Homoleptic Optically Active Ditungsten and Dimolybdenum Alkoxides. The Crystal Structure of $(+)[W_2(OC_{10}H_{19})_6]$†

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Reaction of optically resolved menthol (1*R*,2*S*,5*R* or 1*S*,2*R*,5*S*) with $[M_2(NMe_2)_6]$ or $[M_2(OBu^t)_6]$ (M = Mo or W) in hexane produces (+)- or (−)-$[M_2(OC_{10}H_{19})_6]$ respectively in high yield (86–98%). The $[M_2(OC_{10}H_{19})_6]$ compounds are air sensitive, extremely soluble in hydrocarbon solutions and have decomposition points of 174–177 °C. Characterization was achieved by ^1H, ^{13}C, $^{13}C-\{^1H\}$ NMR, IR, CD, ORD, UV and mass spectrometry. For $(+)[W_2(OC_{10}H_{19})_6]$ X-ray crystallography revealed two independent molecules in the unit cell, both d^3–d^3 ethane-like dimers: space group *P*1, *a* = 15.439(3), *b* = 15.883(3), *c* = 13.684(3) Å, α = 104.4(1), β = 99.10(1), γ = 94.27(1)°, *Z* = 2; W≡W 2.338 (average), W–O 1.88 Å (average). Reaction of $[W_2(NMe_2)_6]$ with neomenthol produces $[W_2(NMe_2)(OC_{10}H_{19})_5]$ in high yield. Reaction of $[W_2(OC_{10}H_{19})_6]$ with MeCN produces $[\{WN(OC_{10}H_{19})_3\}_x]$ and $[W(CMe)(OC_{10}H_{19})_3]$ and with hex-3-yne produces $[W(CEt)(OC_{10}H_{19})_3]$ and polyhexyne. Reaction of $(+)[W_2(OC_{10}H_{19})_6]$ with 6 equivalents of L-$HOC_{10}H_{19}$ produces racemic $[W_2(OC_{10}H_{19})_6]$ in less than 5 min. Treatment of $[\{MoN(OBu^t)_3\}_x]$ with menthol produces the optically active polymer $[\{MoN(OC_{10}H_{19})_3\}_x]$.

Chirality is an integral part of nature. For example, the human body is composed largely of L-amino acids.[1] Enormous effort has been made in organic and biological chemistry to reproduce nature's efficient formation of enantiomerically pure materials.[2] Indeed, reactions with the wrong diastereomer may fail to occur or can lead to different product distributions. Inorganic chemistry has played a role in such reactivity studies, highlighted by the achievement of enantiomeric control in olefinic epoxidation using optically active titanium tartrate complexes.[3]

Heppert *et al.*[4] have demonstrated the formation of the first class of optically active dimetallic bis(naphtholate) *tert*-butoxide complexes. Unfortunately, the enantiomerically pure starting material is expensive and the dimetallic compounds are formed in moderate yield. Introduction of chiral agents in dimetallic chemistry is advantageous because such systems are known to promote reactions such as polymerization and carbon monoxide cleavage.[5] In many instances an active catalyst is generated which can perform multiple reactions. In such systems a variety of organic products are produced, for example polyacetylene, stilbenes, alkanes and alkenes, which are often difficult to prepare by conventional routes.[6] Although the amounts of organic materials produced so far are small, and isolation non-trivial, the introduction of chirality into organic fragments would be extremely advantageous.[7] By using a chiral dimetallic compound it may be possible to induce a particular geometric isomer or stereoisomer in these transformations.

To this end we describe here the high-yield synthesis (86–98%) of homoleptic optically active mentholate (2-isopropyl-5-methylcyclohexanolate) complexes of ditungsten and dimolybdenum starting from D- or L-menthol. Further the reactions of these compounds with unsaturated hydrocarbons and acetonitrile are described.

Results and Discussion

Synthesis.—Reaction of D- or L-menthol with $[M_2(NMe_2)_6]$ (M = Mo or W) in hexane produces optically pure $[M_2(OC_{10}H_{19})_6]$ in high yield (95%), equation (1). The

$$[M_2(NMe_2)_6] + 6HOC_{10}H_{19} \xrightarrow{\text{hexane}} 6NMe_2H + [M_2(OC_{10}H_{19})_6] \quad (1)$$

reaction, which may be monitored by ^1H NMR spectroscopy, showed the formation of dimethylamine gas and a number of intermediates, postulated as $[M_2(NMe_2)_2(OC_{10}H_{19})_4]$ and $[M_2(NMe_2)_4(OC_{10}H_{19})_2]$. The reaction of $[M_2(OBu^t)_6]$ (M = Mo or W) with D- or L-menthol proceeds analogously and with comparable yields, equation (2). The time required for

$$[M_2(OBu^t)_6] + 6HOC_{10}H_{19} \xrightarrow{\text{hexane}} 6HOBu^t + [M_2(OC_{10}H_{19})_6] \quad (2)$$

complete alcoholysis of complexes such as $[M_2(NMe_2)_6]$ and $[M_2(OR)_6]$ (M = Mo or W) is dependent on the steric size of the alcohol, with small alcohols requiring shorter reaction times. Alcoholysis of $[W_2(NMe_2)_6]$ by menthol proceeds in a few hours. The reaction is both favoured entropically, due to the loss of NMe_2H (g), and enthalpically, since the metal–oxygen bonds formed are stronger than the metal–nitrogen bonds broken. Mentholysis of $[W_2(OBu^t)_6]$ requires ⩾6 h for completion. Indeed removing the solvent *in vacuo* and redissolving the residue several times eliminates Bu^tOH and accelerates the reaction. The rate of reaction is slow because of the similar steric size of menthol and Bu^tOH.

Complexes of the type $[M_2(OC_{10}H_{19})_6]$ are exceedingly air sensitive, both as solids and in solution, decomposing to brown oils or brown solutions after a few seconds exposure to air. They are extremely soluble in hydrocarbon solvents (*ca.* 1 g per 3 cm^3) and ethers. Sublimation of $[M_2(OC_{10}H_{19})_6]$ at 110 °C (1×10^{-4} Torr) is accompanied by significant decomposition. The $[M_2(OC_{10}H_{19})_6]$ complexes have comparable melting points (174–7 °C) to those of $[M_2(OC_6H_{11})_6]$ (M = Mo or W).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: Torr = 133 Pa.

Table 1 Circular dichroism, optical rotatory dispersion and ultraviolet data for the new complexes

	CD			ORD			UV	
Compound	λ/nm	$[\psi]_\lambda$[a]	$[\theta]_\lambda$[a]	λ/nm	$[\alpha]_\lambda$[a]	$[M]_\lambda$[a]	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
$(+)[W_2(OC_{10}H_{19})_6]$	447	(+)179	(+)2330	495	(+)113	(+)1470	436	600
	385	(−)221	(−)2890	415	(−)167	(−)2180	358	1550
$(-)[W_2(OC_{10}H_{19})_6]$	447	(−)179	(−)2330	495	(−)113	(−)1470	436	600
	385	(+)221	(+)2890	415	(+)167	(+)2180	358	1550
$(+)[Mo_2(OC_{10}H_{19})_6]$	452	(+)124	(+)1400				392	1200
$(-)[Mo_2(OC_{10}H_{19})_6]$	452	(−)124	(−)1400				392	1200
$(-)[MoN(OC_{10}H_{19})_3]$	286	(−)120	(−)694					
	262	(+)195	(+)1130					
$[W_2(neo\text{-}NMe_2)(OC_{10}H_{19})_5]$	470	(+)24.6	(+)332	505	(+)62	(+)830		
	417	(+)29.6	(+)400	455	(+)55	(+)726		
	377	(−)31.6	(−)426	430	(+)61	(+)748		
				355	(+)86	(+)1143		

[a] $[\Psi]_\lambda$ = specific ellipticity, $[\theta]_\lambda$ = molar ellipticity, $[\alpha]_\lambda$ = specific rotation and $[M]_\lambda$ = molar rotation = $[\alpha]_\gamma \times M/100$, units are deg cm^2 dmol^{-1}, [b] For $[W_2(OC_{10}H_{19})_6]$, λ_{max} = 264 nm, ε = 4000 dm^3 mol^{-1} cm^{-1}; for $[Mo_2(OC_{10}H_{19})_6]$, λ_{max} = 275nm, ε = 6400 dm^3 mol^{-1} cm^{-1}.

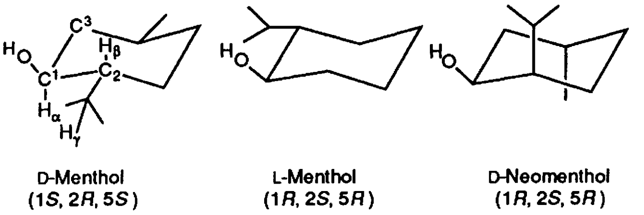

Fig. 1 Stick drawing of the different forms of menthol with the atom numbering referred to in the Discussion

Spectroscopic Characterization.—Characterization of $[M_2(OC_{10}H_{19})_6]$ (M = Mo or W; D- or L-mentholate) was achieved by IR, UV, CD/ORD, ^{1}H and ^{13}C NMR spectroscopy and in the case of $(+)[W_2(OC_{10}H_{19})_6]$ by X-ray crystallography. The infrared spectra showed the expected menthoxide vibrations and were almost identical to that of the starting menthol with the exception of the O–H stretch.

The ^{1}H NMR spectra of $[W_2(OC_{10}H_{19})_6]$ show characteristic menthoxide resonances. A triplet of doublets at δ 5.14 is indicative of H_α (Fig. 1) and is deshielded by 1.8 ppm compared to menthol. A septet of doublets is seen at δ 2.57, with an integrated intensity of one, attributable to H_γ, whilst a broad doublet at δ 2.65 of integral one is presumably due to H_β. Three doublets due to methyl groups are observed, indicating that all the menthoxide ligands are equivalent on the ^{1}H NMR timescale. Proton NMR spectra of (+)- and $(-)$-$[W_2(OC_{10}H_{19})_6]$ are identical and invariant with temperature (−75 to +45 °C). Similarly the spectra of (+)- and $(-)$-$[Mo_2(OC_{10}H_{19})_6]$ are identical to each other and closely resemble those of their tungsten counterparts.

