Reaction of the tetralin complex **11** with lithioacetonitrile afforded the 5-cyanomethyl product **21**. A minor product from this reaction showed a molecular ion peak in the mass spectrum at $m/z$ 301 and was identified as the bis-adduct **38**. Unexpectedly, reactions of the complexes **7** with lithioacetonitrile gave only the uncomplexed arene **2**.

Attempted generation of 2-lithio-2-methyl-1,3-dithiane by use of lithium diisopropylamine (LDA) [30] instead of butyllithium, followed by reaction with the complexes **7** and then iodine, resulted in capture of an iodine atom by the nucleophilic lithiated diterpenoid complex to give a mixture of the iodo adduct **5** and its C(14) regioisomer. Lithiation of the complexes **7** by a modification of the methods of Uemura et al. [31] and Fukui et al. [32] followed by quenching with an excess of methyl triflate gave an inseparable mixture of methyl 13-methylpodocarpa-8,11,13-trien-19-oate (**6**) and its C(14) regioisomer. Also isolated was the novel diterpenoid ketone **39** (10%), again as a mixture of arene regioisomers. The structure of **39** was deduced from its spectral properties. Thus, the $^1$H NMR spectrum no longer showed a methoxycarbonyl singlet but showed methyl group singlets at 1.02 and 1.03 ppm (3H(20)), 1.26 and 1.27 ppm (3H(18)), and 2.27 and 2.28 ppm (aryl Me). The aromatic region contained only three protons in a multiplet which was similar to the corresponding signals in the spectrum of **6** and its C(14) regioisomer. The IR spectrum showed ketone absorption (1705 cm$^{-1}$), while the mass spectrum showed peaks at $m/z$ 326 ($M^{+\cdot}$) and a fragment at $m/z$ 255 corresponding to $\alpha$-cleavage of the five carbon aliphatic moiety from the ketone carbonyl group. Formation of **39** necessitates nucleophilic attack at the methoxycarbonyl group by a butyl anion, followed by deprotonation with butyllithium and

then alkylation of the $\alpha$-anion with methyl triflate. The competitive nucleophilic attack on the methoxycarbonyl group relative to deprotonation of the coordinated arene nucleus, allied with lack of regioselectivity of electrophilic attack on the aromatic ring, restricts the synthetic applicability of the arene lithiation-electrophilic trapping reaction sequence. However, attachment of the three-carbon synthons to afford **23** and **33** via addition–oxidation sequences occurred regioselectively at C(13), consonant with the prediction from $^1$H NMR studies on the complexes **7**.

## Experimental

For general experimental details see ref. 1. Melting points were determined on a Reichert–Kofler block and are uncorrected. IR spectra were recorded in $CHCl_3$ (unless otherwise stated) on a Perkin–Elmer 397 spectrophotometer. UV spectra of solutions in $CHCl_3$ were recorded with a Varian DMS 100 spectrophotometer. Analytical thin layer chromatography (TLC) was conducted on 0.2 mm layers of Kieselgel$_{254}$ (Merck); the fractions were detected by spraying with 2-methoxybenzaldehyde and heating. Preparative layer chromatography (PLC) was carried out on 1 mm thick layers of Kieselgel $PF_{254+366}$ (Merck) using the solvent system indicated. Flash chromatography was conducted using Kieselgel 60 (230–400 mesh ASTM, Merck) under a nitrogen pressure of 4 kgf cm$^{-2}$ (4 lb in$^{-2}$).

Butyllithium (nominally 2.6 mol l$^{-1}$ solution in hexanes, Aldrich Chemical Co.) was transferred to a Schlenk tube under argon, and titrated against 1,3-diphenyl-2-propanone toluene-*p*-sulfonylhydrazone [33] for accurate determination of its concentration.

*General procedure for reaction of ($\eta^6$-arene)tricarbonylchromium(0) complexes*

Reactions were conducted in oven-dried, side-arm flasks containing a magnetic stirrer and fitted with a parafilm-sealed, wired-on serum cap. The apparatus was flame-dried under vacuum, flushed with dry nitrogen, and evacuated ($\times$4), and a dry inert atmosphere established. Immediately before the addition of the ($\eta^6$-arene)tricarbonylchromium(0) complex, the flask was covered with aluminium foil. Reagents were pre-cooled to the reaction temperature immediately prior to their addition and were transferred to the solution from dry, round-bottom flasks that had been purged thoroughly with dry nitrogen via a syringe, either neat or as solutions in THF. Syringes and needles were oven-dried and purged with dry nitrogen immediately before use.

*Methyl podocarpa-8,11,13-trien-19-oate (**2**)*

This compound was prepared by hydrogenolysis of the tetrazolyl ether **8** [2], using a 2/1 ratio by weight of 8 to 10% palladium-charcoal in ethanol at 50 p.s.i. and 45 °C for 40 h. It crystallized from methanol as orthorhombic needles, m.p. 140–143 °C (lit. [2] 140–142 °C); $\nu_{max}$ (KBr) 1722 cm$^{-1}$ ($CO_2Me$). $\delta$(H) (ppm) 1.04, s, 3H(20); 1.09, dxt, *J* 4, 14 Hz, 1H; 1.28, s, 3H(18); 1.39, dxt, *J* 4, 14 Hz; 1.55, dxd, *J* 2, 12 Hz, 1H; 1.62, m, 1H; 1.99, m, 2H (6$\beta$); 2.18, dxd, *J* 6, 14 Hz, H(6$\alpha$); 2.28, d, *J* 13 Hz, 2H; 2.81, dxt, *J* 6, 15 Hz, H(7$\alpha$); 2.91, dxd, *J* 4, 17 Hz, H(7$\beta$); 3.68, s, $CO_2Me$; 7.04, br d, *J* 9 Hz, H(14); 7.08; dxt, *J* 1, 7 Hz, H(13); 7.13, br t, *J* 7 Hz, H(12); 7.27, br d, *J* 8 Hz, H(11). $\delta$(C) (ppm) 20.0, C(2); 20.9, C(6); 23.0, C(20); 28.5, C(18); 32.0, C(7); 37.6, C(3); 38.4, C(10); 39.3, C(1); 44.0, C(4); 51.3, C(21);

52.8, C(5); 125.4, C(13); 125.6, C(12); 125.8, C(11); 129.1, C(14); 135.4, C(8); 148.0, C(9); 177.9, C(19). *m/z* 272 (9, $M^+$), 257, 240, 197.

*Tricarbonyl[(8,9,11,12,13,14-η)-methyl podocarpa-8,11,13-trien-19-oate]chromium(0) (7)*

The ester **2** (0.61 g, 2.26 mmol) and hexacarbonylchromium(0) (0.58 g, 2.64 g) were treated with dibutyl ether (54 ml) and then THF (4.5 ml), and the solution was heated under reflux under nitrogen. The reaction was monitored by TLC (hexane/ether, 9/1) and by the disappearance of a white vapour halo of hexacarbonylchromium(0) in the condenser. After 24 h, the solution was filtered rapidly under nitrogen through Celite into an aluminium foil-covered flask. The Celite was washed with ether and the solvents were removed immediately from the combined filtrates by rotary evaporation in vacuo at ca. 60 °C to give a yellow crystalline mass. Flash chromatography and development with hexane resolved two yellow bands, the first of which was eluted with hexane/ether (4/1) and was identified as the complex **10** (from benzene contaminant in dibutyl ether). Elution with ether gave a mixture of the α- and β-stereoisomers (7/3, $^1$H NMR) of tricarbonyl[(8,9,11,12,13,14-η)-methyl podocarpa-8,11,13-trien-19-oate]chromium(0) (0.80 g, 90%). Isopiestic crystallization (ethyl acetate/hexane) at 4 °C gave the α-isomer as yellow prisms, m.p. 173.5–175 °C (decomp.) (Found: C, 61.5; H, 6.2; Cr, 13.0. $C_{21}H_{24}CrO_5$ calcd.: C, 61.8; H, 6.0; Cr, 12.7%). $\nu_{max}$ 1961 (CO), 1886 (CO), 1719 ($CO_2$Me). $\nu_{max}$ (KBr) 1963 (CO), 1875, 1854 (CO), 1714 $cm^{-1}$ ($CO_2$Me). $\lambda_{max}$ 315 (log ε 4.00), 258sh (4.01), 217 nm (4.51).

