Preparation and characterisation of dimolybdenum complexes containing fluorophenylimide ligands

Pravat Bhattacharyya,* John Fawcett, John H. Holloway, Eric G. Hope and Graham C. Saunders

Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK

The arylimido complexes $[Mo_2O_2(\mu\text{-}NR)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ and $[\{MoO(\mu\text{-}NR)(\eta^5\text{-}C_5H_4Me)\}_2]$ (R = C_6H_4F-2 or $C_6H_4CF_3$-2) were obtained from the reaction between $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_3\}_2]$ and the appropriate nitrobenzene RNO_2. In contrast, the corresponding reaction between $O_2NC_6H_3F_2$-2,6 and $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_3\}_2]$ generated two isomeric bis(imido) complexes $[\{MoO(\mu\text{-}NC_6H_3F_2\text{-}2,6)(\eta^5\text{-}C_5H_4Me)\}_2]$, which were separated by column chromatography. Hydrogen-1 and ^{19}F NMR spectroscopic studies suggested that $[\{MoO(\mu\text{-}NC_6H_4CF_3\text{-}2)(\eta^5\text{-}C_5H_4Me)\}_2]$ exists in two chemically inseparable isomeric forms. The molecular structures of $[Mo_2O_2(\mu\text{-}NC_6H_4F\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$, $[Mo_2O_2(\mu\text{-}NC_6H_4CF_3\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ and the centrosymmetric isomer of $[\{MoO(\mu\text{-}NC_6H_4CF_3\text{-}2)(\eta^5\text{-}C_5H_4Me)\}_2]$ have been determined by single-crystal X-ray diffraction. In each structure the central $Mo_2(\mu\text{-}O)(\mu\text{-}NR)$ or $Mo_2(\mu\text{-}NR)_2$ core is planar with a *trans* configuration of methylcyclopentadienyl ligands and a substantial twist angle between the phenyl rings and the metallacycle planes.

Substitution of hydrogen atoms by fluorine in the backbone of a ligand often leads to profound changes in co-ordination properties; for example tris(pentafluorophenyl)phosphine is more sterically demanding than PPh_3 by virtue of the *o*-fluorine atoms and, additionally, is a weaker σ-donor ligand.[1,2] More recently we have reported that while $P(OC_6H_3F_2\text{-}2,6)_3$ is endowed with great steric bulk by the *o*-fluorine atoms its σ-donor/π-acceptor properties are comparable to those of $P(OPh)_3$.[3–5] Metal complexes of fluorinated alkoxides and β-diketonates are recognised in materials chemistry as important precursors for the growth of thin films of metallic oxides, because of their increased volatility compared with the analogous perprotio compounds.[6–8] Furthermore, additional stabilisation of metal centres by long-range metal–fluorine interactions has been established crystallographically in a number of complexes.[9–12] The $[Mo_2X(X')(\mu\text{-}Y)(\mu\text{-}Y')(\eta^5\text{-}C_5H_4R)_2]$ system [R = H, Me or Pr^i; X, X′ = O or NR (R = aryl); Y, Y′ = O or NR],[13–19] which exists in one of two geometries depending upon the nature of the bridging Y, Y′ groups, is ideal to study the electronic and steric effects of fluorine substitution in arylimide ligands. Where X, X′ = Y, Y′ = O a puckered $Mo_2(\mu\text{-}O)_2$ core with a *cis* arrangement of the C_5H_4R rings is adopted.[13] In contrast, replacement of one or both of the bridging oxide ligands by an arylimido group results in a planar metallacyclic $Mo_2(\mu\text{-}Y)(\mu\text{-}Y')$ core and a *trans* arrangement of the cyclopentadienyl rings.[14–17] This has been attributed both to the greater steric bulk and the stronger π-donor ability of the imide ligand.

We have recently reported the isolation and single-crystal structure of $[\{MoO(\mu\text{-}NC_6F_5)(\eta^5\text{-}C_5H_4Me)\}_2]$[20] which, exceptionally for a dioxodiimido complex, has a puckered $Mo_2(\mu\text{-}NR)_2$ metallacyclic core and a *cis* arrangement of the methylcyclopentadienyl rings. In order to determine the extent to which the steric and electronic effects of fluorine atoms can dictate the structures of these complexes, we have prepared a range of μ-arylimido dimolybdenum complexes from the reaction between $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_3\}_2]$ and fluorinated nitrobenzenes.

Experimental

General techniques

All syntheses were carried out under an atmosphere of dry dinitrogen, subsequent work-up being performed in air. The nitrobenzenes and $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_3\}_2]$ were used as received (Aldrich). Toluene was distilled from sodium–benzophenone, other solvents were unpurified. Chromatography was performed on columns of deactivated alumina (6% w/w water) made up with light petroleum (b.p. 60–80 °C). The ^1H (250.13 MHz) and $^{19}F\text{-}\{^1H\}$ NMR (235.33 MHz) spectra were recorded in $CDCl_3$ on a Bruker ARX250 spectrometer. All chemical shifts are reported using the high-frequency-positive convention; ^1H NMR spectra were referenced externally to $SiMe_4$ (δ 0), ^{19}F spectra to $CFCl_3$ (δ 0). Abbreviations for NMR spectral multiplicities are: s = singlet, m = multiplet, vt = virtual triplet, vq = virtual quartet. Infrared spectra were recorded as Nujol mulls (KBr plates) on a Digilab FTS-40 spectrometer, positive-ion FAB mass spectra (3-nitrobenzyl alcohol matrix) on a Kratos Concept 1H spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd., Middlesex.

