Oxo- and Imido-molybdenum(VI) and -tungsten(VI) Functionalities supported by Diacetoneglucose†

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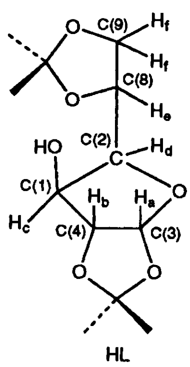
The synthesis of novel complexes of Mo^{VI} and W^{VI} containing oxo- and imido-functionalities was undertaken using the carbohydrate derivative diacetoneglucose (1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) (HL) as a ligand. Starting from the oxo chlorides $MoOCl_4$, $WOCl_4$ and MoO_2Cl_2, the complexes $[MOL_4]$ (M = Mo **1** or W **2**) and $[MoO_2L_2]$ were obtained by reaction with the previously reported lithium derivative LiL. Complexes **1** and **2** reacted with pyridine forming the adducts $[MOL_4(py)]$. The complex $[MoO_2L_2]$ also acts as a Lewis acid towards 1,10-phenanthroline (phen) to yield $[MoO_2L_2(phen)]$ and the sodium salt of dibenzoylmethane Na(dbm) affording the heterobimetallic complex $[MoO_2L_2\{(dbm)Na\}]$. Reaction of LiL with $W(NC_6H_4Me\text{-}p)Cl_4$ gave the imido derivative $[W(NC_6H_4Me\text{-}p)L_4]$. All the complexes have been characterized by means of ^1H and ^{13}C NMR spectroscopy and gave correct elemental analyses. The specific rotations $[\alpha]^{298}_{589}$ have been measured and are briefly discussed. The crystal structures of $[MoO_2L_2]$ and $[MoO_2L_2(phen)]$ have been determined. In the former the *cis*-MoO_2 fragment is bonded to two bidentate L ligands. The octahedral co-ordination of molybdenum is achieved *via* two weak Mo···O interactions, displaced by phen in the latter complex.

High-oxidation-state transition metals bearing multiply bonded ligands[2] are of great interest in organometallic chemistry as catalysts in olefin-metathesis reactions and as model compounds for the active catalyst site in important industrial oxidation processes. In particular, oxo complexes are widely employed as oxidizing agents and as oxygen carriers. Imido complexes have been postulated as intermediates for industrial processes, such as ammoxidation of propylene, and have been used as stabilizing ligands in metal–alkylidene complexes.[3] Alkoxides[4] are widely employed ancillary ligands in combination with multiply bonded functionalities. Their π-donor ability alters the Lewis acidity of the metal centre and allows a fine tuning of the reactivity of the metal–carbon multiple bond. In addition to these properties, the easy availability of homochiral alkoxide ligands offers the possibility to control the stereochemistry of living polymerization. Despite great interest in such a possibility, only a handful of examples of chiral alkoxide-containing complexes have been reported in this field, mainly by Heppert[5] and Schrock and co-workers.[6] Sugar derivatives, although widely employed in organic chemistry as chiral auxiliaries,[7] have seldom been used in organometallic chemistry apart from a few successful cases in metal-assisted enantioselective organic chemistry.[8] The lack of prior investigation into the co-ordination chemistry of sugars prompted us to study the reciprocal influences of these spatially very demanding, oxygen-rich compounds with transition metals and the different co-ordination geometries imposed by particular oxidation states and co-ordination numbers of these metals.[9] The carbohydrate derivative we used in our studies is diacetoneglucose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL), which proved to be the most suitable, because of its high steric requirements, oxygen-rich periphery, and lack of acidic protons. The arrangement of the ligands about the metal centres could result in cavities capable of acting as binding sites for metal ions and other molecules being hydrogen bonded. These cavities, due to the chiral nature of the ligand, could further prove important in the field of chiral recognition.



HL

This report deals with the synthesis and characterization of new complexes of Group 6 transition metals bearing oxo and imido functionalities. We envisaged that the steric requirements and characteristics of the ligand L should give rise to novel interesting molecular architectures along with possibilities of structural modification and synthetic exploitation of the multiply bonded functionalities.

Results and Discussion

Oxoalkoxide complexes of Mo have been reported by Chisholm *et al.*[10] to be liquids or low-melting solids and were obtained by dioxygen oxidation of the corresponding molybdenum(IV) complexes. The synthesis of our oxo complexes $[MOL_4]$ (M = Mo **1** or W **2**) was accomplished by chloride displacement from

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the derivatives $MOCl_4$ (M = Mo[11] or W[12]), with the previously reported lithium derivative LiL[9c] [equation (1)].

$$MOCl_4 + 4LiL \xrightarrow{Et_2O} [MOL_4] + 4LiCl \qquad (1)$$

Both reactions were carried out in diethyl ether and the two extremely soluble derivatives were recrystallized from hexane at low temperature.

