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Preliminary Communication

Synthesis and crystal structure of dioxobis(μ-pentafluorophenylimido)di-(η-methylcyclopentadienyl)dimolybdenum

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Abstract

The reaction between $C_6F_5NO_2$ and $[(\eta\text{-}MeC_5H_4)Mo(CO)_3]_2$ yields the dioxobisimido complex, $[(\eta\text{-}MeC_5H_4)MoO(\eta\text{-}NC_6F_5)]_2$ (**1**). The X-ray crystal structure of compound **1** shows a *cis* arrangement of the methylcyclopentadienyl ligands and a puckered metallacyclic core.

Key words: Molybdenum; Imide; Oxo; Pentafluorophenyl; Crystal structure

There is considerable interest in the electronic and geometric properties of cyclopentadienylmolybdenum dimers of the form $[(\eta\text{-}C_5H_4R)_2Mo_2(X)(X')(\mu\text{-}Y)(\mu\text{-}Y')]$ (R = H, Me, ^{i}Pr, X, X′ = O, N-aryl; Y, Y′ = O, N-aryl) [1–6]. This intriguing series of complexes displays two structural types. The tetraoxo complex $[(\eta\text{-}C_5H_5)MoO(\mu\text{-}O)]_2$ contains a puckered metallacyclic core with a *cis* arrangement of the cyclopentadienyl ligands (*cis*-puckered) [1]. Replacement of one or more of the oxo ligands by arylimido ligands yields complexes with planar metallacyclic cores and *trans* arrangement of the cyclopentadienyl ligands (*trans*-planar), as found for $[(\eta\text{-}C_5H_5)MoO]_2(\mu\text{-}O)(\mu\text{-}N\text{-}p\text{-}tolyl)$ [2], $[(\eta\text{-}MeC_5H_4)MoO]_2(\mu\text{-}O)(\mu\text{-}NPh)$ [5], $[(\eta\text{-}MeC_5H_4)MoO(\mu\text{-}NPh)]_2$ [5] and $[(\eta\text{-}MeC_5H_4)Mo(NPh)(\mu\text{-}NPh)]_2$ [3,4]. The difference in structure between the tetraoxo complex and the arylimido-containing complexes has been ascribed to the greater bulk of the bridging arylimido ligands than of oxo ligands, which favours a *trans* disposition of the cyclopentadienyl ligands, and also the better π-donor ability of the imido ligand than of the oxo ligand. The latter is reflected in the Mo–Mo distances, which increase with successive substitution of oxo by imido ligands (2.602(1) Å for $[(\eta\text{-}C_5H_5)MoO(\mu\text{-}O)]_2$ ranging to 2.717(1) Å for $[(\eta\text{-}MeC_5H_4)Mo(NPh)(\mu\text{-}NPh)]_2$), and in the electrochemical properties of the complexes [6]. As part of our continuing study of the effect on transition metal complexes of the presence of fluorine in a ligand, we have prepared the bis(pentafluorophenyl)imido complex, $[(\eta\text{-}MeC_5H_4)MoO(\mu\text{-}NC_6F_5)]_2$ (**1**). Herein we report the synthesis and structure of complex **1**.

The complex $[(\eta\text{-}MeC_5H_4)MoO(\mu\text{-}NC_6F_5)]_2$ (**1**) was isolated in very low yield (*ca.* 2%) following chromatography of the complex mixture of products obtained by treatment of $[(\eta\text{-}MeC_5H_4)Mo(CO)_3]_2$ with $C_6F_5NO_2$ in refluxing toluene. The structure of complex **1** was determined by single-crystal X-ray crystallography *, and is shown in Fig. 1. Unlike perprotio arylimido-containing $[(\eta\text{-}RC_5H_4)_2Mo_2XX'(\mu\text{-}Y)(\mu\text{-}$

