Camphor-derived β-Ketophosphonate Complexes of Molybdenum(VI) and Titanium(IV); Crystal and Molecular Structure of Dichloro[(1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor]dioxomolybdenum(VI) †

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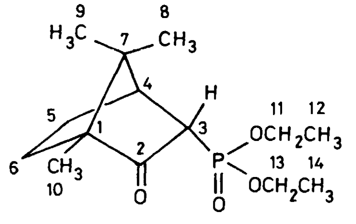
Reaction of (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor (L) with MoO_2Cl_2 gives $[MoO_2Cl_2L]$ with *cis* oxygen and *trans* chloro ligands if the stoicheiometry is 1 : 1 whilst 2 equivalents of L give $[MoO_2Cl_2L_2]$. On reaction with 1 equivalent of L, $TiCl_4$ gives $[TiCl_4L]$. The complexes were characterised by i.r., ^1H, and ^{31}P n.m.r. spectroscopy, and shown to contain bidentate binding (through the phosphoryl and carbonyl oxygen atoms) except for $[MoO_2Cl_2L_2]$, where binding is only through the phosphoryl oxygen. The compound $[MoO_2Cl_2L]$ has been characterised crystallographically. Crystals are orthorhombic (space group $P2_12_12_1$) with a = 15.528(2), b = 13.721(2), c = 9.777(1) Å, and Z = 4. The structure was obtained from 1 664 observed intensities measured on a diffractometer and refined to an R value of 0.043. The complex is distorted octahedral about molybdenum with mutually *cis* oxygen atoms and mutually *trans* chlorine atoms although the O–Mo–O angle is 102.8(5)° and the Cl–Mo–Cl angle is only 158.0(1)°. The organic ligand is bound through the phosphoryl and carbonyl oxygen atoms and the geometry of the ligand is little distorted from that of *e.g.* 3-bromocamphor. The bite angle for the bidentate ligand is 78.6(3)° and the Mo–O(phosphoryl) bond length [2.183(7) Å] is significantly shorter than that to the carbonyl oxygen [2.402(7) Å]. The known absolute configurations of the chiral centres have been confirmed as (1*R*), (3*S*), and (4*S*).

The co-ordination chemistry of neutral donor β-ketophosphonate ligands $[(RO)_2P(O)CH_2C(O)R]$ has been investigated for elements such as Ti^{IV} and Sn^{IV} (ref. 1) and some studies have been carried out on β-ketophosphine oxide complexes.[2] Complexes of the deprotonated form of β-ketophosphonates $[(RO)_2P(O)CHC(O)R]^-$ with Cr^{III}, Co^{II}, and Zn^{II} have been investigated by Cotton and Schunn.[3]

Much interest has developed in the structurally related carbamoylmethylphosphonates $(RO)_2P(O)CH_2C(O)NR_2$ and their complexes, particularly with a number of lanthanide and actinide elements[4—7] because of the use of such ligands as extractants of the metal ions from radioactive waste solutions.[8] Solution equilibrium analyses carried out by Horwitz and co-workers[9] on U^{VI} and Th^{IV} have shown the interesting and complex molecular operation of these ligands. It has been found by Paine and co-workers that the carbamoylmethylphosphonate $(Pr^iO)_2P(O)CH_2C(O)NEt_2$[10] and diethyl(diethylcarbamoylmethyl)thiophosphonate $(RO)_2P(S)CH_2C(O)NEt_2$[11] will form complexes with dichlorodioxomolybdenum(VI).

As part of a study into new catalytic systems for asymmetric epoxidation, we have been investigating the ligand behaviour of chiral β-ketophosphonates with some high-valent early transition-metal species. We report here on the preparation, isolation, and characterisation of new complexes of Mo^{VI} and Ti^{IV} which demonstrate that (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor, L (camphor = bornan-2-one), can act as a unidentate or a bidentate ligand with co-ordination through P=O alone or through P=O and C=O. Spectroscopic and crystallographic studies suggest that co-ordination has little effect on the electronic and steric properties of the ligand.