The ^1H NMR spectra of complexes **1** and **2** display very similar chemical shifts; the proton H_c (the one closest to the M–O bond) is shifted downfield about 1 ppm (δ 5.5 *vs.* 4.4) compared to the free sugar and about 0.7 ppm compared to our starting material [LiL, δ(H_c) 4.72]. An analogous trend is observed for the H_b protons, 0.8 ppm downfield (δ 5.2 *vs.* 4.4) compared to free HL and LiL for complex **2**, whereas for **1** the shift is 0.6 ppm. Unfortunately, the ^1H spectrum of $[MoOL_4]$ shows only broad signals, which do not decoalesce even at low temperature. In order to gain more structural information about these complexes, as well as to obtain crystalline and more easily handled products, both complexes **1** and **2** were recrystallized in the presence of 1 equivalent of pyridine (py) [equation (2)].

$$[MOL_4] + py \xrightarrow{toluene} [MOL_4(py)] \qquad (2)$$

$$\mathbf{3}\ M = Mo$$
$$\mathbf{4}\ M = W$$

The ^1H NMR spectra of the two complexes show one co-ordinated pyridine molecule and a single set of sugar (L) peaks independent of the temperature. These data are consistent with an axially bound pyridine molecule embedded in the cage formed by the four sugar ligands. Although the H_c resonances are found at δ 5.5 for both complexes, H_b is not shifted (δ 5.2) in the case of **3** but is shifted downfield (δ 5.5) in the case of **4**.

Analogous to these complexes is the *p*-tolylimido derivative $[W(NC_6H_4Me\text{-}p)L_4]$ **5** which was obtained by chloride metathesis from $W(NC_6H_4Me\text{-}p)Cl_4$[13] with LiL in diethyl ether [equation (3)]. The pure product is obtained by recrystallization from hexane. The ^1H NMR spectrum reveals the presence of two different sets of sugar signals in a 1 : 3 ratio. This fact can be explained by invoking the closer proximity of one of the four sugar ligands to the bulky aromatic ring of the imido substituent. The fact that this set of protons is shifted to lower field would suggest a shielding effect by the π electrons of the tolyl ring. This effect is more pronounced on the protons H_c and on the two diastereotopic protons of the methylene group which are shielded by 0.25 ppm for H_c and about 0.4 ppm for the H_f protons. A variable-temperature NMR study was undertaken to determine any possible variation of the ratio, but no significant difference was observed.

$$W(NC_6H_4Me\text{-}p)Cl_4 + 4LiL \xrightarrow{Et_2O} \underset{\mathbf{5}}{[W(NC_6H_4Me\text{-}p)L_4]} + 4LiCl \qquad (3)$$

Another very important class of Group 6 complexes of multiply bonded ligands are those of the general formula $MX(Y)(OR)_2$ where X and Y can be oxide, imide or alkylidene. In order to obtain a deeper insight into the binding mode of our ligand L, and, if possible, to explore subsequent reactivity, we undertook the synthesis of various molybdenum derivatives. The first complex isolated was $[MoO_2L_2]$ **6** obtained by the reaction of MoO_2Cl_2[12] with LiL in diethyl ether and purified from the inorganic salts by extraction with diethyl ether [equation (4)]. The ^1H NMR spectrum shows a H_c proton at δ 5.4 and H_b at δ 4.3, in good agreement with data for the other complexes. Complex **6** can even be obtained by dioxygen oxidation of the derivative $[Mo_2L_6]$[1] according to the Chisholm procedure[10] [equation (4)]. Crystals suitable for X-ray diffraction were obtained by slow extraction into CH_2Cl_2–Et_2O (1 : 1).

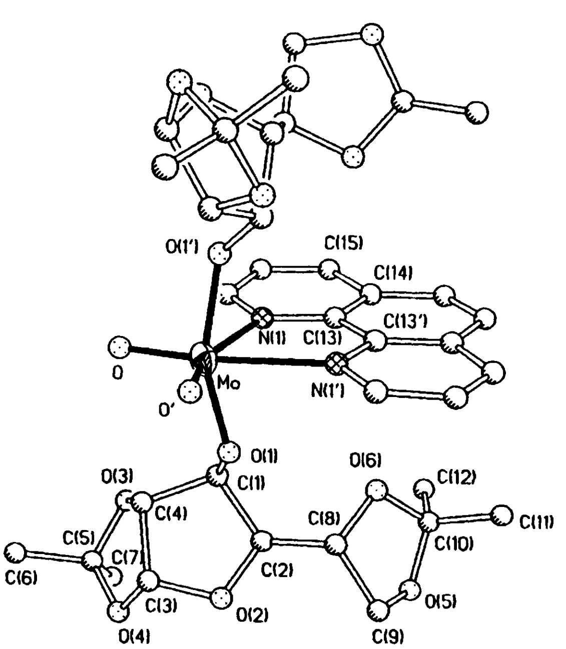

Fig. 1 View of complex **6** with the labelling scheme adopted

Table 1 Relevant bond lengths (Å) and angles (°) for $[MoO_2L_2]$ **6**

Mo–O(1)	1.687(2)	Mo–O(2)	1.683(2)
Mo–O(1a)	1.909(2)	Mo–O(1b)	1.924(2)
Mo · · · O(6a)	2.484(2)	Mo · · · O(6b)	2.568(2)
O(1)–Mo–O(2)	105.0(1)	O(1)–Mo–O(1a)	101.6(1)
O(2)–Mo–O(1a)	100.7(1)	O(1)–Mo · · · O(6a)	87.5(1)
O(2)–Mo · · · O(6a)	167.3(1)	O(1a)–Mo · · · O(6a)	74.1(1)
O(1b)–Mo · · · O(6a)	80.4(1)	O(1)–Mo–O(1b)	102.4(1)
O(2)–Mo–O(1b)	98.7(1)	O(1a)–Mo–O(1b)	143.9(1)
O(1)–Mo · · · O(6b)	166.3(1)	O(2)–Mo · · · O(6b)	88.4(1)
O(1a)–Mo · · · O(6b)	78.2(1)	O(1b)–Mo · · · O(6b)	72.1(1)
O(6a) · · · Mo · · · O(6b)	79.2(1)	Mo–O(1a)–C(1a)	123.1(2)
Mo–O(1b)–C(1b)	121.5(2)		

$$\begin{tikzcd}
MoO_2Cl_2 + 2LiL \arrow[rd, "Et_2O", "-2LiCl"'] & \\
 & \underset{\mathbf{6}}{[MoO_2L_2]} + \text{phen} \arrow[d, "\text{benzene}"] \\
{[Mo_2L_6]} \arrow[ru, "O_2", "\text{hexane}"'] & \underset{\mathbf{7}}{[MoO_2L_2(\text{phen})]} \quad (4)
\end{tikzcd}$$