The ^{13}C-{^{1}H} and ^{13}C NMR spectra of (+)- or (−)-$[Mo_2(OC_{10}H_{19})_6]$ and (+)- or $(-)$-$[W_2(OC_{10}H_{19})_6]$ are very similar and both show ten resonances due to the menthoxide groups in the range of δ +82.6 to +16.4. The apical carbon atom is deshielded from δ +71.2 for menthol to +82.6 for the complex $[W_2(OC_{10}H_{19})_6]$. This is due to an inductive electron withdrawal towards the tungsten atom, and appears as a doublet in the proton-coupled spectrum (split by H_α) with $^1J(^{13}C-^1H)$ 146 Hz. The C^2 and C^3 carbons (Fig. 1) are deshielded by 2 and 2.5 ppm with respect to the corresponding carbon atoms of free menthol, whilst the other carbon atoms have essentially the same chemical shifts as that of the free ligand.

Optical spectroscopy. The UV spectra of $[M_2(OC_{10}H_{19})_6]$ are presented in Table 1. For $[W_2(OC_{10}H_{19})_6]$ two absorption bands in the region 800–300 nm are observed at 436 and 358 nm, whilst $[Mo_2(OC_{10}H_{19})_6]$ has only one band at 392 nm. The absorption coefficients for these bands are quite weak (600–1550 dm^3 mol^{-1} cm^{-1}) and analogous to those of other $[M_2(OR)_6]$ complexes, where they have been previously assigned as metal-based π–π* and $^3(\pi$–π*) transitions.[8]

Circular dichroism (CD) and optical rotatory dispersion (ORD) spectroscopic data are given in Table 1 for the $[M_2(OC_{10}H_{19})_6]$ and $[MoN(OC_{10}H_{19})_3]$ complexes. Fig. 2 gives the combined CD/ORD spectra for (+)- and $(-)$-$[W_2(OC_{10}H_{19})_6]$ and Fig. 3 the spectra for $(+)$-$[Mo_2(OC_{10}H_{19})_6]$. Fig. 2 shows that the (+)/(−) forms of $[W_2(OC_{10}H_{19})_6]$ are exact mirror images of each other with respect to the CD/ORD behaviour. The CD spectrum of $[W_2(OC_{10}H_{19})_6]$ shows two absorptions at 447 and 385 nm respectively, which correspond to absorptions at 436 and 365 nm in the UV spectrum. For $(+)[W_2(OC_{10}H_{19})_6]$ the first peak has a (+) Cotton effect whilst the second has a (−)Cotton effect; the opposite is true for $(-)[W_2(OC_{10}H_{19})_6]$. The spectrometer was capable of scanning to 250 nm, although no CD peaks were observed for either (+) or (−) forms between 385 and 250 nm. Menthol and neomenthol have no CD absorptions between 700 and 200 nm, thus the bands observed for $[M_2(OC_{10}H_{19})_6]$ complexes are consistent with p_π–d_π ligand-to-metal charge transfer or mixing of ligand-orbital character in the M–M multiple bond.[8]

There is no alteration in the CD or ORD spectra of $(+)[W_2(OC_{10}H_{19})_6]$ on changing solvent from hexane to toluene. Formation of a racemic $(\pm)[W_2(OC_{10}H_{19})_6]$ complex by treating equal amounts of (+)- and (−)-menthol with $[W_2(NMe_2)_6]$ gave no CD or ORD spectra in the range 700–250 nm but it did give a similar UV spectrum to those of (+)- and $(-)$-$[W_2(OC_{10}H_{19})_6]$.

The CD spectrum of $(+)[Mo_2(OC_{10}H_{19})_6]$ shows only one band in the region 700–330 nm at 452 nm with a (+)Cotton effect. As for the tungsten analogue, $(-)[Mo_2(OC_{10}H_{19})_6]$ was found to be the mirror image of $(+)[Mo_2(OC_{10}H_{19})_6]$. In the UV spectra two absorptions are observed at 392 and 275 nm for $[Mo_2(OC_{10}H_{19})_6]$. In the UV spectra two absorptions are observed at 392 and 275 nm for $[Mo_2(OC_{10}H_{19})_6]$ The high-intensity UV absorption of $(+)[Mo_2(OC_{10}H_{19})_6]$ at 275 nm does not correspond to a CD measurement, indicating that this transition is metal-based on orbitals that are little mixed with those of the ligands.

$(+)[W_2(NMe_2)(neo\text{-}OC_{10}H_{19})_5]$.—Reaction of $[W_2(NMe_2)_6]$ with (six-fold excess) neomenthol for 16 h at room temperature (r.t.) produces $(+)[W_2(NMe_2)(neo\text{-}OC_{10}H_{19})_5]$ in high yield (90%), equation (3). Allowing a longer reaction time (10 d), heating (65 °C) and addition of excess of neomenthol does not force complete substitution.

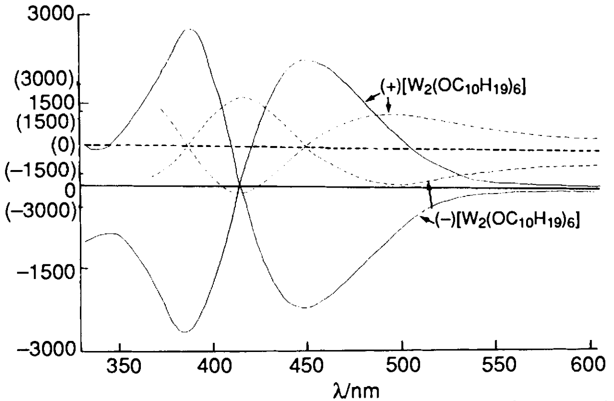

Fig. 2 Combined CD (——) and ORD (– – –) spectra of (+)- and (−)-$[W_2(OC_{10}H_{19})_6]$

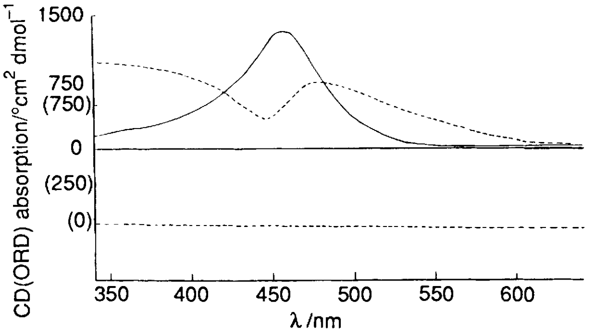

Fig. 3 The CD (——) and ORD (– – –) spectra of (+)$[Mo_2(OC_{10}H_{19})_6]$

The orange-red solid formed on removal of the solvent *in vacuo* equation (3) is extremely soluble in hydrocarbon solvents

$$[W_2(NMe_2)_6] + 6\textit{neo}\text{-}HOC_{10}H_{19} \xrightarrow{\text{hexane}} 5NMe_2H + HOC_{10}H_{19} + (+)[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5] \quad (3)$$

and is air and moisture sensitive. It can be grown as large orange plate-like crystals by slowly cooling saturated hexane solutions from +65 °C to r.t. The product (+)$[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5]$ was characterized by microanalysis, m.p., IR, ^1H, ^{13}C and $^{13}C\text{-}\{^1H\}$ NMR, and CD/ORD/UV spectroscopies. The ^1H NMR spectrum is complex but does show five resonances (each a triplet of doublets) in the region δ 5.4–4.1, attributable only to the α-protons (the remaining protons on a co-ordinated neomenthoxide ligand occur below δ 2.4). Two further resonances at δ 4.05 and 2.10 respectively, each of relative integral ratio three, show temperature-variant behaviour with a coalescence point of 85 °C. No other regions of the spectrum show temperature-dependent behaviour over the range 20–110 °C in toluene. This observation is explained by the presence of proximal and distal diastereotopic methyl groups on a co-ordinated dimethylamide ligand, which become equivalent on raising the temperature.[9]

The co-ordinated dimethylamide ligands in $[W_2(NMe_2)_6]$ are formally doubly bonded to the metal. On heating, the π component of the M=N bond is broken and the dimethylamides rotate about the M–N bond at a rate measurable by ^1H NMR spectroscopy, thus equilibrating the proximal and distal groups.[10]

The $^{13}C\text{-}\{^1H\}$ NMR spectrum of (+)$[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5]$ shows ten resonances of approximate intensity five and two resonances of intensity one. There are five carbon resonances in the region of δ +81.9 to 73.7 due to C^1, consistent with five inequivalent neomenthoxide ligands (Fig. 1). The gated coupled spectra showed that all five resonances split into doublets with a ^1J(C–H) coupling constant of 146 Hz. Indeed all of the other neomenthoxide carbon atoms appear as a cluster of five lines or an overlap of five lines except for the two resonances at δ 59.4 and 40.4 which are assigned to the dimethylamide proximal and distal carbons and split into quartets in the gated coupled spectra with ^1J(C–H) 130 and 132 Hz respectively.

The IR spectrum of (+)$[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5]$ is much more complicated than those of the homoleptic $[W_2(OC_{10}H_{19})_6]$ complexes although the dimethylamide vibrations could not be discerned with accuracy. The melting point is 125 °C and is lower than that of (+)$[W_2(OC_{10}H_{19})_6]$.

