

# Preparation and crystal structure of an oxoimido complex of molybdenum containing the 2,4,6-triphenylimide ligand

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Reaction of 2,4,6-triphenylaniline with Na<sub>2</sub>MoO<sub>4</sub> in the presence of SiMe<sub>3</sub>Cl and NEt<sub>3</sub> in 1,2-dimethoxyethane (dme) gave the oxoimido complex [MoCl<sub>2</sub>(NC<sub>6</sub>H<sub>2</sub>Ph<sub>3</sub>-2,4,6)O(dme)]. Its crystal structure determination showed a distorted octahedron with mutually *cis*-oxo and imido groups, *trans*-chloride ligands and the dme oxygen atoms *trans* to the oxide and imide ligands. The Mo–N<sub>imido</sub> and Mo–O<sub>oxo</sub> bond lengths [1.756(7) and 1.700(6) Å] are consistent with four- and two-electron donor ligands, respectively. The phenyl ring of the imide ligand orientates with the face of one *ortho* substituent phenyl ring pushing away from a chloride ligand and tilted towards the oxide ligand. The second such phenyl ring tilts away from a chloride ligand but does not push away from the side of the molecule. This occurs as the imido group bends towards the other side of the molecule [Mo–N–C 172.2(7)°] and a methyl group of the dme ligand is severely distorted to remove an interaction with the phenyl ring.

Use of 2,6-diisopropylphenylimide as ligand has given rise to a variety of unusual bis and tris complexes.<sup>1</sup> This is particularly so when the complexes involve low co-ordination numbers. However, our recent work<sup>2</sup> has shown that for tungsten, where only one such ligand is present, the chemistry is not significantly different from that with phenylimide as ligand, where sterically hindering groups are absent. We were thus interested in preparing phenylimido complexes with substituents in the 2,6 positions which might prove to be significantly more sterically demanding than isopropyl groups. To date, we have been unable to form complexes containing 2,4,6-tri-*tert*-butylphenylimide but have had more success with the 2,4,6-triphenyl-substituted analogue. We report here the preparation and structural properties of an oxoimido complex of molybdenum containing this phenyl-substituted ligand.

## Results and Discussion

2,4,6-Triphenylaniline can be prepared in multigram quantities by nitration of commercially available 1,3,5-triphenylbenzene followed by reduction with zinc metal and concentrated HCl. While the nitration<sup>3</sup> is straightforward, the reduction, carried out in glacial acetic acid, requires successive additions of granular zinc and concentrated HCl with monitoring by NMR spectroscopy to achieve good yields. We have found that this method is superior to that of using tin where filtration problems are experienced.

Reaction of Na<sub>2</sub>MoO<sub>4</sub> with 2 equivalents of 2,4,6-triphenylaniline in the presence of 8 equivalents of SiMe<sub>3</sub>Cl and 4 equiv. of NEt<sub>3</sub> in 1,2-dimethoxyethane (dme)<sup>4</sup> at 70–80 °C for 3 d led to a dark red solution and a copious precipitate of NEt<sub>3</sub>·HCl. Crystallisation of the red solid obtained from the solution gave a complex analysing as [MoCl<sub>2</sub>(NC<sub>6</sub>H<sub>2</sub>Ph<sub>3</sub>-2,4,6)O(dme)]. The <sup>1</sup>H NMR spectrum was consistent with a 1:1 ratio of 2,4,6-triphenylphenylimide and dme ligands. The methyl-group protons appeared as a very broad resonance with a slightly broadened singlet for the CH<sub>2</sub>CH<sub>2</sub> group. The phenyl protons cannot be assigned unambiguously, but a four-proton doublet downfield of the remaining resonances [δ 7.80, <sup>3</sup>J(HH) 7.6 Hz] is assigned to the *o*-protons of the 2,6-phenyl substituents. In the <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum the dme CH<sub>3</sub> and