α-Isomer: δ(H) (ppm) 1.06, s, 3H(20); 1.28, s, 3H(18); 2.04, dxd, *J* 7, 14 Hz, H(6α); 2.72, m, 2H(7α,7β); 3.66, s, $CO_2$Me; 5.00, t, *J* 6 Hz, H(12); 5.05, d, *J* 6 Hz, H(14); 5.51, t, *J* 7 Hz, H(13); 5.53, d, *J* 6 Hz, H(11). δ(C) (ppm) 19.8, (C(2)); 20.0, (C(6)); 24.3, (C(20)); 28.5, C(18); 29.4, (C(7)); 37.2, (C(3)); 37.5, (C(10)); 39.0, (C(1)); 44.0, (C(4)); 50.1, (C(21)); 51.4, (C(5)); 88.4, (C(12)) *; 90.3, (C(14) *; 92.7, (C(11)) *, 95.1, (C(13)) *; 111.3, (C(8)); 122.4, (C(9)); 177.3, (C(19)); 234.0, (C(22,23,24)). δ(C) ($C_6D_6$) (ppm) 20.1, (C(2)); 20.3, (C(6)); 24.2, (C(20)); 28.4, (C(18)); 29.5, (C(7)); 37.3 (C(3)); 37.6, (C(10)); 39.2, (C(1)); 88.4, (C(12)) *; 90.3, (C(14)) *; 92.8, (C(11)) *; 95.0, (C(13)) *; 111.1, (C(8)); 122.3, (C(9)); 176.7, (C(19)); 234.6, (C(22,23,24)).

β-Isomer: δ(H) (ppm) 1.14, s, 3H(20); 1.25, s, 3H(18); 2.72, m, 2H(7α,7β); 3.69, s, $CO_2$Me; 4.93, d, *J* 6 Hz, H(14); 5.04, t, *J* 6 Hz, H(12); 5.48, t, *J* 6 Hz, H(13); 5.66, d, *J* 7 Hz, H(11). δ(C) (ppm) 20.0, (C(2)); 20.4, (C(6)); 25.1, (C(20)); 28.5, (C(18)); 32.8, (C(7)); 37.3, (C(3)); 37.5, (C(10)); 40.9, (C(1)); 43.7, (C(4)); 51.4, (C(21)); 53.2, (C(5)); 86.7, (C(12)) *; 87.9, (C(14)) *; 94.5, (C(11)) *; 96.9, (C(13)) *; 112.9, (C(8)); 123.0, C(9)); 177.2, (C(19)); 233.6, (C(22,23,24)). δ(C) ($C_6D_6$) (ppm) 20.2, (C(2)); 20.6, (C(6)); 25.2, (C(20)); 28.1, (C(18)); 32.7, (C(7)); 37.3, (C(3)); 37.4, (C(10)); 40.6, (C(1)); 43.7, (C(4)); 50.9, (C(21)); 53.0, (C(5)); 86.5, (C(12)) *; 87.9, (C(14)) *; 94.6, (C(11)) *; 96.9, (C(13)) *; 112.9, (C(8)); 123.0, (C(9)); 176.5, C(19)); 234.1, (C(22,23,24)).

*Tricarbonyl[(4a,5,6,7,8,8a-η)-1,2,3,4-tetrahydronaphthalene]chromium(0) (11)*

This compound was prepared as for **7** using hexacarbonylchromium(0) (2.0 g, 9.0 mmol) and 1,2,3,4-tetrahydronaphthalene (10.0 ml, 73 mmol) in dibutyl ether (60

* Tentative assignments.

ml) and THF (5 ml). Flash chromatography (hexane/ether, 4/1) yielded tricarbonyl[(4a,5,6,7,8,8a-$\eta$)-1,2,3,4-tetrahydronaphthalene]chromium(0) (2.47 g, 100%) as yellow crystals, m.p. 114.5–115.5 °C (lit. [7] 116–117.5 °C). $\nu_{max}$ (KBr) 1962(CO), 1884 $cm^{-1}$ (CO). $\delta$(H)(ppm) 1.75, m, 4H(2,3); 2.62, m, 4H(1,4); 5.22, s, 4H(5,6,7,8). $\delta$(C) (ppm) 22.0, t, $^1J$(CH) 131 Hz, C(2,3); 28.1, t, $^1J$(CH) 130 Hz, C(1,4); 91.9, dxt, $^1J$(CH) 174 Hz, $^2J$(CH) 5 Hz, C(6,7); 93.9, dxd, $^1J$(CH) 171 Hz, $^2J$(CH) 8 Hz, C(5,8); 109.7, s, C(4a,8a); 233.7, s, CO.

*2-Phenyl-1,3-dithiane (**14**)*

Butyllithium (1.2 mol $l^{-1}$, 1.17 ml, 1.40 mmol) was added dropwise to a solution of 1,3-dithiane [3] (0.21 g, 1.75 mmol) in THF (7 ml) at −23 °C ($CCl_4$/dry ice) under nitrogen and the solution was stirred for 2 h. The solution was cooled to −78 °C and dry hexamethylphosphoric triamide (HMPT) (3.2 ml, 18 mmol) was added. After 1 h the solution was treated dropwise with a solution of (benzene)tricarbonylchromium(0) (0.30 g, 1.40 mmol) in THF (3 ml), and stirred at −78 °C for 20 min and then at 0 °C for 4 h. The solution was treated at −78 °C with a solution of iodine (2.1 g, 8.4 mmol) in THF (15 ml), allowed to warm to room temperature, and stirred for 15 h. The mixture was then diluted with ether and the solution washed successively with aqueous sodium hydrogensulfite solution (5%), water, and brine, then dried. Removal of solvent in vacuo gave a solid, PLC (hexane/ether, 19/1) of which yielded (i) 2-phenyl-1,3-dithiane (0.16 g, 60%) as white needles, m.p. 69–72 °C (lit. [25] 74 °C). $\nu_{max}$ 1601, 1582 (aryl C=C), 905 $cm^{-1}$ (CS). $\delta$(H) (ppm) 2.07, m, 2H(5); 2.97, m, 4H(4,6); 5.15, s, H(2); 7.38, m, 5(aryl H). *m/z* 196 ($M^+$), 121, 77, 45; and (ii) biphenyl (30 mg, 14%) as a white solid, $\delta$(H) 7.5, m, 10H.

Repetition of the experiment in the absence of HMPT [17] for 30 min at 0 °C, followed by flash chromatography yielded a mixture ($^1$H NMR) of 1,3-dithiane (43 mg, 20%) and **14** (27 mg, 10%).

*2-[5-(1,2,3,4-Tetrahydronaphthalenyl)]-1,3-dithiane (**17**)*

2-Lithio-1,3-dithiane, prepared in THF (6 ml) from butyllithium (1.27 mol $l^{-1}$, 0.88 ml, 1.12 mmol) and 1,3-dithiane (0.15 g, 1.22 mmol) as above, was treated with HMPT (3 ml, 17 mmol), and the solution was stirred at −78 °C for 1.5 h. A solution of tricarbonyl[(4a,5,6,7,8,8a-$\eta$)-1,2,3,4-tetrahydronaphthalene]chromium(0) (0.30 g, 1.12 mmol) in THF ( 3 ml) was added slowly, and the solution was stirred at −78 °C for 1 h, and then at 0 °C for 4 h. The solution was treated at −78 °C with a solution of iodine (1.7 g, 6.7 mmol) in THF (15 ml), allowed to warm to room temperature, and stirred for 16 h. Work-up gave an oil (86 mg), PLC (hexane/ether, 4/1) of which gave a white solid (20 mg) which was shown ($^1$H NMR) to be an unstable mixture (7/1) of (i) 2[5-(1,2,3,4-tetrahydronaphthalenyl][-1,3-dithiane, $\delta$(H) (ppm) 1.82, m, 6H(2′,3′,5); 2.90, m, 8H(1′,4′,4,6); 5.32, s, H(2); 7.4, m, 3(ArH). $\delta$(H) (ppm) 7.01, d, *J* 7.6 Hz, H(8′); 7.12, t, *J* 7.7 Hz, H(7′); 7.44, d, *J* 7.4 Hz, H(6′). *m/z* 250 ($M^+$), 175, 131; and (ii) 5,6,7,8-tetrahydro-1-naphthalenecarboxyaldehyde (**19**), $\delta$(H) (ppm) 10.26, s, CHO. *m/z* 160 ($M^+$), 145, 131, 117, 91.

Repetition of the experiment at 0 °C for 24 h prior to the addition of iodine at −78 °C afforded 1,3-dithiane and 2,2′-bi-1,3-dithiane (**16**), as a white solid, m.p. 118–125 °C (lit. [35] 143–145 °C). $\delta$(H) (ppm) 2.08, m, 4H(5,5′); 2.85, m, 8H(4,4′,6,6′); 4.30, s, 2H(2,2′). *m/z* 119 (94, $M^+ - \dot{C}HS(CH_2)_3\dot{S}^{\cdot}$).

*2-Methyl-2-phenyl-1,3-dithiane (**15**)*

2-Lithio-2-methyl-1,3-dithiane, prepared in THF (2 ml) from butyllithium (1.03 mol $l^{-1}$, 0.42 ml, 0.43 mmol) and 2-methyl-1,3-dithiane [36,37] (57 μl), was treated with HMPT (1.0 ml) and (benzene)tricarbonylchromium(0) (93 mg, 0.43 mmol) in THF (2 ml) as above. The solution was stirred at 0 °C for 40 h and a solution of iodine (0.66 g, 2.6 mmol) in THF was added to the cooled (−78 °C) solution during 2 min, and the mixture was allowed to warm to room temperature. After 20 h the solution was worked up to give an oil, PLC (hexane/ether, 9/1) of which yielded 2-methyl-2-phenyl-1,3-dithiane, (18 mg, 20%) as a yellow oil, b.p. 98–101 °C, 0.1 mmHg. δ(H) (ppm) 1.81, s, 3H(Me); 2.6–2.8, m, 4H(4,6); 4.2–8.0, m, 5(aryl H). *m/z* 210 ($M^+$), 195, 136, 121, 105, 77.