L

Results and Discussion

(*a*) *Ligand Synthesis*.—(1*R*)-*endo*-(+)-3-(Diethoxyphosphoryl)camphor (L) was synthesised from optically pure (1*R*)-*endo*-(+)-3-bromocamphor by a method[12] involving reaction with sodium diethyl phosphite followed by rearrangement of the (+)-enol phosphate using lithium di-isopropylamide.

(*b*) *Synthesis of Complexes*.—Reaction of MoO_2Cl_2 with 1 equivalent of L in tetrahydrofuran (thf) gives a blue solution from which pale blue ‡ cuboid crystals of a product analysing

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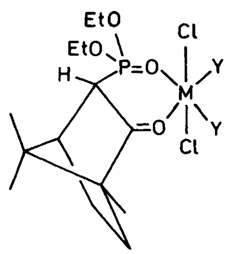
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

‡ Pure crystals of the complex are colourless but they become pale blue on contact with even traces of air.

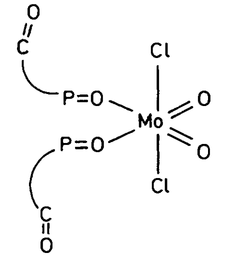
Table 1. Spectroscopic data for ligand L and its complexes with MoO_2Cl_2 and $TiCl_4$

	Multiplicity	L	$[MoO_2Cl_2L]$	$[MoO_2Cl_2L_2]$	$[TiCl_4L]$
ν(M–Cl)/cm^{-1}			346s 304m	336s 273m	360s(br)
ν(Mo=O)/cm^{-1}			967s 923s	943s 910s	
ν(P=O)/cm^{-1}		1 251s	1 171s 1 152s	1 205s 1 187s 1 173s	1 120s 1 096s
ν(C=O)/cm^{-1}		1 742s	1 697s	1 748s	1 675s
$\delta(^{31}P)$/p.p.m.	s	23.1	24.3	24.5	23.9
$\delta(^{1}H)$[a]					
$CH_3(8)$	s	0.86 (0.62)[b]	0.95	0.91	0.98
$CH_3(10)$	s	0.92 (0.8)	1.08	0.99	1.09
$CH_3(9)$	s	1.00 (1.03)	1.12	1.05	1.11
$CH_3(12)$[c]	t	1.34 (1.28)	1.40	1.38	1.46
$CH_3(14)$[c]	t	1.35 (1.35)	1.48	1.40	1.49
$H(6)_{endo}$	m	1.63 (1.55)	1.58[d]	1.58	1.6[d]
$H(6)_{exo}$	dt	1.69 (1.95)	1.92[d]	1.78	2.05[d]
$H(5)_{exo}$	m	1.92 (1.81)	*e*	1.91	1.98
$H(5)_{endo}$	m	2.13 (2.62)	2.09[d]	2.06	2.12[d]
H(4)	t	2.40 (2.32)	2.45	2.50	2.63
H(3)	dd	2.93 (3.12)	3.85	3.40(br)	4.06
$CH_2(11, 13)$	m[f]	4.1 (4.12) (4.15) (4.39) (4.50)	4.40	4.35	4.54

[a] In $CDCl_3$ at 298 K, assignments based on those for 3-bromocamphor (fully assigned by two-dimensional COSY). [b] Numbers in parentheses refer to chemical shifts in C_6D_6. [c] Assignments are arbitrary. [d] Resonances are simpler than in the spectra of the other compounds. [e] Not observed. [f] Complex multiplet made up of four different signals.



(**1**) M = Mo, Y = O
M = Ti, Y = Cl



(**2**)

= L

as $[MoO_2Cl_2L]$ can be isolated in high yield. Using 2 equivalents of L, a second complex of formula $[MoO_2Cl_2L_2]$ is formed. Similarly, reaction of $TiCl_4$ with 1 equivalent of L gives yellow $[TiCl_4L]$. These complexes have been fully characterised spectroscopically and, in the case of $[MoO_2Cl_2L]$, by single-crystal *X*-ray diffraction.

