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Dimolybdenum oxo-imido complexes: crystal structures of $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ and $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$

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Abstract

Oxidation of $[(MeC_5H_4)Mo(CO)_3]_2$ (**1**) by nitrobenzene in refluxing toluene affords three dimolybdenum oxo-imido complexes $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**2**), $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$ (**3**), and $[(MeC_5H_4)_2Mo_2O(NPh)(\mu\text{-}O)(\mu\text{-}NPh)]$ (**4**). Complexes **3** and **4** are isomers but do not interconvert. Complex **4** undergoes facile hydrolysis in hydrocarbon solvents giving **2** and aniline. The X-ray crystal structures of compounds **2** and **3** have been determined. Both structures display a *trans*-disposition of methylcyclopentadienyl ligands and terminal oxo ligands. The $Mo_2(\mu\text{-}X)_2$ metallacore geometries are rigorously planar with the phenyl substituent(s) of the imido ligands being tilted slightly out of this plane. The Mo–Mo distances correspond to normal single bonds.

Introduction

The chemistry of transition metal complexes containing oxo and imido ligands continues to attract considerable attention [1]. Those containing both oxo and imido functionalities are of particular interest since they are potential reagents towards the oxyamination of unsaturated organic compounds. To date such oxyamination has only been achieved using osmium reagents such as $OsO_3(NR)$ [2]. We have recently synthesised a number of mixed oxo-imido complexes of molybdenum [3]. In this paper we describe the crystal structures of two of these complexes namely $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**2**) and $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$ (**3**), the synthesis of a third new complex $[(MeC_5H_4)_2Mo_2O(NPh)(\mu\text{-}O)(\mu\text{-}NPh)]$ (**4**) and their interconversions. To date, attempts to utilise these complexes towards the oxyamination of alkynes has proved unsuccessful.

Experimental

General comments. All reactions were carried out under an N_2 atmosphere using predried solvents unless otherwise stated. NMR spectra were recorded on a Varian VXR 400 spectrometer. IR spectra were recorded as KBr disks on a Perkin–Elmer

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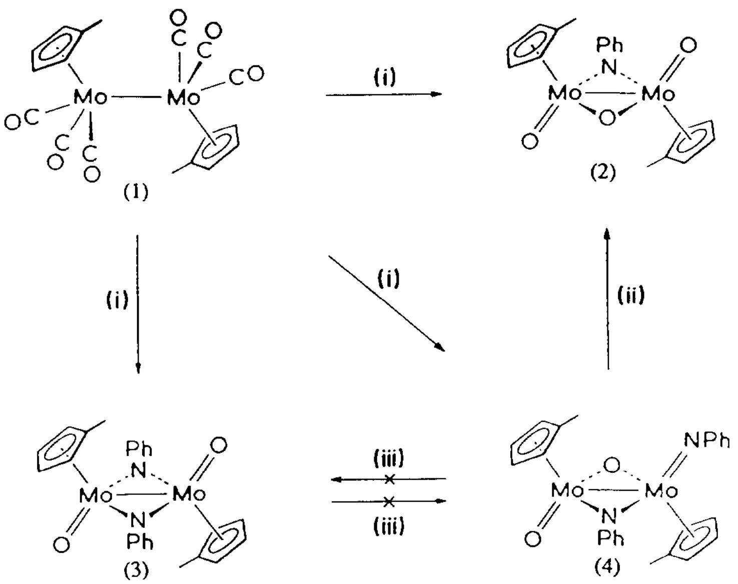

Scheme 1. (i) $PhNO_2$, toluene, 110 °C; (ii) $CDCl_3$, H_2O; (iii) toluene, 110 °C.

983 spectrometer. Column chromatography was carried out on columns of deactivated alumina (6% w/w water) and thin layer chromatography on silica (120 mesh) made up in a slurry in deionised water and activated by heating at 110 °C. Elemental analysis was performed within the chemistry department of University College. The compound $[(MeC_5H_4)Mo(CO)_3]_2$ (1) was prepared by the literature method [4].