*Reaction of 2-lithio-2-methyl-1,3-dithiane with complex **11***

2-Lithio-2-methyl-1,3-dithiane, prepared in THF (0.8 ml) from butyllithium (0.21 ml, 0.27 mmol) and 2-methyl-1,3-dithiane (34 μl, 0.29 mmol) was treated with tricarbonyl[(4a,5,6,7,8,8a-η)-1,2,3,4-tetrahydronaphthalene]chromium(0) (50 mg, 0.19 mmol) and HMPT (0.6 ml) as above. The mixture was warmed to 0 °C, stirred for 4 h, and then cooled to −78 °C. Iodine (0.42 g, 1.65 mmol) in THF (3 ml) was added over 2 min, and the solution was allowed to warm to room temperature and set aside for ca. 10 h. Work-up gave an oil, PLC (hexane/ether, 9/1) of which yielded (i) 5-acetyl-1,2,3,4-tetrahydronaphthalene (***20***) (19 mg, 59%) as an oil (Found: $M^{+\cdot}$ 174.1037. $C_{12}H_{14}O$ calcd.: *M*, 174.1045). $\nu_{max}$ 1676 (conj. CO), 1572 $cm^{-1}$ (aryl C=C). δ(H) (ppm) 1.75, m, 4H(2,3); 2.57, s, COMe; 2.8, m, 4H(1,4); 7.3, m, 3(aryl H). *m/z* 174 ($M^+$), 159, 131, 129, 115, 103, 91, 77; and (ii) 5-(2′-methyl-1′,3′-dithianyl)-1,2,3,4-tetrahydronaphthalene (**18**) (11 mg, 22%) as an oil (Found: $M^{+\cdot}$ 264.1011. $C_{15}H_{20}S_2$ calcd.: *M*, 264.1007). $\nu_{max}$ 1600(aryl C=C), 1359(dithianyl), 900 $cm^{-1}$ (dithianyl). δ(H) (ppm) 1.8, m, 6H(2,3,5′); 2.12, s, 3H(Me); 3.0, m, 8H(1,4,4′,6′); 7.1, m, 2H(7,8); 7.8, m, H(6). *m/z* 264 ($M^+$), 189, 175, 129, 115, 91, 77.

*6-Acetyl-1,2,3,4-tetrahydronaphthalene*

Acylation of 1,2,3,4-tetrahydronaphthalene with acetyl chloride and anhydrous aluminium trichloride yielded 6-acetyl-1,2,3,4-tetrahydronaphthalene (90%) as an oil (lit. [21] m.p. 53 °C) $\nu_{max}$ (neat) 1676(conj. CO), 1598 $cm^{-1}$ (aryl C=C). δ(H) (ppm) 1.8, m, 4H(2,3); 2.53, s, COMe; 2.9, m, 4H(1,4); 7.3, m, H(8); 7.75, m, 2H(5,7).

*Methyl 13-(2′-methyl-1′,3′-dithianyl)podocarpa-8,11,13-trien-19-oate (**22**)*

2-Lithio-2-methyl-1,3-dithiane, prepared in THF (0.8 ml) from butyllithium (0.21 ml, 0.27 mmol) and 2-methyl-1,3-dithiane (34 μl, 0.29 mmol), was treated with the complexes **7** (76 mg, 0.19 mmol) and then HMPT (0.6 ml) as above. The mixture was warmed to 0 °C, stirred for 6 h, cooled to −78 °C, and treated with a solution of iodine (0.42 g, 1.65 mmol) in THF ( 3 ml) over 2 min. The solution was allowed to warm to room temperature, set aside for 18 h, and worked up to give an oil which after PLC (hexane/ether, 9/1) yielded (i) a mixture (2/1) of methyl 13-acetylpodocarpa-8,11,13-trien-19-oate (**3**) and its C(14) regioisomer, (7 mg, 12%) (Found: $M^{+\cdot}$ 314.1911. $C_{20}H_{26}O_3$ calcd.: *M*, 314.1882). $\nu_{max}$ 1718 ($CO_2Me$), 1671 (COMe), 1604 (aryl C=C), 1565 $cm^{-1}$ (aryl C=C). δ(H) (ppm) 1.04 and 1.05, s, 3H(20); 1.28 and 1.29, s, 3H(18); 2.55 and 2.57, s, COMe; 2.7–3.0, m, 2H(7); 3.66 and 3.67, s,

3H($CO_2$Me); 7.5, m, 3(aryl H). *m/z* 314 ($M^+$), 299, 239, 197, 155, 141, 43; and (ii) a mixture (2/1) of methyl 13-(2′-methyl-1′,3′-dithianyl)podocarpa-8,11,13-trien-19-oate (**22**) and its C(14) regioisomer, (29 mg, 39%) (Found: $M^{+\cdot}$ 404.1830. $C_{23}H_{32}O_2S_2$ calcd.: *M*, 404.1844). $\nu_{max}$ 1715 ($CO_2$Me), 1599(aryl C=C), 1373(dithianyl), 1270(dithianyl), 904 $cm^{-1}$ (dithianyl). δ(H) (ppm) 1.03 and 1.05, s, 3H(20); 1.29, s, 3H(18); 1.82, s, 3H(Me); 2.8, m, 6H(7,4′,6′); 3.66 and 3.67, s, 3H($CO_2$Me); 7.0–7.8, m, 3(aryl H). *m/z* 404 ($M^+$), 389, 330, 315, 299, 255, 211, 174, 159, 131, 115.

*2-(2,2-Dimethoxyethyl)-1,3-dithiane (**24**)*

*(a) Using $BF_3 \cdot Et_2O$/HOAc as catalyst.* A stirred mixture of chloroform (4 ml), boron trifluoride etherate (1.2 ml, 0.01 mol), and glacial acetic acid (2.4 ml, 0.04 mol) was maintained at reflux temperature under nitrogen while a solution of 1,1,3,3-tetramethoxypropane (6.6 ml, 0.04 mol) and 1,3-propanedithiol (1.0 ml, 0.01 mol) in chloroform (15 ml) was added during 2.25 h. The cooled solution was diluted with chloroform (30 ml) and worked up to yield a liquid (1.26 g ). Distillation (120 °C, 0.5 mmHg) gave a yellow liquid containing 1,1,3,3-tetramethoxypropane (0.39 g, 6%) and 2-(2,2-dimethoxyethyl)-1,3-dithiane (0.87 g, 42%) which were inseparable by TLC.

*(b) Using thionyl chloride-silica gel as catalyst.* Thionyl chloride (3.05 ml) was added dropwise to a stirred suspension of silica gel (5 g, Kieselgel 60, 230–400 mesh) in dichloromethane (10 ml) and after 1 h, the solvent was removed in vacuo to give a flowing white solid (4.73 g). The solid (0.61 g) was added to a stirred mixture of 1,1,3,3-tetramethoxypropane (0.50 ml, 3.05 mmol) in benzene (15 ml) followed by 1,3-propanedithiol (0.31 ml, 3.05 mmol). The mixture was stirred at room temperature under argon for 5 h, the catalyst was filtered off and washed with ether, and the combined filtrate and washings were washed successively with aqueous sodium hydroxide solution (5%), water, and brine, then dried. Solvent was removed in vacuo to give an oil containing ($^1$H NMR) **24** and 1,1,3,3-tetramethoxypropane. A stirred solution of this mixture in benzene (10 ml), was treated with the thionyl chloride/silica gel catalyst (0.16 g) and 1,3-propanedithiol (78μl, 0.78 mmol) and the mixture was stirred overnight at room temperature, under argon. Workup as above gave a yellow oil (0.46 g) which on Kugelrohr distillation (140 °C, 3 mmHg) yielded 2-(2,2-dimethoxyethyl)-1,3-dithiane (0.24 g, 38%) as an oil. $\nu_{max}$ 2845 (acetal $CH_3$), 1060(acetal CO), 907 $cm^{-1}$ (CS). δ(H)(ppm) 2.05, m, 4H(5,1′); 2.85, m, 4H(4,6); 3.35, s, 6H(OMe); 4.10, t, *J* 7 Hz, H(2); 4.67, t, *J* 6 Hz, H(2′). *m/z* 208 ($M^+$), 176, 119, 75.

Variation of the procedure using 1,3-propanedithiol (7.92 mmol), thionyl chloride/silica gel catalyst (1.22 g), and benzene (25 ml) for 24 h, yielded a mixture of **24** (0.60 g, 80%) and **27** (0.18 g, 20%).