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* Crystal data: $C_{24}H_{14}F_{10}Mo_2N_2O_2$, $M = 744.3$, monoclinic, space group $P2_1/c$; $a = 6.517(1)$, $b = 31.684(4)$, $c = 11.979(1)$ Å, $\beta = 90.83(0)°$, $V = 2473.2(5)$ Å^3, $Z = 4$, $D_c = 1.999$ Mg m^{-3}, Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 1.117$ mm^{-1}, $T = 293$ K, $F(000) = 1448$, The crystals were yellow needles. The crystal used for data collection had the dimensions $0.70 \times 0.15 \times 0.13$ mm. Accurate unit cell parameters were determined by least-squares refinement of the optimised setting angles of 45 reflections in the range $10 \leq 2\theta \leq 25°$. The intensities of 8338 reflections were collected at room temperature on a Siemens P4 diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) using an ω-scan technique (range $4 \leq 2\theta \leq 59°$; $-1 \leq h \leq 8$, $-1 \leq k \leq 43$, $-16 \leq l \leq 16$). Three standard check reflections monitored every 100 reflections indicated no crystal decay. The data merged to give 6470 unique reflections ($R_{int} = 0.029$) and were corrected for Lorentz and polarization effects to yield 4669 data have $I > 2\sigma(I)$ regarded as observed. A semi-empirical absorption correction was applied to the data with the maximum and minimum transmission factors of 0.975 and 0.653 respectively.

The structure was solved by direct methods using the TREF option of SHELXTL-PC [7] and refined by full matrix least squares. Hydrogen atoms were included in calculated positions (C–H = 0.95 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. The final $R = 0.0536$ and $R_w = 0.0511$ (where $w = 1/\sigma^2 F$) for 365 variables, $(\Delta/\sigma)_{max} = 0.003$. The final Fourier showed $+1.8$ eÅ^{-3} peaks at 0.8 Å from both Mo atoms. An analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ was satisfactory.

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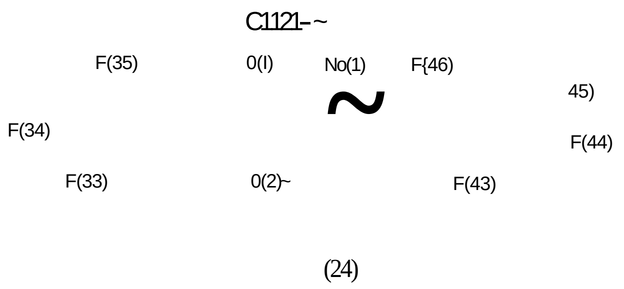

Fig. 1. Molecular structure of [~/-MeCsHg)MoCK/z-NC6Fs)]2(1). Selected bond distances (,~):' Mo(1)-N(1) 1.967(4), Mo(1)-N(2) 1.963(4), Mo(2)-N(1) 1.969(4), Mo(2)-N(2) 1.982(4), Mo(1)-O(1) 1.703(4), Mo(2)-O(2) 1.688(4), N(1)-C(31) 1.40~7), N(2)-C(41) 1.392(7), Mo(1)-(MeCsH4)centroid 2.091, Mo(2)-(MeCsH4)eentroid 2.075. Selected bond angles (°): Mo(1)-N(1)-Mo(2) 86.1(2), Mo(1)-N(2)-Mo(2) 85.8(2), N(1)-Mo(1)-N(2) 92.3(2), N(1)-Mo(2)-N(2) 91.6(2), Mo(2)-Mo(1)-O(1) 105.2(1), Mo(1)-Mo(2)-O(2) 106.3(1), Mo(1)-N(1)-C(31) 140.9(4), Mo(2)-N(1)-C(31) 132.6(3), Mo(1)-N(2)-C(41) 141.7(3), Mo(2)-N(2)-C(41) 132.4(3), N(1)-C(31)-C(32) 121.1(5), N(1)-C(31)-C(36) 122.3(5), N(2)-C(41)-C(42) 121.2(5), N(2)-C(41)-C(46) 122.7(5).