Reaction of $[(MeC_5H_4)Mo(CO)_3]_2$ (1) with nitrobenzene

A toluene solution (100 cm^3) of **1** (1.44 g, 2.85 mmol) and nitrobenzene (0.35 cm^3, 3.40 mmol) was refluxed for 6 h whilst purging with nitrogen. A colour change from red to yellow was noted. A sample was withdrawn and the solvent removed under reduced pressure. The ^1H NMR spectrum of this sample was recorded in $CDCl_3$ revealing the presence of **2**, **3**, and **4**, in the ratios 3 : 1 : 1 respectively. No other methylcyclopentadienyl containing products were observed. The solvent was removed from the bulk of the material under reduced pressure. Chromatography eluting with light petroleum (b.p. 40–60 °C)–dichloromethane (1 : 1) yielded a yellow band which afforded **3** (280 mg, 18%) as a bright yellow solid. Crystals suitable for X-ray diffraction were grown from a saturated acetone solution at −20 °C. Further elution with dichloromethane–acetone (99 : 1) gave an orange band which yielded **4** (320 mg, 20%). Crystallisation was effected from a saturated light petroleum solution at −20 °C. Anal. Found: C, 51.09; H, 4.24; N, 4.82. $Mo_2C_{24}H_{24}N_2O_2$ calcd.: C, 51.06; H, 4.26; N, 4.96%. ^1H NMR ($CDCl_3$): δ 1.64 (3H, s, CH_3); 1.84 (3H, s, CH_3); 5.04 (1H, q, *J* 2, C_5H_4); 5.30 (1H, q, *J* 2, C_5H_4); 5.69 (1H, q, *J* 2, C_5H_4); 5.82 (1H, q, *J* 2, C_5H_4); 5.92 (1H, q, *J* 2, C_5H_4); 6.07 (2H, m, C_5H_4); 6.42 (1H, q, *J* 2, C_5H_4); 6.42 (1H, q, *J* 2, C_5H_4); 6.80 (2H, d, *J* 7, C_6H_5); 6.95 (2H, t, *J* 7, C_6H_5); 7.13 (2H, m, C_6H_5); 7.47 (2H, t, *J* 7, C_6H_5); 7.79 (2H, d, *J* 7, C_6H_5). IR: 1574(m), 1469(s), 1438(m), 1325(s), 1263(s), 1161(w), 1068(m), 1027(m), 994(w), 971(m), 885(s), 823(m), 799(s), 753(s), 690(s) cm^{-1}. By this method of purification complex **2** was not isolated.

Complex **2** was isolated by use of TLC from an analogous experiment carried out on a smaller scale. From **1** (0.8 g, 1.54 mmol), orange **2** (0.42 g, 56%) was isolated by TLC eluting with a 1 : 1 mixture of light petroleum and diethyl ether. Crystals suitable for X-ray analysis were grown from a saturated petroleum ether solution at −20 ° C. Anal. Found: C, 44.95; H, 3.80; N, 2.69. $Mo_2C_{18}H_{19}O_3$ calcd.: C, 44.17; H, 3.89; N, 2.86%. ^1H NMR ($CDCl_3$): δ 1.92 (6H, s, CH_3); 5.36 (2H, q, J 2, C_5H_4); 5.81 (2H, q, J 2, C_5H_4); 6.08 (4H, m, C_5H_4); 7.15 (1H, t, J 7, C_6H_5); 7.56 (2H, t, J 7, C_6H_5); 7.83 (2H, d, J 7, C_6H_5). IR 1582(m), 1469(s), 1438(m), 1263(s), 1068(w), 1025(m), 889(s), 819(s), 803(s), 756(m), 690(s) cm^{-1}.

Hydrolysis of 4 giving 2

Complex **4** (100 mg, 0.17 mmol) dissolved in undried CH_2Cl_2 was left open to the atmosphere for one week, additional solvent being added as necessary. TLC afforded **2** (80 mg, 92%). This conversion was conveniently monitored by ^1H NMR spectroscopy. Thus a $CDCl_3$ solution of **4** converted cleanly to **2** over a period of 3 days. Aniline was also formed stoichiometrically as shown by integration.

Reaction of 2 with nitrobenzene

A toluene solution (50 cm^3) of **2** (100 mg, 0.20 mmol) and nitrobenzene (0.04 cm^3, 0.40 mmol) was refluxed overnight whilst purging with a steady stream of nitrogen. A sample was withdrawn and the ^1H NMR spectrum recorded. The major component of the mixture was **2**, and while some new peaks appeared in the spectrum, complexes **3** and **4** were not present.