Preparations of complexes

$[\{MoO(\mu\text{-}NC_6H_4F\text{-}2)(\eta^5\text{-}C_5H_4Me)\}_2]$ 1 and $[Mo_2O_2(\mu\text{-}NC_6H_4F\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ 2. A solution of $[\{Mo(\eta^5\text{-}C_5H_4Me)(CO)_3\}_2]$ (1.5 g, 2.9 mmol) and $O_2NC_6H_4F$-2 (0.82 g, 5.8 mmol) in degassed toluene (150 cm^3) was heated at reflux for 18 h, during which time it changed from purple to brown. The reaction mixture was cooled to room temperature, the solvent removed under reduced pressure and the products extracted into warm light petroleum (10 × 50 cm^3). Column chromatography using dichloromethane gave complex **1** (50 mg, 3%), and diethyl ether eluted **2** (27 mg, 2%). The complexes were recrystallised by slow evaporation of concentrated toluene solutions at room temperature.

A similar procedure was adopted for R = $C_6H_4CF_3$-2 and $C_6H_3F_2$-2,6 giving **3** and **4** and **5a** and **5b**; no monoimido complex could be isolated from $O_2NC_6H_3F_2$-2,6.

$[\{MoO(\mu\text{-}NC_6H_4F\text{-}2)(\eta^5\text{-}C_5H_4Me)\}_2]$ **1**: orange-brown crystals (Found: C, 48.2; H, 3.6; N, 4.7. $C_{24}H_{22}F_2Mo_2N_2O_2$ requires C, 48.0; H, 3.7; N, 4.7%); δ_H 7.88 (2 H, m, C_6H_4), 7.34 (4 H, m, C_6H_4), 7.20 (2 H, m, C_6H_4), 5.77 [4 H, vt, J(H−H) 2.4, η^5-C_5H_4], 5.54 [4 H, vt, J(H−H) 2.5 Hz, η^5-C_5H_4] and 1.86 (6 H, s, CH_3); δ_F −121.1 (s); IR 1481s, 1466s, 1378m, 1288m, 1279m, 1254m, 1206w, 1191w, 1104w, 1032m, 931m, 885s, 846w, 810m, 800m, 761m, 723w and 676w cm^{-1}; FAB *m/z* 601 (*M* + H).

$[Mo_2O_2(\mu\text{-}NC_6H_4F\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ **2**: red crystals (Found: C, 42.7; H, 3.6; N, 2.8. $C_{18}H_{18}FMo_2NO_3$ requires C, 42.6; H, 3.6; N, 2.8%); δ_H 7.52 (1 H, m, C_6H_4), 7.23 (3 H, m, C_6H_4), 6.09 [4 H, vt, J(H–H) 2.4, η^5-C_5H_4], 5.15 [4 H, vt, J(H–H) 2.4 Hz, η^5-C_5H_4] and 2.15 (6 H, s, CH_3); δ_F −121.45 (s); IR 1464s, 1377s, 1294w, 1252w, 1204w, 1102w, 1024w, 939w, 901s, 884w, 826w, 798w, 759m, 723w and 562w cm^{-1}; FAB *m/z* 508 (*M* + H).

[{MoO(μ-$NC_6H_4CF_3$-2)(η^5-C_5H_4Me)}$_2$] **3**: red crystals, yield 58 mg (3%) (Found: C, 44.1; H, 2.9; N, 4.0. $C_{26}H_{22}F_6Mo_2N_2O_2$ requires C, 44.6; H, 3.2; N, 4.0%); δ_H 7.80 (4 H, d, C_6H_4), 7.64 (8 H, m, C_6H_4), 7.25 (4 H, m, C_6H_4), 5.82 [2 H, vt, J(H–H) 2.5, η^5-C_5H_4], 5.78 (6 H, m, η^5-C_5H_4), 5.05 [2 H, vt, J(H–H) 2.5, η^5-C_5H_4], 4.92 (4 H, m, η^5-C_5H_4), 4.69 [2 H, vt, J(H–H) 2.5 Hz, η^5-C_5H_4], 2.10 (3 H, s, CH_3) and 2.02 (9 H, s, CH_3); δ_F −58.4 (3 F, s) and −59.2 (3 F, s); IR 1464s, 1449s, 1377s, 1319s, 1243s, 1176m, 1153m, 1125m, 1110s, 1058m, 1033m, 920w, 893s, 844w, 808s, 781m, 771m, 723w, 667w, 650w, 627w, 600w and 532w cm^{-1}; FAB *m/z* 701 (*M* + H).