The formation of (+)$[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5]$ is very unusual and is possibly the first example of a singly co-ordinated dimethylamide ligand left during an alcoholysis reaction of $[W_2(NMe_2)_6]$ with an excess (> six-fold) of alcohol. Typically, alcohol substitution reactions of $[W_2(NMe_2)_6]$ go to completion as is the case for Bu^tOH, neopentanol and cyclohexanol. Alternatively, the dimethylamides are replaced in a pairwise manner.[11] For example, reaction of excess (> six-fold) Ph_3COH with $[M_2(NMe_2)_6]$ replaces two dimethylamide groups to form $[M_2(NMe_2)_4(OCPh_3)_2]$ (M = Mo or W), whilst reaction with triphenylsilanol forms $[M_2(NMe_2)_2(OSiPh_3)_4]$ through the isolable intermediate $[M_2(NMe_2)_4(OSiPh_3)_2]$.[12] The reason for incomplete alcoholysis with neomenthol is undoubtedly steric in orgin. The Pr^i and methyl substituent groups on neomenthol are in the axial position, thus making the molecule more sterically demanding than menthol. This steric factor is unique in allowing replacement of only five dimethylamides; the access of a sixth neomenthol is blocked by crowding at the W_2 core.

The ORD/CD spectra of (+)$[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5]$ are different to that of optically pure (+)$[W_2(OC_{10}H_{19})_6]$. The magnitude of both CD and ORD effects is between $\frac{1}{2}$ and $\frac{1}{3}$ of those measured for either (+)$[Mo_2(OC_{10}H_{19})_6]$ or (+)-$[W_2(OC_{10}H_{19})_6]$ and this corresponds to the weaker ORD effect of D-neomenthol compared to D-menthol, α(589.3 nm, 23 °C) = +48° and α(589.3 nm, 22 °C) = +17.3°. Three CD peaks are observed for (+)$[W_2(NMe_2)(\textit{neo}\text{-}OC_{10}H_{19})_5]$ at 470(+), 417(+) and 377 nm (− Cotton effect).

Menthol Exchange Reactions.—Addition of a twelve-fold excess of D-menthol to a hexane solution of (−)$[W_2(OC_{10}H_{19})_6]$ and immediately obtaining the CD spectrum shows approximately a one-third concentration of (+)$[W_2(OC_{10}H_{19})_6]$. This indicates that the exchange rate of D- and L-menthol in $[W_2(OC_{10}H_{19})_6]$ is extremely rapid.

Mixing (+)$[W_2(OC_{10}H_{19})_6]$ with exactly 6 equivalents of L-menthol generates no CD spectrum. The ^1H NMR spectrum of this mixture displays eight resonances of unequal intensity for the α-hydrogen from δ 5.7 to 4.5. This suggests that the racemic (±) complex contains both D- and L-menthoxide groups on the same dimetallic core, otherwise only one α-hydrogen resonance would be observed.

The (±)$[W_2(OC_{10}H_{19})_6]$ compound made by treating $[W_2(NMe_2)_6]$ with equimolar quantities of D- and L-menthol shows eight resonances of unequal intensity for C^1 in the $^{13}C\text{-}\{^1H\}$ NMR spectra and eight resonances for the C^2 peak. The other carbon resonances are broadened and fine detail is more difficult to discern. For C^1 the resonances occur in the range of δ +87.3 to +78.5. This indicates that the racemic compound consists of a statistical mix of (+) and (−) isomers [*i.e.* 6(+),0(−); −0(+),6(−)] on each W_2 unit, since if only all (+) or all (−) species were present only one resonance at δ 82.6 would be observed for C^1. Having mixed-chirality menthoxides on a W_2 unit would interfere with the free rotation of these ligands and orient the Pr^i groups differently to those observed in pure (+)- or pure (−)-$[W_2(OC_{10}H_{19})_6]$ complexes.

For steric reasons it would be unlikely that $[W_2(OC_{10}H_{19})_6$-

$(HOC_{10}H_{19})_n]$ (n = 1 or 2) could form and be responsible for the observed CD and ^{1}H NMR spectra of the mixed-ligand complex. Indeed, a solution of (+)[$W_2(OC_{10}H_{19})_6$] and D-menthol gives no evidence for a co-ordinated menthol by ^{1}H or ^{13}C NMR spectroscopy. There is no contact shift for menthol and no change in the [$W_2(OC_{10}H_{19})_6$] NMR spectra are noted.

Addition of 6 equivalents of D-$HOC_{10}H_{19}$ to a solution of (−)[$W_2(OC_{10}H_{19})_6$] shows a complete scrambling after 5 min (or less), with the observation of only racemic (±)[$W_2(OC_{10}H_{19})_6$] and free menthol by ^{1}H NMR spectroscopy. This indicates that the rate of alcohol exchange in these complexes is extremely rapid. Previous studies have indicated that dinuclear tungsten compounds can undergo self-exchange reactions either by intermolecular exchange *via* alkoxide bridges or by reversible cluster (tetranuclear W_4 core) formation.[11]

The ^{1}H NMR spectrum (in C_6D_6) of crystals containing equimolar quantities of (+)- and (−)-[$W_2(OC_{10}H_{19})_6$] indicates that no measurable interchange to the racemic (±)[$W_2(OC_{10}H_{19})_6$] species (*i.e.* both D- and L-menthol on the same core) occurs 5 min after mixing. After a period of 14 h approximately 50% conversion has taken place, and the solution contains 25% (+)-, 25% (−)- and 50% (±)-[$W_2(OC_{10}H_{19})_6$]. This process of intimate racemization is slow and is probably due to a trace of free menthol or some minute hydrolysis products catalysing the exchange. It would seem unlikely that alkoxide bridge formation or a dimer–tetramer equilibrium were present, as the rate of racemization is so slow at room temperature.[11]

The melting point of (+)- or (−)-[$W_2(OC_{10}H_{19})_6$] is 174–177 °C (decomp.), the racemic compound (±)[$W_2(OC_{10}H_{19})_6$] melts at a lower temperature, 85–90 °C (decomp.).

Reaction of (+)[$W_2(OC_{10}H_{19})_6$] *with Acetonitrile*.—Ditungsten hexaalkoxides are known to undergo metathesis cleavage reactions with nitriles to form a metal nitride and metal alkylidyne;[13] the products may be easily separated, as only the alkylidyne is hexane soluble. Reaction of (−)[$W_2(OC_{10}H_{19})_6$] with acetonitrile produced two main products by ^{1}H and ^{13}C NMR spectroscopy consistent with a mixture of [$WN(OC_{10}H_{19})_3$] and [$W(CMe)(OC_{10}H_{19})_3$] [equation (4)]. The

$$[W_2(OC_{10}H_{19})_6] + MeC{\equiv}N \xrightarrow{\text{hexane}} [WN(OC_{10}H_{19})_3] + [W(CMe)(OC_{10}H_{19})_3] \quad (4)$$

high hexane solubility of both [$WN(OC_{10}H_{19})_3$] and [$W(CMe)(OC_{10}H_{19})_3$] made separation difficult; sublimation also provided ineffective and differential crystallization from a saturated hexane solution produced two types of very pale yellow crystals.

Reaction of (+)[$W_2(OC_{10}H_{19})_6$] *with hex-3-yne*.—Addition of an excess (>six-fold) of hex-3-yne to (−)[$W_2(OC_{10}H_{19})_6$] in hexane produces a colourless amorphous air-stable solid, characterized by IR spectroscopy to be poly(hex-3-yne). The addition of 1.2 molar equivalents of hex-3-yne to (−)[$W_2(OC_{10}H_{19})_6$] causes a darkening in the colour of the solution from orange to brown. Reducing the solvent volume by half *in vacuo* followed by cooling to −20 °C produces pale yellow rod-shaped crystals. These were assigned as [$W(CEt)(OC_{10}H_{19})_3$] on the basis of ^{13}C, ^{13}C-{^{1}H}, ^{1}H NMR and IR spectroscopy [equation (5)].

$$[W_2(OC_{10}H_{19})_6] + EtC{\equiv}CEt \xrightarrow{\text{hexane}} 2[W(CEt)(OC_{10}H_{19})_3] \quad (5)$$

The ^{13}C-{^{1}H} NMR spectrum of [$W(CEt)(OC_{10}H_{19})_3$] showed the characteristic ten menthoxide ligand resonances and three other peaks of about one-third intensity at δ 350.4, 22.4 and 15.2. The peak at δ 350.4 is unsplit in the proton-coupled spectrum and is of the correct chemical shift for a tungsten alkylidyne resonance.[14] The resonances and δ 22.4 and 21.5 are due to the Et groups and are as such consistent in the proton-coupled spectra. The C^1 carbon of the menthoxide ligands, which occurs at δ 86.5, is deshielded with respect to free menthol and optically resolved [$M_2(OC_{10}H_{19})_6$] complexes. This is due to the higher formal oxidation state of the metal in [$W(CEt)(OC_{10}H_{19})_3$]. The ^{1}H NMR spectrum of [$W(CEt)(OC_{10}H_{19})_3$] shows only one type of α-hydrogen at δ 4.6 as a doublet of triplets. The rest of the spectrum is characteristic for the menthoxide ligands with the addition of a resonance at δ 2.4 possibly due to the CH_2 group of the alkylidyne chain.

Addition of excess of hex-3-yne to a 'polymerically active' solution (one that has already promoted polymerization) does produce further poly(hex-3-yne). The ^{1}H NMR shows the presence of [$W(CEt)(OC_{10}H_{19})_3$], although it is not clear if this is the active polymerization catalyst.

Formation of [{$MoN(OC_{10}H_{19})_3$}$_x$] *and* [{MoN(*neo*-$OC_{10}H_{19})_3$}$_x$].—Reaction of [{$MoN(OBu^t)_3$}$_x$] with D-, L-menthol or (+)-neomenthol in toluene at 40 °C for 12 h produces [{$MoN(OC_{10}H_{19})_3$}$_x$] in nearly quantitative yield [equation (6)]. The reaction can be followed by ^{1}H NMR

$$[\{MoN(OBu^t)_3\}_x] + 3HOC_{10}H_{19} \xrightarrow{\text{toluene}} [\{MoN(OC_{10}H_{19})_3\}_x] + 3Bu^tOH \quad (6)$$

spectroscopy which shows a variety of resonances due to intermediates, possibly [{$MoN(OBu^t)_2(OC_{10}H_{19})$}$_x$] and [{$MoN(OBu^t)(OC_{10}H_{19})_2$}$_x$]. Alcohol-exchange reactions of [$MoN(OBu^t)_3$] have been studied[14] with neopentanol and ethanol to produce a range of other molybdenum nitrides, for example [{$MoN(OCH_2Bu^t)_3$}$_x$] and [{$MoN(OEt)_3$}$_x$].