(*c*) *Spectroscopic Properties.*—(*i*) *Infra-red.* Table 1 lists selected i.r. vibrations for the various complexes. For both of the molybdenum species, the observation of two ν(M=O) suggests a *cis*-dioxo arrangement and the positions of these bands are similar to those observed for other complexes containing this unit.[13,14] Two ν(Mo–Cl) might also be seen as indicative of mutually *cis* chlorides, but *X*-ray studies clearly reveal them to be *trans* in $[MoO_2Cl_2L]$ and the similarity of the spectra of the two molybdenum compounds in this region, together with their similarity to the spectra of $[MoO_2Cl_2L_2]$ [L = Ph_3PO,[15] ν(Mo–Cl) 295 and 320; L_2 = 2,2′-bipyridyl,[16] ν(Mo–Cl) 342 and 318 cm^{-1}], which in the case of L = Ph_3PO is known to have mutually *trans* chlorides from *X*-ray studies, confirm *trans* chlorides in $[MoO_2Cl_2L_2]$ also. The observation of the symmetric stretch as a relatively strong band suggests that the Cl–Mo–Cl angle is significantly different from 180° in both complexes (*X*-ray studies show it to be 158° for $[MoO_2Cl_2L]$). For $[TiCl_4L]$, the observation of a broad structured ν(M–Cl) at 360 cm^{-1} is consistent with a non-planar arrangement of the four chloride ligands.

Of more importance, however, are the vibrations of the ligand C=O and P=O groups. In both $[MoO_2Cl_2L]$ and $[TiCl_4L]$ there is a marked shift to lower frequency on co-ordination of L both of ν(C=O) (-45 and -67 cm^{-1} respectively) and of ν(P=O), which becomes a split band (-89* and -143 cm^{-1} respectively). The splitting of ν(P=O) in complexes of β-keto-phosphonates is well documented although its origin remains obscure.[1,10]

The shifts to low frequency of ν(C=O) and ν(P=O) on co-ordination of L are similar to those observed[10] for carbamoylmethylphosphonate complexes of Mo^{VI} (-52 and -72 cm^{-1} respectively). Lanthanide complexes of such ligands also show this shift to lower frequency [-30, ν(C=O); -50 cm^{-1}, ν(P=O)] as does $[TiCl_4\{(Pr^iO)_2P(O)CH_2COMe\}]$ (-40 and -115 cm^{-1} respectively).[1] We conclude that $[MoO_2Cl_2L]$ and $[TiCl_4L]$ have structure (**1**), with bidentate binding of L.

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* The average position of the split band is used for calculation of the shift.

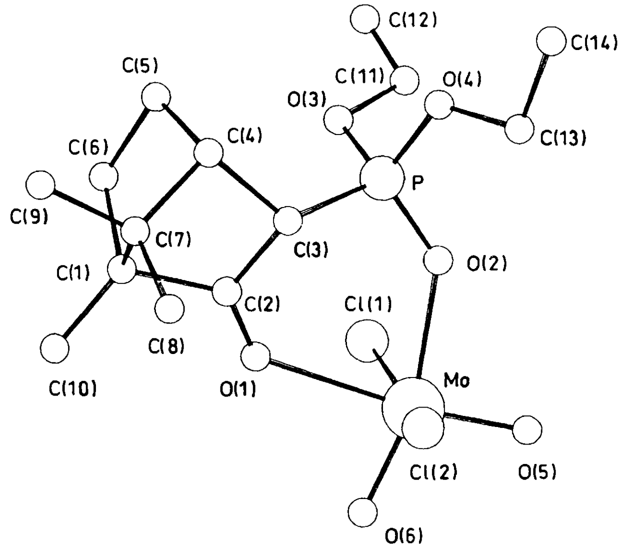

Figure. Single-crystal *X*-ray structure and numbering scheme for $[MoO_2Cl_2L]$; H atoms have been omitted for clarity