Using 1,3-propanedithiol (6.7 mmol), thionyl chloride/silica gel catalyst (1.22 g ) and benzene (30 ml) for 5.5 h followed by flash chromatography (hexane/ether, 4/1) and Kugelrohr distillation (120 °C, 1 mmHg) gave **24** (0.42 g, 67%).

*(c) From 2-lithio-1,3-dithiane.* Butyllithium (1.27 mol $l^{-1}$, 0.99 ml, 1.25 mmol) was added to a stirred solution of 1,3-dithiane (0.15 g, 1.24 mmol) in THF (5 ml) at −23 °C under nitrogen, the solution was stirred for 2 h, and HMPT (1.7 ml, 9.8 mmol) was then added. After 30 min the mixture was cooled to −78 °C, 2-chloro-1,1-dimethoxyethane (0.16 ml, 1.3 mmol) was added dropwise, the mixture stirred for 10 min, then warmed to −23 °C, stirred for 2 h, allowed to warm to room

temperature, and stirred for 18 h. The solution was diluted with ether (30 ml) and worked up to give a mixture ($^1$H NMR) of 1,3-dithiane (30 mg, 20%) and **24** (79 mg, 31%).

*(d) Acetalisation of 1,3-dithiane-2-acetaldehyde (25).* To 1,3-dithiane-2-acetaldehyde (0.82 g, 5 mmol) was added a solution of cerium(III) chloride heptahydrate (1.86 g, 5 mmol) in methanol (12.5 ml, 0.3 mol) followed immediately by trimethyl orthoformate (4.4 ml, 0.04 mol), and the solution was stirred at room temperature for 3 days. The mixture was poured into aqueous sodium hydrogencarbonate (ca. 25 ml), and the aqueous layer was extracted with ether. Work up gave a yellow oil (0.44 g, 42%) containing mainly **24** ($^1$H NMR).

*1,3-Dithiane-2-acetaldehyde (25)*

A solution of 1,3-propanedithiol (1.00 ml, 0.01 mol), boron trifluoride etherate (1.23 ml, 0.01 mol), and glacial acetic acid (2.46 ml, 0.04 mol) in chloroform (15 ml) was added during 2 h to a refluxing solution of 1,1,3,3-tetramethoxypropane (1.65 ml, 0.01 mol) in chloroform (5 ml), under nitrogen. The solution was diluted with chloroform, and worked up to give a liquid (1.50 g) which on flash chromatography (hexane/ether, 7/3) yielded (i) 1,3-dithiane-2-acetaldehyde (0.82 g, 51%) as a brown oil. $\nu_{max}$ 1734 (CHO), 901 cm$^{-1}$ (CS). $\delta$(H) (ppm) 2.07, m, 2H(5′); 2.90, m, 6H(2,4′,6′); 4.52, t, *J* 7 Hz, H(2′); 9.77 br s, H(1). *m/z* 162 ($M^+$), 133, 119; and (ii) **27** (0.52 g, 41%) as pale yellow needles (hexane/ether), m.p. and mixed m.p. 114–116°C.

*2,2′-Methylenebis(1,3-dithiane) (27)*

*(a) Using $BF_3 \cdot Et_2O$/HOAc as catalyst.* A solution of 1,1,3,3-tetramethoxypropane (1.65 ml, 0.01 mol) and 1,3-propanedithiol (2.01 ml, 0.02 mol) mol) in chloroform (15 ml) was added during 2 h to a stirred, refluxing mixture of chloroform (5 ml), boron trifluoride etherate (1.23 ml, 0.01 mol) and glacial acetic acid (2.46 ml, 0.04 mol) under nitrogen. The cooled solution was worked up to give a solid (3.17 g) which on flash chromatography (hexane/ether, 4/1) and crystallization from hexane/ether yielded 2,2′-methylenebis(1,3-dithiane) (2.07 g, 82%) as white crystals, m.p. 114–115.5°C (lit. [23] 110–114°C). $\nu_{max}$ 901 cm$^{-1}$ (CS). $\delta$(H)(ppm) 2.12, m, 6H(5,5′,1″); 2.88, m, 8H(4,4′,6,6′); 4.28, t, *J* 7 Hz, 2H(2,2′). $\delta$(C) (ppm) 25.8, C(5,5′); 29.5 C(4,4′,6,6′); 40.4, C(1″); 43.3, C(2,2′). *m/z* 252 ($M^+$), 177, 145, 119.

*(b) Using thionyl chloride-silica gel as catalyst.* 1,3-Propanedithiol (0.67 ml, 6.7 mmol) was added to a stirred mixture of 1,1,3,3-tetramethoxypropane (0.50 ml, 3.05 mmol) and thionyl chloride/silica gel catalyst (1.22 g) in benzene (30 ml), and the mixture was stirred at room temperature under argon for 5.5 h. Workup gave a yellow oil (0.78 g) which on flash chromatography (hexane/ether, 4/1) gave a mixture ($^1$H NMR, MS) of 2-(2,2-dimethoxyethyl)-1,3-dithiane (0.38 g, 60%) and **27** (0.23 g, 30%).

*2-(2,2-Dimethoxyethyl)-2-phenyl-1,3-dithiane (26)*

Butyllithium (1.7 mol l$^{-1}$, 0.33 ml, 0.56 mmol) was added to 2-phenyl-1,3-dithiane (0.10 g, 0.56 mmol) in THF (3 ml) at −23°C, HMPT (1 ml, 5.8 mmol) was added, and after 30 min the solution was treated dropwise at −78°C with 2-chloro-1,1-dimethoxyethane (64 μl, 0.56 mmol). The solution was warmed to

−23° C, stirred for 2 h, and then warmed to room temperature and stirred for 19 h. The solution was worked up to give an oil (0.12 g), PLC (hexane/ether, 4/1) of which yielded 2-(2,2-dimethoxyethyl)-2-phenyl-1,3-dithiane (74 mg, 46%) as a pale yellow oil, b.p. 170° C, 0.5 mmHg (Found: C, 59.8; H, 7.1; S, 23.0%, $M^{+\cdot}$ 284.0907. $C_{14}H_{20}O_2S_2$ calcd.: C, 59.1; H, 7.19; S, 22.5%; *M* 284.0905). $\nu_{max}$ 1515 (aryl C=C), 1035 (CO), 901 $cm^{-1}$ (CS). δ(H) (ppm) 1.98, m, 2H(5); 2.34, d, *J* 5 Hz, 2H(1′); 2.69, m, 4H(4,6); 3.19, s, 6H($OCH_3$); 4.38, t, *J* 5 Hz, H(2′); 7.32, m, 3(aryl H); 7.95, m, 2 (aryl H). A trace of aldehyde impurity was also detected, $\nu_{max}$ 1714 $cm^{-1}$.

*2-Phenyl-2,2′-methylenebis(1,3-dithiane) (**29**)*

Butyllithium (1.20 mol $l^{-1}$, 2.33 ml, 2.80 mmol) was added to **27** (0.35 g, 1.40 mmol) in THF (7 ml), and after 2.75 h at −23° C the mixture was treated with HMPT (6.5 ml, 37 mmol) at −78° C. The mixture was stirred at −78° C for 2 h, a solution of (benzene)tricarbonylchromium(0) (0.30 g, 1.40 mmol) in THF (3 ml) was added dropwise, and the mixture was stirred at −78° C for 1 h, left to stand at 0° C for 15 h, and cooled to −78° C. Trifluoroacetic acid (104 μl, 1.40 mmol) was added dropwise and the solution was stirred at −78° C for 1 h, treated with a solution of iodine (2.1 g, 8.4 mmol) in THF (15 ml), warmed to room temperature, and stirred for 5.5 h. Workup and flash chromatography (hexane/ether, 9/1) gave (i) biphenyl (34 mg, 31%); and (ii) a liquid (0.20 g) which on PLC (benzene/hexane, 1/1) gave: (i) a solid mixture (90 mg) of 2-[2-(1,3-dithianylmethylidene)]-1,3-dithiane (**30**), δ(H) (ppm) 2.1, m, 4H(5,5″); 2.9, m, 9H(4,6,4″,6″,2); 5.18, s, H(1′). δ(C) (ppm) 24.9, C(5″); 26.3, C(5); 29.0, C(4″ or 6″); 29.3, C(6″ or 4″); 29.9, C(4,6); 44.0, C(2); 125.3, C(1′); 135.1, C(2″). *m/z* 250 ($M^+$), 217, 176, 164, 129; and (ii) an inseparable mixture ($^1$H NMR) of **27** (28 mg, 8%) and 2-phenyl-2,2′-methylenebis(1,3-dithiane) (0.13 g, 29%). δ(H)(ppm) 1.93, m, 4H(5,5′); 2.45, d, *J* 5 Hz, 2H(1″); 2.78, m, 8H(4,4′,6,6′); 4.08, t, *J* 5 Hz, H(2′); 7.32, m, 3H(*meta, para*); 7.92, m, 2H(*ortho*). δ(C) (ppm) 24.5, C(5′); 24.9, C(5); 27.8, C(4′,6′); 30.6, C(4,6); 42.2, C(2′); 50.5, C(1″); 58.0, C(2); 127.3, C(*para*); 128.4, C(*ortho, meta*); 140.9, C(*ipso*).

