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AN UNUSUAL ROUTE TO THE ISOPOLYMOLYBDATES; OCTAMOLYBDATE β-$[Mo_8O_{26}]^{4-}$ AND HEXAMOLYBDATE $[Mo_6O_{19}]^{2-}$. REACTION OF DIOXOMOLYBDENUM COMPLEXES WITH TRIPHENYLPHOSPHONIUM YLIDES. CRYSTAL STRUCTURES OF THE SALTS $[PPh_3CH_2COOEt]^+{}_2[NH_2Et]^+{}_2$ $[Mo_8O_{26}]^{4-}$, $[PPh_3CH_2COOEt]^+{}_2$ $[Mo_6O_{19}]^{2-}$, AND $[PPh_3CH_2Ph]^+{}_2$ $[Mo_6O_{19}]^{2-}$

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Summary

Isopolymolybdate anions with various counterions have been obtained from the reaction of dioxomolybdenum(VI) compounds and the triphenylphosphonium ylides $RCH{=}PPh_3$ (R = Ph, COOEt, H) in dichloromethane. The polyoxoanions are of two types, β-$[Mo_8O_{26}]^{4-}$ and $[Mo_6O_{19}]^{2-}$, depending on the starting molybdates. X-ray structure determinations have been performed on the salts $[PPh_3CH_2COOEt]^+{}_2$ $[NH_2Et]^+{}_2$ $[Mo_8O_{26}]^{4-}$, $[PPh_3CH_2COOEt]^+{}_2$ $[Mo_6O_{19}]^{2-}$, and $[PPh_3CH_2Ph]^+{}_2$ $[Mo_6O_{19}]^{2-}$.

Introduction

Isopolymolybdates are obtained from simple molybdates in aqueous systems by acidification. Their degree of aggregation and their structures are directly dependent upon the acidity of the medium [1].

We describe below the formation of such isopolymolybdates from dioxomolybdenum(VI) complexes in the complete absence of water or acid. During a study of alkylation reactions of oxomolybdenum complexes we observed the formation of hexamolybdate or octamolybdate anions when dioxomolybdenum(VI) complexes were treated with triphenylphosphonium ylides. The occurrence of these reactions in the absence of any protonating species and above all the apparent transformation of an "MoO_2" species into an "MoO_3" aggregate without any extraneous source of oxygen atoms, prompted us to study several dioxomolybdenum(VI)/phosphonium ylide systems.

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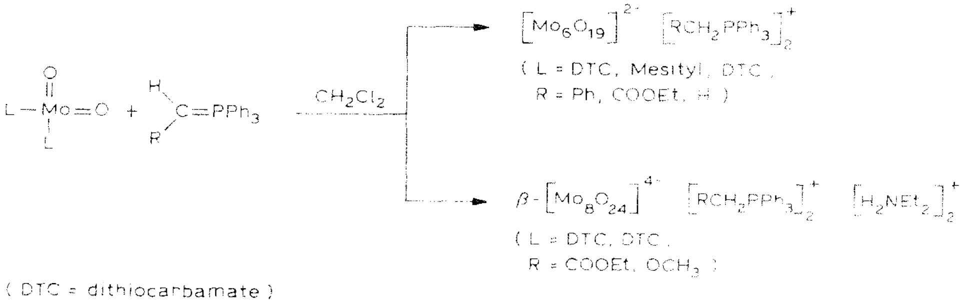

SCHEME 1

Experimental

All solvents were freshly distilled in an inert atmosphere prior to use. The ^{1}H, ^{13}C ^{31}P and ^{95}Mo NMR spectra were recorded on Bruker AM 200, Varian XL 200 and Varian FT 80 A spectrometers, and IR spectra (1000–600 cm^{-1} range) on a Nicolet MX 5 spectrometer. Elemental analyses were performed by Alfred Bernhardt Analytische Laboratorium, Engelskirchen, West Germany.