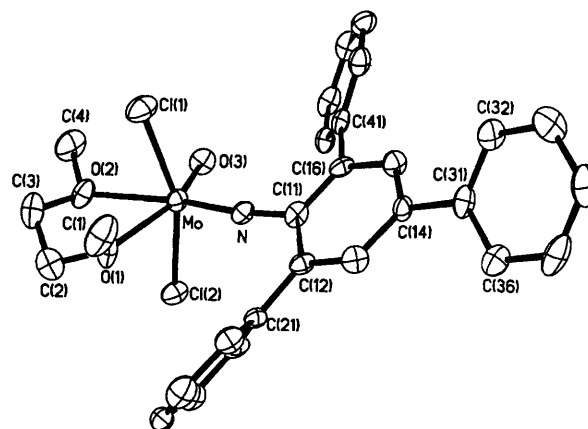


Fig. 1 Molecular structure of complex 1; atoms are represented as 50% probability surfaces

CH<sub>2</sub> carbon resonances are slightly broadened and there is only one set of aromatic ring-carbon resonances for the ligand, characteristic of a symmetrical molecule. The quaternary carbons all lie well downfield of the CH carbon resonances in comparison with the spectrum of 2,4,6-triphenylaniline where quaternaries apparently associated with the *p*-phenyl substituent lie near or within the CH resonance manifold. A resonance at δ 150.08 is assigned to the imido *ipso*-carbon on the basis of peak height and position compared with those of phenylimido complexes, particularly of tungsten(vi).<sup>5</sup>

A crystal structure determination confirmed the complex as [MoCl<sub>2</sub>(NC<sub>6</sub>H<sub>2</sub>Ph<sub>3</sub>-2,4,6)O(dme)] 1. Bond lengths and angles are given in Table 1. The structure (Fig. 1) consists of a distorted-octahedral array about the molybdenum atom, with *cis* orientated organoimide and oxide ligands, *trans* chloride ligands and with the oxygen atoms of dme lying *trans* to the oxide and imide ligands. The structure is similar to that found for the only other crystallographically studied oxoimidomolybdenum complex [MoCl<sub>2</sub>(NH)O(OPPh<sub>2</sub>Et)<sub>2</sub>]<sup>6</sup> and also one study for tungsten, namely [WCl<sub>2</sub>(NCMe<sub>3</sub>)O(bipy)]<sup>7</sup> (bipy = 2,2'-bipyridyl). In view of the rarity of structural details for

**Table 1** Selected bond lengths (Å) and angles (°) for complex **1**

Mo–N	1.756(7)	Mo–Cl(2)	2.375(3)
Mo–O(3)	1.700(6)	Mo–O(1)	2.301(7)
Mo–Cl(1)	2.386(3)	Mo–O(2)	2.297(7)
N–Mo–O(3)	104.2(4)	O(2)–Mo–Cl(2)	82.0(2)
N–Mo–O(1)	95.5(3)	O(2)–Mo–O(1)	70.6(2)
N–Mo–Cl(1)	95.2(3)	C(1)–O(1)–Mo	121.8(8)
N–Mo–Cl(2)	98.5(3)	C(4)–O(2)–Mo	119.2(7)
N–Mo–O(2)	165.9(3)	C(1)–O(1)–C(2)	113.2(9)
O(3)–Mo–Cl(1)	94.9(2)	C(3)–O(2)–C(4)	112.8(8)
O(3)–Mo–Cl(2)	96.3(2)	C(2)–O(1)–Mo	114.8(7)
O(1)–Mo–Cl(1)	81.9(2)	C(3)–O(2)–Mo	115.2(6)
O(1)–Mo–Cl(2)	81.1(2)	Mo–N–C(11)	172.2(7)
O(1)–Mo–O(3)	160.3(3)	C(11)–C(12)–C(21)	121.6(10)
Cl(1)–Mo–Cl(2)	159.7(1)	C(11)–C(16)–C(41)	125.0(8)
O(2)–Mo–O(3)	89.7(3)	C(14)–C(31)–C(32)	119.8(8)
O(2)–Mo–Cl(1)	81.1(2)	C(14)–C(31)–C(36)	122.2(9)

oxoimido complexes and the steric implications of the 2,4,6-triphenylphenylimide ligand, a detailed structural analysis for complex **1** is now presented.

