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Preparation and X-ray structure determination of an aryltrioxomolybdenum(VI) anion

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Abstract

The reaction of dimesityldioxomolybdenum(VI) with ethylidenetriethylphosphorane in tetrahydrofuran at 0 °C yields the mesityltrioxomolybdate (VI) anion, resulting from an oxygen atom transfer from one molybdenum atom to another. The molecular and crystal structure of the anion was determined by X-ray diffraction on the tetraphenylphosphonium salt. The structure was solved via standard heavy atom procedure, completed by subsequent difference Fourier method and refined to $R=0.033$ using 4300 reflections. The crystal system is triclinic $P\bar{1}$ with $a=10.523(3)$, $b=15.061(5)$, $c=10.248(3)$ Å, $\alpha=108.90(5)$, $\beta=97.47(5)$ and $\gamma=102.11(5)°$. The molecular conformation features a single plane including the aromatic ring and one Mo=O bond; this allows the existence of an interaction between an oxygen atom and a methyl carbon.

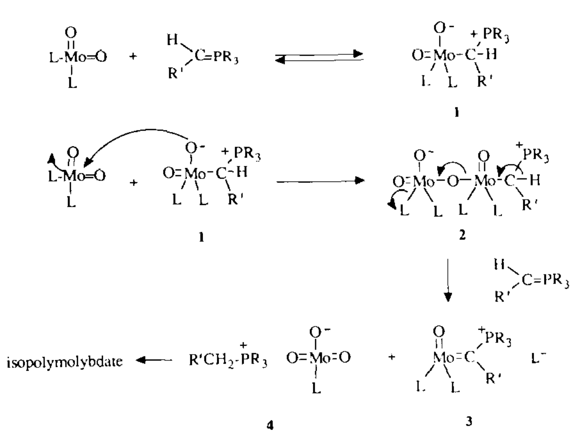
Introduction

Transition metal–oxo chemistry has encountered increasing interest in the past few years [1, 2]. This is due to the relevance of the M=O function not only in oxidation processes but also in many other catalytic reactions. The importance of metal–oxo complexes bearing one or several alkyl or aryl groups is particularly pronounced since these can be considered as excellent models for catalytic reaction intermediates. The majority of known oxoalkyl or aryl complexes contain one or two oxo groups. Trioxoalkyl or aryl species are more uncommon [3–6] and none has been fully structurally characterized. We report here the isolation and first X-ray structure determination of an aryltrioxometal complex: $[PPh_4][Mo(\eta^1\text{-}1,3,5\text{-}C_6H_2Me_3)(O_3)]$.

Results and discussion

The reaction of molybdenum(VI) dioxo complexes with triphenylphosphonium ylids leads, by a redistribution of oxygen atoms, to isopolymolybdate anions [7]. If one considers these species in terms of a juxtaposition of 'MoO_3' building blocks [8], this reaction implies indeed an oxygen atom transfer from one metal center to another and is schematized in Scheme 1.

This could thus be regarded as a potential route to alkyl or aryltrioxo species if one could stop at the intermediate **4**. This was found to be the case by choosing the appropriate phosphorous ylid. When dimesityldioxomolybdenum(VI) was reacted with trialkylphosphonium ylids [9, 10], the phosphonium dioxomolybdenum(VI) ylid complex corresponding to intermediate **1** could either be isolated or it could directly undergo further reaction to the desired product **4**.



Scheme 1.

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In a typical experiment dimesityldioxomolybdenum(VI) (L = 1,3,5-$C_6H_2Me_3$ in Scheme 1) (0.82 g, 2.24 mmol) in 20 ml of tetrahydrofuran was reacted at 0 °C for 4 h with ethylidenetriethylphosphorane (R = C_2H_5, R′ = CH_2 in Scheme 1) (0.33 g, 2.26 mmol). The white solid obtained upon removal of tetrahydrofuran under reduced pressure was washed with n-pentane. Recrystallization from tetrahydrofuran/n-pentane at 0 °C yielded a white crystalline solid (0.28 g, 30%). IR (KBr disc): ν(Mo=O) 920(s), 880(vs), 850(m) cm^{-1}. NMR spectra ($CDCl_3$): $^{31}P\{^1H\}$ d 38.9; $^{13}C\{^1H\}$ d 21 (CH_{3p}), 27.9 (CH_{3o}), 126.5 (CH_{arom}), 138.6, 145.2 (C_{quat}).