Reaction of bis(N,N-diethyldithiocarbamate)dioxomolybdenum(VI) with carbethoxymethylenetriphenylphosphorane

A typical experiment: At 20°C a dichloromethane solution (30 ml) of carbethoxymethylenetriphenylphosphorane (purchased from Lancaster Synthesis and used as received) (0.232 g, 6.7 mmol) was added to a thoroughly degassed dichloromethane solution (30 ml) of bis(*N*,*N*-diethyldithiocarbamate)dioxomolybdenum(VI) [2] (0.284 g, 6.7 mmol). There was a rapid change in color from orange to red. Stirring was continued as a white crystalline solid slowly precipitated out during four days. This solid was filtered off, washed with dichloromethane and analyzed (Compound **A**) *. IR (KBr): 940vs, 910vs, 870m, 830s, ~ 700vs(br), 650m cm^{-1}. NMR (DMSO-d_6): ^{1}H $\nu(CH_3)$ 1.35, 1.66 (t), $\nu(CH_2)$ 3.15, 3.96 (quad), $\nu(PCH_2)$ 5.32 (d, J(PH) 10 Hz), $\nu(CH)$ (aromatic) ~ 7.0 (m), $\nu(NH)$ 7.5 (b), ^{13}C $\nu(CH_3CH_2)$ 11.21, 17.41, $\nu(\mathrm{CH_3CH_2})$ 62.32, 92.52, $\nu(\mathrm{PCH_2})$ 29.30 (d J(PC) 75.2 Hz), ν(PC) (aromatic) 118.1 (d J(PC) 102 Hz), $\nu(CH)$ (aromatic) 130.1–135.3, ^{31}P 20.11. Anal. Found: C, 30.85; H, 3.35; O, 24.16; N, 1.51; P, 3.78; Mo, 36.82. $C_{26}H_{34}O_{15}N_1P_1Mo_4$ calcd. C, 31.7; H, 3.35; O, 24.4; N, 1.42; P, 3.15; Mo, 39.03%. A crystal was chosen for X-ray analysis.

Reaction of bis(N,N-diethyldithiocarbamate)dioxomolybdenum(VI) with benzylidenetriphenylphosphorane

The reaction was carried out similarly with 0.57 g (12.9 mmol) of bis(*N*,*N*-diethyldithiocarbamate)dioxomolybdenum(VI) [2] and freshly prepared benzylidenetriphenylphosphorane ** (0.45 g, 12.9 mmol) and gave a yellow crystalline

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* A trace amount of a yellow solid, similar to the main product of the reaction described below, was also obtained. IR (KBr): 950vs, 910m, 790vs cm^{-1}.

** Obtained by adding 12.9 mmol of "instant ylide" purchased from Fluka and used as received, (benzylidenetriphenylphosphonium bromide + sodium amide) to 50 ml of freshly distilled tetrahydrofuran, followed by filtration of the bright orange suspension and evaporation of the solvent under vacuum.

product (compound **C**). (A trace amount of a white solid, similar to the main product of the reaction described above, was also obtained. IR (KBr): 940vs, 910vs, 840s, 700vs(br), 650m(br) cm^{-1}.)

Compound **C**: IR (KBr): 950s, 935m, 795vs cm^{-1}. NMR (DMSO-d_6): ^1H $\nu(PCH_2)$ 5.2 (d, J(P–H) 15 Hz), $\nu(CH)$ (aromatic) 6.8–7.3 (m, ^{13}C $\nu(PCH_2)$ 28.5 (d J(PC) 47.0 Hz) $\nu(C)$ (aromatic) 117–131 (m). ^{31}P 20.71. ^{95}Mo, 125 *. Anal. Found: C, 37.84; H, 2.75; Mo, 35.28. $C_{50}H_{44}O_{19}P_2Mo_6$ calcd.: C, 37.85; H, 2.77; Mo, 36.32%. A crystal (yellow) was chosen for X-ray analysis.