The compound [{$MoN(OC_{10}H_{19})_3$}$_x$] was characterized by microanalysis, melting point, CD, IR, ^{1}H and ^{13}C NMR spectroscopy. It is white, very air sensitive, both as a solid and in solution, and sublimes with some decomposition at 110 °C at 1 × 10^{-3} Torr. It is very soluble in aromatic hydrocarbon solvents and much more soluble than [$MoN(OBu^t)_3$] in hexane (*ca.* 2 g per 100 cm^3). The compound decomposes on melting around 180 °C. Crystals of (+)[{$MoN(OC_{10}H_{19})_3$}$_x$] could be grown as long white needles (*ca.* 1–2 cm in length) by slowly cooling a hexane solution from 65 °C to room temperature. Unfortunately these were unsuitable for X-ray diffraction.

The infrared spectrum of (+)[{$MoN(OC_{10}H_{19})_3$}$_x$] showed essentially menthoxide vibrations with possibly a metal–nitrogen stretch, tentatively assigned at 1005 cm^{-1}. Other M≡N stretches (M = Mo or W) have been observed[14] from 1030 to 970 cm^{-1}. The circular dichroism spectra of (−)[{$MoN(OC_{10}H_{19})_3$}$_x$] showed a negative Cotton effect at 286 nm and a positive Cotton effect at 262 nm.

The ^{1}H NMR spectra of (−)- and (+)-[{$MoN(OC_{10}H_{19})_3$}$_x$] were identical and showed a characteristic doublet of triplets at δ 5.15 assigned as the α-proton of the menthoxide ligands (Fig. 1). The higher-frequency end of the spectra, although characteristic of menthoxide groups, was complicated by overlapping resonances. Resonances due to the methyl group, however, can be readily observed as three sets of doublets, which suggest that on the ^{1}H NMR time-scale only one type of menthoxide ligand is present. The ^{13}C-{^{1}H} and ^{13}C NMR spectra allow structural connectivity assignments. The α-carbon (C^1 on Fig. 1) is most deshielded at δ 96.8 and is a doublet in the proton coupled spectra with ^1J(C–H) of 140 Hz. This carbon is more deshielded than in the parent menthol (δ 71.6) and [$W_2(OC_{10}H_{19})_6$] (δ 82.8), probably because molybdenum has a higher formal oxidation state. The other nine resonances fall in the range δ 50–16.4 and have similar chemical shifts (within 1–2 ppm) and splitting patterns in the proton-coupled spectrum as for [$W_2(OC_{10}H_{19})_6$].

The reaction of neomenthol with [{$MoN(OBu^t)_3$}$_x$] proceeds

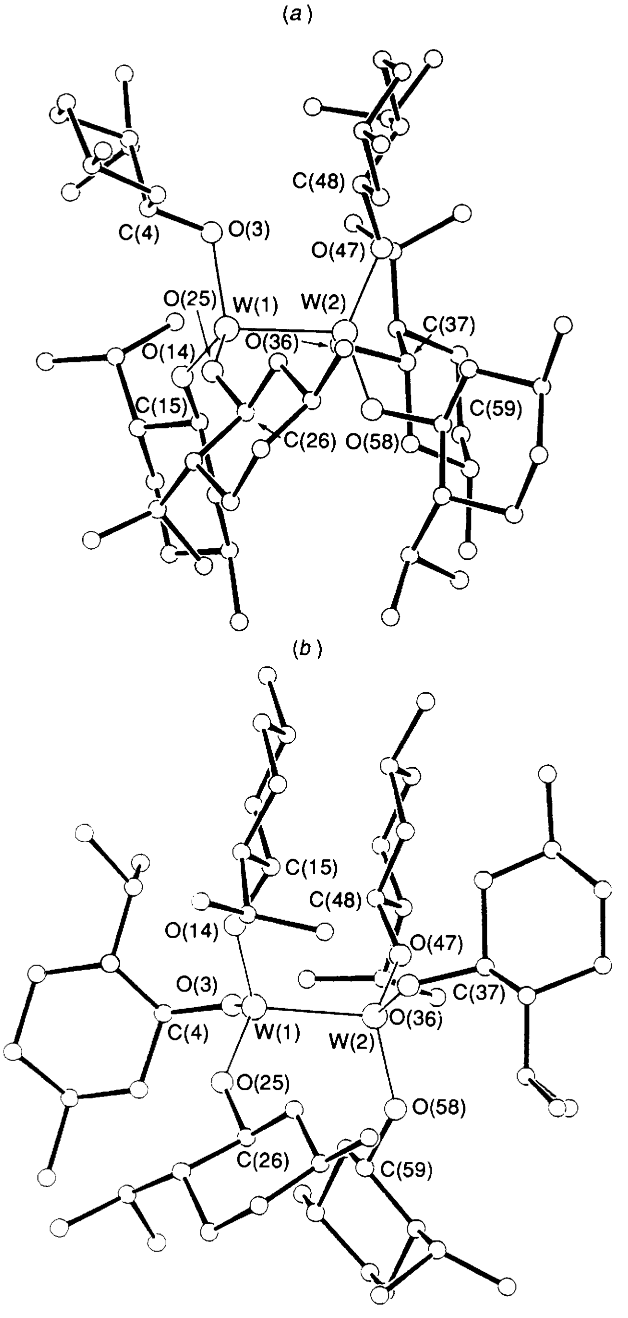

Fig. 4 Ball and stick diagrams of (+)[$W_2(OC_{10}H_{19})_6$] perpendicular to the W–W vector: (*a*) molecule A, (*b*) molecule B

analogously to the other menthol reactions. The ^1H NMR spectrum of the product, [{$MoN(\textit{neo}\text{-}OC_{10}H_{19})_3$}$_x$], has resonances characteristic of ligated neomenthoxide groups. It is different to that of [{$MoN(OC_{10}H_{19})_3$}$_x$] since neomenthol has a different ^1H NMR spectrum to menthol. Crystals suitable for X-ray diffraction were grown from hexane–neomenthol on slow cooling of a saturated hexane solution. Unfortunately, the *a* axis had a length of 54 Å, precluding a structural determination. The molecule possibly adopts a polymeric structure analogous to that of [{$MoN(OBu^t)_3$}$_x$]. Indeed, the long unit-cell axis would be consistent with this view perhaps with either a helical twist in the chain or a staggered 'rotation' of neomenthoxide groups about the *a* axis with a 54 Å repetition.

Crystallographic Studies.—Crystals of (+)- and (−)-[$W_2(OC_{10}H_{19})_6$] were grown by slowly cooling a saturated hexane solution (1 g per 3 cm^3) from +65 °C to room temperature. Both compounds have the same unit-cell dimensions. The structure of the (+) form was fully solved and showed two independent molecules in the unit cell; both are of d^3–d^3 ditungsten centres supported by menthoxide ligands in an ethane-like conformation.

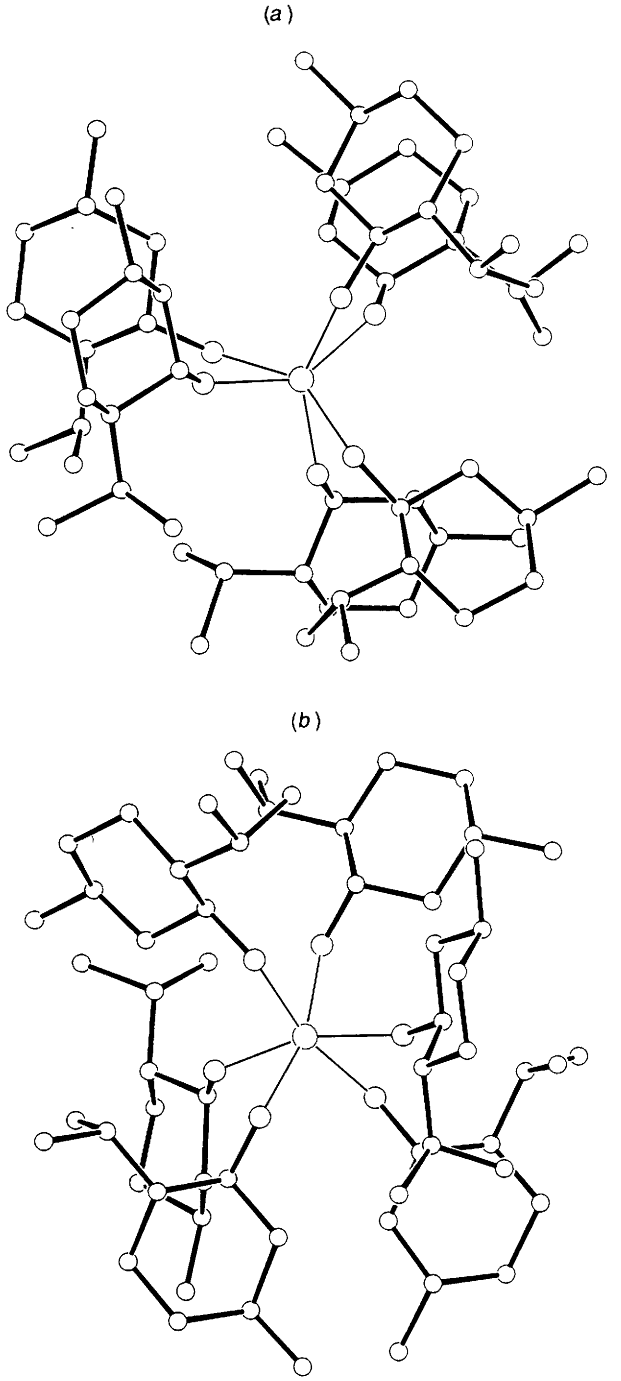

Fig. 5 Ball and stick diagrams of (+)[$W_2(OC_{10}H_{19})_6$] parallel to the W–W vector: (*a*) molecule A, (*b*) molecule B

The first independent molecule A is shown in Fig. 4(*a*) perpendicular and Fig. 5(*a*) parallel to the metal–metal axis. This shows a staggered conformation with a torsional angle O(3A)–W(1A)–W(2A)–O(47A) of 19.58° (Table 2). The Pr^i groups of the menthoxide ligands in molecule A are orientated on either tungsten such that two point in one direction and the remaining group is directed in a 'clockwise' fashion.*

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* Clockwise refers to the direction of rotation down the M–M vector when starting from the cyclohexane ring and moving to the extremity of the Pr^i group, as viewed in Fig. 5.