The structure is shown in Fig. 1 and the most relevant bond distances and angles are listed in Table 1. The molecule possesses a non-crystallographic C_2 symmetry with the pseudo-two-fold axis passing through Mo and bisecting the O(1)=Mo=O(2) angle. The metal atom links two L units and has a distorted-octahedral co-ordination with two *cis* double bonds to O(1) [1.687(2) Å] and O(2) [1.683(2) Å], two *trans* single bonds to O(1a) [1.909(2) Å] and O(1b) [1.924(2) Å] and two weak *cis* contacts with O(6a) [2.484(2) Å] and O(6b) [2.568(2) Å]. The Mo=O bond lengths agree with those in the literature[14] and the Mo–O(1*n*) values are in keeping with those found in $[Mo_2L_6]$.[1] The most relevant angular distortion is due to a bending of the O(1a)–Mo–O(1b) line [143.9(1)°] with the oxygens tilted away

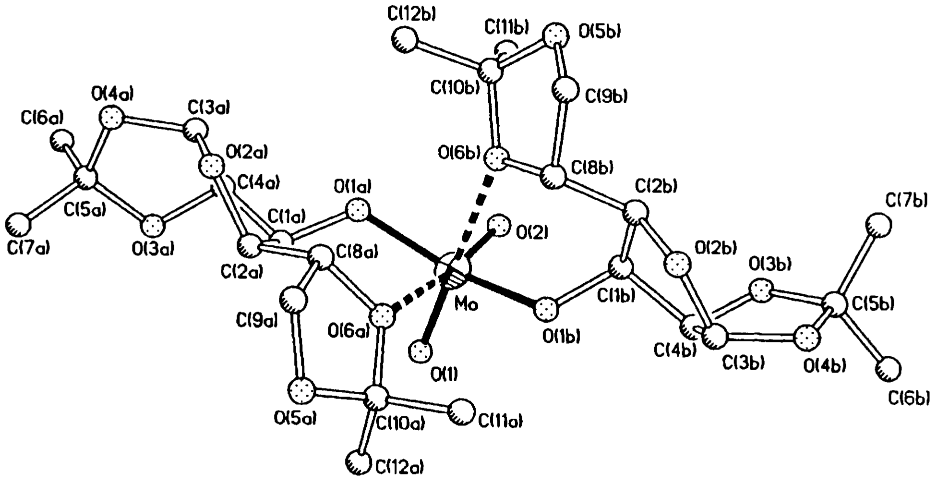

Fig. 2 View of complex **7** with the labelling scheme adopted. Primed atoms refer to atoms related by the two-fold symmetry axis

Table 2 Relevant bond lengths (Å) and angles (°) for $[MoO_2L_2(phen)]$ **7**

Mo–O	1.703(3)	Mo–O(1)	1.944(3)
Mo–N(1)	2.374(4)		
O–Mo–O(1)	97.7(1)	O–Mo–N(1)	91.3(1)
O(1)–Mo–N(1)	81.4(1)	O–Mo–O′	108.5(2)
O(1)–Mo–O′	96.8(1)	N(1)–Mo–O′	160.1(1)
O(1)–Mo–O(1′)	154.9(2)	N(1)–Mo–O(1′)	77.9(1)
N(1)–Mo–N(1′)	68.9(2)	Mo–O(1)–C(1)	130.8(3)
Mo–N(1)–C(13)	117.9(3)	Mo–N(1)–C(17)	123.7(3)

Table 3 Specific rotations

Compound	$[\alpha]^{298}_{589}$/deg cm^3 g^{-1} dm^{-1}	Concentration in thf/g dl^{-1}
$[MoOL_4(py)]$	−169.5	4.29
$[WOL_4]$	−70.45	2.2
$[WOL_4(py)]$	−98.2	2.38
$[W(NC_6H_4Me\text{-}p)L_4]$	−101.9	2.62
$[MoO_2L_2]$	+3	2.02
$[MoO_2L_2(phen)]$	−89.8	1.08

from O(1) and O(2). The *cis* octahedral angles range from 72.1 to 105.0° (for O=Mo=O).

As already mentioned, the sugars behave as bidentate ligands through O(1*n*) and O(6*n*) and their disposition around Mo corresponds to a helical Λ configuration. The six-membered rings [Mo–O(1*n*)–C(1*n*)–C(2*n*)–C(8*n*)–O(6*n*)] resulting from the double co-ordination assume a twisted-boat conformation, as found in other diacetoneglucose complexes.[9c]

Recrystallization of complex **6** in the presence of 1,10-phenanthroline (phen) yielded crystals of the adduct **7** [equation (4)]. The ^1H NMR spectrum of **7** does not differ substantially from that of **6** for H_a and H_b. One particular feature is the upfield shift of the two H_f protons: δ 3.18 for **7** *versus* δ 3.65 for **6**. This shift can be explained by the proximity of these protons to the aromatic ring of the phenanthroline moiety.