Reaction of 2 with phenylisocyanate

A THF solution (10 cm^3) of **2** (25 mg, 0.05 mmol) and phenylisocyanate (0.1 cm^3) was stirred at room temperature for 1 week. After removal of solvent and excess isocyanate the ^1H NMR spectrum was recorded. This revealed **2** ($>$ 70%), the complete absence of **3** and **4**, and a small amount ($\sim$ 10%) of the tetraimido complex $[(MeC_5H_4)Mo(NPh)(\mu\text{-}NPh)]_2$ (**5**), together with other unidentified products.

Attempted interconversion of 3 and 4

A toluene solution (75 cm^3) of **4** (100 mg, 0.18 mmol) was refluxed for 17 h. Removal of the solvent under reduced pressure yielded an oily orange solid. The ^1H NMR spectrum showed unreacted **4**, a small amount ($\sim$ 10%) of **2** (formed via hydrolysis), and the complete absence of **3**. Similarly, a toluene solution (50 cm^3) of **3** (100 mg, 0.18 mmol) was refluxed for 17 h. Removal of solvent under reduced pressure led to the quantitative recovery of the starting material.

Reaction of 4 with diphenylacetylene

A THF solution (20 cm^3) of **4** (79 mg, 0.14 mmol) and diphenylacetylene (34 mg, 1.91 mmol) was refluxed for 24 h. ^1H NMR spectroscopy revealed only the presence of starting materials.

Reaction of 3 with phenylacetylene

A THF solution (100 cm^3) of **3** (100 mg, 0.18 mmol) and phenylacetylene (0.5 g, 4.90 mmol) was irradiated for 3 h. ^1H NMR spectroscopy revealed only the presence of starting materials.

X-ray data collection

An orange crystal of **2** of approximate dimensions 0.80 × 0.55 × 0.15 mm was mounted on a glass fibre. All geometric and intensity data were taken from the crystal using an automated four-circle diffractometer (Nicolet R3mV) equipped with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Important crystallographic parameters are presented in Table 3. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. Axial photography was used to verify Laue class and unit cell dimensions. The $\bar{\omega}-2\theta$ technique was used to measure 3443 reflections (3101 unique) in the range $5 \leq 2\theta \leq 50°$. Three standard reflections were measured every 97 reflections, and showed no sign of loss of intensity during data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied. There are 2743 unique reflections with $I \geq 1.5\sigma(I)$. Structure determination and refinement was successfully accomplished in the space group $P2/c$.

A yellow crystal of **3** of approximate size 0.70 × 0.36 × 0.10 mm mounted on a glass fibre was treated as detailed above. Of 10721 reflections measured 10158 were unique with 8305 falling in the range $I \geq 1.5\sigma(I)$. The structure was solved and refined in the space group $P\bar{1}$.

Structure solution and refinement

The asymmetric unit of **2** contains two independent half molecules. The positions of the molybdenum atoms were obtained by direct methods. The remaining non-hydrogen atoms were found by iterative application of least-squares refinement and difference Fourier analysis. All non-hydrogen atoms were refined anisotropically. The final/least squares refinement included 221 parameters for 2743 variables. The last cycle gave $R = 0.054$ and $R_w = 0.065$, quality of fit 2.11 and did not shift any parameter by more than 0.001 times its estimated standard deviation. The final difference Fourier contained a peak above 1 e$Å^{-3}$ close to Mo(2). Attempts to rectify this by altering the weighting system proved unsuccessful. The structure of **3** was solved similarly. The asymmetric unit contains one complete molecule and two independent half molecules. The final least-squares refinement included 550 parameters for 8305 reflections. The last cycle of refinement gave $R = 0.039$ and $R_w =$ 0.039, quality of fit 1.65. During the refinement of **3** it became apparent that the methyl substituent of the cyclopentadienyl ring bound to Mo(2) was disordered. Refinement of C(20) in two sites, namely C(20a) and C(20b), of equal occupancy was therefore necessary.