The Mo–N bond length [1.756(7) Å] is similar to that found for the molybdenum complexes [Mo(NCPh<sub>3</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub>]-BF<sub>4</sub><sup>8</sup> and [MoCl<sub>2</sub>(NPh)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]<sup>9</sup> [M–N 1.731(2) and 1.734(4) Å, respectively] which are 18-electron species in which the single organoimide ligand functions as a four-electron donor (1σ, 2π donor interactions). These bond lengths contrast to the Mo–N bond length in [MoCl<sub>4</sub>(NC<sub>6</sub>H<sub>4</sub>Me-*p*)-(thf)]<sup>10</sup> (thf = tetrahydrofuran) [1.717(3) Å] where the nitrogen ligand is more tightly held and where π loading from the chloride ligands is required to obtain an 18-electron count. For complex **1** the Mo–N bond length and the Mo–N–C(11) bond angle [172.2(7)°] are similar in magnitude to those of the ‘linear’ imide ligand in [Mo(NPh)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]<sup>11</sup> [Mo–N 1.754(4) Å, Mo–N–C 169.4(4)°] which also contains a ‘bent’ two-electron-donor (1σ, 1π donor interaction) imide ligand [Mo–N 1.789(4) Å, Mo–N–C 139.4(4)°]. To obtain an overall 18-electron count for complex **1** and taking into regard the data for these other complexes, the terminal oxo group in **1** must act essentially as a two-electron donor (1σ, 1π interaction). This is represented in the complex by an Mo–O bond length of 1.700(6) Å which compares with 1.66(1) Å in [MoCl<sub>2</sub>(NH)O-(OPPh<sub>2</sub>Et)<sub>2</sub>]<sup>6</sup> taking into account the poor refinement of this structure.

The imide and oxide ligands in complex **1** cannot, however, be regarded strictly as four- and two-electron donors, respectively, as some metal-orbital sharing will occur with *cis*-orientated π-donor ligands. In bis(organoimido) complexes of tungsten such as [WCl<sub>2</sub>(NPh)(NBu<sup>1</sup>)(bipy)]<sup>12</sup> extensive sharing of the tungsten orbital occurs with lengthened W–N bonds observed, representing a bond order of 2.5 per W–N bond.

The bonding situation in oxoimido and bis(imido) complexes is further complicated by the ability of chloride ligands competitively to donate electrons to the metal π-acceptor orbitals involved in the W–N and W–O π-bonding system. The extent of Cl-to-Mo π bonding is difficult to assess but in complex **1** is expected to be small. The averaged Mo–Cl bond lengths [2.381(4) Å] are slightly shorter than those found for the bis(imido) complex [MoCl<sub>2</sub>(NC<sub>10</sub>H<sub>15</sub>)(NC<sub>6</sub>F<sub>5</sub>)(dme)]<sup>4</sup> (C<sub>10</sub>H<sub>15</sub> = adamantyl) and the oxoimido complex [MoCl<sub>2</sub>(NH)O(OPPh<sub>2</sub>Et)<sub>2</sub>]<sup>6</sup> [average Mo–Cl 2.397(2) and 2.391(7) Å, respectively] but are significantly longer than those found for [MoCl<sub>4</sub>(NC<sub>6</sub>H<sub>4</sub>Me-*p*)-(thf)]<sup>10</sup> which is a 16-electron species in the absence of Cl-to-Mo π donation.