Attempted hydrolysis of the mixture gave no identifiable products.

*2,2′-Methylenebis-1,3-dithiane tetrasulfoxide (**32**)*

A solution of sodium metaperiodate (1.28 g, 6 mmol) in water (5 ml) was added to a stirred solution of **27** (0.51 g, 2.0 mmol) in methanol (50 ml) and the mixture was stirred for 48 h. The mixture was filtered, the residue was washed with chloroform (40 ml), and solvent was removed from the filtrate in vacuo to give a solid which crystallized from chloroform/hexane to give 2,2′-methylenebis-1,3-dithiane tetrasulfoxide (92 mg, 19%) as a pale yellow powder, m.p. 195° C (decomp) (Found: C, 34.3; H, 5.1; S, 39.6. $C_9H_{16}O_4S_4$ calcd.: C, 34.2; H, 5.1; S, 40.5%). *m/z* 300 ($M^+ - O^{\cdot}$), 284, 267, 249, 106, 41.

*2-[13-(Methyl podocarpa-8,11,13-trien-19-oate)]-2,2′-methylenebis(1,3-dithiane) (**33**)*

2,2′-Dilithio-2,2′-methylenebis-1,3-dithiane, prepared in THF (3 ml) from butyllithium (1.7 mol $l^{-1}$, 0.61 ml, 1.04 mmol) and 2,2′-methylenebis-1,3-dithiane (0.13 g, 0.52 mmol) at −23° C for 2 h was treated with HMPT (4 ml, 23 mmol) at −78° C, and after 1 h a solution of the complexes **7** (0.21 g, 0.52 mmol) in THF (3 ml) was added. The mixture was stirred at −78° C for 30 min, and at 0° C for 5.5 h, then

treated dropwise at −78°C with trifluoroacetic acid (0.04 ml, 0.52 mmol). A solution of iodine (0.79 g, 3.1 mmol) in THF (10 ml) was added and the mixture was warmed to room temperature and stirred for 17.5 h. Work-up gave an oil (0.30 g) which was dissolved in chloroform (5 ml) and stirred in air for 21 h. Removal of the solvent in vacuo yielded an oil, PLC (hexane/ether, 9/1) of which gave (i) 2,2′-methylenebis-1,3-dithiane (62 mg, 43%); (ii) ester **2** (62 mg, 44%); and (iii) 2-[13-(methyl podocarpa-8,11,13-trien-19-oate)]-2,2′-methylenebis(1,3-dithiane) (36 mg, 13%) as an oil (Found: C, 62.7; H, 7.4. $C_{27}H_{38}S_4O_2$ calcd.: C, 62.0; H, 7.3%). $\nu_{max}$ 1717($CO_2Me$), 1516 (aryl C=C), 902 $cm^{-1}$(CS). $\delta$(H) (ppm) 1.03, s, 3H(20‴); 1.28, s, 3H(18‴); 2.42, d, *J* 5 Hz, 2H(1″); 2.73–2.92, m, 2H(7‴α,7‴β); 3.67, s, 3H($CO_2$*Me*); 4.14, t, *J* 5 Hz, H(2′); 7.25, d, *J* 8 Hz, H(11‴); 7.56, d, *J* 2 Hz, H(14‴); 7.63, d (*J* 2 Hz) x d (*J* 8 Hz), H(12‴). $\delta$(C) (ppm) 20.4, C(2‴); 21.5, C(6‴); 23.4, C(20‴); 25.0, C(5′); 25.6, C(5); 28.4, C(4′,6′); 29.0, C(18‴); 31.2, C(4,6); 32.7, C(7‴); 38.1, (C 3‴); 38.7, C(10‴); 39.7, C(1‴); 43.0, C(2′); 44.4, C(4‴); 50.7, C(1″); 51.7, ($CO_2$*Me*); 53.1, C(5‴); 58.5, C(2); 126.2, C(11‴); 126.4, C(12‴); 129.3, C(14‴); 136.0, C(13‴); 138.5, C(8‴); 147.8, C(9‴); 178.4, C(19‴). *m/z* 522 ($M^+$), 416, 271, 211.

*2-(2,2-Dimethoxyethyl)-2-phenyl-1,3-dithiane (**26**)*

2-Lithio-2-(2,2-dimethoxyethyl)-1,3-dithiane, prepared in THF (4 ml) at −23°C from butyllithium (1.7 mol $l^{-1}$, 0.45 ml, 0.77 mmol), and 2-(2,2-dimethoxyethyl)-1,3-dithiane (0.16 g, 0.77 mmol), after 2 h was treated at −78°C with HMPT. The mixture was stirred at −78°C for 1 h then treated with a solution of the complex **10** (0.16 g, 0.77 mmol) in THF (2 ml), stirred at −78°C for 1 h, and at 0°C for 4 h, then treated at −78°C with a solution of iodine (1.2 g, 4.6 mmol) in THF (7 ml). The solution was allowed to warm to room temperature, stirred for 16 h, and worked up to give an oil (0.18 g), PLC (hexane/ether, 9/1) of which gave 2-(2,2-dimethoxyethyl)-2-phenyl-1,3-dithiane (52 mg, 24%) as an oil (correct IR and $^1$H NMR spectra).

*2-(2,2-Dimethoxyethyl)-2-[13-(methyl podocarpa-8,11,13-trien-19-oate)]-1,3-dithiane (**23**)*

2-Lithio-2-(2,2′-dimethoxyethyl)-1,3-dithiane, prepared in THF (3 ml) at −23°C from butyllithium (1.7 mol $l^{-1}$, 0.13 ml, 0.23 mmol) and compound **24** (47 mg, 0.23 mmol), after 2 h was treated at −78°C with HMPT (1.5 ml, 8.6 mmol). After 1 h, a solution of the complexes **7** (92 mg, 0.23 mmol) in THF (1.5 ml) was added and the solution was stirred at −78°C for 1 h, and at 0°C for 4 h, and then treated at −78°C with a solution of iodine (0.35 g, 1.4 mmol) in THF (5 ml). The solution was allowed to warm to room temperature, stirred for 15 h, and worked up to give an oil (90 mg), PLC hexane/ether, 4/1), of which yielded (i) ester **2** (19 mg, 30%); and (ii) 2-(2,2-dimethoxyethyl)-2-[13-(methyl podocarpa-8,11,13-trien-19-oate)]-1,3-dithiane (26 mg, 24%) (Found: $M^{+\cdot}$ 478.2161. $C_{26}H_{38}O_4S_2$ calcd.: *M* 478.2178). $\nu_{max}$ 2860 (acetal $CH_3$), 1718 ($CO_2Me$), 1490 (aryl C=C), 1068 (CO), 902 $cm^{-1}$ (CS). $\delta$(H) (ppm) 1.03, s, 3H(20″); 1.28, s, 3H(18″); 2.79, m, 2H(7″α,7″β); 3.20, s, 6H(OMe); 3.67, s, 3H($CO_2$*Me*); 4.38, t, *J* 5 Hz, H(2′); 7.25, d, *J* 8 Hz, H(11″); 7.56, d, *J* 2 Hz, H(14″); 7.63, d (*J* 2 Hz) x d (*J* 8 Hz), H(12″). $\delta$(C) (ppm) 19.9, C(2″); 21.0, (C 6″); 22.9, C(20″); 24.8, C(5); 27.6, C(4,6); 28.5, C(18″); 32.2, C(7″); 37.6, C(3″); 38.2, C(10″); 39.3, C(1″); 44.0, C(4″); 47.9, C(1′); 51.2, C(2′);

52.7, (C 5″, $CO_2Me$); 56.1, C(2); 101.7, (OMe); 125.8, C(11″); 126.0, C(12″); 129.1, C(14″); 135.3, C(13″); 138.2, C(8″); 146.9, C(9″); 177.9, C(19″).