Results and discussion

Thermolysis of a toluene solution of $[(MeC_5H_4)Mo(CO)_3]_2$ (**1**) *and nitrobenzene* led to the isolation of three products. The spectroscopic characterisation of two of these, namely $[(MeC_5H_4)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}NPh)]$ (**2**) and $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$

(3) has previously been described [3] and their solid-state structures are discussed later. A third, [$(MeC_5H_4)_2Mo_2O(NPh)(\mu$-$O)(\mu$-$NPh)$] (4), was isolated in yields of up to 20% and characterised by spectroscopic and analytical techniques. Thus, in the IR spectrum peaks were observed which were assigned to both bridging and terminal oxo (823 and 885 cm^{-1}) and imido (1263 and 1325 cm^{-1}) [5] moieties respectively. In the ^1H NMR spectrum of **4** the presence of two different imido ligand environments is clearly seen, resonances attributable to the bridging moiety being shifted to low field, while the observation of two methyl resonances is indicative of inequivalent molybdenum centres. All eight of the CH cyclopentadienyl protons are inequivalent being observed over a 1.5 ppm range indicating that the molecule contains neither a mirror plane or an inversion centre consistant with the proposed structure. Although the bisimido-bisoxo complexes **3** and **4** are structural isomers attempts to interconvert them under the conditions of their formation (i.e. toluene reflux) proved unsuccessful and thus their relative thermodynamic stabilities are unknown. Both are however stable crystalline solids and thus it appears that at least at the dimolybdenum(V) centre, no strong preference exists for either oxo or imido moieties to occupy terminal or bridging position.

The nature of the oxidation of **1** by nitrobenzene remains obscure although Alper and coworkers have shown that reaction proceeds via initial loss of carbonyl to form the multiply bonded dimer [$(MeC_5H_4)Mo(CO)_2]_2$ [6]. Complexes **3** and **4** are formally related to **2** via substitution of a bridging and terminal oxo moiety respectively by a phenylimido ligand however nitrobenzene does not effect this transformation. Thus, thermolysis of a toluene solution of **2** with excess nitrobenzene failed to yield either **3** or **4**. We have, however, previously noted that upon thermolysis with excess phenylisocyanate, **2** can be converted in high yield to the tetraimido complex [$(MeC_5H_4)Mo(NPh)(\mu$-$NPh)]_2$ (5), a process which involves complete substitution of both bridging and terminal oxo moieties [3]. The isolation of isomers **3** and **4** allowed us to test whether initial substitution of a terminal or the bridging oxo moiety of **2** was favoured. Room temperature reaction of **2** with phenylisocyanate for one week resulted in the recovery of starting material (~ 70%) and the complete absence by ^1H NMR of either **3** or **4**. The tetraimido complex **5** was however detected (~ 10%). While this result is inconclusive it does indicate that if formation of **5** proceeds via either of the bisoxo-bisimido complexes then later substitutions are strongly favoured.

Complex **4**, unlike isomeric **3**, is strongly susceptible to hydrolysis. Thus dissolution in CH_2Cl_2 and exposure to air led to the quantitative formation of **2**. This process was conveniently monitored by ^1H NMR spectroscopy which also revealed the stoichiometric formation of aniline. Thus, the overall conversion is that of nitrobenzene to aniline. To date the attempted oxyamination of alkynes utilising dimolybdenum oxo-imido complexes has been singularly unsuccessful. Thus, thermolysis of **4** with diphenylacetylene led only to the recovery of starting material as did the photolytic reaction of **3** with phenylacetylene.

X-ray crystal structures of 2 and 3

The results of X-ray diffraction studies on **2** (Fig. 1) and **3** (Fig. 2) are summarised in Tables 1 and 2 respectively. Complex **2** crystallises in the space group $P2/c$, the asymmetric unit contains two half molecules. Complex **3** crystallises in the space group $P\bar{1}$, the asymmetric unit containing one complete and two