The structure of complex **7** is shown in Fig. 2 and the most relevant bond distances and angles are listed in Table 2. In this complex the Mo atom also assumes an octahedral co-ordination with two terminal oxygens [Mo=O 1.703(3) Å], two sugars as terminal ligands [Mo–O(1) 1.944(3) Å] and the 1,10-phenanthroline as a bidentate ligand co-ordinating through the nitrogen atoms. The weak *cis* interactions with O(6*n*) in complex **1** are substituted by bonding interactions with the N_{phen} atoms; the Mo–N distance [2.374(4) Å] is significantly longer than the value of 2.275 Å reported in ref. 14.

In this case the C_2 symmetry is imposed by a two-fold crystallographic axis through Mo and bisecting both the O=Mo=O and the N–Mo–N angles. The asymmetric unit is therefore formed by one half of a Mo atom, one terminal oxygen, one sugar molecule, and one half of a phen ligand.

With respect to complex **6**, as a consequence of the insertion of the planar phenanthroline, the O(1)–Mo–O(1′) angle is widened by nearly 11°. At the same time the sugar molecule undergoes the following rearrangements: (*i*) rotations of about 71° around the O(1)–C(1) bond and of nearly 20° around C(2)–C(8) which move the O(6) atoms away from the metal and bring the mean plane through the sugar ligand from a nearly perpendicular to an almost parallel disposition with respect to the O=Mo=O plane; (*ii*) widening of the Mo–O(1)–C(1) angle from 122.3 (average) to 130.8°. Finally, the O=Mo=O angle is increased from 105.0 to 108.5°.

The reaction of complex **6** with the anion of dibenzoylmethane (Hdbm) in toluene [equation (5)] afforded the adduct **8** as a

$$\underset{\mathbf{6}}{[MO_2L_2]} + Na(dbm) \xrightarrow{\text{toluene}} \underset{\mathbf{8}}{[MO_2L_2\{(dbm)Na\}]} \quad (5)$$

pale yellow solid. The ^1H NMR spectrum shows the co-ordinated dibenzoylmethane moiety with two broad singlets at δ 8.05 and 7.53 and a singlet at δ 6.86 for the proton between the two acyl groups. The protons H_a and H_b of the sugar ligand are broadened and appear at δ 5.6 and 4.86 in methylene chloride. The co-ordination of Na(dbm) shows the ability of our metal sugar complexes to act as carriers for alkali-metal species in hydrocarbons, where these species are normally not soluble, and to solvate them in a chiral environment.

Specific rotations for all the complexes were measured and their values are summarized in Table 3. A comparison of these values with those of other L complexes reveals some similarities, *e.g.* $[VL_3(py)_2]$[9a] ($[\alpha]^{298}_{589}$ = −201), $[W_2L_6]$[1] ($[\alpha]^{298}_{589}$ = −58.4) and $[Mo_2L_6]$[1] ($[\alpha]^{298}_{589}$ = +53.4 deg cm^3 g^{-1} dm^{-1}).

Conclusion

Our initial idea to develop a synthetic methodology for the synthesis of diacetoneglucose complexes bearing oxo and imido functionalities on the metal centre proved accessible from commonly encountered starting materials. The complexes revealed interesting chemical properties and more interesting stereochemical features which may prove exploitable in some organometallic processes.

Experimental

General Procedures.—All operations were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods and freshly distilled prior to use. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, ^{1}H NMR spectra on a 200-AC Bruker [^{1}H (200.13 MHz), ^{13}C (50.32 MHz)] and on a 400 ARX Bruker spectrometer [^{1}H (400.13 MHz), ^{13}C (100.62 MHz)].

Syntheses.—[$MoOL_4$] **1**. To a solution of $MoOCl_4$ (2.58 g, 10.18 mmol) in diethyl ether (100 cm^3), a solution of LiL (10.84 g, 40.77 mmol) in diethyl ether was added dropwise over 20 min. An immediate reaction ensued, the mixture was allowed to warm to room temperature and stirred for 2 h during which time a green solution and a pale precipitate formed. Filtration and removal of the solvent from the mother-liquor under vacuum gave an oily green solid which was extracted at room temperature into pentane (80 cm^3), filtered and stored at −20 °C. An oily green crude product was collected at low temperature and dried *in vacuo*. Yield 7.2 g (62%) (Found: C, 51.25; H, 7.25. $C_{48}H_{76}MoO_{25}$ requires C, 50.15; H, 6.70%). ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ 1.08 (s, 3 H, Me), 1.35 (s, 6 H, Me), 1.47 (s, 3 H, Me), 4.07 (s, br, 2 H), 4.56 (br, 2 H), 4.97 (br, 1 H), 5.58 (br, 1 H) and 6.06 (br, 1 H).