Reaction of dimesityldioxomolybdenum(VI) with carbethoxymethylenetriphenylphosphorane

This reaction was also carried out similarly with 1.26 g (3.4 mmol) of dimesityldioxomolybdenum(VI) [3] and 1.2 g (3.4 mmol) of carbethoxymethylenetriphenylphosphorane, and gave a yellow crystalline product ** (compound **B**) IR (KBr): 960s, 950s, 795vs cm^{-1}. NMR (DMSO-d_6) ^1H, $\nu(CH_3)$ 0.97 (t), $\nu(CH_2)$ 4.06 (q), $\nu(PCH_2)$ 5.3 (d J(PH) 13.8 Hz). ^{13}C $\nu(CH_3)$ 13.55, $\nu(CH_2)$ 62.4, $\nu(PCH_2)$ 29.0 (d) J(PC) 96.0 Hz), $\nu(PC)$ (aromatic) 118.2 (d J(PC) 88.7 Hz), $\nu(C)$ (aromatic) 130.0–135.2 ^{31}P 21.7. ^{95}Mo 125.7. Anal. Found: C, 33.51; H, 2.81; O, 21.45; P, 4.15; Mo, 38.10. $C_{44}H_{44}O_{23}P_2Mo_6$ calcd.: C, 33.47; H, 2.79; O, 23.33; P, 3.92; Mo, 36.46%. A crystal was chosen for X-ray analysis.

*Reaction of bis(N,N)-diethyldithiocarbamate)dioxomolybdenum(VI) [2] with methylenetriphenylphosphorane ****

This reaction was carried out similarly to give a red-violet solution, from which a yellow solid slowly separated. IR (KBr): 950vs, 935vs, 795vs, 740m cm^{-1}. No crystallographic analysis was performed: the infrared data and color of the solid suggest a $[Mo_6O_{19}]^{2-}$ species analogous to that obtained from bis(*N,N*-diethyldithiocarbamate)dioxomolybdenum(VI) and benzylidenetriphenylphosphorane.

Reaction of bis (N,N-diethyldithiocarbamate)dioxomolybdenum(VI) [2] with methoxymethylenetriphenylphosphorane §

This reaction was carried out similarly to give a white solid. IR (KBr): 940s, 910s, 840m, 700vs(br) cm^{-1}). No crystallographic analysis was performed. The infrared data and color of the solid suggest a β-$[Mo_8O_{26}]^{4-}$ species analogous to those described above.

Collection and reduction of X-ray data

Diffraction data were collected at 20°C on an Enraf–Nonius CAD4 diffractometer equipped with a monochromator for Mo-K_α radiation (λ 0.7107 Å). Crystal data and details of the data collection are listed in Table 1. Lattice constants were obtained by least-squares fit of 25 carefully centered reflections for each compound. The intensities were measured by the θ–2θ technique with a scan width of

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* Relative to Na_2MoO_4.

** The yield was lower than in the reactions described above.

*** Obtained from a methylenetriphenylphosphonium bromide-sodium amide mixture (Fluka instant ylide).

§ Obtained from a methoxymethylenetriphenylphosphonium bromide - sodium amide mixture (Fluka instant ylide).

TABLE 1

CRYSTAL DATA, DATA COLLECTION PARAMETERS AND REFINEMENT RESULTS

	A	B	C
Formula	$Mo_8P_2O_{30}N_2C_{52}H_{68}$	$Mo_6P_2O_{23}C_{44}H_{44}$	$Mo_6P_2O_{19}C_{50}H_{44}$
Structural Formula	$[Mo_8O_{26}]^4$ $[PPh_3CH_2COOCH_2CH_3]_2^{+}[NH_2(CH_2CH_3)_2]_2^{+}$	$[Mo_6O_{19}]^2$ $[PPh_3CH_2COOCH_2CH_3]_2^{+}$	$[Mo_6O_{19}]^2$ $[PPh_3CH_2Ph]_2^{+}$
Formula weight	1968.6	1678.4	1586.5
Crystal dimensions	0.15 × 0.10 × 0.4 mm	0.25 × 0.25 × 0.30 mm	0.20 × 0.25 × 0.40 mm
d_{calcd} (g/cm^3)	1.894	1.981	1.927
Space group	$P1$	$P2_1/n$	$P1$
a (Å)	10.562(4) 111.37(4)	11.747(5)	11.015(5) 66.02(3)
b (Å)	12.898(5) 101.72(4)	14.113(6) 101.84(4)	12.194(5) 69.28(4)
c (Å)	14.555(5) 101.36(4)	16.299(6)	12.246(5) 69.94(4)
α (deg) β (deg) γ (deg) (e.s.d.)			
Number of molecule per unit cell	1	2	1
$F(000)$	970	1548	778
μ (cm^{-1})	14.5	14.8	14.3
$2\theta_{max}$ (deg)	58	44	54
Scan time (s)	45	60	60
Reflections measd.	6071	3852	6475
Number of unique reflections	5607	3230	5405
Number of refl $I > 3\sigma(I)$ used in the refinement	5183	2672	4154
R	0.037	0.028	0.032
R_w	0.046	0.037	0.037
Error in observation of unit weight	2.669	2.78	1.608
Number of variables	397	340	352