[Mo_2O_2(μ-$NC_6H_4CF_3$-2)(μ-O)(η^5-C_5H_4Me)$_2$] **4**: dark red crystals, yield 21 mg (1%) (Found: C, 41.4; H, 3.1; N, 2.5. $C_{19}H_{18}F_3Mo_2NO_3$ requires C, 40.95; H, 3.3; N, 2.5%); δ_H 7.78 (1 H, d, C_6H_4), 7.56 (2 H, m, C_6H_4), 7.27 (1 H, m, C_6H_4), 6.19 [2 H, vq, J(H–H) 2.5, η^5-C_5H_4], 5.84 [1 H, vq, J(H–H) 2.5, η^5-C_5H_4], 5.78 [1 H, vq, J(H–H) 2.8, η^5-C_5H_4], 5.66 [1 H, vq, J(H–H) 2.7, η^5-C_5H_4], 5.49 [1 H, vq, J(H–H) 2.8, η^5-C_5H_4], 5.24 [1 H, vq, J(H–H) 2.2, η^5-C_5H_4], 5.14 [1 H, vq, J(H–H) 2.4 Hz, η^5-C_5H_4], 2.00 (3 H, s, CH_3) and 1.97 (3 H, s, CH_3); δ_F −58.6 (s); IR 1463s, 1377s, 1315m, 1251m, 1161m, 1128m, 1111m, 1059m, 1033m, 916s, 895s, 873m, 846m, 820s, 774s, 722m, 694s, 664w, 649w, 629w, 613w, 599w and 533w cm^{-1}; FAB *m/z* 588 (*M* + H).

[{MoO(μ-$NC_6H_3F_2$-2,6)(η^5-C_5H_4Me)}$_2$] **5a**: orange crystals, yield 48 mg (3%) (Found: C, 45.9; H, 3.1; N, 4.5. $C_{24}H_{20}F_4Mo_2N_2O_2$ requires C, 45.3; H, 3.2; N, 4.4%); δ_H 7.07 (6 H, m, C_6H_3), 5.77 [4 H, vt, J(H–H) 2.4, η^5-C_5H_4], 5.44 [4 H, vt, J(H–H) 2.5 Hz, η^5-C_5H_4] and 1.86 (6 H, s, CH_3); δ_F −116.8 (s); IR 1467s, 1377s, 1340w, 1280m, 1246m, 1236m, 1152w, 1064w, 1030w, 997s, 923m, 896s, 847m, 810s, 780s, 736m, 725s, 669m and 553m cm^{-1}; FAB *m/z* 637 (*M* + H).

[{MoO(μ-$NC_6H_3F_2$-2,6)(η^5-C_5H_4Me)}$_2$] **5b**: orange crystals, yield 34 mg (2%) (Found: C, 45.9; H, 3.2; N, 4.5%); δ_H 7.05 (6 H, m, C_6H_3), 6.09 [4 H, vt, J(H–H) 2.4, η^5-C_5H_4], 5.15 [4 H, vt, J(H–H) 2.5 Hz, η^5-C_5H_4] and 2.15 (6 H, s, CH_3); δ_F −117.5 (s); IR 1464s, 1377s, 1287m, 1263m, 1235m, 1152w, 1000s, 929w, 910s, 902s, 826m, 819m, 778s, 731s, 621w, 585w, 555w and 505w cm^{-1}; FAB *m/z* 637 (*M* + H).

Crystallography

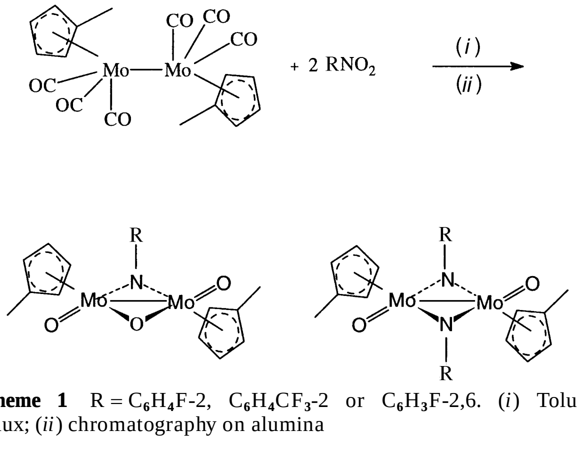
Crystals of complexes **2**, **3a** and **4** suitable for X-ray crystallographic analysis were grown by slow evaporation of concentrated diethyl ether solutions at room temperature. The crystal data, a summary of the data collection and the structure refinement for these compounds are given in Table 1. All data sets were corrected for Lorentz-polarisation effects and empirical absorption corrections were applied based on ψ-scan data. The structures were solved by Patterson methods using the program SHELXTL-PC[21] and refined using full-matrix least squares on F^2 with the program SHELXL 93.[22] For all structures all hydrogen atoms were included in calculated positions (C–H 0.96 Å) with a fixed isotropic displacement parameter (0.08 e Å^{-2}). All non-hydrogen atoms were refined with anisotropic displacement parameters.

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/297.