[WOL_4] **2**. A solution of LiL (4.59 g, 17.25 mmol) in diethyl ether (80 cm^3) was added dropwise to a stirred, chilled suspension of $WOCl_4$ (1.47 g, 4.24 mmol) in diethyl ether (30 cm^3). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. A white fine precipitate in a colourless solution was formed. The solid was filtered off and the solvent removed under reduced pressure. The white oily residue was extracted into hexane (50 cm^3) and cooled to −10 °C to yield white crystals of [WOL_4] which were collected at low temperature. Yield 3.1 g (58%) (Found: C, 45.75; H, 6.50. $C_{48}H_{76}O_{25}W$ requires C, 46.60; H, 6.20%). NMR (C_6D_6, 298 K): ^{1}H (200.13 MHz), δ 1.11 (s, 12 H, Me), 1.34 (s, 12 H, Me), 1.37 (s, 12 H, Me), 1.47 (s, 12 H, Me), 4.07 (m, 8 H, H_f), 4.51 [dd, 4 H, H_d, $J(H_dH_e) = 9.0$, $J(H_cH_d) = 2.6$], 4.59 (m, 4 H, H_e), 5.20 [d, 4 H, H_b, $J(H_bH_a) = 3.6$], 5.51 [d, 4 H, H_c, $J(H_cH_d) = 2.6$] and 6.13 [d, 4 H, H_a, $J(H_aH_b) = 3.6$ Hz]; ^{13}C (50.13 Hz), δ 25.9, 26.7, 27.4, 27.9, 68.8, 74.0, 84.3, 85.1, 88.7, 106.5, 111.2 and 112.7.

[$MoOL_4(py)$] **3**. To a stirred solution of complex **1** (5.0 g, 4.35 mmol) in toluene (80 cm^3), pyridine (0.4 g, 5.19 mmol) was added dropwise *via* a syringe. After the resulting green solution was stirred for 6 h, the volatiles were removed under vacuum to afford an oily green solid. The solid was then washed with hexane (80 cm^3) to afford a lime-green powder. Yield 4.2 g (79%) (Found: C, 51.85; H, 7.05; N, 1.00. $C_{53}H_{81}MoNO_{25}$ requires C, 51.85; H, 6.65; N, 1.15%). NMR (C_6D_6, 298 K): ^{1}H (200.13 MHz), δ 1.12 (s, 12 H, Me), 1.26 (s, 12 H, Me), 1.37 (s, 12 H, Me), 1.42 (s, 12 H, Me), 4.03 (m, 8 H), 4.48 (s br, 8 H), 5.27 (d, 4 H, $J_{CH} = 3.6$), 5.59 (s br, 4 H), 6.20 (d, 4 H, $J = 3.2$), 6.89 (d, 2 H, $J = 4.2$), 7.01 (t, 1 H, $J = 4.2$ Hz) and 9.04 (s br, 2 H); ^{13}C (50 MHz), δ 27.0, 27.3, 27.7, 28.4, 68.6, 73.6, 84.0, 90.3, 106.7, 110.0, 112.4, 124.7, 138.6 and 150.7.

[$WOL_4(py)$] **4**. Pyridine (0.4 g, 5.19 mmol) was added dropwise *via* a syringe to a stirred solution of [WOL_4] (5.95 g, 4.81 mmol) in toluene (70 cm^3). An immediate reaction ensued with the formation of a pale, blue-purple solution. The mixture was allowed to stir at room temperature for 1 h and then the volatiles were removed *in vacuo* to afford an oily, pale, purple solid. The solid was extracted into hexane (100 cm^3) and slowly cooled to −10 °C to afford needles of [$WOL_4(py)$]. Yield 4.5 g (71%) (Found: C, 49.05; H, 6.35; N, 0.95. $C_{53}H_{81}NO_{25}W$: C, 48.35; H, 6.20; N, 1.05%). NMR (C_6D_6, 298 K): ^{1}H (200.13 MHz), δ 1.13 (s, 12 H, Me), 1.22 (s, 12 H, Me), 1.37 (s, 12 H, Me), 1.40 (s, 12 H, Me), 4.00 (m, 4 H, H_f), 4.13 (m, 4 H, $H_{f'}$), 4.47 (m, 8 H, H_d, H_e), 5.49 [d, 4 H, H_b, $J(H_bH_a) = 3.6$], 5.53 [d, 4 H, H_c, $J(H_cH_d) = 1.6$], 6.28 [d, 4 H, H_a, $J(H_aH_b) = 3.6$], 6.96 (m, 3 H, H_{py}), 9.10 [d, 2 H, H_{py}, $J = 4.4$ Hz]; ^{13}C (50.13 MHz), δ 26.4, 26.9, 27.6, 27.8, 68.7, 73.5, 83.4, 84.4, 87.5, 106.4, 110.0, 112.4, 138.8 and 151.0.