$0.8 + 0.35 \tan \theta$ and a variable scan time. The orientation was checked after every 200 reflections by using three orientation standards, and reorientation by centering 25 reflections was carried out if any of them were significantly off-center. The intensities of three standard reflections measured after 10000 seconds of X-ray exposure showed no significant variation.

Solution and refinement of the structures

All calculations were performed on a PDP 11/44 computer using the SDP software [4]. The structures were solved by conventional Multan [5], Patterson and Fourier methods and refined by full-matrix least squares. The minimized function was: $M = \Sigma\ w(|F_o| - |F_c|)^{-2}$ with $w\ 1/\sigma^2(F_0)$. Atomic scattering factors were taken from International Tables for X-ray crystallography [6]; absorption and extinction corrections were not applied. The hydrogen atoms were generated geometrically and included in the last cycles of refinement but not refined. Results of refinements are given in Table 1. Final difference maps were featureless with peaks ranging between ± 0.4 e Å^3.

Atomic coordinates with equivalent values, anisotropic thermal parameters, parameters for H atoms, bond distances and bond angles, listings of observed and calculated structure factors are available from the authors.

Discussion

The polyanions β-$[Mo_8O_{26}]^{4-}$ in compound **A** and $[Mo_6O_{19}]^{2-}$ in compounds **B** and **C** are represented in Fig. 1 and 2. These anions have several times been crystallographically characterised [7–20] and only some especially interesting features are considered here. Because of the location of the anions at centers of symmetry, four molybdenum atoms are crystallographically independent in Mo_8O_{26} and three in Mo_6O_{19}. Relevant bond distances and bond angles for distorted MoO_6 octahedra are listed in Table 2 and are consistent with values in the literature. The octahedral coordination of the molybdenum atoms is different in the two polyanions.

In Mo_8O_{26} (Fig. 3 and Table 2) the terminal oxygen atom shown on Mo(1) is actually a bridging atom shared with Mo(4), and thus the Mo(1)=O(c) distance (1.757 Å) is slightly longer than other Mo=O distances. In Mo_6O_{19} (Fig. 3 and Table 3) each molybdenum atom forms one short Mo–O bond (mean value 1.677 Å), four medium Mo–O bonds (mean value 1.925 Å) and one long Mo–O bond (mean value 2.316 Å. In both polyanions the spread of the Mo–O distances for the bridging oxygen atoms reflects the distorsion of the MoO_6 octahedra [8,9].

The cation $[PPh_3CH_2COOCH_2CH_3]^+$ in compounds **A** and **B** and the cation $[PPh_3CH_2Ph]^+$ in compound **C** are compared in Table 4. Bond distances and bond angles in $[NH_2(CH_2CH_3)_2]^+$ are given in Fig. 4. All the compounds are simple cationic species with no significant short non-bonded contacts.

All known isopolymolybdates have been obtained by acidification of aqueous molybdate [1], by hydrolysis of esters of molybdic acids in organic solvents [21–25] or by treatment of molybdenum oxide with organic bases [9,26,27]. More recently isopolymolybdates containing organic moieties have attracted increasing interest because of their possible role as intermediates in catalytic oxydation reactions [10,28,29]. Again the isopolymolybdate compounds were obtained either by *O*-al-