The *trans*-chloride ligands in complex **1** push slightly further away from the oxo and imido functions than in [MoCl<sub>2</sub>(NH)O(OPPh<sub>2</sub>Et)<sub>2</sub>]<sup>6</sup> [Cl–Mo–Cl 159.7(1) *versus* 162.4(2)°, respectively] and these angles are both wider than the

equivalent bond angle in [MoCl<sub>2</sub>(NC<sub>10</sub>H<sub>15</sub>)(NC<sub>6</sub>F<sub>5</sub>)(dme)]<sup>4</sup> [equivalent bond angle 157.71(3)°]. The two chloride ligands push slightly further away from the imido nitrogen than the oxo oxygen [relevant angles 193.7(4) *versus* 191.2(3)°] whereas in [MoCl<sub>2</sub>(NH)O(OPPh<sub>2</sub>Et)<sub>2</sub>]<sup>6</sup> these angles are similar at 190.9(7) and 191.2(6)°.

The phenyl ring of the imide ligand in complex **1** orientates so that one of the *ortho*-substituent phenyl rings is nearly midway above O(3) and Cl(1) with the face of the phenyl ring tilted towards Cl(1) possibly to remove any interaction of a C–H bond with this atom. The C(11)–C(16)–C(41) bond angle of 125.0(8)° is significantly different from the equivalent sp<sup>2</sup> bond angle for the *p*-phenyl substituent [average C(14)–C(31)–C(32) and C(14)–C(31)–C(36) 121.0(8)°] reflecting the proximity of Cl(1), when the imide ligand itself pushes towards O(3) more than Cl(1) [Mo–N–C(11) 172.2(7)°].

The second *o*-phenyl substituent [C(12)] tilts more towards Cl(2) than O(1) of the dme ligand but does not push significantly away from these groups [C(11)–C(12)–C(21) 121.6(10)°]. While the N–Mo–O(3) angle is opened out more than that of N–Mo–O(1) [104.2(4) *versus* 95.5(3)°], the tilt of the imide ligand towards O(3) and Cl(1) apparently reduces any congestion between the C(12) phenyl ring and Cl(2) or O(1).

The Mo–O bond lengths for the dme ligand in complex **1** are equivalent [2.301(7) and 2.297(7) Å] and much shorter than those observed for [MoCl<sub>2</sub>(NC<sub>10</sub>H<sub>15</sub>)(NC<sub>6</sub>F<sub>5</sub>)(dme)]<sup>4</sup> where the Mo–O bond *trans* to the electron-releasing adamantyl group [bond length average 2.370(2) Å] experiences a greater *trans* influence than that *trans* to the pentafluorophenyl ligand [Mo–O 2.346(2) Å]. The close approach of O(1) and O(2) to the molybdenum centre in complex **1** is facilitated by the O(2) methyl group moving slightly towards the Cl(1) side of O(3) while the O(1) methyl group is highly distorted towards Cl(1) which minimises interaction with the C(12) phenyl group of the imide ligand. This interaction is also reduced by the opening out of the N–Mo–O(1) angle compared with O(3)–Mo–O(2) [95.5(3) *versus* 89.7(3)°, respectively]. However, the C(1)–O(1)–C(2) bond angle is still similar to that of C(4)–O(2)–C(3) [113.2(9) *versus* 112.8(8)°] in the presence of the distorted C(1) methyl group.

## Conclusion

This first study of a complex containing the 2,4,6-triphenylphenylimide ligand indicates that steric pressure will result where ligands in *cis* positions are larger than one-atom species such as oxide or chloride ligands. Thus, complexes containing large ligands *cis* to the imido function, such as those found in d<sup>2</sup>-imido complexes of molybdenum,<sup>1</sup> are expected to be severely distorted or become co-ordinatively unsaturated to accommodate the imide ligand *o*-phenyl rings. Examination of the present structure shows that the imide ligand as a whole is spatially wider than the 2,6-diisopropylphenylimide ligand. Molecular models indicate that severe steric pressure would result when bis(organo)imide ligands are present in a molecule. Studies are at present underway to evaluate these aspects.