TABLE 1. Crystallographic data, data collection parameters and refinement results

Formula	$[PPh_4][Mo(C_6H_2(CH_3)_3)(O)_3]$
Formula weight (g mol^{-1})	590.52
Space group	$P\bar{1}$
a (Å)	10.523(3)
b (Å)	15.061(4)
c (Å)	10.248(3)
α (°)	108.90(5)
β (°)	97.47(5)
γ (°)	102.11(5)
V ($Å^3$)	1467.5(6)
Density calc. (g cm^{-3})	1.336
Density obs. (g cm^{-3})	1.34(2)
Z	2
Crystal size (mm)	0.4 × 0.5 × 0.3
μ(Mo Kα) (cm^{-1})	5.17
Data collection instrument	Enraf-Nonius CAD-4
Radiation	Mo Kα (0.71073 Å)
Orientation reflections, no., range, 2θ (°)	25, 20–32
Temperature (°C)	20
Scan method	ω–2θ
Scan range, 2θ (°)	2–48, $h_{max} = \pm 11$, $k_{max} = \pm 16$, $l_{max} = 11$
No. unique data	$3\sigma(F_o^2)$ 4300, 3418
No. parameters refined	343
R	0.033
R_w	0.054
Quality of fit indicator	2.15
Largest shift/e.s.d., final cycle	0.20
largest peak (e/$Å^3$)	0.42

TABLE 2. Positional and thermal parameters for the anion [Mo(η^1-1,3,5-$C_6H_2Me_3$)(O_3] with e.s.d.s in parentheses

Atom	x	y	z	B ($Å^2$)
Mo	0.10553(3)	0.24172(2)	0.21401(7)	3.117(7)
O1	0.2192(4)	0.3396(3)	0.3445(4)	6.07(9)
O2	0.1843(4)	0.1588(2)	0.1268(4)	6.81(9)
O3	0.0169(3)	0.2793(2)	0.0983(3)	4.56(7)
C1	−0.0336(4)	0.1784(3)	0.3194(4)	3.07(9)
C2	−0.0535(4)	0.0833(3)	0.3205(4)	3.48(9)
C3	−0.1413(5)	0.0520(3)	0.37787(4)	4.2(1)
C4	−0.2104(4)	0.1116(4)	0.4745(4)	4.3(1)
C5	−0.1914(4)	0.2047(4)	0.4717(4)	4.2(1)
C6	−0.1038(4)	0.2397(3)	0.3974(4)	3.5(1)
C7	0.0169(5)	0.0113(3)	0.2399(5)	5.3(1)
C8	−0.3025(5)	0.0765(5)	0.5602(5)	6.5(1)
C9	−0.0857(5)	0.3437(3)	0.4036(5)	5.0(1)

These data are well in accord with the tetraethylphosphonium mesityltrioxomolybdate(VI) complex (5) implying one oxygen atom transfer and loss of one mesityl group*. This was confirmed by an X-ray structure determination of the anion**. Crystal data and details of the data collection are listed in Table 1. Positional parameters and interatomic distances and angles of the anion [Mo(η^1-1,3,5-$C_6H_2Me_3$(O)$_3$] are given in Tables 2 and 3, respectively. The structure was solved via standard heavy atom procedure and completed by subsequent difference Fourier method. The structure was refined by least-squares refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of all non-hydrogen atoms. The hydrogen atoms were introduced, after inspection of the electron density map, at idealized positions in the calculations before last refinement cycles but not refined. Full least-squares refinement minimized the function: $S\ w(F_o - F_c)^2$, $w = 1/s^2$, with F_o and F_c the observed and calculated structure factors and s the estimated standard deviations on F_o. Final refinement converged with $R = 0.034$ ($R_w = 0.055$), $S = 2.15$, $(D/s)_{max} = 0.12$; a final difference synthesis did not reveal any peak of density > 0.32 e $Å^{-3}$ [11, 12]. The central part of the anion shows a symmetry very close to C_{3v}. The three Mo–O bonds are nearly equal, 1.721 ± 0.3 Å on average, and the three O–Mo–O angles have an average value of 110.8 ± 0.4° showing no significant differences. The Mo atom is at 0.538(2) Å of the plane formed by the three oxygen atoms. The Mo–C1 bond shows a slight but significant departure from the normal to the oxygen plane: 2.8(4)°. Thus the C1–Mo–O angles are not equal, they scatter from 106.1(2)° for O1–Mo–C1 to 110.9(2)° for O2–Mo–C1,