*Reaction of complex* ***11*** *with 2-lithio-2-methyl-1,3-dithiane and methyl trifluoromethanesulfonate*

2-Lithio 2-methyl-1,3-dithiane, prepared in THF (0.8 ml) from buttyllithium (0.58 ml, 0.49 mmol) and 2-methyl-1,3-dithiane (60 μl, 0.51 mmol), was treated with tricarbonyl[(4a,5,6,7,8,8a,η)-1,2,3,4-tetrahydronaphthalene]chromium(0) (0.12 g, 0.47 mmol) and then HMPT (0.8 ml) as above. The mixture was warmed to 0 °C, stirred for 4 h, and then cooled to −78 °C. A CO atmosphere was established, methyl trifluoromethanesulfonate (154 μl, 1.36 mmol) was added dropwise, and the solution was stirred at 0 °C for 4 h, and treated at −78 °C with a solution of triphenylphosphine (0.61 g, 2.32 mmol) in THF (1 ml) over 2 min. The mixture was stored at 0 °C for 54 h, and worked up to give a yellow oil. PLC (hexane/ether, 9/1) yielded (i) 6-acetyl-5-(2′-methyl-1,3-dithianyl)-1,2,3,4,5,6-hexahydronaphthalene (**36**), (34 mg, 24%) as an oil. δ(H) (ppm) 1.30, s, 3H(Me); 2.42, s, COMe; 4.4, m, 2H(5,6); 6.9, m, 2, vinyl H. *m/z* 293 ($M^+ - {}^{\cdot}Me$), 174, 159, 139, 133, 131, 115, 91, 43; and (ii) 5-acetyl-6-(2′-methyl-1′,3′-dithianyl)-1,2,3,4,5,6-hexahydronaphthalene (**37**), (37 mg, 26%) as an oil. δ(H) (ppm) 1.48, s, 3H(Me); 2.18, s, COMe; 5.17, s, vinyl H; 5.73, s, vinyl H. *m/z* 174 ($M^+ - C_5H_9S_2{}^{\cdot} - H^{\cdot}$), 159, 133, 131, 115, 91, 77, 43.

*Methyl 13-t-butylpodocarpa-8,11,13-trien-19-oate (****4****)*

A solution of the complexes **7** (41 mg, 0.10 mmol) in THF (1.0 ml) was added dropwise to a solution of t-butyllithium (1.06 mol $l^{-1}$, 0.15 ml, 0.16 mmol) in THF (0.8 ml) at −78 °C under argon, followed by HMPT (0.4 ml). The mixture was warmed to 0 °C until homogeneous, recooled to −78 °C, stirred for 90 min, and treated dropwise with methyl trifluoromethanesulfonate (28 μl, 0.25 mmol). The mixture was warmed to 0 °C, stirred for 18 h, and a solution of triphenylphosphine (0.14 g) in THF (2 ml) was added to the mixture over 2 min. The mixture was kept at 0 °C for 45 h, and worked up to give an oil which on PLC (hexane/ether, 9/1) yielded methyl 13-t-butylpodocarpa-8,11,13-trien-19-oate, (11 mg, 34%) as a cream solid, m.p. 103–107 °C (Found: $M^{+\cdot}$ 328.2426. $C_{22}H_{32}O_2$ calcd.: *M*, 328.2402). $\nu_{max}$ 1714 $cm^{-1}$ (CO). δ(H) (ppm) 1.06, s, 3H(20); 1.29, s, 3H(18); 1.33, s, t-Bu; 2.7–3.0, m, 2H(7); 3.70, s, $CO_2Me$; 7.0–7.6, m, 3(aryl H). *m/z* 328 ($M^+$), 272, 257, 197, 131, 57.

*5-Cyanomethyl-1,2,3,4-tetrahydronaphthalene (****21****)*

Lithioacetonitrile, prepared in THF (1.0 ml) from butyllithium (0.26 ml, 0.34 mmol), diisopropylamine (48 μl, 0.34 mmol), and acetonitrile (18 μl, 0.34 mmol) at −78 °C for 30 min, was treated with HMPT (0.5 ml) followed by a solution of the complex **11** (61 mg, 0.23 mmol) in THF (1.0 ml). The mixture was stirred at −78 °C for 1 h, a solution of iodine (0.52 g, 2.05 mmol) in THF (3 ml) was added during 2 min, and the mixture was warmed to room temperature and left to stand for 5 h. The solution was then worked up to give 5-cyanomethyl-1,2,3,4-tetrahydronaphthalene (27 mg, 69%) which crystallized from hexane as orthorhombic crystals, m.p. 65–68 °C (Found: $M^{+\cdot}$ 171.1052. $C_{12}H_{13}N$ calcd.: *M*, 171.1048). $\nu_{max}$ (KBr) 2245 (CN), 1585 $cm^{-1}$ (aryl C=C). δ(H) (ppm) 1.7, m, 4H(2,3); 2.5, m, 4H(1,4); 3.61, s, $CH_2CN$; 7.2, m, 3(aryl H). *m/z* 171 ($M^+$), 144, 131, 115, 103, 91, 77.

Repetition of the experiment yielded **21** (8 mg, 10%) and bis(1,2,3,4-tetrahydronaphthalenyl)acetonitrile (**38**) (25 mg, 36%) m.p. 150–154.5°C (Found: $M^{+\cdot}$ 301.1842. $C_{22}H_{23}N$ calcd.: $M$, 301.1831). $\delta$(H) (ppm) 1.8, m, 8H(2,3,2′,3′); 2.8, m, 8H(1,4,1′,4′); 5.30, s, CHCN; 7.15, m, 6(aryl H). $m/z$ 301 ($M^+$), 300, 273, 169, 131, 115, 91, 77.

*Reaction of complexes 7 with lithium diisopropylamide and iodine*

A mixture of butyllithium (1.57 mol $l^{-1}$, 0.49 ml, 0.77 mmol), diisopropylamine (126 $\mu$l, 0.76 mmol), in THF (2.0 ml) at 0°C under argon, was stirred for 30 min, cooled to −78°C, and treated dropwise with 2-methyl-1,3-dithiane (82 $\mu$l, 0.70 mmol). The mixture was stirred for 30 min, and a solution of tricarbonyl[(8,9,11,12,-13,14-$\eta$)-methyl podocarpa-8,11,13-trien-19-oate]chromium(0) (0.16 g, 0.38 mmol) in THF (2.0 ml) added dropwise. The mixture was stirred at −78°C for 1 h, a solution of iodine (0.95 g, 3.74 mmol) in THF (4 ml) added during 2 min, and the mixture was allowed to warm to room temperature and set aside for 20 h. It was then worked up to yield (i) the ester **2** (28 mg, 27%); and (ii) a mixture of methyl 13-iodopodocarpa-8,11,13-trien-19-oate (**5**) (45 mg, 29%) and its C(14) regioisomer. $\delta$(H) 1.01, s, 3H(20); 1.27, s, 3 H(18); 2.8, m, 2H(7); 3.65, s, 3H, $CO_2Me$; 7.2, m, 3(aryl H). $m/z$ 398 ($M^+$), 323, 257, 197, 131.

*Reaction of complexes 7 with butyllithium/TMEDA and methyl trifluoromethanesulfonate*

Butyllithium (0.84 mol $l^{-1}$, 0.11 ml, 92 $\mu$mol) was added dropwise to a solution of the complexes **7** (35 mg, 86 $\mu$mol) and dry TMEDA (38 $\mu$l, 93 $\mu$mol) in THF (0.7 ml) at −78°C under argon, and the solution was stirred for 4 h. Methyl trifluoromethanesulfonate (98 $\mu$l, 0.60 mmol) was added dropwise and stirring was continued at −78°C for 1 h and then at 0°C for 2 h. The mixture was diluted with ether (10 ml), warmed to room temperature, exposed to light, and an oxygen atmosphere established. After 6 h, work up gave an oil, which on PLC (hexane/ether, 9/1) yielded (i) a mixture of methyl 13/14-methylpodocarpa-8,11,13-trien-19-oates (9 mg, 37%), as an oil (Found: $M^+$ 286.1935. $C_{19}H_{26}O_2$ calcd.: $M$, 286.1933). $\nu_{max}$ 1716 $cm^{-1}$ (CO). $\delta$(H) (ppm) ($CCl_4$) 1.02 and 1.03, s, 3H(20); 1.26 and 1.27, s, 3H(18); 2.27 and 2.28, s, aryl Me; 2.8, m, 2H(7); 3.61, s, 3H, $CO_2Me$; 7.05, m, aryl H. $m/z$ 286 ($M^+$), 271, 211, 197; and (ii) a mixture of 13/14-methyl-19-(1′-methylbutyl)podocarpa-8,11,13-trien-19-one (**39**), (3 mg, 10%) as an oil (Found: $M^{+\cdot}$ 326.2615. $C_{23}H_{34}O$ calcd.: $M$, 326.2609). $\nu_{max}$ 1705 $cm^{-1}$ (CO). $\delta$(H) (ppm) 1.09, s, 3H(20); 1.25, s, 3H(18); 2.23, br s, aryl Me; 3.0, m, 2H(7); 7.0, m, 3 (aryl H). $m/z$ 326 ($M^+$), 255, 227, 197, 145, 131.