Results and Discussion

The reaction between [{Mo(η^5-C_5H_4Me)(CO)$_3$}$_2$] and nitrobenzenes RNO_2 containing either one fluorine atom or a trifluoromethyl group in the *ortho* position of the phenyl ring led to a mixture of products from which the bis(imido) complexes [{MoO(μ-NR)(η^5-C_5H_4Me)}$_2$] (R = C_6H_4F-2 **1** or $C_6H_4CF_3$-2 **3**) and the monoimido species [Mo_2O_2(μ-NR)(μ-O)(η^5-C_5H_4Me)$_2$] (R = C_6H_4F-2 **2** or $C_6H_4CF_3$-2 **4**) are isolable as analytically pure materials in small yields following column chromatography (Scheme 1); the compounds are analogous to those obtained using non-fluorinated nitrobenzenes,[14–20] but are produced in greatly reduced yield. No further methylcyclopentadienyl- or imido-containing species were recovered upon elution with more polar solvents. The complexes are air- and moisture-stable solids which are soluble in most organic solvents. Positive-ion FAB mass spectrometry confirms the identity of the products as dimolybdenum complexes containing either one or two imide ligands, the calculated isotopomeric distribution being in good agreement with that experimentally observed for ions of composition [*M* + H]$^+$. The reaction between 2,6-difluoronitrobenzene and [{Mo(η^5-C_5H_4Me)(CO)$_3$}$_2$] yields two distinct dioxobis(imido) complexes of formulation [{MoO(μ-$NC_6H_3F_2$-2,6)(η^5-C_5H_4Me)}$_2$]. The first, **5a**, is eluted by dichloromethane whereas the more polar isomer, **5b**, requires diethyl ether for elution. In each case identical elemental analyses and a prominent peak in both mass spectra at *m/z* 637, corresponding to a protonated bis(imido) complex, support the formulation. Notably no monoimido complex was isolated, mimicking the reactivity of $C_6F_5NO_2$, for which only a bis(imido) complex [{MoO(μ-NC_6F_5)(η^5-C_5H_4Me)}$_2$] was isolated from the corresponding reaction.[20] The IR spectra of **1**–**5** show absorptions characteristic of (arylimido) dimolybdenum complexes.[14–20]

In the cyclopentadienyl region of the ^{1}H NMR spectra (250 MHz) of complexes **1** and **2** a pair of virtual triplets of equal intensity are observed, and the ^{19}F NMR spectrum of each complex shows a singlet, confirming that **1** and **2** are single isomers with equivalent C_5H_4Me rings as a result of free rotation about the N–C bond. The δ(CH_3) values for **1** (1.86) and **2** (2.15) lie to high frequency of those for the corresponding phenylimido complexes [{MoO(μ-NPh)(η^5-C_5H_4Me)}$_2$][14] (δ 1.77) and [Mo_2O_2(μ-NPh)(μ-O)(η^5-C_5H_4Me)$_2$][17] (δ 1.92). There is a low-frequency shift in δ_F upon conversion of the nitrobenzene into the μ-imide ligand. The ^{1}H NMR spectrum of **4** contains virtual quartets in the cyclopentadienyl region, spanning a 1 ppm range, which arise from coupling of each hydrogen nucleus to three inequivalent ring protons, and two methyl signals of equal intensity (Fig. 1), indicating restricted rotation about the N–C bond and inequivalent methylcyclopentadienyl rings. The spectrum is qualitatively similar in appearance to that of [Mo_2O(S)(μ-NPh)(μ-O)(η^5-C_5H_4Me)$_2$][19] in which the two molybdenum centres are rendered inequivalent



Scheme 1 R = C_6H_4F-2, $C_6H_4CF_3$-2 or $C_6H_3F_2$-2,6. (*i*) Toluene, reflux; (*ii*) chromatography on alumina

Table 1 Details of the data collection and refinement parameters for complexes $[Mo_2O_2(\mu\text{-}NC_6H_4F\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ **2**, $[\{MoO(\mu\text{-}NC_6H_4CF_3\text{-}2)(\eta^5\text{-}C_5H_4Me)\}_2]$ **3a** and $[Mo_2O_2(\mu\text{-}NC_6H_4CF_3\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ **4**[a]

	2	**3a**	**4**
Empirical formula	$C_{18}H_{18}FMo_2NO_3$	$C_{26}H_{22}F_6Mo_2N_2O_2$	$C_{19}H_{18}F_3Mo_2NO_3$
M	507.22	700.34	557.22
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Crystal size/mm	0.57 × 0.41 × 0.35	0.54 × 0.50 × 0.39	0.64 × 0.54 × 0.48
a/Å	9.480(1)	8.876(1)	8.199(1)
b/Å	21.781(3)	10.387(2)	16.634(1)
c/Å	9.451(1)	14.030(2)	14.651(3)
β/°	109.69(1)	105.17(1)	99.21(1)
U/Å^3	1837.4(4)	1248.4(3)	1972.4(5)
Z	4	2	4
D_c/Mg m^{-3}	1.834	1.863	1.877
T/K	293	190	293
μ/mm^{-1}	1.390	1.078	1.318
$F(000)$	1000	692	1096
Empirical T_{max}, T_{min}	0.842, 0.703	0.815, 0.734	0.792, 0.706
θ Range/°	2.79–25.50	3.01–25.99	2.45–29.66
h,k,l Ranges	−11 to 11, −26 to 1, −1 to 9	−1 to 10, −1 to 12, −17 to 17	−1 to 10, −1 to 20, −18 to 18
Total data	3997	3264	5036
Unique data (R_{int})	3165 (0.0230)	2443 (0.0226)	3860 (0.0195)
a,b[c] in weighting scheme	0.030, 2.12	0.050, 2.00	0.042, 12.35
Goodness of fit on F^2	1.104	1.116	1.058
No. parameters refined	236	172	254
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0295, 0.0718	0.0349, 0.0976	0.0510, 0.1246
(all data)	0.0362, 0.1022	0.0386, 0.1004	0.0564, 0.1290
Max, min $\Delta\rho$/e Å^{-3}	0.438, −0.468	0.832, −0.506	2.755, −1.932[b]

Details in common: Siemens P4 diffractometer; Mo-Kα radiation ($\lambda = 0.7107$ Å), graphite monochromated; monoclinic. [a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n = number of reflections and p = total number of parameters refined. [b] 0.81 Å from Mo(1) (possibly due to trace of tungsten impurity). [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