Table 2. Bond lengths (Å) for $[MoO_2Cl_2L]$

Cl(1)–Mo	2.343(5)	Cl(2)–Mo	2.358(5)
O(1)–Mo	2.402(7)	O(2)–Mo	2.183(7)
O(5)–Mo	1.658(8)	O(6)–Mo	1.655(9)
O(2)–P	1.472(7)	O(3)–P	1.558(10)
O(4)–P	1.533(9)	C(3)–P	1.783(10)
C(2)–O(1)	1.202(10)	C(11)–O(3)	1.519(24)
C(13)–O(4)	1.406(15)	C(2)–C(1)	1.538(14)
C(6)–C(1)	1.580(19)	C(7)–C(1)	1.601(18)
C(10)–C(1)	1.497(15)	C(3)–C(2)	1.509(14)
C(4)–C(3)	1.592(15)	C(5)–C(4)	1.538(22)
C(7)–C(4)	1.589(16)	C(6)–C(5)	1.567(23)
C(8)–C(7)	1.540(20)	C(9)–C(7)	1.568(16)
C(12)–C(11)	1.121(29)	C(14)–C(13)	1.525(21)

In contrast, only a small shift in ν(C=O), + 6 cm^{-1}, is observed on co-ordination of L in $[MoO_2Cl_2L_2]$ whilst ν(P=O) is shifted (− 62 cm^{-1}) and split into three bands, the greater degeneracy presumably arising from there being 2 P=O in the molecule. These shifts are similar to those observed for $[TiCl_4\{(Pr^iO)_2P(O)CH_2COMe\}_2]$ (+ 2 and − 130 cm^{-1} respectively), in which co-ordination is only through the phosphoryl oxygen atom.[1] We conclude that $[MoO_2Cl_2L_2]$ contains the β-ketophosphonate co-ordinated as a unidentate ligand through the phosphoryl oxygen and that it has structure (**2**). Interestingly, in the related $[MoO_2Cl_2\{(EtO)_2P(S)CH_2C(O)NEt_2\}_2]$[11] binding of the organic ligand is unidentate through the carbonyl oxygen, presumably because the class A Mo^{VI} prefers binding to the hard oxygen rather than the soft sulphur centre. The preference for binding to the phosphoryl rather than the carbonyl oxygen in L suggests that the phosphoryl oxygen is the harder centre.

(*ii*) *N.m.r.* Table 1 lists ^1H and ^{31}P n.m.r. shifts and assignments for L and its complexes. In the ^1H-decoupled ^{31}P n.m.r. spectra all complexes show a singlet shifted only slightly to higher frequency compared with the free ligand, suggesting only a slight change in electron density at phosphorus on co-ordination. In each case only one isomer is present in solution. Similar small shifts to higher frequency have previously been noted on co-ordination of carbamoylmethylphosphonates to UO_2^{2+},[5] Th^{IV},[7] or Mo^{VI}.[11,12]

Table 3. Bond angles (°) for $[MoO_2Cl_2L]$

Cl(2)–Mo–Cl(1)	158.0(1)	O(1)–Mo–Cl(1)	81.0(3)
O(1)–Mo–Cl(2)	80.6(3)	O(2)–Mo–Cl(1)	83.0(3)
O(2)–Mo–Cl(2)	81.5(3)	O(2)–Mo–O(1)	78.6(3)
O(5)–Mo–Cl(1)	97.8(4)	O(5)–Mo–Cl(2)	98.8(4)
O(5)–Mo–O(1)	172.6(3)	O(5)–Mo–O(2)	94.0(4)
O(6)–Mo–Cl(1)	96.4(4)	O(6)–Mo–Cl(2)	93.9(4)
O(6)–Mo–O(1)	84.6(4)	O(6)–Mo–O(2)	163.1(3)
O(6)–Mo–O(5)	102.8(5)	O(3)–P–O(2)	113.3(5)
O(4)–P–O(2)	113.9(5)	O(4)–P–O(3)	103.8(6)
C(3)–P–O(2)	107.6(5)	C(3)–P–O(3)	108.9(6)
C(3)–P–O(4)	109.2(5)	C(2)–O(1)–Mo	132.3(5)
P–O(2)–Mo	137.7(4)	C(11)–O(3)–P	118.5(9)
C(13)–O(4)–P	122.9(9)	C(6)–C(1)–C(2)	102.3(9)
C(7)–C(1)–C(2)	98.3(8)	C(7)–C(1)–C(6)	103.8(11)
C(10)–C(1)–C(2)	115.2(10)	C(10)–C(1)–C(6)	114.9(11)
C(10)–C(1)–C(7)	119.7(10)	C(1)–C(2)–O(1)	125.5(9)
C(3)–C(2)–O(1)	126.3(8)	C(3)–C(2)–C(1)	108.2(8)
C(2)–C(3)–P	111.6(7)	C(4)–C(3)–P	122.5(8)
C(4)–C(3)–C(2)	101.6(8)	C(5)–C(4)–C(3)	110.9(11)
C(7)–C(4)–C(3)	98.1(9)	C(7)–C(4)–C(5)	104.3(13)
C(6)–C(5)–C(4)	102.9(11)	C(5)–C(6)–C(1)	104.5(13)
C(4)–C(7)–C(1)	92.9(10)	C(8)–C(7)–C(1)	112.9(10)
C(8)–C(7)–C(4)	118.1(13)	C(9)–C(7)–C(1)	110.2(12)
C(9)–C(7)–C(4)	110.7(11)	C(9)–C(7)–C(8)	110.8(12)
C(12)–C(11)–O(3)	105.4(27)	C(14)–C(13)–O(4)	108.9(13)