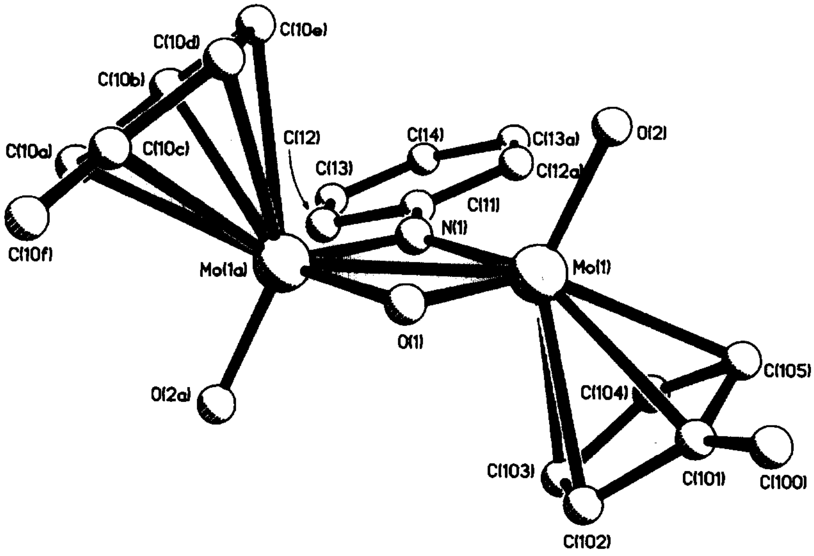

Fig. 1. Molecular structure of one of the crystallographically unique molecules of 2.

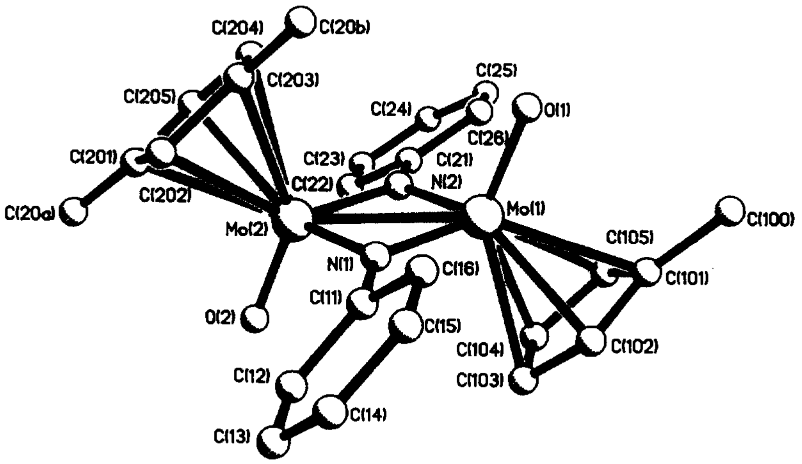

Fig. 2. Molecular structure of one of the crystallographically unique molecules of 3.

Table 1

Selected bond lengths (Å) and angles (°) for 2

Mo(1)–Mo(1A)	2.645(1)	Mo(1A)–Mo(1)–N(1)	47.6(1)
Mo(1)–N(1)	1.960(5)	Mo(1A)–Mo(1)–O(1)	46.9(1)
Mo(1)–O(1)	1.935(4)	Mo(1)–N(1)–Mo(1A)	84.8(3)
Mo(1)–O(2)	1.699(6)	Mo(1)–O(1)–Mo(1A)	86.2(2)
N(1)–C(11)	1.382(10)	Mo(1A)–Mo(1)–O(2)	113.1(2)

Table 2

Selected bond lengths (Å) and angles (°) for **3**

Mo(1)–Mo(2)	2.691(1)	Mo(2)–Mo(1)–N(1)	46.3(1)
Mo(1)–N(1)	1.931(4)	Mo(2)–Mo(1)–N(2)	46.7(1)
Mo(1)–N(2)	1.959(4)	Mo(1)–N(1)–Mo(2)	87.9(2)
Mo(2)–N(1)	1.948(4)	Mo(1)–N(2)–Mo(2)	86.7(2)
Mo(2)–N(2)	1.961(4)	Mo(2)–Mo(1)–O(1)	113.8(1)
Mo(1)–O(1)	1.717(3)	Mo(1)–Mo(2)–O(2)	114.4(1)
Mo(2)–O(2)	1.686(3)		
N(1)–C(11)	1.406(6)		
N(2)–C(21)	1.385(6)		

half independent molecules. In both structures no significant differences were observed in bond lengths or angles of crystallographically independent molecules. Relevant crystallographic details are given in Table 3.