## Experimental

General procedures and instrumentation have been described.<sup>13</sup> Proton and <sup>13</sup>C-<sup>1</sup>H NMR spectra were recorded at 400 and 100 MHz, respectively, in CDCl<sub>3</sub>. Analytical data were obtained by Dr. A. Cunninghame and associates, University of Otago, New Zealand. 1,2,3-Triphenylbenzene (Aldrich) was used without further purification. 1,2-Dimethoxyethane and diethyl ether were distilled from sodium wire and triethylamine from freshly crushed CaH<sub>2</sub> granules. Chlorotrimethylsilane was distilled prior to use.

**2,4,6-Triphenylnitrobenzene.** This compound was prepared by a modification of the reported procedure.<sup>3</sup> 1,3,5-Triphenylbenzene (100 g, 0.326 mol) was heated in glacial acetic acid (1000 cm<sup>3</sup>) until dissolution was complete and the solution allowed to cool to approximately 75 °C. The rapidly stirred solution was treated over 30 min with fuming nitric acid (250 cm<sup>3</sup>,  $d = 1.52 \text{ g cm}^{-3}$ ), stirred for a further hour at 75 °C and allowed to stand at room temperature overnight. The solution and precipitated solid were poured into iced water (500 g ice, 2 l water) and the solid collected and dried under vacuum. Crude yield 110 g, 96%. The product is sufficiently pure at this stage for further use but may be recrystallised from boiling glacial acetic acid if required. NMR: <sup>1</sup>H,  $\delta$  7.42 (m, 13 H, aromatic H) and 7.61 (m, 4 H, aromatic H); <sup>13</sup>C-<sup>1</sup>H,  $\delta$  127.26, 128.07, 128.46, 128.58, 128.67, 128.74 and 129.01 (aromatic CH); 135.05, 136.51, 138.82, 142.99 and 148.59 (aromatic C).

**2,4,6-Triphenylaniline.** 2,4,6-Triphenylnitrobenzene (105 g, 0.299 mol) was refluxed in glacial acetic acid (800 cm<sup>3</sup>). After all the solid had dissolved, zinc granules (5 g) were added followed by concentrated aqueous HCl (10 cm<sup>3</sup>) and the mixture refluxed vigorously with stirring. After the metal was consumed the process was repeated up to five times with the reaction monitored by <sup>1</sup>H NMR spectroscopy. When the reaction was essentially complete further zinc granules (10 g) were added and the solution refluxed gently overnight. The cooled solution was poured into iced water (2 l), the solution made basic with 0.1 mol dm<sup>-3</sup> NaOH and the solid collected and dried under vacuum. Crystallisation from ethanol-water solution gave colourless crystals which were dried under vacuum. Further product was obtained by heating the mother-liquor and adding water. Yield: 76.8 g, 79.9%. NMR: <sup>1</sup>H,  $\delta$  7.21–7.26 (t, 1 H, aromatic H), 7.32–7.40 (m, 6 H, aromatic H), 7.41–7.57 (t, 4 H, aromatic H) and 7.51–7.59 (m, 6 H, aromatic H); <sup>13</sup>C-<sup>1</sup>H,  $\delta$  126.34, 126.38, 127.39 (aromatic CH); 128.26 (aromatic C); 126.36, 128.66, 128.90, 129.32 (aromatic CH); 131.01, 139.64, 140.29, 140.82 (aromatic C).