The ^1H n.m.r. spectra are complex. The spectrum of the free ligand was interpreted by comparison with that of (+)-3-bromocamphor which exists in the *endo* configuration. Full assignment of the ^1H spectrum of the latter was achieved using two-dimensional ^1H-^{13}C correlation spectroscopy (COSY) and nuclear Overhauser enhancement (n.O.e.) difference spectroscopy. In a difference spectrum of the ligand significant enhancement at H(3) was observed on saturation of C(8), confirming the *exo* configuration of H(3). In addition, it has been shown that the diethoxyphosphoryl group of $[MoO_2Cl_2L]$ is *endo* and so the chiral centres of the ligand and complexes are as shown for L and (**1**), respectively.

As would be expected, in the ^1H n.m.r. spectra of the complexes the most significant shift to higher frequency compared with the ligand is of H(3) and it is greater for the bidentate complexes (≈ 1 p.p.m.) than for $[MoO_2Cl_2L_2]$ (≈ 0.5 p.p.m.) where evidence from i.r. spectroscopy indicates binding solely through P=O. Differences in multiplicities of certain resonances of the bidentate complexes compared with those of the free ligand may be caused by minor changes in bond lengths and angles resulting from complexation. The non-equivalence of CH_3 and CH_2 resonances of the ethoxy groups is a consequence of the chirality of the ligand and in C_6D_6 solution all four proton resonances of the two CH_2 groups of the free ligand can be recognised.

(*d*) X-*Ray Crystallographic Studies on* $[MoO_2Cl_2L]$.—The main features of the solid-state structure of $[MoO_2Cl_2L]$ are shown in the Figure and bond lengths and angles in Tables 2 and 3. The arrangement of the donor atoms about the central molybdenum(VI) is typical of oxomolybdenum(VI) complexes having a six-co-ordinate distorted octahedral geometry.[15] Both the terminal oxygen atoms O(5) and O(6) and the (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor oxygen atoms O(1) and O(2) are *cis* to one another while the halogen ligands Cl(1) and Cl(2) are *trans* to one another. Previous workers have shown that in mixed-ligand complexes of Mo^{VI} the π bonding is concentrated in bonds to terminal oxygen atoms at the expense of bonds to other atoms.[10,17,18] The present compound is no exception to this observation which is shown up most clearly in the significant lengthening of bonds *trans* to the terminal oxygen atoms. The phosphoryl oxygen atom makes a Mo–O(2) bond distance of 2.183(7) Å which is comparable to that found[17] for the monodentate $\mathrm{Ph_3PO}$ ligand [2.169(1) Å] in the complex $[\mathrm{MoO_2Cl_2(Ph_3PO)_2}]$, whilst the carbonyl oxygen atom of camphor makes a Mo–O(1) bond distance of 2.402(7) Å which is significantly longer than the Mo–O(C) bond distance in the related bidentate complex[10] $[\mathrm{MoO_2Cl_2\{(Pr^iO)_2P(O)CH_2C(O)NEt_2\}}]$, consistent with weaker binding than of the harder phosphoryl oxygen.