Table 2 Selected bond distances (Å) and angles (°) in (+)[$W_2(OC_{10}H_{19})_6$]

W(1A)–W(2A)	2.3383(6)	W(1B)–O(14B)	1.882(8)	O(47A)–C(48A)	1.472(15)
W(1A)–O(3A)	1.916(8)	W(1B)–O(25B)	1.880(8)	O(58A)–C(59A)	1.440(14)
W(1A)–O(14A)	1.878(8)	W(2B)–O(36B)	1.914(8)	O(3B)–C(4B)	1.454(14)
W(1A)–O(25A)	1.840(9)	W(2B)–O(47B)	1.884(7)	O(14B)–C(15B)	1.453(14)
W(2A)–O(36A)	1.886(9)	W(2B)–O(58B)	1.899(8)	O(25B)–C(26B)	1.449(15)
W(2A)–O(47A)	1.870(8)	O(3A)–C(4A)	1.416(13)	O(36B)–C(37B)	1.515(22)
W(2A)–O(58A)	1.933(8)	O(14A)–C(15A)	1.454(14)	O(47B)–C(48B)	1.432(14)
W(1B)–W(2B)	2.3367(8)	O(25A)–C(26A)	1.466(14)	O(58B)–C(59B)	1.426(14)
W(1B)–O(3B)	1.903(9)	O(36A)–C(37A)	1.514(15)		
W(2A)–W(1A)–O(3A)	100.81(24)	O(3B)–W(1B)–O(14B)	116.0(3)	W(1B)–O(3B)–C(4B)	128.9(8)
W(2A)–W(1A)–O(14A)	107.73(22)	O(3B)–W(1B)–O(25B)	117.4(3)	W(1B)–O(14B)–C(15B)	139.6(7)
W(2A)–W(1A)–O(25A)	107.73(25)	O(14B)–W(1B)–O(25B)	108.4(3)	W(1B)–O(25B)–C(26B)	141.7(7)
O(3A)–W(1A)–O(14A)	116.1(3)	W(1B)–W(2B)–O(36B)	102.77(24)	W(1B)–O(36B)–C(37B)	114.0(9)
O(3A)–W(1A)–O(25A)	112.7(3)	W(1B)–W(2B)–O(47B)	106.93(23)	W(1B)–O(47B)–C(48B)	143.4(7)
O(14A)–W(1A)–O(25A)	110.8(4)	W(1B)–W(2B)–O(58B)	107.44(24)	W(1B)–O(58B)–C(59B)	140.5(7)
W(1A)–W(2A)–O(36A)	98.94(24)	O(36B)–W(2B)–O(47B)	111.8(3)		
W(1A)–W(2A)–O(47A)	107.60(26)	O(36B)–W(2B)–O(58B)	114.9(3)	O(3A)–W(1A)–W(2A)–O(47A)	19.58
W(1A)–W(2A)–O(58A)	100.06(23)	O(47B)–W(2B)–O(58B)	112.1(4)	O(14A)–W(1A)–W(2A)–O(36A)	24.49
O(36A)–W(2A)–O(47A)	112.5(4)	W(1A)–O(3A)–C(4A)	118.9(7)	O(25A)–W(1A)–W(2A)–O(58A)	22.40
O(36A)–W(2A)–O(58A)	118.9(3)	W(1A)–O(14A)–C(15A)	138.8(7)	O(3B)–W(1B)–W(2B)–O(47B)	42.15
O(47A)–W(2A)–O(58A)	115.6(3)	W(1A)–O(25A)–C(26A)	143.7(7)	O(14B)–W(1B)–W(2B)–O(36B)	39.82
W(2B)–W(1B)–O(3B)	96.86(24)	W(2A)–O(36A)–C(37A)	119.5(7)	O(25B)–W(1B)–W(2B)–O(58B)	43.81
W(2B)–W(1B)–O(14B)	107.98(23)	W(2A)–O(47A)–C(48A)	140.0(8)		
W(2B)–W(1B)–O(25B)	109.03(25)	W(2A)–O(58A)–C(59A)	123.2(7)		

The second independent molecule B is shown in Fig. 4(*b*) perpendicular and Fig. 5(*b*) parallel to the metal–metal axis. This molecule has a more staggered geometry looking down the M–M vector with a torsional angle O(25B)–W(1B)–W(2B)–O(58B) of 43.8°. In this case all the isopropoxide groups of the menthoxide ligand centred on one tungsten atom point in the same direction, generating a 'clockwise' orientation, whilst on the remaining tungsten two menthoxide isopropoxide groups point in an 'anticlockwise' direction and the other in a 'clockwise sense'. The difference between the two independent molecules A and B is the change in orientation of two menthoxide groups so that the Pr^i groups are aligned in an opposite sense. The resulting increase in steric non-bonding repulsion promotes a more staggered geometry for molecule B.

The M–M distance, of 2.3383(6) Å in molecule A and 2.3367(8) Å in B are identical within the 3σ criteria and at the long end of a tungsten–tungsten triple bond (2.30 Å).[15] The W–O distances within the structure vary from 1.840(9)–1.933(8) Å in molecule A to 1.880(8)–1.914(8) Å in B. These distances are almost all equivalent and typical of a W–O bond length, in which there is some π donation from an occupied oxygen lone pair to the tungsten, indicating a degree of p_π–d_π multiple bonding.[16]

In molecule A three menthoxide ligands are distal and three proximal with respect to the dimetallic core. The distal groups have W–O–C angles of 118–123°, whilst the proximal groups have angles of 138.8–140.3°. Two proximal groups are present on one tungsten atom. In molecule B four of the menthoxide ligands are proximal to the metal–metal core with W–O–C angles of 141° (average) and two are distal with comparable angles of 120° (average). The distal menthoxide groups are orientated in an *anti* conformation with respect to each other about the metal–metal core.

Conclusion

The reaction of optically resolved menthol with [$M_2(NMe_2)_6$] or [$M_2(OBu^t)_6$] (M = Mo or W) produces [$M_2(OC_{10}H_{19})_6$], the first homoleptic optically active dimetallic compounds in high yield. Treatment of [$M_2(NMe_2)_6$] with neomenthol produces [$M(NMe_2)(OC_{10}H_{19})_5$] a rare example of an incomplete alcoholysis reaction, probably due to steric protection in the axially substituted menthol. The [$M_2(OC_{10}H_{19})_6$] complexes undergo metathesis cleavage with alkynes and nitriles to give optically active metal alkylidynes and nitrides. Exchange reactions of D- for L-menthoxide indicate that self-exchange is extremely rapid in [$M_2(OC_{10}H_{19})_6$] complexes but may require a proton source (either menthol or partially hydrolysed complex).

Metal–metal multiple bonds are known to undergo a variety of reactions with ketones, aldehydes and small molecules like NO and CO. Often this leads to formation of synthetically useful organic reagents. Such optically active dimetallic complexes may be capable of inducing chirality into organic fragments. Since [$M_2(OC_{10}H_{19})_6$] complexes are relatively inexpensive to synthesise they may find applications in asymmetric synthesis.

Experimental

General Procedures.—All manipulations were performed using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were distilled over sodium–benzophenone and then stored over 3 Å molecular sieves. Ditungsten hexa-*tert*-butoxide, [$\{MN(OBu^t)_3\}_x$] and [$M_2(NMe_2)_6$] (M = Mo or W) were made by standard procedures and recrystallized from hexane prior to use.[14,17] D-Neomenthol (1*S*,2*S*,5*R*) (>97%), D-menthol (1*S*,2*R*,5*S*) (>99%), L-menthol (1*R*,2*S*,5*R*) (>99%) and hex-3-yne were purchased from Aldrich Chemical and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as pressed KBr discs, UV spectra on a Hewlett-Packard 4852A spectrophotometer and CD/ORD spectra on a JASCO 20A instrument; ORD measurements were calibrated using L-sucrose of known concentrations. Proton and ^{13}C-{^1H} NMR spectra were obtained in C_6D_6 or $C_6D_5CD_3$ and referenced to internal solvent peaks on a Varian 300 spectrometer at 299.66 and 75.14 MHz respectively. Additional proton and carbon NMR spectra were obtained on a JEOL FX-90Q instrument at 89.99 and 22.17 MHz. Variable-temperature ^1H NMR spectra were recorded on the Varian 300 in $C_6D_5CD_3$ and the temperature calibrated with an external methanol standard. Microanalyses were provided by Oneida Research Services, Whiteboro, NY and Medac, Brunel University, Uxbridge, Middlesex. Mass spectra were provided by the SERC service in Swansea.

$[W_2(OC_{10}H_{19})_6]$.—The same general procedure was adopted for both D- and L-menthol, and is illustrated below for the D-isomer.