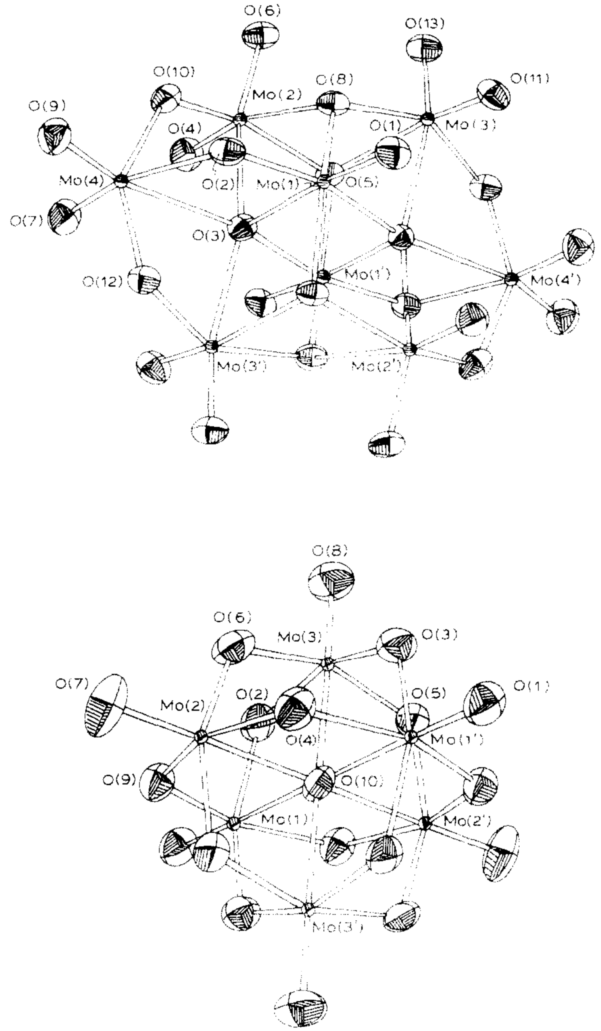

Fig. 1. ORTEP views of the anions β-$[Mo_8O_{26}]^{4-}$ (compound **A**), and $[Mo_6O_{19}]^{2-}$ (compound **B**).

kylation of already formed isopolymolybdates or directly from molybdenum oxides.

The main feature of isopolymolybdates is that they can be considered as consisting of aggregates of MoO_6 octehedra, and in a simplified view their formation can be thought of in terms of juxtaposition of "MoO_3" building blocks [1]. Formation of such compounds starting from species bearing only two oxygen atoms per molybdenum was therefore unexpected at first, it strongly implied a redistribution of oxygen atoms between two molybdenum centers in order to attain the "MoO_3" unit required for an isopolymolybdate structure.

The presence of a phosphonium ylide seems essential * and suggests that the initial step is the nucleophilic attack of the ylide onto the MoO_2 to give an

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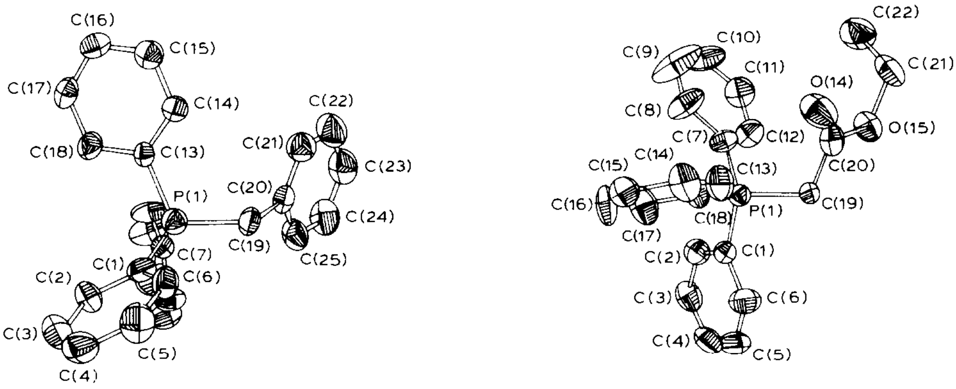
* Control experiments showed that the dioxomolybdenum compounds either alone or in the presence of a phosphonium salt did not generate isopolymolybdic species.