## X-Ray crystal structure

A suitable crystal of the $\alpha$-diastereomer of tricarbonyl[(8,9,11,12,13,14-$\eta$)methyl podocarpa-8,11,13-trien-19-oate]chromium(0) (**7**) was mounted on a nylon fibre, and placed on a Nonius CAD-4 diffractometer. Accurate unit cell dimensions were derived by a least squares fit to the observed setting angles of 25 reflections representative of all regions of reciprocal space. Details of the data collection and unit cell parameters are given in Table 2. The crystal belongs in the monoclinic system (two molecules per unit cell) with systematic absences ($0k0$, $k = 2n + 1$)

Table 2

Summary of crystal data and intensity data collection for the α-diastereomer of **7**

| | |
|---|---|
| Formula | $C_{21}H_{24}CrO_5$ |
| Molecular weight (g mol$^{-1}$) | 408.42 |
| Crystal habit and colour | multifaceted prisms, yellow |
| $a$ (Å) | 8.079(4) |
| $b$ (Å) | 14.691(2) |
| $c$ (Å) | 8.310(1) |
| $\beta$ (°) | 100.58(2) |
| $V$ (Å$^3$) | 969.6 |
| Space group | $P2_1$ |
| $Z$ | 2 |
| $\rho_c$ (g cm$^{-3}$) | 1.399 |
| $\rho_o$ (g cm$^{-3}$) | 1.395 (aq.KI/KCl) |
| λ(Mo-$K_\alpha$) (Å) | 0.7107 |
| $\theta_{max}$ (°) | 30 |
| Total reflections | 3113 |
| Observed reflections | 2582 |
| Temperature (K) | 291 |
| Transmission coefficients | min. 98.86%<br>max. 99.94% |

Table 3

Atomic positions (×10$^4$) as fraction of the unit cell for the α-diastereomer of **7**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cr | −164(1) | −2500(0) | −1211(1) |
| C(1) | −3024(6) | −2341(3) | −5409(5) |
| C(2) | −4635(7) | −2195(3) | −6670(6) |
| C(3) | −5844(6) | −1560(4) | −6037(6) |
| C(4) | −5086(5) | −638(3) | −5397(5) |
| C(5) | −3421(5) | −824(3) | −4169(5) |
| C(6) | −2559(6) | 19(3) | −3313(6) |
| C(7) | −1357(7) | −264(4) | −1764(7) |
| C(8) | −223(6) | −1042(3) | −2067(6) |
| C(9) | −603(5) | −1613(3) | −3456(5) |
| C(10) | −2152(5) | −1444(3) | −4826(5) |
| C(11) | 531(5) | −2327(4) | −3641(5) |
| C(12) | 2041(5) | −2444(5) | −2471(5) |
| C(13) | 2361(6) | −1890(4) | −1102(6) |
| C(14) | 1251(5) | −1206(3) | −892(6) |
| C(18) | −6368(6) | −170(4) | −4499(6) |
| C(19) | −4836(5) | 31(3) | −6726(6) |
| C(20) | −1418(6) | −1004(4) | −6249(5) |
| C(21) | −5144(8) | 324(4) | −9560(6) |
| C(22) | 430(6) | −2803(3) | 965(6) |
| C(23) | −626(7) | −3702(4) | −1701(6) |
| C(24) | −2293(6) | −2376(5) | −849(5) |
| O(1) | −4291(5) | 786(3) | −6472(4) |
| O(2) | −5326(5) | −293(2) | −8258(4) |
| O(3) | 756(6) | −2988(3) | 2330(4) |
| O(4) | −931(6) | −4453(3) | −2010(5) |
| O(5) | −3660(4) | −2285(4) | −623(5) |

Table 4

Bond lengths for the α-diastereomer of **7**

| Atoms | Bond lengths (Å) | Atoms | Bond lengths (Å) |
|---|---|---|---|
| Cr–C(8) | 2.254(5) | C(6)–C(7) | 1.521(7) |
| Cr–C(9) | 2.249(4) | C(7)–C(8) | 1.515(7) |
| Cr–C(11) | 2.208(5) | C(8)–C(9) | 1.414(6) |
| Cr–C(12) | 2.228(5) | C(9)–C(10) | 1.549(5) |
| Cr–C(13) | 2.215(5) | C(9)–C(11) | 1.420(7) |
| Cr–C(14) | 2.210(5) | C(10)–C(11) | 1.531(6) |
| Cr–C(22) | 1.838(5) | C(10)–C(20) | 1.557(6) |
| Cr–C(23) | 1.835(5) | C(11)–C(12) | 1.424(6) |
| Cr–C(24) | 1.809(5) | C(12)–C(13) | 1.384(7) |
| C(1)–C(2) | 1.529(6) | C(13)–C(14) | 1.380(7) |
| C(2)–C(3) | 1.514(8) | C(14)–C(8) | 1.415(6) |
| C(3)–C(4) | 1.540(7) | C(19)–O(1) | 1.197(6) |
| C(4)–C(5) | 1.556(5) | C(19)–O(2) | 1.349(6) |
| C(4)–C(18) | 1.545(7) | C(21)–O(2) | 1.439(7) |
| C(4)–C(19) | 1.520(7) | C(22)–O(3) | 1.149(6) |
| C(5)–C(6) | 1.531(6) | C(23)–O(4) | 1.149(7) |
| C(5)–C(10) | 1.545(6) | C(24)–O(5) | 1.161(6) |

characteristic of the space group $P2_1$. The intensities of 3113 unique reflections were measured using the $2\theta/\omega$ scan technique to a maximum scan angle of $\theta$ 30°. Of these, 2582 were found to have intensities greater than $3\sigma(I)$. The data were corrected for Lorentz, polarization, and absorption effects. The $x$ and $z$ coordinates of the chromium atom were deduced from a three dimensional Patterson synthesis,

Table 5

Bond angles for the α-diastereomer of **7**

| Atoms | Angles (°) | Atoms | Angles (°) |
|---|---|---|---|
| C(1)–C(2)–C(3) | 111.8(4) | C(9)–C(11)–C(12) | 120.3(4) |
| C(2)–C(3)–C(4) | 114.9(4) | C(10)–C(1)–C(2) | 112.3(4) |
| C(3)–C(4)–C(5) | 108.3(4) | C(10)–C(5)–C(6) | 111.5(3) |
| C(3)–C(4)–C(18) | 107.4(4) | C(10)–C(9)–C(11) | 119.3(4) |
| C(3)–C(4)–C(19) | 114.5(4) | C(11)–C(12)–C(13) | 119.9(5) |
| C(4)–C(5)–C(6) | 115.3(4) | C(12)–C(13)–C(14) | 120.3(4) |
| C(4)–C(5)–C(10) | 115.0(3) | C(13)–C(14)–C(8) | 121.4(4) |
| C(4)–C(19)–O(1) | 124.4(4) | C(14)–C(8)–C(9) | 119.5(4) |
| C(4)–C(19)–O(2) | 113.7(4) | C(18)–C(4)–C(5) | 109.7(3) |
| C(5)–C(6)–C(7) | 109.7(4) | C(18)–C(4)–C(19) | 104.6(4) |
| C(5)–C(10)–C(1) | 108.8(3) | C(19)–C(4)–C(5) | 112.1(4) |
| C(5)–C(10)–C(9) | 109.5(3) | C(19)–O(2)–C(21) | 115.7(4) |
| C(5)–C(10)–C(20) | 113.2(3) | C(20)–C(10)–C(1) | 109.6(3) |
| C(6)–C(7)–C(8) | 112.2(4) | C(22)–Cr–C(23) | 89.5(2) |
| C(7)–C(8)–C(9) | 122.4(4) | C(22)–Cr–C(24) | 86.9(2) |
| C(7)–C(8)–C(14) | 118.1(4) | C(23)–Cr–C(24) | 88.5(3) |
| C(8)–C(9)–C(10) | 122.0(4) | O(3)–C(22)–Cr | 178.1(5) |
| C(8)–C(9)–C(11) | 118.6(4) | O(4)–C(23)–Cr | 179.4(5) |
| C(9)–C(10)–C(1) | 110.9(3) | O(5)–C(24)–Cr | 179.2(6) |
| C(9)–C(10)–C(20) | 104.9(3) | O(1)–C(19)–O(2) | 121.9(4) |

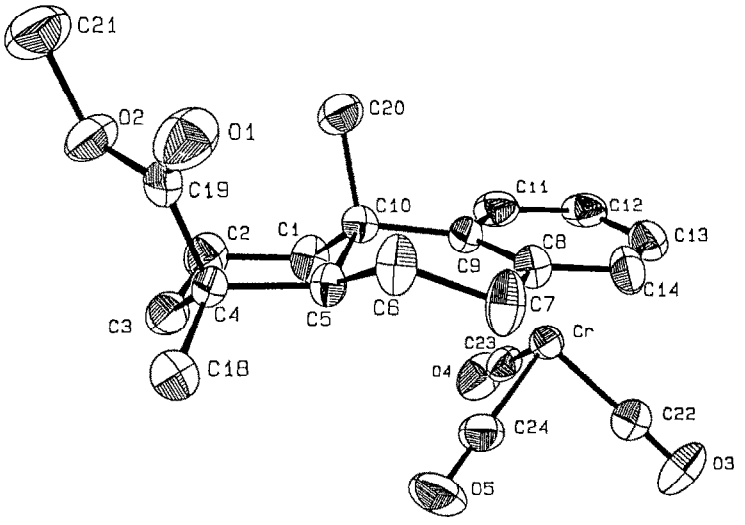



Fig. 1. The molecular geometry and atomic numbering of the α-diastereomer of 7. Anisotropic ellipses represent 50% probability surfaces.