[$W(NC_6H_4Me\text{-}p)L_4$] **5**. A solution of LiL (4.42 g, 16.6 mmol) in diethyl ether (80 cm^3) was added *via* a cannula to a stirred green suspension of $W(NC_6H_4Me\text{-}p)Cl_4{\cdot}Et_2O$ (2.10 g, 4.15 mmol) in diethyl ether (50 cm^3) chilled to −20 °C. The resulting mixture was allowed to warm to room temperature during which time a reaction took place accompanied by a change from green, through red and finally to yellow, with precipitation of a pale solid. The mixture was stirred for 2 h and the solid carefully filtered off. The solvent was removed under reduced pressure and the yellow oily solid extracted into hexane (100 cm^3). Concentration of the solution, followed by standing at room temperature, yielded pale yellow crystals of [$W(NC_6H_4Me\text{-}p)L_4$]. A further crop of crystals can be obtained by cooling the solution to −20 °C. Overall yield 4.72 g (85%) (Found: C, 49.60; H, 6.80; N, 0.75. $C_{55}H_{83}NO_{24}W$: C, 49.80; H, 6.30; N, 1.05%). NMR (C_6D_6, 298 K): ^{1}H (400.13 MHz), δ 1.20 (s, 9 H, Me), 1.24 (s, 3 H, Me), 1.34 (s, 3 H, Me), 1.39 (s, 9 H, Me), 1.42 (s, 9 H, Me), 1.48 (s, 3 H, Me), 1.50 (s, 12 H, Me), 2.21 (s, 3 H, *Me*C_6H_4N), 3.73 [dd, 1 H, $H_{f'}$, $J(H_{f'}H_{e'}) = 9$, $J(H_{f'}H_{f''}) = 6$], 3.96 [dd, 1 H, $H_{f'}$, $J(H_{f'}H_e) = 8$, $J(H_{f'}H_{f'}) = 6$], 4.15 [dd, 3 H, H_f, $J(H_fH_e) = 9$, $J(H_fH_f) = 6$], 4.29 [dd, 3 H, H_f, $J(H_fH_e) = 9$, $J(H_fH_f) = 6$], 4.39 [dd, 1 H, $H_{d'}$, $J(H_{d'}H_{e'}) = 6$, $J(H_{d'}H_{c'}) = 3$], 4.47 [dd, 3 H, H_d, $J(H_dH_e) = 8$, $J(H_dH_c) = 3$], 4.60 (m, 1 H, $H_{e'}$), 4.71 (m, 3 H, H_e), 5.10 [d, 1 H, $H_{c'}$, $J(H_{c'}H_{d'}) = 3$], 5.32 [d, 3 H, H_b, $J(H_bH_a) = 4$], 5.54 [d, 1 H, $H_{b'}$, $J(H_{b'}H_{a'}) = 4$], 5.78 [d, 3 H, H_c, $J(H_cH_d) = 3$], 6.20 [d, 1 H, $H_{a'}$, $J(H_{a'}H_{b'}) = 4$], 6.24 [d, 3 H, H_a, $J(H_aH_b) = 4$], 7.07 (d, 2 H, C_6H_4, $J = 8$) and 7.69 (d, 2 H, C_6H_4, $J = 8$ Hz); ^{13}C (50.13 MHz), δ 21.4, 23.7, 26.0, 26.2, 27.2, 27.8, 28.0, 28.1, 32.6, 67.8, 68.7, 73.8, 76.0, 79.5, 81.8, 84.2, 86.2, 86.3, 86.5, 105.7, 106.0, 110.8, 111.4, 111.7, 111.9, 128.9, 131.1, 138.3 and 149.7.

[MoO_2L_2] **6**. *Method A*. A solution of LiL (15.2 g, 57.1 mmol) in diethyl ether (150 cm^3) was added *via* a cannula to a suspension of MoO_2Cl_2 (5.6 g, 28.1 mmol) in diethyl ether (50 cm^3) chilled to −20 °C. The resulting mixture was allowed to warm to room temperature, during which time a pale green suspension formed which was stirred at room temperature overnight. The suspension was filtered into an extractor and the solid extracted with the same Et_2O solution for 24 h. The resulting suspension was concentrated to about 70 cm^3 and the precipitate collected on a filter and dried *in vacuo*. Yield 13.5 g (74%) (Found: C, 46.10; H, 6.05. $C_{24}H_{38}MoO_{14}$ requires C, 44.60; H, 5.90). NMR (C_6D_6, 298 K): ^{1}H (200.13 MHz), δ 1.10 (s, 6 H, Me), 1.25 (s, 6 H, Me), 1.39 (s, 6 H, Me), 1.70 (s, 6 H, Me), 3.65 [dd, 2 H, H_f, $J(H_fH_e) = 9.6$, $J(H_fH_f) = 5.8$], 3.91 (m, 4 H, H_f, H_e), 4.26 [d, 2 H, H_b, $J(H_bH_a) = 3.6$], 4.59 [dd, 2 H, H_d, $J(H_dH_e) = 8.2$, $J(H_dH_c) = 3.8$], 5.42 [d, 2 H, H_c, $J(H_cH_d) = 3.8$] and 5.71 [d, 2 H, H_a, $J(H_aH_b) = 3.6$ Hz]; ^{13}C (50.13 MHz), δ 25.0, 27.0, 27.7, 28.2, 68.2, 77.3, 83.9, 86.9, 94.2, 107.0 and 112.7.

Method B. To a degassed suspension of [Mo_2L_6] (4.26 g, 2.44 mmol) in hexane (*ca*. 100 cm^3) was added dry molecular oxygen. The mixture was stirred for 12 h, during which time it changed from orange to red, with the precipitation of a pale powder. The solid was collected as a pale brown powder and analysed as [MoO_2L_2] (0.66 g, 42%). A further quantity of [MoO_2L_2] can be obtained by cooling the mother-liquor. No other products were isolable. When the reaction was carried out using a gas burette 1.5–2.0 mol of O_2 were consumed per mol of [Mo_2L_6]. ^{1}H NMR (C_6D_6, 200 MHz): δ 1.10 (s, 6 H, Me), 1.25 (s, 6 H, Me), 1.39 (s, 6 H, Me), 1.70 (s, 6 H, Me), 3.65 [dd, 2 H, H_f, $J(H_fH_{f'}) = 5.8$, $J(H_fH_e) = 9.6$], 3.91 (m, 4 H, H_e, H_f), 4.26

[d, 2 H, H_b, $J(H_bH_a)$ = 3.6], 4.59 [dd, 4 H, H_d, $J(H_dH_e)$ = 8.2, $J(H_dH_c)$ = 3.8], 5.42 [d, 2 H, H_c, $J(H_cH_d)$ = 3.0] and 5.71 [d, 2 H, H_a, $J(H_aH_b)$ = 3.6 Hz] (Found: C, 47.05; H, 6.30. $C_{24}H_{38}MoO_{14}$ requires C, 44.60; H, 5.90%).