Both **2** and **3** contain a *trans*-planar dimolybdenum dicyclopentadienyl core geometry as previously observed for the tetraimido complex $[(MeC_5H_4)Mo(NPh)(\mu\text{-}NPh)]_2$ (**5**) [3]. The dimolybdenum distances do however vary becoming longer with

Table 3

Crystallographic data for **2** and **3**

	2	**3**
Formula	$C_{18}H_{19}NO_3Mo_2$	$C_{24}H_{24}N_2O_2Mo_2$
fw	489.26	564.38
a, Å	9.333(1)	10.196(3)
b, Å	14.204(2)	14.185(3)
c, Å	13.850(2)	15.982(5)
α, deg	90.0	77.58(2)
β, deg	106.67(1)	85.06(2)
γ, deg	90.0	82.44(2)
U, Å^3	1759.1	2212.0
Z	4	4
$F(000)$	968	1128
d_{calc}, g/cm^3	1.85	1.69
cryst. size, mm	0.80×0.55×0.15	0.70×0.36×0.10
μ(Mo-K_α), cm^{-1}	14.07	11.18
data collection instrument	Nicolet R3mV	Nicolet R3mV
Radiation	Mo-K_α ($\lambda = 0.71073$)	Mo-K_α ($\lambda = 0.71073$)
Orient. reflections: no.; range	30; $14 \leq 2\theta \leq 29$	30; $7 \leq 2\theta \leq 29$
temp., °C	19	19
No. of unique data	3101	10158
total with $I \geq 1.5\sigma(I)$	2743	8305
No. of parameters	221	550
R [a]	0.054	0.039
R [b]	0.065	0.039
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.001131F^2$	$w^{-1} = \sigma^2(F) + 0.000359F^2$
largest shift/esd, final cycle	0.001	0.13
largest peak, e/Å^3	1.92	0.71

[a] $R = \Sigma[|F_c|]/\Sigma|F_o|$. [b] $R' = \Sigma[|(F_o - F_c)| \cdot w^{1/2}]/\Sigma[F_o, w^{1/2}]$.

successive substitutions of oxo for phenylimido ligands (average Mo–Mo distances: **2**, 2.662(1) Å; **3**, 2.691(1) Å; **5**, 2.717(1) Å [3]). This effect may be a result of the better π-donor ability of the imido versus the oxo ligand, the better donor ligand decreasing the need for a strong metal–metal interaction. In both **2** and **3** each molybdenum atom is bound to a terminal oxo ligand, the molybdenum-oxygen distances of between 1.717(3) and 1.686(3) Å being typical [1]. Similarly both structures contain one or more bridging phenylimido moieties with molybdenum–nitrogen distances of between 1.961(4) and 1.931(4) Å [3,6]. We have previously discussed the bonding in the related tetraimido complex **5** in terms of a delocalised system in which each multiply bonded ligand formally acts as a three electron donor [3]. The planarity of the bridging nitrogen atom(s) in **2** and **3** indicates that a similar bonding picture can be invoked. The phenyl substituent in each case is twisted slightly out of the plane of the metallacore an effect previously noted for **5** and attributed to electronic effects.

Complex **2** also contains a bridging oxo ligand the Mo(1)–O(1) distance of 1.935(4) Å within the expected range [6,7]. The presence in **2** of two different bridging ligands incurs stereochemical activity to the molecule (*RR/SS*). The other diastereoisomer, namely *RS/SR* is precluded since this would involve a *cis*-configuration of cyclopentadienyl rings. Alper and coworkers have previously characterised a derivative of **2** namely $[(C_5H_5)_2Mo_2O_2(\mu\text{-}O)(\mu\text{-}N\text{-}p\text{-tolyl})]$ (**6**) synthesised via the same method [6] and bond lengths and angles do not differ significantly between these two structures.

References

1 W.A. Nugent and J.M. Mayer, Metal–Ligand Multiple Bonds, Wiley–Interscience, New York, 1988 and references therein.
2 S.G. Hentges and K.B. Sharpless, J. Org. Chem., 45 (1980) 2257.
3 M.L.H. Green, G. Hogarth, P.C. Konidaris and P. Mountford, J. Chem. Soc., Dalton Trans., submitted.
4 R. Birdwhistell, P. Hackett and A.R. Manning, J. Organomet. Chem., 157 (1978) 239.
5 J.H. Osborne and W.C. Trogler, Inorg. Chem., 24 (1985) 3098.
6 H. Alper, J.-F. Petrignani, F.W.B. Einstein and A.C. Willis, J. Am. Chem. Soc., 105 (1983) 1701.
7 See for example: C. Couldwell and K. Prout, Acta. Crystallogr., Sect. B, 34 (1978) 933; H. Arzoumanian, A. Baldy, M. Pierrot and J.-F. Petrignani, J. Organomet. Chem., 294 (1985) 327; R. Korswagen, K. Weidenhammer and M.L. Ziegler, Acta. Crystallogr., Sect. B, 35 (1979) 2554.