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*The fate of the mesityl anion, although not totally elucidated, could be rationalized in terms of oxidative coupling to bimesitylene or protonation to mesitylene; both hydrocarbons were detected by GC-MS but not quantified.

**The X-ray analysis was performed on a good quality single crystal of the tetraphenylphosphonium salt 6. Spectroscopic data concerning the anionic portion of it were nearly identical with those of the tetraethylphosphonium salt 5. IR (KBr disc): ν(Mo=O) 920(s), 880(vs), 850(m) cm^{-1}. NMR spectra (CD_3CN): $^{13}C\{^1H\}$ δ 21.2 (CH_{3p}), 28.3 (CH_{3o}), 127.3 (CH_{arom}), 136.8, 148.2 (C_{quat}); $^1H(CD_3CN)$: δ 2.27 (3H, s, CH_{3p}), 2.55 (6H, s, CH_{3o}), 6.89 (2H, s, CH_{arom}).

TABLE 3. Interatomic distances (Å) and angles (°) of anion $[\mathrm{Mo}(\eta^1\text{-}1,3,5\text{-}\mathrm{C_6H_2Me_3})(\mathrm{O})_3]$

Distances					
Mo–O1	1.721(3)	C3–C4	1.380(7)	C4–C5	1.381(8)
Mo–O2	1.718(4)	C1–C6	1.414(7)	C4–C8	1.516(8)
Mo–O3	1.723(3)	C2–C3	1.404(7)	C5–C6	1.394(7)
Mo–C1	2.171(4)	C2–C7	1.524(7)	C6–C9	1.518(8)
C1–C2	1.408(6)				
Angles					
O1–Mo–O2	110.4(2)	Mo–C1–C6	116.7(3)	C3–C4–C8	120.8(6)
O1–Mo–O3	110.9(2)	C2–C1–C6	118.6(4)	C5–C4–C8	121.0(5)
O2–Mo–O3	111.1(2)	C1–C2–C3	119.6(5)	C4–C5–C6	122.0(4)
O1–Mo–C1	106.1(2)	C1–C2–C7	122.8(4)	C1–C6–C5	119.8(4)
O2–Mo–C1	110.9(2)	C3–C2–C7	117.6(4)	C1–C6–C9	121.6(4)
O3–Mo–C1	107.5(2)	C2–C3–C4	122.1(5)	C5–C6–C9	118.7(4)
Mo–C1–C2	124.7(4)	C3–C4–C5	118.1(4)		

with an average value of 108.2 ± 2.7°; C1 is closer to O1 (3.122(5) Å) and O3 (3.152(6) Å) than to O2 (3.214(6) Å).