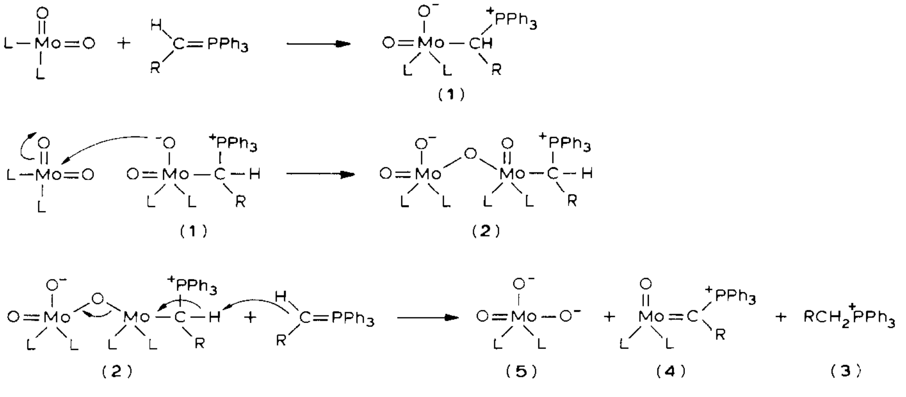


(cation C) (cation A)

Fig. 2. ORTEP view of the cations $Ph_3PCH_2Ph^+$ (compound C) and $Ph_3PCH_2CO_2Et^+$ (compound A).

"oxometallobetaïne" (**1**). This is analogous to the well documented reaction of ylides with transition metal complexes; the main difference arises from the marked nucleophilic character of the Mo–O$^-$ group, which could attack a second mole of dioxomolybdenum complex, as is shown in Scheme. 2. Such attack could well be the key step in the initiation of the formation of an isopolymolybdate species.

The presence in the products of phosphonium cations (**3**) implies the occurrence of a transylidation reaction, such as is often encountered in ylide-transition metal chemistry [30,31]. This transylidation, involving the intermediate **2** as shown in Scheme 2, could plausibly be followed by rearrangement to two distinct molybdenum compounds. The monooxo compound **4** was not isolated under the conditions used, but only observed as a transient species by NMR *. Its proposed structure is based on analogy with a recently isolated dioxomolybdenum-alkylidene compound formed in similar reaction with tributylphosphonium ylids [32]. Compounds of type **5**, on the other hand, can be thought of as being the first step in the formation of an



SCHEME 2

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* Transient peaks in the range 165–238 ppm in the ^{13}C $\{^1H\}$ NMR spectra assignable to metal-alkylidene carbon atoms were observed in several cases.

(a) (b)

Fig. 3. Labeling scheme and Mo–O bonding system of octahedric MoO$_6$ (a) in Mo$_8$O$_{26}$ and (b) in Mo$_6$O$_{19}$: =, – and . . . refer to short, medium and long distances respectively. Oxygen atoms O(a) and O(c) in (a) and O(a) in (b) are terminal atoms, other oxygen atoms are bridging atoms shared by several MoO$_6$ octahedra. Oxygen O(b) in Mo$_6$O$_{19}$ is a central atom located at the symmetry center of the polyanion.

isopolymolybdate anion, in a manner similar to that in the usual aqueous isopolymolybdate synthesis.

Scheme 2 although speculative, takes account of most of the available observations. The nature of the isopolymolybdates obtained must depend on factors such as the mode of aggregation and the rate of crystallization; it also involves loss of ligands initially present on molybdenum. There are several possibilities for the mode of departure of the ligands. In the case of the *N*,*N*-diethyldithiocarbamate this process results in the formation of carbon disulfide and diethylamine; both of these compounds are found in the reaction medium and suggest an ionic process. In

TABLE 2

RELEVANT Mo–O DISTANCES (Å) AND O–Mo–O ANGLES IN Mo$_8$O$_{26}$ (°) (A) [a]