Method 1. To a solution of $[W_2(NMe_2)_6]$ (1.000 g, 1.582 mmol) dissolved in hexane (25 cm^3) at 35 °C was added D-menthol (1.400 g, 9.50 mmol) in hexane (30 cm^3). The solution was magnetically stirred for 16 h at room temperature with the colour gradually darkening from yellow to orange and finally to red. The solvent was removed *in vacuo* to leave $[W_2(OC_{10}H_{19})_6]$ as an orange semicrystalline solid (2.004 g, 1.544 mmol, 98% yield), m.p. 174–177 °C (decomp.) (Found: C, 54.95; H, 9.00. $C_{60}H_{114}O_6W_2$ requires C, 55.10; H, 8.85%). $\delta_H(C_6D_6)$ δ 5.14 (6 H, d of t), 2.77 (6 H, d), 2.65 (6 H, d), 2.57 (6 H, d of spt), 1.69 (24 H, m) and 1.11 (72 H, m, br) $\delta_C(C_6D_6)$ 82.7 (6 C, d, 148), 52.1 (6 C, d, *J* 125), 48.1 (6 C, t, 127), 35.2 (6 C, t, 126), 32.7 (6 C, d, 125), 25.5 (6 C, d, 132), 23.6 (6 C, t, 130), 22.7 (6 C, q, 130), 21.9 (6 C, q, 130) and 16.8 (6 C, q, 130 Hz). UV and ORD/CD results are presented in Table 1, and in Figs. 2 and 3. IR (ν_{max}): 2925s, 2875s, 2840s, 2760w, 1440s, 1360s, 1335m, 1310m, 1250w, 1220w, 1170m, 1140m, 1050s, 1020vs (br), 980vs, 910s, 870m, 840s, 860m, 690vs, 610m, 540w, 480m, 440 (sh), 390w and 320m cm^{-1}.

Crystals suitable for X-ray diffraction were obtained by slow cooling of a concentrated hexane solution (1 g per 3 cm^3) of $[W_2(OC_{10}H_{19})_6]$ from 65 °C to room temperature over a period of 16 h. The L-menthol form of $[W_2(OC_{10}H_{19})_6]$ has identical physical properties (^1H, ^{13}C NMR, m.p., IR, UV) as the D-menthol form with the exception of the CD/ORD results which are shown in Table 1, and was made in comparable yield.

Method 2. To a solution of $[W_2(OBu^t)_6]$ (0.200 g, 0.248 mmol) dissolved in hexane (3 cm^3) was added L-menthol (0.232 g, 1.49 mmol) in hexane (3 cm^3). The solution was magnetically stirred for 8 h at room temperature during which time the colour lightened from red to orange. The solvent was removed *in vacuo* to leave an oily orange solid. This was redissolved in hexane (3 cm^3) and the solvent stripped *in vacuo* giving $[W_2(OC_{10}H_{19})_6]$ (0.306 g, 0.236 mmol, 95%). The compound obtained by this method had the same physical characteristics (^1H, ^{13}C NMR, ORD/CD spectra) as that prepared from $[W_2(NMe_2)_6]$.

$(\pm)[W_2(OC_{10}H_{19})_6]$.—To $[W_2(NMe_2)_6]$ (0.300 g, 0.47 mmol) in hexane (15 cm^3) at 60 °C was added L-menthol (0.22 g, 1.41 mmol) and D-menthol (0.22 g, 1.41 mmol) in hexane (10 cm^3). The mixture was stirred for 24 h at r.t. and the solvent removed *in vacuo* to form $(\pm)[W_2(OC_{10}H_{19})_6]$ (0.58 g, 95%), m.p. = 85–90 °C (Found: C, 55.4; H, 8.80. $C_{60}H_{114}O_6W_2$ requires C, 55.10; H, 8.85%). $\delta_H(C_6D_6)$ 5.62 (1 H, d of t), 5.48 (1 H, d of t), 5.24 (1 H, d of t), 5.18 (1 H, m), 5.05 (1 H, m), 4.92 (1 H, m), 4.83 (2 H, m), 2.80 (6 H, m), 2.60 (6 H, m) and 1.11 (94 H, m).

$[Mo_2(OC_{10}H_{19})_6]$.—The same general procedure was used for both D- and L-menthol forms of $[Mo_2(OC_{10}H_{19})_6]$. To a solution of $[Mo_2(NMe_2)_6]$ (0.200 g, 0.44 mmol) in hexane (5 cm^3) at 50 °C was added L-menthol (0.370 g, 2.37 mmol). The solution was magnetically stirred for 4 h and allowed to cool to room temperature. After 6 h it had changed from yellow to orange and the solvent was then removed *in vacuo* to leave a yellow semicrystalline solid. The compound $[Mo_2(OC_{10}H_{19})_6]$ can be recrystallized as cubic yellow crystals by slowly cooling a saturated solution (1 g per 3 cm^3) in hexane from 65 °C to room temperature (0.428 g, 0.38 mmol, 86.4%) (Found: C, 63.7; H, 9.8. $C_{60}H_{114}Mo_2O_6$ requires C, 63.9; H, 9.7%). $\delta_H(C_6D_6)$ 5.15 (6 H, d of t), 2.65 (6 H, d), 2.57 (6 H, d of spt), 1.65 (24 H, m) and 1.10 (72 H, m). $\delta_C(C_6D_6)$ 81.8 (6 C, d, *J* 146), 52.2 (6 C, d, 132), 47.8 (6 C, t, 132), 35.2 (6 C, t, 130), 32.6 (6 C, d, 132), 25.7 (6 C, d, 136), 23.6 (6 C, t, 133), 22.7 (6 C, q, 132), 22.0 (6 C, q, 132) and 16.8 (6 C, q, 132 Hz) ν_{max}: 2940s, 2900s, 2870s, 2850s, 1450m, 1440vs, 1380w, 1360s, 1355m, 1310m, 1253m, 1220w, 1170m, 1140w, 1090m, 1070m, 1035vs, 1015vs, 990s, 970s, 910s, 870m, 842s, 860m, 690vs, 610m, 540w, 485m, 440m, 390m and 320m cm^{-1}. The CD/ORD and UV spectra are reported in Table 1 and in Fig. 3.

$[W_2(NMe_2)(neo\text{-}OC_{10}H_{19})_5]$.—To $[W_2(NMe_2)_6]$ (1.00 g, 1.58 mmol) dissolved in hexane (20 cm^3) at 45 °C was added D-neomenthol (1.50 g, 9.61 mmol) in hexane (5 cm^3). The mixture was vigorously magnetically stirred at 45–50 °C for 2 h and then at room temperature for 12 h, during which time the solution evolved from yellow to a dark orange. The solvent was removed *in vacuo* to leave an orange semicrystalline solid. This was washed with a small amount of cold hexane (1 cm^3 at 0 °C) and dried *in vacuo*, affording $[W_2(NMe_2)(neo\text{-}OC_{10}H_{19})_5]$ as a crystalline solid. It can be recrystallized by slowly cooling a saturated (1 g per 3 cm^3) solution in hexane from 65 to 25 °C, giving orange plate-like crystals (1.68 g, 1.41 mmol, 90%), m.p. 124–126 °C (decomp.) (Found: C, 52.85; H, 8.35; N, 1.65. $C_{52}H_{101}O_5W_2$ requires C, 52.55; H, 8.50; N, 1.20%). IR (ν_{max}): 2980m, 2920m, 2900m, 2825m, 2786m, 1540w, 1480s, 1454s, 1435vs, 1365s, 1355s, 1320s, 1240s, 1210m, 1180vs, 1140s, 1090m, 1040m, 1015vs, 985m, 950vs, 930s, 920s, 880vs, 860vs, 820vs, 760m, 710vs, 670w, 600s, 535s, 510s, 440w, 430w, 365s, 325s, 310s and 240m cm^{-1}. $\delta_H(C_6D_6$, 25 °C) 5.4 (1 H, s), 5.3 (1 H, s), 5.07 (1 H, s), 4.68 (1 H, s), 4.1 (1 H, s) 4.05 (3 H, s), 3.6 (1 H, s), 2.1 (3 H, m), 1.5 (26 H, m, br) and 0.8 (63 H, m); T_c = 85 °C, $\Delta\nu$ = 549 Hz, $\Delta G^\ddagger$ = 68 kJ mol^{-1}. $\delta_C(C_6D_6)$ 81.9 (1 C, d), 80.7 (1 C, d), 79.0 (1 C, d), 77.5 (1 C, d), 73.7 (1 C, d), 59.4 (1 C, q), 50.8 (1 C, d), 50.5 (1 C, d), 50.4 (1 C, d), 50.3 (1 C, d), 50.0 (1 C, d), 45.9 (1 C, t), 45.7 (1 C, t), 45.6 (2 C, t), 45.3 (1 C, t), 40.4 (1 C, q), 36.0 (5 C, t), 29.6 (1 C, d), 29.4 (1 C, d), 29.3 (1 C, d), 29.0 (1 C, d), 28.9 (1 C, d), 26.3 (1 C, d), 26.0 (3 C, d), 25.9 (1 C, d), 25.0 (1 C, t), 24.8 (1 C, t), 24.6 (1 C, t), 24.5 (2 C, t), 24.0 (1 C, t), 22.9 (1 C, q), 21.9 (1 C, q), 21.8 (1 C, q) and 21.2 (3 C, q). The CD/ORD results are reported in Table 1.