But the most striking feature of the molecular conformation is the fact that the mesityl group lies exactly in the same plane as the Mo–O2 bond: the dihedral angle between the mesityl plane and the C1–Mo–O2 plane is 2.6(7)°. Oxygen O1 is 1.487(4) Å below and oxygen O3 1.344(3) Å above the mean mesityl–Mo–O2 plane. This conformation allows the existence of an interaction between the oxygen O2 and the methyl carbon C7. When looking at the electron density map it appears probable that the equilibrium position of the hydrogen HC71 may also lie in the O2–Mo mesityl plane. Thus a hydrogen bond between O2 and C7 can be postulated with an O2–HC71 distance of 2.245(5) Å and an O2–C7 distance of 3.154(7) Å. However the strength of this bond is considerably weakened by a twist of the benzene cycle including an opening of the Mo–C1–C2 angle: 124.7(4)° and a concomitant narrowing of the Mo–C1–C6 angle: 116.7(3)°. Crystals of the title compound are composed of individual entities: one $[\mathrm{Mo}(\eta^1\text{-}1,3,5\text{-}\mathrm{C_6H_2Me_3})(\mathrm{O})_3]^-$ anion for one $[\mathrm{PPh_4}]^+$ cation which are packed without remarkable features. See also 'Supplementary material'.

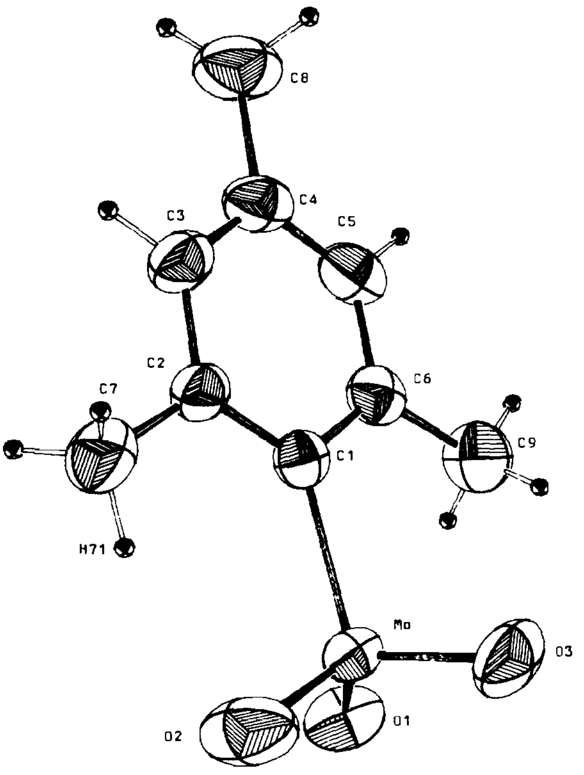

Fig. 1. ORTEP view of $[\mathrm{Mo}(\eta^1\text{-}1,3,5\text{-}\mathrm{C_6H_2Me_3})(\mathrm{O})_3]^-$ in **6** with atom numbering scheme.

Supplementary material

Structure factors as well as bond distances and angles for the $[\mathrm{PPh_4}]^+$ cation may be obtained from the authors on request.

References

1 R. H. Holm, *Chem. Rev.*, *87* (1987) 1401.
2 F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, *28* (1988) 339.
3 I. R. Beattie and P. J. Jones, *Inorg. Chem.*, *18* (1979) 2318.
4 W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, *27* (1988) 1297, and refs. therein.
5 I. Feinstein-Jaffe, J. C. Dewan and R. R. Schrock, *Organometallics*, *4* (1985) 1189.

6 G. N. Schrauzer, L. A. Hughes and N. Strampach, *Z. Naturforsch., Teil B, 37* (1982) 380.

7 H. Arzoumanian, A. Baldy, R. Laï, A. Odreman, J. Metzger and M. Pierrot, *J. Organomet. Chem., 295* (1985) 343.

8 K. H. Tytko and O. Glemser, *Adv. Inorg. Chem. Radiochem., 19* (1976) 239.

9 H. Arzoumanian, A. Baldy, R. Laï, J. Metzger, M. L. Nkeng Peh and M. Pierrot, *J. Chem. Soc., Chem. Commun.*, (1985) 1151.

10 R. Laï, S. Le Bot, A. Baldy, M. Pierrot and H. Arzoumanian, *J. Chem. Soc., Chem. Commun.*, (1986) 1208.

11 B. A. Frenz, Enraf-Nonius CAD4 SDP, in H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G. C. Bassi (eds.), *Computing in Crystallography,* Delft University Press, Delft, 1978.

12 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974. (Present distributor Kluwer, Dordrecht, The Netherlands.)