The Mo–Cl bond distances 2.343(5) and 2.358(5) Å are slightly shorter than the corresponding distances in $[\mathrm{MoO_2Cl_2\{(Pr^iO)_2P(O)CH_2C(O)NEt_2\}}]$, 2.376(1) and 2.384(1) Å, and $[\mathrm{MoO_2Cl_2(Ph_3PO)_2}]$, 2.397(1) and 2.388(1) Å. The Cl(1)–Mo–Cl(2) bond angle of 158.0(1)° is comparable to those found in the above complexes [162.2(2) and 161.3°]. The expansion from 90° of the O(5)–Mo–O(6) angle to 102.8(5)° is again typical when compared with those observed for the above complexes [102.8(1) and 102.2(7)° for the *cis* molybdenyl], although the observed M=O(5),(6) bond distances of 1.658(8) and 1.655(9) Å are slightly shorter than the corresponding distances [1.687(2) and 1.677(2),[10] 1.695(1) and 1.673(1) Å[17]]. This expansion of the O–Mo–O angle to *ca.* 103° means that the O(1)–Mo–O(2) angle of the co-ordinated phosphorylcamphor group is compressed to 78.6(3)°, giving a very distorted $[\mathrm{MoO_2Cl_2L}]$ octahedron. This bite angle for the ligand is similar to that found for $[\mathrm{MoO_2Cl_2\{(Pr^iO)_2P(O)CH_2C(O)NEt_2\}}]$ [78.9(1)°] and even that for $[\mathrm{MoO_2Cl_2(Ph_3PO)_2}]$ [77.81(5)°] where these donor phosphoryl oxygen atoms are not constrained in a bidentate ligand.

The P=O(2) bond distance, 1.472(7) Å, is only slightly longer than that expected for an unco-ordinated P=O (*ca.* 1.46 Å), similarly the carbonyl C(2)–O(1) bond distance, 1.202(10) Å, is essentially identical with that observed in free 3-bromocamphor [1.200(15) Å].[19]

The remaining bond distances and angles in the (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor fragment are consistent with those observed in 3-bromocamphor.[19] The known absolute configurations at the chiral carbon atom centres C(1), C(3), and C(4) have been confirmed to be (1*R*),(3*S*), and (4*S*).

Experimental

Microanalyses were by the University of St. Andrews Microanalytical Services. I.r. spectra were recorded on Perkin-Elmer 1710 (Fourier transform) and 1330 (dispersion) spectrometers as Nujol mulls between CsI plates, n.m.r. spectra on a Bruker AM 300 spectrometer operating in the Fourier-transform mode with (for $^{31}\mathrm{P}$) proton decoupling. Melting points were determined on a Gallenkamp apparatus in air and are uncorrected.

All solvents were carefully dried and degassed by distillation from sodium diphenylketyl [thf, diethyl ether, light petroleum (b.p. 40—60 °C)] or $\mathrm{CaH_2}$ ($\mathrm{CH_2Cl_2}$) before use. All manipulations were carried out under dry oxygen-free nitrogen (purified by passing over a $\mathrm{Cr^{2+}}$-on-silica column) by standard Schlenk-line and catheter-tubing techniques.

The compounds $\mathrm{MoO_2Cl_2}$ (Alfa), $\mathrm{TiCl_4}$ (BDH), diethyl phosphite (Aldrich), (1*R*)-*endo*-(+)-3-bromocamphor, n-butyl-lithium (10 mol $\mathrm{dm^{-3}}$ in hexane, Aldrich), sodium hydride (60% dispersion in mineral oil, Aldrich), and di-isopropylamine (Aldrich) were reagent grade and were used without further purification.