$[MoO_2L_2(phen)]$ **7**. 1,10-Phenanthroline (0.585 g, 3.25 mmol) was added in one portion to a solution of $[MoO_2L_2]$ (2.06 g, 3.19 mmol) in benzene (50 cm^3). On standing overnight the product crystallized as colourless cubes and was collected on a filter and dried *in vacuo*. Yield 1.95 g (74%) (Found: C, 52.45; H, 5.65; N, 3.65. $C_{36}H_{46}MoN_2O_{14}$ requires C, 52.30; H, 5.60; N, 3.40%). NMR (C_6D_6, 298 K): ^1H (200.13 MHz), δ 0.53 (s, 6 H, Me), 0.86 (s, 6 H, Me), 1.04 (s, 6 H, Me), 1.32 (s, 6 H, Me), 3.18 (m, 4 H, H_f), 3.90 (m, 2 H, H_e), 4.01 [dd, 2 H, H_d, $J(H_dH_e)$ = 6.4, $J(H_dH_c)$ = 2.6], 4.63 [d, 2 H, H_c, $J(H_cH_d)$ = 2.6], 5.21 [d, 2 H, H_b, $J(H_bH_a)$ = 3.6] and 5.82 [d, 2 H, H_a, $J(H_aH_b)$ = 3.6 Hz]; ^{13}C (50.13 MHz), δ 24.98, 26.27, 26.76, 27.16, 66.47, 73.06, 82.50, 85.19, 86.96, 105.71, 107.56, 111.16, 124.48, 126.66, 137.81 and 151.01.

$[MoO_2L_2\{dbm)Na\}]$ **8**. The salt Na(dbm) (0.806 g, 3.28 mmol) was added in one portion to a pale green solution of $[MoO_2L_2]$ (2.12 g, 3.28 mmol) in toluene (100 cm^3). The resulting suspension was stirred at room temperature and after 4 h a cloudy orange solution was obtained. Stirring was continued overnight and the solution was then filtered. Removal of the solvent *in vacuo* and washing of the residue with hexane (70 cm^3) afforded a yellow solid. Yield 2.4 g (82%) (Found: C, 52.25; H, 5.75. $C_{39}H_{49}O_{16}MoNa$ requires C, 52.45; H, 5.55%). NMR (CD_2Cl_2, 298 K): ^1H (200.13 MHz), δ 1.12 (s, 3 H, Me), 1.16 (s, 6 H, Me), 1.34 (s, 3 H, Me), 3.88 (m, 4 H, H_f), 3.98 [dd, 2 H, H_d, $J(H_dH_e)$ = 8, $J(H_dH_c)$ = 2.8], 4.05 (m, 2 H, H_e), 4.64 [d, 2 H, H_c, $J(H_cH_d)$ = 2.8 Hz], 4.86 (br s, 2 H, H_b), 5.60 (br s, 2 H, H_a), 6.86 (s, 1 H, PhCOC*H*COPh), 7.53 (br s, 6 H, *Ph*COCHCO*Ph*) and 8.05 (br s, 4 H, *Ph*COCHCO*Ph*); ^{13}C (50.13 MHz), δ 26.8, 27.8, 28.2, 28.5, 68.9, 84.3, 86.7, 87.4, 107.2, 111.0, 113.0, 129.3, 130.4, 134.0, 141.0, 186.8 and 209.7.

Table 4 Experimental data for the X-ray diffraction studies on complexes **6** and **7**

Complex	**6**	**7**
Formula	$C_{24}H_{38}MoO_{14}$	$C_{36}H_{46}MoN_2O_{14}$
M	646.5	826.7
Crystal symmetry	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12$ (no. 18)
a/Å	12.043(2)	22.870(8)
b/Å	12.898(2)	8.304(2)
c/Å	18.605(2)	10.047(3)
U/Å^3	2841(2)	1908(1)
Z	4	2
D_c/g cm^{-3}	1.511	1.439
μ/mm^{-1}	0.529	0.413
Crystal dimensions/mm	0.40 × 0.60 × 0.70	0.10 × 0.26 × 0.40
F(000)	336	430
Transmission coefficients	0.36–0.38	0.63–0.66
*R**	0.032	0.037
*R'**	0.041	0.041

* $R = \Sigma|\Delta F|/\Sigma|F_o|$, $R' = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