and $y$ was set at 0.2500. False symmetry in the heavy-atom electron density map was broken by locating the six atoms of the arene ring lying off the false mirror plane. The remaining atoms were found in subsequent 'difference' electron density maps. Refinement was by full-matrix least-squares techniques. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors and dispersion corrections were for neutral atoms. After initial isotropic refinement, anisotropic thermal parameters were assigned to the heavier atoms, and hydrogen atoms were included in calculated positions. The atom coordinates were then passed through a centre of symmetry to generate the correct diastereomer, indicating the wrong set of carbon atoms had been chosen originally from the first Fourier difference map. Refinement

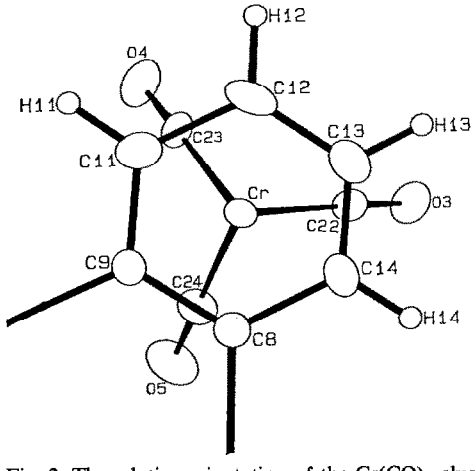



Fig. 2. The relative orientation of the $Cr(CO)_3$ cluster.

converged with $R$ and $R'$ 0.0335 and 0.0319 respectively. Atomic thermal parameters, hydrogen atom positions, and tables of observed and calculated structure factor amplitudes are available on request from the authors (G.R.C.).

Atom coordinates, bond lengths and bond angles are listed in Tables 3–5. The molecular geometry is shown in Fig. 1. The $\alpha$-stereochemistry is confirmed, with the tricarbonylchromium(0) moiety located on the face opposite the C(10)-methyl group. The aromatic ring is symmetrically bonded to the chromium atom with an average $Cr-C_{arene}$ bond length of 2.23 Å, typical of ($\eta^6$-arene)tricarbonylchromium(0) complexes. The C–C arene bond lengths range from 1.380 to 1.424 Å, and show no discernable increase from the free ligand. The tricarbonylchromium(0) group possesses a 'piano-stool' arrangement, and planes taken through the CO ligand carbon atoms and oxygen atoms are parallel with respect to the aromatic ring. The average $Cr-C_{CO}$ bond length is 1.63 Å, while the average C–O bond length is 1.15 Å. This suggests less transfer of electron density from the aromatic nucleus to the chromium atom for utilization in $\pi$-acceptor bonding by the CO ligands compared with other ($\eta^6$-arene)tricarbonylchromium(0) complexes. It should be noted however, that the $Cr-C_{CO}$ bond length is appreciably shorter than that for hexacarbonylchromium(0) (1.92 Å) reflecting the relative electron donor properties of the arene ligand.

The X-ray crystal structure allowed a definitive conformational analysis of the $\alpha$-diastereomer of **7** in the solid state. With no arene heteroatom substituents present, there are no strong electronic contributions which can cause a particular eclipsed conformation to be adopted. Likewise, steric interactions in the $\alpha$-diastereomer of **7** are minimal. Thus it is not surprising that the staggered conformation shown in Fig. 2 is observed. Staggering through the C(8)–C(9) bond reduces the potential steric interactions between the *o*-disubstituted alkyl groups and the carbonyl ligand. The crystal structure agrees with the preferred rotamer of the $\alpha$-diastereomer of **7** in solution phase deduced above from the 400 MHz $^1$H NMR data. Interestingly, the $Cr(CO)_3$ tripod is not symmetrically staggered, but exhibits partial eclipsing towards C(8), C(11), and C(13). This may be the result of interaction between the CO ligand staggered through the C(8)–C(9) bond with the benzylic C(7$\alpha$) proton which projects below the plane of the diterpenoid molecule. Moreover, the relative orientation of the carbonyl ligands differs from that determined for the $\alpha$-diastereomer of the 12-methoxy derivative [4]. In the latter case the methoxy substituent exerts a dominant electronic effect which results in near eclipsing of C(9), C(12), and C(14).

## References


1 R.C. Cambie, P.S. Rutledge, M. Tercel, and P.D. Woodgate, J. Organomet. Chem., 315 (1986) 171.
2 R.C. Cambie, K.P. Mathai, and A.W. Missen, Aust. J. Chem., 25 (1972) 1253.
3 W. Strohmeier, Chem. Ber., 94 (1961) 2490.
4 R.C. Cambie, G.R. Clark, A.C. Gourdie, P.S. Rutledge, and P.D. Woodgate, J. Organomet. Chem., 297 (1985) 177.
5 C.A.L. Mahaffy and P.L. Pauson, Inorg. Synth., 19 (1979) 154.
6 E.P. Kundig, C. Perret, S. Spichiger, and G. Bernadinelli, J. Organomet. Chem., 286 (1985) 183.
7 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551.
8 W.R. Jackson, B. Nicholls, and M.C. Whiting, J. Chem. Soc. I, (1960) 469.
9 M.P. Williamson, R.J. Kostelnik, and S.M. Castellano, J. Chem. Phys., 49 (1968) 2218.
10 E. Wenkert, A. Afonso, P. Beak, R.W.J. Carney, P.W. Jeffs, and J.D. McChesney, J. Org. Chem., 30 (1965) 713.

11 S.F. Dyke, A.J. Floyd, M. Sainsbury, and R.S. Theobald, Organic Spectroscopy: An Introduction, Longman Group, 1978, p. 172.
12 E. Wenkert, B.L. Buckwalter, I.R. Burfitt, M.J. Gǎsić, H.E. Gottlieb, E.W. Hagaman, F.M. Schell, and P.M. Wovkulich, Topics in Carbon-13 NMR Spectroscopy, 2 (1976) 81.
13 K.S. Seshadri, R.G. Ruberto, D.M. Jewell, and H.P. Malone, Fuel, 57 (1978) 111.
14 F. Van Meurs, J.M. Van der Toorn, and H. Van Bekkum, J. Organomet. Chem., 113 (1976) 341.
15 A. Solladié-Cavallo, and J. Suffert, Org. Mag. Res., 14 (1980) 426.
16 E.P. Kundig, Pure Appl. Chem., 57 (1985) 1855.
17 M.F. Semmelhack, H.T. Hall Jr., R. Farina, M. Yashifuji, G.R. Clark, T. Bargar, K. Hirotsu, and J. Clardy, J. Am. Chem. Soc., 101 (1979) 3535.
18 F. Sher, J.L. Isidor, H.R. Taneja, and R.M. Carlson, Tetrahedron Lett., (1973) 577.
19 R.M. Carlson and P.M. Helquist, J. Org. Chem., 33 (1968) 2596.
20 R.C. Cambie, R.C. Hayward, and A.W. Missen, Aust. J. Chem., 27 (1974) 2413.
21 M.S. Newman and H.V. Zahm, J. Am. Chem. Soc., 65 (1943) 1097.
22 W.A. Szarek, A. Zamojski, K.N. Tiwari, and E.R. Ison, Tetrahedron Lett., 27 (1986) 3827.
23 R.H. Shapiro, T.E. McEntee Jr., and D.L. Coffen, Tetrahedron, 24 (1968) 2809.
24 J-L. Luche and A.L. Gemal, J. Chem. Soc. Chem. Commun., (1978) 976.
25 Y. Kamitori, M. Hojo, R. Masuda, T. Kimura, and T. Yoshida, J. Org. Chem., 51 (1986) 1427.
26 E.J. Corey and D. Seebach, Angew. Chem. Int. Ed., 4 (1965) 1075.
27 T. Mukaiyama, K. Narasaka, and M. Furusato, J. Am. Chem. Soc., 94 (1972) 8641.
28 E.P. Kundig and D.P. Simmons, J. Chem. Soc. Chem. Commun., (1983) 1320.
29 M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thebtaranonth, W. Wulff, and A. Yamashita, Tetrahedron, 37 (1981) 3957.
30 R.R. Fraser and T.S. Mansour, J. Organomet. Chem., 310 (1986) C60.
31 M. Uemura, N. Nishikawa, K. Take, M. Ohnishi, K. Hirotsu, T. Higuchi, and Y. Hayashi, J. Org. Chem., 48 (1983) 2349.
32 M. Fukui, T. Ikeda, and T. Oishi, Chem. Pharm. Bull., 31 (1983) 466.
33 M.F. Lipton, C.M. Sorenson, A.C. Salder, and R.H. Shapiro, J. Organomet. Chem., 186 (1980) 155.
34 E.J. Corey and D. Seebach, Org. Synth., 50 (1970) 72.
35 D.R. Williams, D.L. Coffen, P.E. Garrett, and R.N. Schwartz, J. Chem. Soc. B, (1968) 1132.
36 D. Seebach, Synth., 1 (1969) 17.
37 A. Hoppmann, P. Weyerstahl, and W. Zummack, Ann., (1977) 1547.