(1R)-2-[(*Diethoxyphosphoryl*)*oxy*]-1,7,7-*trimethylbicyclo*[2.2.1]*hept*-2-*ene*.[12]—Sodium hydride (60% dispersion in mineral oil, 80 g, 2 mol) was washed three times with diethyl ether to remove the oil. Dry diethyl ether (100 $\mathrm{cm^3}$) was added. To this suspension was added slowly a solution of diethyl phosphite (165.6 g, 1.2 mol) in diethyl ether (100 $\mathrm{cm^3}$). Two hours later, when all hydrogen evolution had ceased, a solution of (1*R*)-*endo*-(+)-3-bromocamphor (277 g, 1.2 mol) in ether (150 $\mathrm{cm^3}$) was added. Several hours later the products were filtered through a sinter funnel and saturated aqueous ammonium chloride (100 $\mathrm{cm^3}$) was added carefully to the organic phase which was extracted with diethyl ether and dried over anhydrous magnesium sulphate. Vacuum-pump distillation [110 °C, 0.1 Torr (*ca.* 13.3 Pa)] gave (1*R*)-2-[(diethoxyphosphoryl)oxy]-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (211.2 g, 0.77 mol, 61.1%). The spectroscopic data were essentially identical to those in the literature,[12] $\alpha = +16.06°$ (5.3 g per 100 $\mathrm{cm^3}$ in MeOH, 589 nm).

(1R)-endo-(+)-3-(*Diethoxyphosphoryl*)*camphor*.[12]—Lithium di-isopropylamide (0.49 mol) was prepared by the slow addition of n-butyl-lithium (46 $\mathrm{cm^3}$, 0.49 mol, 10 mol $\mathrm{dm^{-3}}$ solution in hexanes) to a solution of di-isopropylamine (68.11 $\mathrm{cm^3}$, 0.49 mol) in thf (100 $\mathrm{cm^3}$) at −78 °C. One hour later (1*R*)-2-[(diethoxyphosphoryl)oxy]-1,7,7-trimethylbicyclo[2.2.1]-hept-2-ene (46.45 g, 0.162 mol) was added. The temperature was maintained at −78 °C for 2 h and then slowly allowed to rise to 20 °C. Twenty four hours later the reaction mixture was carefully poured into a saturated ammonium chloride–water–ice mixture (150 $\mathrm{cm^3}$). Solvent extraction of the organic phase with diethyl ether (3 × 100 $\mathrm{cm^3}$) and drying over anhydrous magnesium sulphate gave, upon distillation [128 °C, 0.05 mmHg (*ca.* 6.7 Pa)], (1*R*)-(+)-*endo*-3-(diethoxyphosphoryl)-camphor (28.55 g, 61% yield). The spectral information was essentially identical to that given in the literature,[12,*] $\alpha = +74.63°$ (5.3 g per 100 $\mathrm{cm^3}$ in MeOH, 589 nm).

Dichloro[(1R)-endo-(+)-3-(*diethoxyphosphoryl*)*camphor*]-*dioxomolybdenum*(VI).—The compound $\mathrm{MoO_2Cl_2}$ (1.5 g, 7.54 mmol) was dissolved in dry thf (30 $\mathrm{cm^3}$). (1*R*)-*endo*-(+)-3-(Diethoxyphosphoryl)camphor (2.17 g, 7.54 mmol) was added with stirring. One hour later the thf was removed to leave an oily residue. Treatment with dry diethyl ether (15 $\mathrm{cm^3}$) gave a solid which was washed with diethyl ether (2 × 5 $\mathrm{cm^3}$ portions) and was found to have m.p. 176—177 °C. Yield 2.67 g, 73% (Found: C, 34.6; H, 5.2. $\mathrm{C_{14}H_{25}Cl_2MoO_6P}$ requires C, 34.5; H, 5.2%).

Dichlorobis[(1R)-endo-(+)-3-(*diethoxyphosphoryl*)*camphor*]-*dioxomolybdenum*(VI).—The compound $\mathrm{MoO_2Cl_2}$ (1.38 g, 6.94 mmol) was dissolved in dry thf (20 $\mathrm{cm^3}$) and (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor (4.00 g, 13.88 mmol) was added with stirring. The solution gradually became greenish blue. Two hours later the thf was removed to leave a dark blue semi-solid and light petroleum (15 $\mathrm{cm^3}$)–thf (4 $\mathrm{cm^3}$) was added to dissolve the product. The flask was placed in a freezer at −25 °C for 2 h whereupon the product formed as fine pale blue needles. These were filtered off while cold, washed twice with 5-$\mathrm{cm^3}$ portions of light petroleum, and dried *in vacuo*, m.p. 103—104 °C. Yield 4.93 g, 91.6% (Found: C, 43.2; H, 6.4. $\mathrm{C_{28}H_{50}Cl_2MoO_{10}P_2}$ requires C, 43.4; H, 6.4%).