X-Ray Analysis for Complexes **6** *and* **7**.—The crystals used were sealed under nitrogen in a Lindemann glass capillary. Crystal data and details of refinements are given in Table 4. Unit-cell parameters were obtained by least-squares refinement on diffractometer angles of automatically centred reflections (25 for complex **6** and 40 for **7**). The data were collected at room temperature on a Siemens P4 diffractometer with ω–2θ mode (scan width 2.2°, scan speed 4.0–20.0° min^{-1}), using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). For complex **6**, 6158 reflections were measured (2.0 ⩽ 2θ ⩽ 55.0°, +*h,k,l*), 5696 of which were unique (merging *R* = 0.036 after absorption correction by the ψ-scan method)[15] giving 4441 with $F > 4.0\sigma(F)$ used for refinement. For complex **7**, 6213 reflections were measured (2.0 ⩽ 2θ ⩽ 55.0°, +*h,k,l*), 2017 of which were unique (merging *R* = 0.074 after absorption correction by the ψ-scan method)[15] giving 2017 with $F > 4.0\sigma(F)$ used for refinement. For both compounds two standard reflections, measured every 50, indicated no intensity decay. The structures were solved by direct methods with initial recycling and refinement.[16] Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions and refined as rigid atoms with fixed U_{iso} = 0.08 Å^2. The function minimized during refinement was $\Sigma w(|F_o - F_c|)^2$ with weighting scheme $w = 1/[\sigma^2(F) + gF^2]$ (*g* = 0.001 for **6** and 0.0004 for **7**) and σ(*F*) from counting statistics. The absolute configuration was defined by the known chirality of the diacetoneglucose molecule and confirmed by refinement of a chirality parameter.[17] The program system used was Siemens SHELXTL IRIS.[18] Final atomic coordinates are listed in Tables 5 and 6 for complexes **6** and **7** respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Table 5 Atomic coordinates (× 10^4) for $[MoO_2L_2]$ **6**

Atom	*x*	*y*	*z*
Mo	12 326(2)	101 741(2)	33 347(1)
O(1)	1 404(2)	10 221(2)	2 435(1)
O(2)	1 170(2)	11 421(2)	3 598(2)
O(1a)	−293(2)	9 786(2)	3 411(1)
O(2a)	−1 737(2)	7 861(2)	3 582(2)
O(3a)	−2 588(2)	9 005(3)	2 293(1)
O(4a)	−3 542(2)	8 309(2)	3 232(1)
O(5a)	1 216(3)	6 584(2)	2 840(2)
O(6a)	1 192(2)	8 255(2)	3 225(1)
C(1a)	−838(3)	9 160(2)	2 897(2)
C(2a)	−799(3)	8 015(2)	3 105(2)
C(3a)	−2 520(3)	8 668(3)	3 495(2)
C(4a)	−2 076(3)	9 398(3)	2 924(2)
C(5a)	−3 608(3)	8 533(3)	2 474(2)
C(6a)	−4 557(3)	9 275(4)	2 356(3)
C(7a)	−3 718(5)	7 536(4)	2 063(3)
C(8a)	233(3)	7 736(2)	3 526(2)
C(9a)	556(3)	6 597(3)	3 474(2)
C(10a)	1 859(3)	7 485(3)	2 844(2)
C(11a)	2 939(3)	7 348(4)	3 276(3)
C(12a)	2 022(6)	7 824(5)	2 076(3)
O(1b)	2 706(2)	9 858(2)	3 669(1)
O(2b)	3 988(2)	9 047(2)	4 971(2)
O(3b)	4 857(2)	11 200(2)	4 631(2)
O(4b)	5 800(2)	9 716(2)	4 913(2)
O(5b)	918(2)	9 754(3)	5 873(1)
O(6b)	1 093(2)	9 645(2)	4 662(1)
C(1b)	3 178(3)	10 378(3)	4 268(2)
C(2b)	3 054(2)	9 742(3)	4 957(2)
C(3b)	4 845(3)	9 419(3)	4 528(2)
C(4b)	4 433(3)	10 412(3)	4 186(2)
C(5b)	5 792(3)	10 823(3)	5 015(2)
C(6b)	6 845(4)	11 244(4)	4 696(4)
C(7b)	5 655(6)	11 066(4)	5 785(3)
C(8b)	2 012(3)	9 079(3)	4 982(2)
C(9b)	1 601(4)	8 880(4)	5 744(2)
C(10b)	327(3)	9 941(3)	5 233(2)
C(11b)	75(4)	11 080(3)	5 177(3)
C(12b)	−712(3)	9 291(4)	5 183(3)

Table 6 Atomic coordinates (× 10^4) for $[MoO_2L_2(phen)]$ **7**

Atom	x	y	z
Mo	0	10 000	83 603(5)
O	−206(1)	8 435(4)	9 351(3)
O(1)	782(1)	9 244(4)	7 941(3)
O(2)	1 985(1)	7 983(4)	8 216(4)
O(3)	1 109(1)	5 093(5)	8 673(3)
O(4)	2 005(2)	5 638(5)	9 503(4)
O(5)	2 292(2)	8 346(4)	4 420(3)
O(6)	1 363(2)	9 019(5)	5 001(3)
C(1)	992(2)	7 685(6)	7 662(5)
C(2)	1 610(2)	7 792(6)	7 075(5)
C(3)	1 740(2)	7 160(7)	9 292(5)
C(4)	1 100(2)	6 774(6)	8 949(5)
C(5)	1 584(2)	4 383(6)	9 394(5)
C(6)	1 383(3)	3 884(7)	10 752(5)
C(7)	1 817(3)	3 006(8)	8 605(6)
C(8)	1 718(2)	9 207(6)	6 167(5)
C(9)	2 337(2)	9 262(6)	5 602(5)
C(10)	1 739(2)	8 721(7)	3 880(5)
C(11)	1 761(3)	10 215(9)	3 023(6)
C(12)	1 519(3)	7 269(8)	3 147(6)
N(1)	−224(2)	8 505(5)	6 412(3)
C(13)	−117(2)	9 201(6)	5 218(4)
C(14)	−248(2)	8 450(7)	4 011(5)
C(15)	−512(3)	6 908(8)	4 085(6)
C(16)	−624(3)	6 240(7)	5 277(6)
C(17)	−471(2)	7 053(6)	6 428(5)
C(18)	−118(3)	9 247(7)	2 795(4)

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