[MoCl<sub>2</sub>(NC<sub>6</sub>H<sub>4</sub>Ph<sub>3</sub>-2,4,6)O(dme)]. 2,4,6-Triphenylaniline (3.12 g, 9.7 mmol) and sodium molybdate (1.0 g, 4.8 mmol) were added to a pressure bottle and degassed several times. 1,2-Dimethoxyethane (50 cm<sup>3</sup>), chlorotrimethylsilane (4.9 cm<sup>3</sup>, 38.8 mmol) and triethylamine (2.7 cm<sup>3</sup>, 19.4 mmol) were added sequentially and the pressure-bottle head fixed in place. The solution was warmed slowly to 70–80 °C and stirred at this temperature for 3 d. The solution was filtered and the solvent removed to give a dark red solid which was refluxed with diethyl ether (250 cm<sup>3</sup>) containing 1,2-dimethoxyethane (2 cm<sup>3</sup>) for 1 h. The hot solution was removed *via* a cannula and allowed to stand for 1 week giving the complex as dark red crystals. Yield 0.7 g, 25% (Found: C, 56.9; H, 4.6; N, 2.5. C<sub>28</sub>H<sub>27</sub>Cl<sub>2</sub>MoNO<sub>3</sub> requires C, 56.8; H, 4.6; N, 2.4%). NMR: <sup>1</sup>H,  $\delta$  3.18 (br, 6 H, Me), 3.62 (s, 4 H, CH<sub>2</sub>), 7.35 (t, 3 H), 7.42–7.48 (m, 6 H), 7.60–7.66 (m, 4 H) and 7.80 [d, <sup>3</sup>J(HH) 7.6, 4 Hz]; <sup>13</sup>C-<sup>1</sup>H,  $\delta$  62.12 (CH<sub>2</sub>); 69.75 (CH<sub>3</sub>); 126.24, 126.46, 126.78, 126.98, 127.16, 127.27, 127.79, 129.99 (aromatic CH); 137.15, 137.94, 140.76, 143.16, 150.08 (aromatic C).

### Crystallography

Crystal data for complex **1** are given in Table 2, together with information on instrumentation, data collection and structure determination. Air-stable crystals of **1** were mounted on silica fibres on a Nonius CAD-4 diffractometer. Room-temperature data collection used graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and  $\omega$ -2 $\theta$  scans. Lorentz-polarisation corrections were applied using locally written programs and absorption corrections applied from empirical  $\psi$  scans.<sup>14</sup> The

**Table 2** Crystallographic data for complex **1**

Formula	C <sub>28</sub> H <sub>27</sub> Cl <sub>2</sub> MoNO <sub>3</sub>
<i>M</i>	592.35
Crystal system	Orthorhombic
Space group	<i>Pna</i> <sub>2</sub>
<i>a</i> /Å	7.290(2)
<i>b</i> /Å	31.672(8)
<i>c</i> /Å	11.165(4)
<i>U</i> /Å <sup>3</sup>	2577.9(13)
<i>Z</i>	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.526
<i>F</i> (000)	1208
$\mu$ /mm <sup>-1</sup>	0.747
2 $\theta$ range/°	3–56
<i>h</i> , <i>k</i> , <i>l</i> Ranges	0–9, –41 to 0, –14 to 10
No. reflections	3266
No. observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2329
Crystal size/mm	0.37 × 0.25 × 0.22
Minimum, maximum absorption correction	0.997, 0.967
Least-squares weights <i>a</i> , <i>b</i>	0.102, 1.89
No. variables	318
Goodness of fit on <i>F</i> <sup>2</sup>	0.948
Function minimised	$\sum w(F_o^2 - F_c^2)^2$
<i>R</i> , <i>wR</i> <sub>2</sub>	0.0535, 0.1274
Maximum, minimum in final density map/e Å <sup>-3</sup>	+0.94, –0.101

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{1.0 / [\sigma^2(F_o^2) + aP^2 + bP]}, \quad P = (F_o^2 + 2F_c^2) / 3.$$

structure was solved from Patterson and heavy-atom electron-density syntheses and refined by full-matrix least squares on *F*<sup>2</sup> using the program SHELXL 93.<sup>15</sup> The heavier atoms were assigned anisotropic thermal parameters and the light atoms were refined isotropically. Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached with a common thermal parameter. The atomic coordinates are for the correct absolute structure as determined by calculations of the Flack *X* parameter.<sup>16</sup>

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/225.

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