Y')] complexes, 1 possesses a c/s disposition of the methylcyclopentadienyl rings and has a puckered MONEMO metallacyclic core (the dihedral angle between the planes Mo(1)-N(1)-Mo(2) and Mo(1)-N(2)-Mo(2) is 158.6°), as shown in Fig. 2. There is almost planar geometry about each nitrogen atom, indicative of significant N(pzr)-Mo(dzr) interactions (deviations of carbon atoms from the Mo-N-Mo planes are 0.117 and 0.015 ,~ for C(31) and C(41) respectively). Furthermore, the Mo-Mo distance is 2.686(1) A, which is similar to that of 2.691(1) ~, the bis(phenylimido) complex, [(~7-MeCsH4)MoO(/z-NPh)]2 [5], suggesting that C6FsN and C6H5N have similar w-donor properties in these complexes. The Mo-N (bridging), Mo-O(terminal) and N-C distances are typical of arylimido-containing [(r/-RCsH4)2Mo2XX'(/~_y)(/~_y,)] complexes. The planes containing each pentafluorophenyl group lie almost perpendicular to the respective Mo-N-Mo planes.

Fig. 2. The geometryof the MoN2Mocore.

The IR and NMR spectroscopic data of complex 1 are entirely consistent with the structure *. The IR spectrum shows bands characteristic of pentafluorophenyl groups, and a strong band at 909 cm-1, which is assigned as v(Mo=O) by comparison with the IR spectrum of [(~7-CsHs)MoO(/~-O)]2 [8]. The 1H NMR spectrum exhibits three resonances assigned to two pairs of cyclopentadienyl hydrogen atoms and the methyl group, consistent with a methylcyclopentadienylmolybdenum dimer with equivalent molybdenum atoms and identical bridging ligands [3,4]. The room temperature 19F NMR spectrum exhibits three multiplets, consistent with the presence of equivalent pentafluorophenylimido ligands. The 19F NMR spectrum recorded at 174 K exhibits two resonances assigned to two pairs of non-equivalent *ortho-fluorine* atoms, indicating that the c/s arrangement of the cyclopentadienyl rings of I is maintained in solution, and also that there is restricted rotation about the N-C bonds, with the conformation of the pentafluorophenyl rings adopted in the solid state being preferred over that in which they would be coplanar with the respective Mo-N-Mo moieties. This is in contrast to the perprotio bridging-arylimido containing [(r/-RCsH4)2-MOEXX'(/z-Y)(~-Y')] complexes, in which the aryl groups adopt conformations in which they are almost coplanar with the respective Mo-N-Mo planes [2-5].

In summary, the bis(pentafluorophenylimido)dimolybdenum complex [(r/-MeCsH4)MoO(~_NC6Fs)]2 has been prepared in low yield and structurally characterized by X-ray crystallography. Complex 1 exhibits a crY-puckered geometry, which is a new structural type for arylimido-containing [(~7-RC5H4)EMOzXX,(~.Y)(/~-Y')] complexes. We are currently carrying out further investigations of fluorophenylimido complexes of this type in order to determine the factors that govern the geometries adopted by these species.

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* Selected spectroscopic data: IH NMR (CDCI3, 300 MHz): 8 6.17 (s, 4H, C5H4), 5.07 (s, 4H, C5H4), 2.24 (s, 6H, CH3). 19F NMR (25°C) (CDCI3, 282.41 MHz): 8 -146.83 [dd, *3J(Fortho-Fmeta) =* 22.7 nz, *5J(Fortho-Fmeta,)=5.1 Hz, 4F, Forthol,* -160.67 [t, *3J(Fpara-Fme,,) =* 21.5 Hz, 2F, *Fp,,ra],* - 162.70 [vtd, 4F, *Fmet,,].* IR (Nujoi, cm-l): 1507 s, 1497 sh, 1447 w, 1367 w, 1319 w, 1187 w, 1036 s, 1016 w, 983 s, 909 s, 901 w, 850 m, 838 m, 828 sh, 733 w, 667 w, 550 w.

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