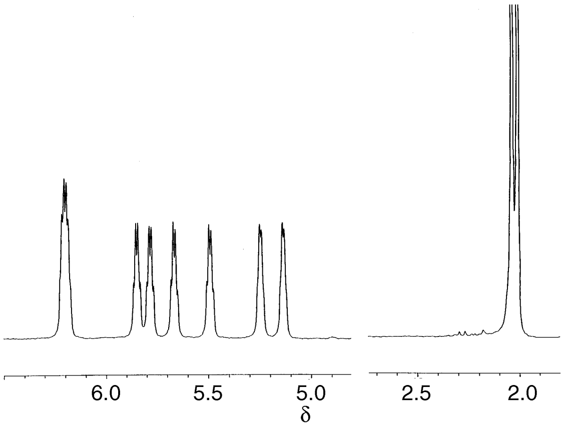


Fig. 1 Proton NMR spectrum (δ 2.0–6.5) of $[Mo_2O_2(\mu\text{-}NC_6H_4CF_3\text{-}2)(\mu\text{-}O)(\eta^5\text{-}C_5H_4Me)_2]$ **4**

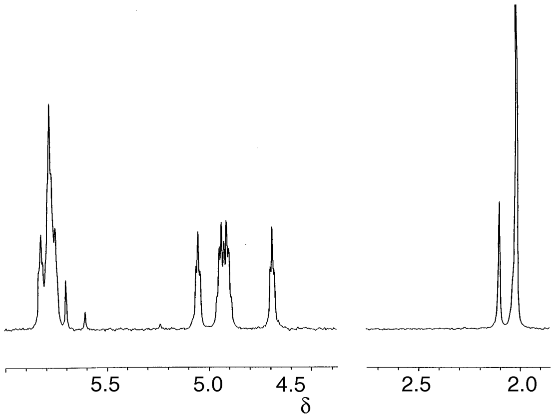
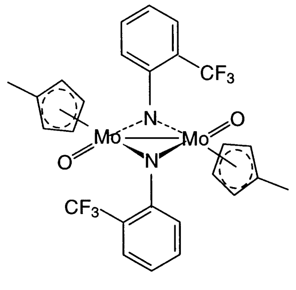
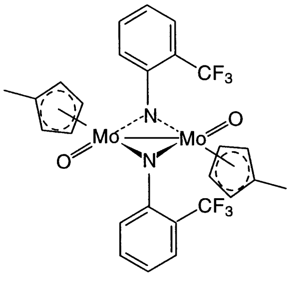


Fig. 2 Proton NMR spectrum (δ 2.0–6.0) of $[\{MoO(\mu\text{-}NC_6H_4CF_3\text{-}2)(\eta^5\text{-}C_5H_4Me)\}_2]$ **3**

by the terminal ligands. The ^{19}F NMR spectrum comprises a singlet at room temperature, indicating rapid rotation within the CF_3 group. In marked contrast, the ^{19}F NMR spectrum of the bis(imido) complex **3** contains two singlets at δ −58.4 and −59.2 in a 1 : 1 ratio, while the ^{1}H NMR spectrum shows two methyl environments at δ 2.10 and 2.02 in the intensity ratio 1 : 3 respectively (Fig. 2). The cyclopentadienyl region is simplified somewhat in comparison to that for **4** by overlap of a number of the resonances. We infer that there are two isomeric forms of complex **3**, present in approximately equal quantities, arising from the same lack of rotation about the N–C bonds identified for **4**. One of these forms, **3a**, has been crystallographically characterised (see below) and is symmetrical (*i* symmetry) with a *trans* arrangement of the CF_3 groups resulting in equivalent C_5H_4Me rings. The single methyl resonance for **3a** is coincident with one of the CH_3 signals of a non-centrosymmetric isomer (σ symmetry), **3b**, in which each phenylimido ring has its CF_3 group oriented on the same side of a planar $Mo_2(\mu\text{-}NR)_2$ core, which renders the molybdenum centres and the methylcyclopentadienyl rings non-equivalent. High-temperature ^{19}F NMR spectroscopy indicates that these two forms do not interconvert at 80 °C. Since the π-donor ability of an imide ligand exceeds that of an oxo group in these systems,[18a] the crystallographically determined planar structure of the trioxomonoimido complex **4** (see below) offers further evidence to support the same geometry for the isomeric dioxodiimido complexes.



3a



3b

The NMR spectra of the isomeric bis(2,6-difluorophenylimido) complexes **5a** and **5b** are similar in appearance to

