Arylalkane Oxidation by Dioxo[4,4′-di(*tert*-butyl)-2,2′-bipyridyl]molybdenum(VI) Complexes

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Arylalkanes are oxidized by dithiocyanato- and dibromo-[4,4′-di(*tert*-butyl)-2,2′-bipyridyl]molybdenum(VI) dioxo complexes either thermally or under UV irradiation.

Transition metal–oxo groups are of particular interest since they are found in many systems ranging from metalloenzymes to solid state reactions on metal oxide surfaces.[1–3] Although this function has many different roles in various catalytic processes,[4–7] its presence in catalytic oxygen atom transfer reactions has been shown to be essential.[1,3] When modelling enzymatic systems for alkane or alkene oxidation, the metals of choice have been chromium, manganese and iron,[1] whereas rhenium–[8] and ruthenium–oxo[9–11] complexes as well as heteropolytungstates[12] have been studied widely as catalysts for alkane or alcohol oxidation.

Molybdenum–oxo compounds also hold an important place in this field since they are present in many enzymatic systems such as molybdenum hydroxylases or oxotransferases,[1,3] however, to our knowledge, no well-defined molybdenum–oxo model able to oxidize an organic substrate has ever been reported. Indeed, the majority of the numerous models studied have been molybdenum–oxo complexes bearing electron-donating sulfur ligands and the substrates oxidized by them were usually phosphines.[1,3,13]

In this context we recently reported the synthesis of a thiocyanatomolybdenum dioxo anion **1** which exhibited remarkable properties of an oxygen atom transfer agent in spite of its anionic character and the fact that no molybdenum–sulfur bond were present:[14]

$$\underset{\mathbf{1}}{[PPh_4]_2[Mo^{VI}(O)_2(NCS)_4]} + PPh_3 \rightarrow [PPh_4]_2[Mo^{IV}O(NCS)_4] + OPPh_3$$
$$\mathbf{2}$$

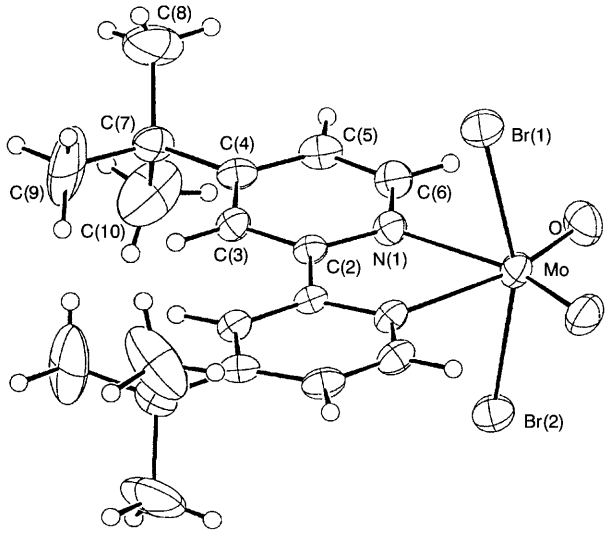


Fig. 1 ORTEP view of **4**. Selected bond distances (Å) and angles (°): Mo–Br(1) 2.5139(9), Mo–Br(2) 2.537(1), Mo–O 1.690(3), Mo–N(1) 2.301(4); Br(1)–Mo–Br(2) 160.74(4), Br(1)–Mo–O 96.3(1), Br(1)–Mo–N(1) 81.57(9), Br(2)–Mo–O 95.1(1), Br(2)–Mo–N(1) 82.61(9), O–Mo–N(1) 92.0(1), O–Mo–N(1) 161.3(1), N(1)–Mo–N(1) 69.3(2), O–Mo–O 106.8(2), Mo–N(1)–C(6) 121.7(3), Mo–N(1)–C(2) 120.5(3).

Since we had also shown that gradual diminishing of the anionic character significantly increases the oxidizing power of similar anions[13] and that bipyridyl ligands were most efficient in this neutralization process,[15] we reacted **1** with various bipyridines[16] and obtained, in the case of 4,4′-di(*tert*-butyl)-2,2′-bipyridine, a neutral dioxo compound **3**† with exceptional oxygen atom transfer properties, not only towards phosphines,[16] but also towards arylalkanes:

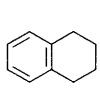
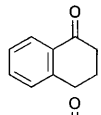
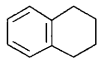
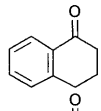
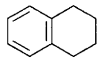
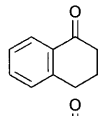
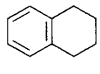
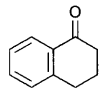
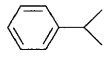
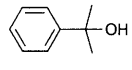
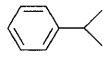
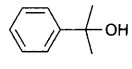
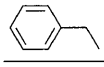
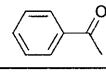
$$\underset{\mathbf{1}}{[PPh_4]_2[Mo^{VI}(O)_2(NCS)_4]} + 4,4'Bu^t_2\text{-bipy} \rightarrow Mo^{VI}(O)_2(NCS)_2(4,4'Bu^t_2\text{-bipy}) + 2\ [PPh_4][SCN]$$
$$\mathbf{3}$$