$[MN(OC_{10}H_{19})_3]$ (M = Mo, D- *or* L-*menthol*, D-*neomenthol*; M = W, L-*menthol*).—The same general procedure was adopted for all $[MN(OC_{10}H_{19})_3]$ complexes and is illustrated here for M = Mo and L-menthol. To $[\{MoN(OBu^t)_3\}_x]$ (1.00 g, 3.04 mmol) suspended in toluene (20 cm^3) at room temperature was added L-menthol (1.42 g, 9 mmol) in hexane (5 cm^3). The resulting slurry was magnetically stirred at room temperature; after 20 min all the $[\{MoN(OBu^t)_3\}_x]$ had dissolved and a pale yellow solution was obtained. This was stirred for 14 h at ambient temperature and then the solvent was removed *in vacuo* to leave a white powder. The product $[\{MoN(OC_{10}H_{19})_3\}_x]$ can be sublimed at 95–110 °C at 1 × 10^{-3} Torr, or recrystallized as long thin needles by cooling a saturated solution in hexane from 60 to 20 °C over a few hours. (1.61 g, 2.79 mmol, 92%) (Found: C, 62.15; H, 9.60; N, 2.30%; M^+ at *m/z* 574. $C_{30}H_{57}MoNO_3$ requires C, 62.60; H, 9.60; N, 2.30%; M^+ at *m/z* 574). ν_{max}: 2990m, 2960m, 2820m, 2790m, 1440s, 1350s, 1240s, 1230s, 1150s, 1070s, 1005vs, 905s, 840w, 780s, 700(sh), 670s, 580s, 505w, 480s, 370vs and 320s cm^{-1}. $\delta_H(C_6D_6)$ 5.15 (3 H, d of t), 2.25 (6 H, m), 1.56 (9 H, m), 1.45 (6 H, m), 1.20 (6 H, m), 1.14 (3 H, d), 1.08 (3 H, d), 1.04 (2 H, d) and 0.9 (1 H, m). $\delta_C(C_6D_6)$ 96.8 (3 C, d), 50.4 (3 C, d), 46.0 (3 C, t), 34.8 (3 C, t), 32.3 (3 C, d), 25.8 (3 C, d), 23.2 (3 C, t), 22.5 (3 C, q), 21.8 (3 C, q) and 16.4 (3 C, q). The D-menthol form of $[MoN(OC_{10}H_{19})_3]$ had an identical m.p., IR and ^1H NMR spectra to those of the L-form.

$[\{MoN(neo\text{-}OC_{10}H_{19})_3\}_x]$. (Found: C, 62.60; H, 10.15; N, 2.20%; M^+ at *m/z* 574. $C_{30}H_{57}MoNO_3$ requires C, 62.60; H, 9.60; N, 2.30%; M^+ at *m/z* 574). $\delta_H(C_6D_6)$ 5.72 (3 H, s), 2.41 (3 H, m), 1.65 (12 H, m), 1.23 (9 H, d) and 0.97 (30 H, m). $\delta_C(C_6D_6)$ 91.3 (3 C, d), 50.2 (3 C, d), 44.6 (3 C, t), 35.8 (3 C, t), 29.6 (3 C, d), 26.4 (3 C, d), 24.8 (3 C, t), 23.0 (3 C, q), 22.2 (3 C, q) and 21.6 (3 C, q). ν_{max}: 2940vs, 2900vs, 2860vs, 2830vs, 1570w, 1460s, 1440s, 1430s, 1380s, 1315s, 1320s, 1300s, 1260m, 1210m, 1190s, 1160s, 1140s, 1090m, 1050s, 1020vs, 1005vs, 980s, 955vs, 935vs, 925vs, 880vs, 860s, 840s, 810s, 760m, 720vs, 605s, 550s, 510s, 400m, 370m, 360m, 335s, 310s, 290m and 250m cm^{-1}. Crystals suitable

Table 3 Crystallographic data collection parameters

Empirical formual	$C_{60}H_{114}O_6W_2$
M	1299.26
Colour of crystal	Amber
Crystal dimensions (mm)	0.24 × 0.28 × 0.32
Space group	$P1$
Temperature (°C)	−157
a/Å	15.439(3)
b/Å	15.883(3)
c/Å	13.684(3)
α/°	104.40(1)
β/°	99.10(1)
γ/°	94.27(1)
Z (molecules per cell)	2
U/Å^3	3186.53
D_c/g cm^{-3}	1.354
λ(Mo-Kα)/Å	0.710 69
μ/cm^{-1}	37.259
Detector to sample distance/cm	22.5
Sample to source distance/cm	23.5
Take-off angle (°)	2.0
Average ω-scan width at half-height	0.25
Scan speed/° min^{-1}	10.0
Scan width/° + dispersion	2.0
Individual background/s	4
Aperture size/mm	3.0 × 4.0
2θ range/(°)	6–45
Total number of reflections collected	15 539
Number unique	15 371
Number with $F > 0.0$	15 154
Number with $F > 3\sigma(F)$	14 836
R	0.0431
R'	0.0443
Goodness of fit for last cycle	1.2032
Maximum shift/error for last cycle	0.01

for X-ray diffraction were grown by leaving a saturated hexane–neomenthol solution of [$\{MoN(\textit{neo}\text{-}OC_{10}H_{19})_3\}_x$] at room temperature for a few weeks. The crystals were colourless cubic rods, unfortunately the *a* axis had a dimension of 54 Å and was unsuitable for X-ray analysis.

[$\{WN(OC_{10}H_{19})_3\}_x$]: $\delta_H(C_6D_6)$ 4.65 (3 H, m), 2.5 (6 H, m), 1.61 (6 H, m), 1.49 (6 H, m), 1.21 (6 H, m), 1.03 (24 H, m) and 0.93 (6 H, m); identical IR spectrum to [$\{MoN(OC_{10}H_{19})_3\}_x$].

[$W(CEt)(OC_{10}H_{19})_3$].—Addition of hex-3-yne (0.020 g, 0.2 mmol) in hexane (3 cm^3) to a solution of (−)[$W_2(OC_{10}H_{19})_6$] (0.250 g, 0.19 mmol) in hexane (5 cm^3) afforded a light brown solution. The mixture was allowed to stand at room temperature for 12 h, during which time a small amount of amorphous white solid was precipitated [0.010 g, polyhex-3-yne)]. This was filtered off and the filtrate reduced to half volume *in vacuo*. On cooling to −20 °C pale yellow crystals of [$W(CEt)(OC_{10}H_{19})_3$] were obtained by decanting the solvent and drying the product *in vacuo* (0.130 g, 0.19 mmol 50%), m.p. 170 °C (decomp.) $\delta_H(C_6D_6)$ 4.5 (6 H, d of t), 2.5 (6 H, m), 2.3 (2 H, m) and 1.5 (49 H, br). $\delta_C(C_6D_6)$ 350.4 (1 C, s), 86.5 (3 C, d, *J* 145), 51.9 (3 C, d, 132), 44.5 (3 C, q, 132), 35.2 (3 C, t, 132), 32.5 (1 C, t, 132), 26.4 (3 C, d, 136), 23.9 (3 C, t, 132), 22.7 (3 C, q, 132), 22.3 (3 C, q, 132), 22.5 (3 C, t, 132), 16.7 (3 C, q, 132) and 14.6 (3 C, q, 132 Hz).

Exchange Studies.—To (+)[$W_2(OC_{10}H_{19})_6$] (0.050 g, 0.04 mmol) dissolved in hexane (10 cm^3) at room temperature was added L-$HOC_{10}H_{19}$ (0.072 g, 0.465 mmol). The mixture was stirred for 1 min then transferred to a CD cell and the spectrum recorded. This showed a (−)Cotton effect for the first peak at 445 nm with $[M]_{445}$ = 750° cm^{-2} mol^{-1}.

Equal molar quantities of crystals of (+) and (−)-[$W_2(OC_{10}H_{19})_6$] were placed in a 5 mm NMR tube, C_6D_6 was added and the ^1H NMR spectra obtained 2 min, 5 h and 10 h after mixing. The spectrum of (+)[$W_2(OC_{10}H_{19})_6$] in C_6D_6 was obtained after addition of 6 equivalents of L-menthol. Successive spectra were obtained at 10 min intervals for a period of 1 h.

Reaction of [$W_2(OC_{10}H_{19})_6$] *with* MeCN.—To (−)[$W_2(OC_{10}H_{19})_6$] (1.00 g, 0.77 mmol) in hexane (5 cm^3) at room temperature was added an excess of MeCN (2 cm^3) in diethyl ether (5 cm^3). This caused an immediate darkening of the solution to brown. The mixture was stirred overnight at room temperature and the solvent removed *in vacuo*. The ^1H NMR spectrum of the residue showed the presence of equimolar amounts of [$WN(OC_{10}H_{19})_3$] and presumably [$W(CMe)(OC_{10}H_{19})_3$]. The residue was redissolved in hexane and small white crystals obtained upon concentration of a saturated solution. The crystals, however, appear to be a mixture of [$WN(OC_{10}H_{19})_3$] and [$W(CMe)(OC_{10}H_{19})_3$] according to spectroscopy.

Crystallography.—An almost equidimensional amber coloured crystal of (+)[$W_2(OC_{10}H_{19})_6$] was selected from the bulk sample using inert-atmosphere handling techniques.[18] It was transferred to the goniostat and cooled to −157 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than $\bar{1}$) and no systematic extinctions. The non-centrosymmetric space group $P1$ was chosen because it was known that the compound was optically active. This choice was confirmed by the successful solution and refinement of the structure.

Data collection was undertaken as detailed in Table 3. A total of 15 539 reflections (including standards) were collected. Following the usual data reduction and Lorentz/polarization corrections a set of 15 371 reflections was obtained. It should be noted, that, since the space group was acentric and we wanted to determine the correct absolute structure, Friedel pairs were not averaged. No correction for absorption was performed. A plot of the four standard reflections monitored every 400 reflections showed no systematic trends.

The structure was solved by locating the four W atoms in an *E* map, using SHELXS.[18] The remainder of the atoms were then located in successive Fourier difference maps. Following initial refinement some hydrogen atoms were evident in a difference map, however it was not possible to include them in fixed positions since our least-squares program allows a maximum of 250 atoms. The full-matrix least-squares refinement was completed using anisotropic thermal parameters for all of the atoms. A weighting scheme of the form $w = k/\sigma(F) + gF^2$ was used. The final R was 0.043 and R' was 0.044. A similar refinement of the inverse structure gave $R = 0.054$ and $R' = 0.057$. A further proof of the correct absolute structure is the fact that the menthol ligands have the correct conformation.

The asymmetric unit contains two independent molecules of the [$W_2(OC_{10}H_{19})_6$] complex. It is interesting that the two molecules are different (see the Figs. 4 and 5 and Table 2). The two molecules are labelled A and B; the numbering schemes are similar, but not identical.