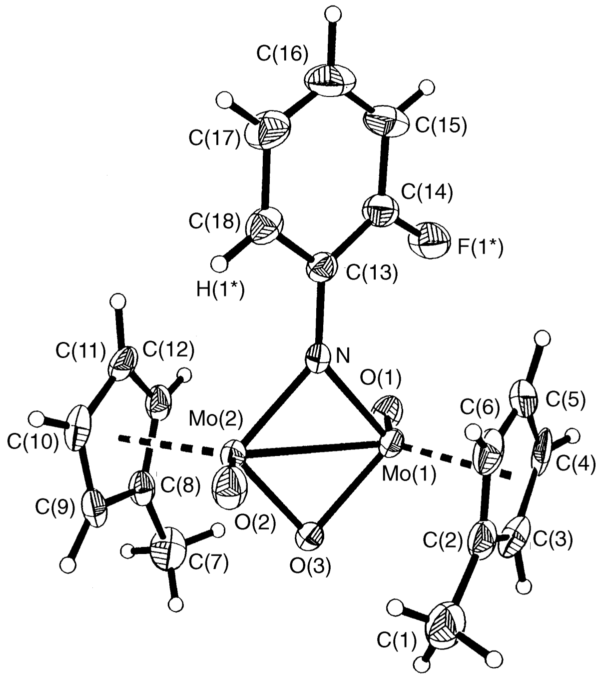


Fig. 3 Crystal structure of $[Mo_2O_2(\mu-NC_6H_4F-2)(\mu-O)(\eta^5-C_5H_4Me)_2]$ **2**. Atoms F(1*) and H(1*) represent the dominant positions of disordered sites, with another orientation of the arylimido ring in which the F and H positions are reversed, in a respective ratio of 58:42. Thermal displacement ellipsoids are drawn at the 30% probability level

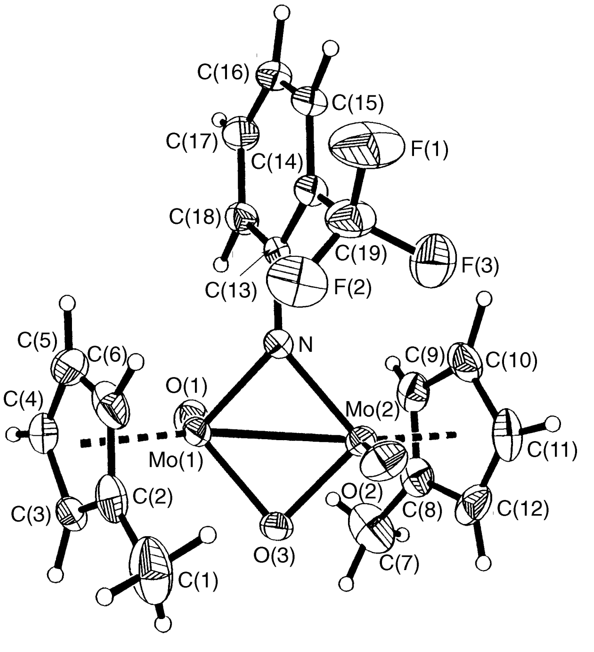


Fig. 4 Crystal structure of $[Mo_2O_2(\mu-NC_6H_4CF_3-2)(\mu-O)(\eta^5-C_5H_4Me)_2]$ **4**. Thermal displacement ellipsoids are drawn at the 30% probability level

Table 2 Selected bond lengths (Å) and angles (°) for complexes **2** and **4**

	2	**4**
Mo(1)–O(3)	1.936(3)	1.940(4)
Mo(2)–O(3)	1.934(3)	1.941(4)
Mo(1)–Mo(2)	2.6499(5)	2.6591(8)
Mo(1)–O(1)	1.708(3)	1.709(5)
Mo(2)–O(2)	1.700(3)	1.694(5)
Mo(1)–N	1.960(3)	1.972(5)
Mo(2)–N	1.961(3)	1.960(5)
N–C(13)	1.389(5)	1.404(7)
Mo(1)–$(C_5H_4Me)_{centroid}$	2.085(5)	2.082(7)
Mo(2)–$(C_5H_4Me)_{centroid}$	2.082(5)	2.083(7)
Mean C–F	1.26	1.33
Mo(1)–N–Mo(2)	85.03(12)	85.1(2)
Mo(1)–O(3)–Mo(2)	86.43(10)	86.5(2)
O(3)–Mo(1)–N	94.24(12)	93.9(2)
O(3)–Mo(2)–N	94.30(12)	94.3(2)
Mo(1)–N–C(13)	138.1(3)	131.9(4)
Mo(2)–N–C(13)	136.8(3)	140.4(4)
O(2)–Mo(2)–O(3)	106.44(14)	104.7(2)
O(1)–Mo(1)–O(3)	105.70(14)	105.0(2)
O(2)–Mo(2)–N	105.33(14)	106.3(2)
O(3)–Mo(2)–Mo(1)	46.82(8)	46.73(12)
O(3)–Mo(1)–Mo(2)	46.76(8)	46.77(13)
O(2)–Mo(2)–Mo(1)	113.57(10)	115.3(2)
O(1)–Mo(1)–Mo(2)	113.25(10)	111.6(2)
N–Mo(1)–Mo(2)	47.49(9)	47.24(14)
N–Mo(2)–Mo(1)	47.48(9)	47.65(14)
O(1)–Mo(1)–N	105.26(14)	106.9(2)
F(2)–C(19)–F(1)		107.1(8)
F(2)–C(19)–F(3)		105.7(7)
F(1)–C(19)–F(3)		105.2(8)

those for **1** and **2**. Integration of the signals in the ^1H NMR spectra indicates equal numbers of arylimido and methyl protons, supporting the microanalytical and mass spectrometric data. We propose that one form has a *trans* geometry of the cyclopentadienyl rings and a planar $Mo_2(\mu-NR)_2$ core, while the other isomer, by analogy with $[\{MoO(\mu-NC_6F_5)(\eta^5-C_5H_4Me)\}_2]$,[20] possesses a puckered metallacycle with *cis* cyclopentadienyl rings. The adoption of both possible metallacyclic geometries is consistent with a weaker *trans* influence for the 2,6-difluorophenylimide ligand than for the 2-fluorophenylimide or 2-(trifluoromethyl)phenylimide ligands due to the electron-withdrawing effects of the two fluorine atoms, and sufficiently similar to that of the oxide ligand to allow both forms to exist. In the absence of a crystal structure no unequivocal assignment of the isomers is forthcoming. Notably the $\delta(CH_3)$ values for the bis(imido) complexes **1**, **3** and **5** are intermediate between those of the corresponding phenylimido complex $[\{MoO(\mu-NPh)(\eta^5-C_5H_4Me)\}_2]$[14] ($\delta$ 1.77) and the pentafluorophenylimido complex $[\{MoO(\mu-NC_6F_5)(\eta^5-C_5H_4Me)\}_2]$[20] ($\delta$ 2.24).