Tetrachloro[(1R)-endo-(+)-3-(*diethoxyphosphoryl*)*camphor*] *titanium*(IV).—To a solution of (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor (1.26 g, 4.38 mmol) in toluene (30 $\mathrm{cm^3}$) was quickly added titanium tetrachloride (0.489 $\mathrm{cm^3}$, 4.38 mmol). The resulting red solution deposited a yellow powder upon cooling. The suspension was filtered and the remaining solid was washed with cold toluene (5 $\mathrm{cm^3}$) and dried for 24 h *in*

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[*] J[H(3)–P] is reported incorrectly in the literature,[12] its actual value being 25 Hz.[20]

Table 4. Fractional atomic co-ordinates (× 10^4) for [MoO_2Cl_2L]

Atom	*x*	*y*	*z*
Mo	3 950.3(5)	2 797.8(6)	1 227.4(7)
P	6 031(2)	2 400(2)	2 222(2)
Cl(1)	4 516(2)	4 359(2)	862(3)
Cl(2)	3 805(2)	1 242(2)	2 225(3)
O(1)	4 345(4)	3 188(4)	3 539(5)
O(2)	5 307(3)	2 382(5)	1 250(6)
O(3)	6 524(5)	3 389(6)	2 234(7)
O(4)	6 735(5)	1 647(6)	1 912(8)
O(5)	3 810(5)	2 490(6)	−397(6)
O(6)	2 977(4)	3 157(6)	1 697(8)
C(1)	5 072(7)	3 227(8)	5 752(9)
C(2)	4 922(5)	2 911(7)	4 262(8)
C(3)	5 606(5)	2 177(7)	3 886(8)
C(4)	6 191(8)	2 180(12)	5 223(9)
C(5)	6 658(8)	3 162(13)	5 385(13)
C(6)	5 898(9)	3 895(12)	5 624(13)
C(7)	5 442(7)	2 219(12)	6 328(9)
C(8)	4 767(9)	1 396(9)	6 321(13)
C(9)	5 821(9)	2 367(13)	7 800(10)
C(10)	4 317(8)	3 697(8)	6 438(9)
C(11)	6 903(11)	3 762(15)	900(24)
C(12)	7 436(17)	4 269(17)	1 205(28)
C(13)	6 563(10)	750(9)	1 273(19)
C(14)	7 382(10)	136(11)	1 281(20)

vacuo, m.p. 98—101 °C. Yield 0.84 g, 40.2% (Found: C, 35.5; H, 5.2. $C_{14}H_{25}Cl_4O_4PTi$ requires C, 35.3; H, 5.3%).

Crystallography of Dichloro[(1R)-endo-(+)-3-(*diethoxyphosphoryl*)*camphor*]*dioxomolybdenum*(VI).—Suitable crystals were obtained from tetrahydrofuran–ether at −5°C.

Crystal data. $C_{14}H_{25}Cl_2MoO_6P$, $M = 487.168$, orthorhombic, space group $P2_12_12_1$, $a = 15.528(2)$, $b = 13.721(2)$, $c = 9.777(1)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 2\,083.03$ Å^3, $D_m = 1.56$ g cm^{-3}, $Z = 4$, $D_c = 1.55$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 8.89$ cm^{-1}, $F(000)$ 992.

Data collection.[21] 2 101 Unique reflections were recorded on a CAD4 diffractometer measuring to $\theta_{max.} = 25°$. Psi-scan absorption corrections were made (minimum 0.9559, maximum 0.9993). The structure was solved by Patterson and Fourier methods. The positional and anisotropic vibrational parameters of all non-hydrogen atoms were refined.

The final R factor was 0.043 and $R' = 1/[\sigma(F_0)^2 + 0.0003\,26F_0^2]$ 0.054 for 1 664 reflections having $F > 3\sigma(F)$. The R value for the enantiomorphic structure was 0.048. The largest peaks in the final difference map were 0.5 e in the vicinity of the carbon atoms. The fractional co-ordinates are in Table 4. Programs and computers used, as well as sources of scattering-factor data were as in ref. 21.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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