The final difference map was essentially featureless, except for residuals of 1.2 e Å^{-3} at the W atoms. Atomic coordinates are given in Table 4.

It should be mentioned here that preliminary data obtained for the L-menthol complex indicated that the unit cells are identical and it would be expected that the compounds are isomorphous.[19]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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Table 4 Atomic coordinates (× 10^4) for (+)[$W_2(OC_{10}H_{19})_6$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1A)	−2 868*	−4 564*	−9 423*	W(1B)	987.9(4)	−1 055.8(4)	−4 656(1)
W(2A)	−4 063.0(4)	−5 646.5(4)	−9 721.3(5)	W(2B)	1 995.6(4)	193.1(4)	−3 872.3(5)
O(3A)	−3 460(6)	−3 624(5)	−9 751(6)	O(3B)	1 689(6)	−1 624(5)	−5 588(6)
C(4A)	−2 950(7)	−2 890(7)	−9 871(10)	C(4B)	1 567(10)	−2 527(8)	−6 208(10)
C(5A)	−2 883(9)	−3 040	−10 994(10)	C(5B)	1 756(11)	−3 142(9)	−5 493(10)
C(6A)	−2 373(10)	−2 272(11)	−11 231(14)	C(6B)	1 693(13)	−4 086(9)	−6 172(13)
C(7A)	−2 749(11)	−1 422(10)	−10 800(14)	C(7B)	755(12)	−4 361(11)	−6 777(18)
C(8A)	−2 837(10)	−1 275(9)	−9 677(12)	C(8B)	567(11)	−3 757(10)	−7 524(14)
C(9A)	−3 431(9)	−2 052(8)	−9 526(11)	C(9B)	678(11)	−2 770(10)	−6 864(11)
C(10A)	−3 640(11)	−1 943(9)	−8 462(10)	C(10B)	478(12)	−2 179(11)	−7 600(12)
C(11A)	−4 260(15)	−1 202(12)	−8 257(16)	C(11B)	1 050(15)	−2 228(14)	−8 385(14)
C(12A)	−2 799(13)	−1 702(12)	−7 538(13)	C(12B)	−513(13)	−2 315(11)	−8 169(19)
C(13A)	−2 345(12)	−2 434(12)	−12 358(14)	C(13B)	1 924(15)	−4 703(11)	−5 418(15)
O(14A)	−2 297(5)	−4 367(5)	−8 054(6)	O(14B)	−58(5)	−697(5)	−5 249(6)
C(15A)	−2 302	−4 766(8)	−7 207(9)	C(15B)	−407(8)	88(7)	−5 388(9)
C(16A)	−1 800(9)	−5 587(8)	−7 485(10)	C(16B)	−450(8)	40(8)	−6 530(9)
C(17A)	−1 681(11)	−6 041(9)	−6 611(12)	C(17B)	−850(9)	842(8)	−6 838(11)
C(18A)	−1 239(11)	−5 379(10)	−5 586(12)	C(18B)	−1 772(9)	887(8)	−6 518(11)
C(19A)	−1 762(10)	−4 579(10)	−5 344(11)	C(19B)	−1 726(9)	920(8)	−5 399(11)
C(20A)	−1 817(8)	−4 125(8)	−6 2343(9)	C(20B)	−1 359(8)	96(8)	−5 144(10)
C(21A)	−2 246(10)	−3 273(8)	−6 013(11)	C(21B)	−1 395(9)	25(8)	−4 062(10)
C(22A)	−1 668(13)	−2 580(9)	−5 094(12)	C(22B)	−2 392(11)	−192(10)	−3 965(13)
C(23A)	−3 246(12)	−3 425(12)	−5 799(17)	C(23B)	−957(11)	873(9)	−3 196(11)
C(24A)	−1 104(15)	−6 809(13)	−6 914(18)	C(24B)	−879(10)	743(8)	−7 973(9)
O(25A)	−2 124(6)	−4 975(5)	−10 313(7)	O(25B)	726(6)	−1 603(5)	−3 650(6)
C(26A)	−1 955(8)	−5 750(7)	−11 066(9)	C(26B)	810(8)	−1 450(8)	−2 548(9)
C(27A)	−2 492(9)	−5 760(9)	−12 087(10)	C(27B)	484(9)	−592(8)	−2 085(10)
C(28A)	−2 318(9)	−6 530(8)	−12 944(10)	C(28B)	546(9)	−399(9)	−960(11)
C(29A)	−1 340(10)	−6 528(9)	−12 955(9)	C(29B)	84(10)	−1 180(10)	−671(11)
C(30A)	−810(10)	−6 546(9)	−11 911(12)	C(30B)	393(10)	−2 054(9)	−1 172(11)
C(31A)	−952(9)	−5 734(9)	−11 068(10)	C(31B)	265(8)	−2 222(8)	−2 348(10)
C(32A)	−409(9)	−5 647(10)	−9 972(10)	C(32B)	528(10)	−3 111(9)	−2 901(11)
C(33A)	−532(12)	−6 482(11)	−9 597(14)	C(33B)	1 510(10)	−3 221(10)	−2 661(12)
C(34A)	580(10)	−5 374(12)	−10 002(13)	C(34B)	−85(12)	−3 890(10)	−2 685(13)
C(35A)	−2 863(12)	−6 526(11)	−13 988(11)	C(35B)	253(11)	455(10)	−477(11)
O(36A)	−4 249(5)	−5 490(5)	−8 361(7)	O(36B)	1 265(6)	1 022(5)	−3 268(6)
C(37A)	−4 880(9)	−6 152(9)	−8 116(10)	C(37B)	1 689(12)	1 964(12)	−2 966(13)
C(38A)	−4 297(9)	−6 839(9)	−7 792(10)	C(38B)	1 133(15)	2 390(10)	−3 874(14)
C(39A)	−4 846(12)	−7 474(10)	−7 342(12)	C(39B)	1 475(15)	3 281(12)	−3 758(15)
C(40A)	−5 251(11)	−6 953(10)	−6 481(11)	C(40B)	1 547(13)	3 855(11)	−2 547(14)
C(41A)	−5 831(11)	−6 293(11)	−6 821(11)	C(41B)	2 141(9)	3 422(8)	−1 898(12)
C(42A)	−5 281(10)	−5 621(9)	−7 227(10)	C(42B)	1 667(13)	2 465(10)	−1 969(14)
C(43A)	−5 828(10)	−4 950(10)	−7 584(11)	C(43B)	2 185(10)	2 036(15)	−1 188(15)
C(44A)	−6 769(10)	−5 296(12)	−8 199(12)	C(44B)	3 203(15)	2 156(15)	−1 037
C(45A)	−6 769(10)	−5 296(12)	−8 199(12)	C(45B)	1 969(15)	2 465(15)	−92(15)
C(46A)	−4 207(16)	−8 105(11)	−6 972(14)	C(46B)	850(19)	3 658(15)	−4 427(18)
O(47A)	−4 999(5)	−5 345(5)	−10 563(6)	O(47B)	2 473(6)	527(5)	−4 923(6)
C(48A)	−5 180(10)	−4 716(9)	−11 177(11)	C(48B)	2 352(9)	396(8)	−6 012(9)
C(49A)	−5 006(12)	−5 172(11)	−12 271(11)	C(49B)	1 903(8)	1 152(8)	−6 286(9)
C(50A)	−5 211(15)	−4 563(12)	−13 009(14)	C(50B)	1 799(10)	1 148(10)	−7 400(11)
C(51A)	−6 158(12)	−4 358(11)	−13 017(14)	C(51B)	2 692(10)	1 082(10)	−7 753(10)
C(52A)	−6 311(11)	−3 897(11)	−11 944(14)	C(52B)	3 160(10)	292(10)	−7 497(11)
C(53A)	−6 109(10)	−4 517(9)	−11 187(12)	C(53B)	3 257(9)	395(8)	−6 330(10)
C(54A)	−6 317(11)	−4 171(10)	−10 134(13)	C(54B)	3 826(11)	−297(9)	−5 986(11)
C(55A)	−7 325(13)	−4 009(12)	−10 160(18)	C(55B)	3 519(13)	−1 226(10)	−6 673(15)
C(56A)	−5 748(12)	−3 309(12)	−9 469(16)	C(56B)	4 839(10)	1(9)	−5 914(12)
C(57A)	−5 034(19)	−5 021(15)	−14 052(15)	C(57B)	1 394(11)	1 978(10)	−7 582(11)
O(58A)	−3 539(6)	−6 665(5)	−10 352(6)	O(58B)	2 871(5)	−113(5)	−2 923(6)
C(59A)	−4 049(9)	−7 485(8)	−10 919(9)	C(59B)	3 284(8)	−853(7)	−2 762(9)
C(60A)	−4 578(9)	−7 386(8)	−11 886(10)	C(60B)	3 707(8)	−1 225(8)	−3 686(9)
C(61A)	−5 041(9)	−8 274(8)	−12 612(9)	C(61B)	4 218(11)	−2 012(10)	−3 530(12)
C(62A)	−4 359(9)	−8 890(7)	−12 868(10)	C(62B)	4 919(10)	−1 697(10)	−2 532(10)
C(63A)	−3 817(9)	−9 025(8)	−11 868(10)	C(63B)	4 460(10)	−1 369(9)	−1 619(10)
C(64A)	−3 368(8)	−8 151(7)	−11 161(8)	C(64B)	3 950(8)	−565(8)	−1 747(9)
C(65A)	−2 746(9)	−8 225(8)	−10 166(10)	C(65B)	3 543(8)	−176(8)	−796(9)
C(66A)	−3 225(10)	−8 753(9)	−9 565(11)	C(66B)	3 057(9)	−907(10)	−385(12)
C(67A)	−1 925(9)	−8 661(9)	−10 483(11)	C(67B)	4 232(10)	416(9)	49(11)
C(68A)	−5 559(10)	−8 092(10)	−13 626(10)	C(68B)	4 712(15)	−2 331(14)	−4 429(14)

* Not varied.

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