The molecular structures of the trioxomonoimido complexes $[Mo_2O_2(\mu-NC_6H_4F-2)(\mu-O)(\eta^5-C_5H_4Me)_2]$ **2** and $[Mo_2O_2(\mu-NC_6H_4CF_3-2)(\mu-O)(\eta^5-C_5H_4Me)_2]$ **4** are given in Figs. 3 and 4 respectively with selected bond lengths and angles in Table 2, and confirm the *trans* planar geometry. In each complex the molybdenum centres are bridged by an oxide ligand O(3) and the nitrogen atom N of an arylimido group, to give a planar $Mo_2(\mu-O)(\mu-NR)$ metallacycle arrangement with a *trans* disposition of the methylcyclopentadienyl rings. The molecular structure of **2** shows disorder of the fluorine-atom position between two possible orientations of the arylimido group about the N–C(13) bond with a ratio of 58:42 between the two sites. The Mo(1)–Mo(2) distances in **2** and **4** [2.6499(5) and 2.6591(8) Å respectively] lie within the observed range for related η^5-cyclopentadienyl μ-imido-dimolybdenum complexes (2.645–2.660 Å),[14–18] indicating the similar π-donor properties of the fluorophenylimide ligands to those of their perprotio counterparts. In each of complexes **2** and **4** there is a small deviation from trigonal geometry at N. The angle between the Mo(1)–Mo(2)–N–O(3) plane and the N–C(13) bond axis is 178.9° for **2**, compared to 169.3° for **4**. The Mo(1)–N–C(13)–C(14) torsion angles are 160.2(6) and 144.0(5)° for **2** and **4**, hence the twist angles between the metallacycle planes and the C(13)–C(18) phenyl ring plane are 19.8(6) and 36.0(5)° respectively. The increased twisting in **4** is attributable to the greater steric bulk of the *o*-CF_3 group. The closest metal–fluorine approach in **4** is between Mo(2) and F(3), 3.391(5) Å. The molecular structure of the dioxodiimido complex $[\{MoO(\mu-NC_6H_4CF_3-2)(\eta^5-C_5H_4Me)\}_2]$ **3a** is shown in Fig. 5; selected bond lengths and angles are in Table 3. Compound **3a**

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

Mo(1)–O(1)	1.706(2)	Mo(1)–N(1)	1.966(3)
Mo(1)–N(1′)	1.971(3)	Mo(1)–Mo(1′)	2.6736(6)
N(1)–C(7)	1.410(4)	Mean C(13)–F	1.34
Mo–$(C_5H_4Me)_{centroid}$	2.078(4)		
O(1)–Mo(1)–N(1)	105.97(12)	O(1)–Mo(1)–N(1′)	104.84(11)
N(1)–Mo(1)–N(1′)	94.47(10)	O(1)–Mo(1)–Mo(1′)	113.03(8)
N(1′)–Mo(1)–Mo(1′)	47.15(8)	N(1)–Mo(1)–Mo(1′)	47.32(7)
C(7)–N(1)–Mo(1′)	130.6(2)	C(7)–N(1)–Mo(1)	140.5(2)
Mo(1)–N(1)–Mo(1′)	85.53(10)	F(2)–C(13)–F(3)	105.8(3)
F(2)–C(13)–F(1)	105.8(4)	F(1)–C(13)–F(3)	104.9(3)

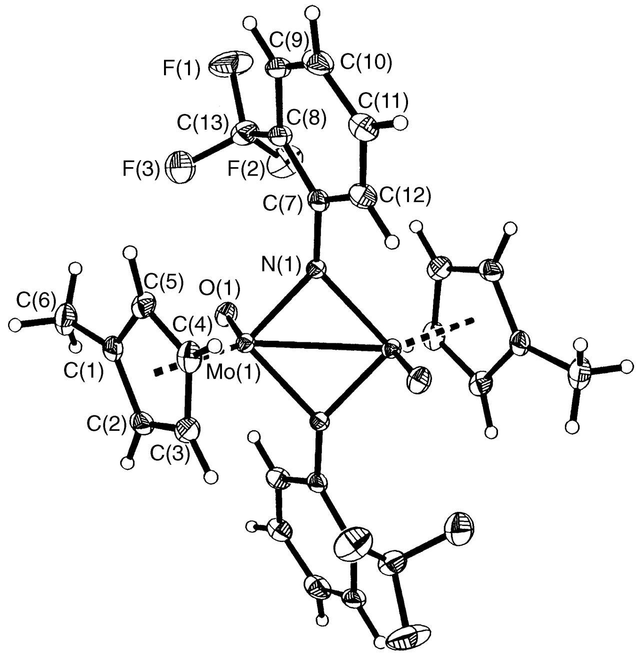


Fig. 5 Crystal structure of [{MoO(μ-$NC_6H_4CF_3$-2)(η^5-C_5H_4Me)}$_2$] **3a**. Details as in Fig. 4