The dibromo analogue **4** was obtained directly from MoO_2Br_2. Just as for the thiocyanato complex, **4** exhibited elemental analysis, IR, ^1H, ^{13}C and ^{95}Mo NMR spectroscopic data in good agreement with a monomeric compound.‡

$$Mo(O)_2Br_2 + 4,4'Bu^t_2\text{-bipy} \rightarrow \underset{\mathbf{4}}{Mo^{VI}(O)_2Br_2(4,4'Bu^t_2\text{-bipy})}$$

This was confirmed by a single-crystal X-ray diffraction analysis.§ The structure given in Fig. 1 shows that the molybdenum atom and the two bromine atoms lie in the same plane of symmetry and therefore have a site occupancy factor of 0.5. This is significantly different from the unsubstituted

Table 1 Oxidation of arylalkanes with $Mo(O)_2(L)_2(4,4'Bu^t_2\text{-bipy})$

Ar–R	L	Conditions[a]	Product	Yield(%)[b]
	NCS **3**	*hν*, r.t.		50[c]
	NCS **3**	100 °C		50[c]
	Br **4**	*hν*, r.t.		50[c]
	NCS **3**	*hν*, r.t. xs. Me_2SO		314
	NCS **3**	*hν*, r.t.		70
	NCS **3**	80 °C		42
	NCS **3**	*hν*, r.t.		22[c]

[a] Reaction time: 6 h; r.t. = room temp. [b] Based on **3** or **4** by GC analysis with an internal standard. [c] Some minor amount of alcohol was also detected.

bipyridyl complex[17] which shows different Mo–N, Mo–O and Mo–Br bond lengths. The very similar values in the IR and NMR *data for* **3** and **4** might suggest an analogy for the actual structure of **3**.

When **3** (10 mg, 0.019 mmol) is reacted with tetraline (2 ml) at room temperature under UV irradiation, the yellow suspension rapidly changes to an intense violet colour which is maintained throughout the reaction (6 h). The yields of oxidized substrates obtained, relative to molybdenum, are given in Table 1. Although no detailed kinetic study has yet been performed, the reaction with **4** is significantly slower (the violet colour begins to appear only after 30 min). Interestingly, this reaction also occurs in the dark at 80–100 °C but at a slightly lower rate. The results obtained with ethylbenzene and cumene are also given in Table 1.

Although the mechanism of the oxygen atom transfer from molybdenum to the arylalkane has not yet been determined, one must note a marked similarity with the reaction of **3** or **4** with triphenylphosphine;[16] this is manifested in the similar colour changes observed and the very similar IR data obtained for the violet solids isolated at the end of both reactions. Furthermore, the oxidation of arylalkanes becomes catalytic in the presence of a large excess (100x) of Me_2SO (Table 1).¶

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Footnotes

† IR (KBr) ν/cm^{-1}: 2011 (NCS); 936, 904 (Mo=O). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.49 (s, CH_3), 7.70 (dd, *J* 5.4, 1.8 Hz, H^5), 8.41 (dd, *J* 1.8, 0.6 Hz, H^3), 9.59 (dd, *J* 5.4, 0.6 Hz, H^6; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 30.6, 36.2, 119.6, 125.1, 150.0, 152.2, 167.0; ^{95}Mo NMR ($CDCl_3$, Na_2MoO_4, pH 11) δ 62.97.

‡ IR (KBr)ν/cm^{-1} 938s and 906s (Mo=O); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.51 (s, CH_3), 7.73 (dd, *J* 5.4, 1.8 Hz, H^5), 8.20 (dd, *J* 1.8, 0.6 Hz, H^3), 9.55 (dd, *J* 5.4, 0.6 Hz, H^6); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 30.1, 35.9, 119.0, 124.5, 149.3, 151.7, 166.3; ^{95}Mo ($CDCl_3$, Na_2MoO_4, pH 11) δ 196.8.

§ *Crystal data* for: **4** $C_{18}H_{24}Br_2MoN_2O_2$, M = 556.15, orthorhombic, space group *Pnma* (No. 62), a = 8.898(5), b = 13.328(3), c = 17.965(4) Å, V = 2130(1) Å^3, D_c = 1.73 g cm^{-3}, Z = 4, crystal size 0.36 × 0.24 × 0.16 mm, μ(Mo-Kα) = 43.3 cm^{-1}, 2168 unique data collected at 22 ± 1 °C on a Rigaku AFC7S diffractometer. 1287 Reflections with $I > 2.00\sigma(I)$ were used to solve the structure to R = 0.029 and R_w = 0.031. All atoms were refined anisotropically; hydrogen atoms were included, but their positions were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ This aspect of the reaction as well as its mechanism is presently being investigated.

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