is centrosymmetric with, as described for **2** and **4**, a torsion angle Mo(1)–N(1)–C(7)–C(12) of 120.1(5)° leading to a twisting of the C(7)–C(12) phenyl ring plane from the central Mo_2(μ-NR)$_2$ plane about N(1)–C(13) by 59.9(5)°, and an angle of 166.7° between the N(1)–C(13) bond and the Mo(1)–Mo(1′)–N(1)–N(1′) plane. The Mo(1)–Mo(1′) separation, 2.6736(6) Å, is smaller than that found in [{Mo(NPh)(μ-NPh)(η^5-C_5H_4Me)}$_2$] [2.7175(5) Å][15] and [{MoO(μ-NPh)(η^5-C_5H_4Me)}$_2$] [2.691(1) Å][17] and the *cis*-puckered bis(pentafluorophenylimido) complex [{MoO(μ-NC_6F_5)(η^5-C_5H_4Me)}$_2$] [2.686(1) Å].[20] The similarity of the internal dimensions of the metallacycle and the exocyclic bond lengths and angles within **2**, **3a** and **4** to those in the perprotio compounds confirm earlier predictions that a single *o*-fluorine atom or *o*-trifluoromethyl group has little influence on the π-donor properties of the phenylimide ligand despite their electron-withdrawing capacity, but that steric effects are of importance.

Conclusion

It is apparent that electronic effects dominate whether a *cis*-puckered or *trans*-planar metallacyclic geometry is adopted, while steric considerations govern the twisting about the N–C bonds. Thus μ-NC_6H_4F-2 and μ-$NC_6H_4CF_3$-2 ligands behave electronically like phenylimide ligands in these cyclopentadienylmolybdenum dimers, leading to planar metallacyclic cores, while μ-NC_6F_5 and μ-$NC_6H_3F_2$-2,6 can be likened to oxide ligands in their electron-withdrawing influence.

Acknowledgements

We are grateful to the Royal Society (E. G. H.), BNFL Fluorochemicals Ltd. (G. C. S.) and the EPSRC (P. B.) for financial support.

References

1 M. J. Atherton, J. H. Holloway, E. G. Hope, D. R. Russell and G. C. Saunders, *Polyhedron*, 1996, **15**, 173.
2 M. J. Atherton, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karacar, L. A. Peck and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1995, 4029.
3 M. J. Atherton, K. S. Coleman, J. H. Holloway, E. G. Hope, D. R. Russell and G. C. Saunders, *Polyhedron*, 1995, **14**, 2107.
4 M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, K. Jones, N. Reeves, D. R. Russell and G. C. Saunders, *Polyhedron*, 1993, **12**, 2681.
5 M. J. Atherton, J. Fawcett, A. P. Hill, J. H. Holloway, E. G. Hope, D. R. Russell and G. C. Saunders, *Acta Crystallogr., Sect. C*, 1996, **52**, 2463.
6 C. J. Willis, *Chem. Soc. Rev.*, 1988, **88**, 133.
7 F. Labrize, L. G. Hubert-Pfalzgraf, J. C. Daran and S. Halut, *J. Chem. Soc., Chem. Commun.*, 1993, 1556.
8 J. C. Plakatouras, I. Baxter, M. B. Hursthouse, K. M. Abdul Malik, J. C. McAleese and S. R. Drake, *J. Chem. Soc., Chem. Commun.*, 1994, 2455.
9 R. J. Kulawiec, E. M. Holt, M. Lavin and R. H. Crabtree, *Inorg. Chem.*, 1987, **26**, 2559.
10 R. M. Catala, D. Cruz-Garritz, A. Hills, D. L. Hughes, R. L. Richards, P. Sosa and H. Torrens, *J. Chem. Soc., Chem. Commun.*, 1987, 261.
11 R. Uson and J. Fornies, *Inorg. Chim. Acta*, 1992, **198**, 165.
12 C. Bartolome, P. Espinet, F. Villafane, S. Giesa, A. Martin and A. G. Orpen, *Organometallics*, 1996, **15**, 2019.
13 C. Couldwell and K. Prout, *Acta Crystallogr., Sect. B*, 1978, **34**, 933.
14 M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Organomet. Chem.*, 1990, **394**, C9.
15 M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3781.
16 H. Alper, J.-F. Petrignani, F. W. B. Einstein and A. C. Willis, *J. Am. Chem. Soc.*, 1983, **105**, 1701.
17 J. Fletcher, G. Hogarth and D. A. Tocher, *J. Organomet. Chem.*, 1991, **403**, 345.
18 (*a*) G. Hogarth, P. C. Konidaris and G. C. Saunders, *J. Organomet. Chem.*, 1991, **406**, 153; (*b*) G. C. Saunders, D.Phil. Thesis, University of Oxford, 1989.
19 J. Fletcher, G. Hogarth and D. A. Tocher, *J. Organomet. Chem.*, 1991, **405**, 207.
20 J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell and G. C. Saunders, *J. Organomet. Chem.*, 1994, **464**, C20.
21 G. M. Sheldrick *SHELXTL-PC Users manual*, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
22 G. M. Sheldrick, SHELXL 93, Program for crystal structure solution, University of Göttingen, 1993.

Received 12*th July* 1996; *Paper* 6/04900A