	Mo(1)	Mo(2)	Mo(3)	Mo(4)
Mo=O(a)	1.694	1.715	1.705	1.695
Mo=O(c)	1.757	1.703	1.698	1.711
Mo–O(d)	1.957	1.993	1.896	1.931
Mo–O(f)	1.939	1.883	1.994	1.916
Mo. . .O(e)	2.160	2.304	2.324	2.301
Mo. . .O(b)	2.362	2.363	2.361	2.445
O(a)–Mo–O(b)	173.9	164.8	162.8	159.9
O(c)–Mo–O(e)	157.1	158.3	162.1	164.4
O(d)–Mo–O(f)	149.7	146.9	145.8	144.3
O(a)–Mo–O(c)	104.8	104.1	105.0	105.5
O(a)–Mo–O(d)	100.2	96.2	100.5	102.6
O(a)–Mo–O(e)	98.0	97.4	92.7	90.0
O(a)–Mo–O(f)	101.7	102.6	97.4	102.9
O(b)–Mo–O(c)	81.3	86.9	90.6	94.5
O(b)–Mo–O(d)	78.1	71.2	83.0	72.8
O(b)–Mo–O(e)	75.9	71.4	71.6	69.9
O(b)–Mo–O(f)	77.9	85.2	72.0	74.7
O(c)–Mo–O(d)	96.9	100.7	101.7	98.7
O(d)–Mo–O(e)	77.6	73.7	77.1	78.5
O(e)–Mo–O(f)	78.2	77.1	73.1	76.8
O(c)–Mo–O(f)	97.4	100.7	101.5	98.1

[a] Estimated standard deviations are 0.002 to 0.003 for distances and 0.1 to 0.2 for angles. See Fig. 3 for labeling.

TABLE 3

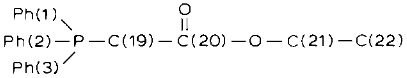
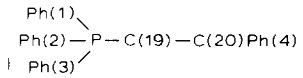
RELEVANT Mo-O DISTANCES AND O-Mo-O ANGLES IN Mo_6O_{19} (**B** and **C**) [a]

	Compound **B**			Compound **C**		
	Mo(1)	Mo(2)	Mo(3)	Mo(1)	Mo(2)	Mo(3)
Distances (Å)						
Mo-O(a)	1.676	1.674	1.678	1.680	1.676	1.676
Mo-O(c)	1.959	1.989	1.890	1.936	1.931	1.907
Mo-O(d)	1.982	1.872	1.989	1.934	1.900	1.916
Mo-O(e)	1.903	1.883	1.966	1.905	1.919	1.932
Mo-O(f)	1.885	1.983	1.865	1.906	1.929	1.939
Mo...O(b)	2.325	2.328	2.309	2.300	2.316	2.320
Angles (°)						
O(a)-Mo-O(b)	178.5	176.1	176.1	178.7	177.7	178.8
O(c)-Mo-O(e)	152.9	152.7	153.5	153.6	153.2	152.9
O(d)-Mo-O(f)	153.3	152.8	154.0	154.1	153.0	153.0
O(a)-Mo-O(c)	102.8	101.4	104.1	103.3	102.7	103.5
O(a)-Mo-O(d)	103.3	104.7	100.8	102.3	105.4	104.4
O(a)-Mo-O(e)	104.2	105.5	101.5	103.0	104.0	103.5
O(a)-Mo-O(f)	103.3	101.8	105.0	103.5	101.5	102.6
O(b)-Mo-O(c)	76.0	75.5	77.7	76.6	76.7	76.4
O(b)-Mo-O(d)	75.7	77.5	75.8	76.5	76.8	76.8
O(b)-Mo-O(e)	77.1	77.5	76.3	77.1	76.6	76.5
O(b)-Mo-O(f)	77.6	75.7	78.8	77.7	76.3	76.2
O(c)-Mo-O(d)	84.0	86.4	85.6	85.7	87.8	87.9
O(d)-Mo-O(e)	86.3	91.5	82.9	87.1	87.8	86.4
O(e)-Mo-O(f)	89.8	87.5	88.8	88.4	86.2	86.4
O(c)-Mo-O(f)	87.6	82.3	91.1	87.2	85.8	86.8

[a] Estimated standard deviations are 0.002 to 0.003 for distances and 0.1 to 0.2 for angles. [b] See Fig. 3 for labeling.

TABLE 4

DISTANCES (Å) AND ANGLES (°) FOUND IN THE CATIONS

			
	Compound **A**	Compound **B**	Compound **C**
P-C$_{Pc}$ mean	1.790±2	1.791±7	1.792±7
P-C(19)	1.819(4)	1.797(4)	1.812(5)
C(19)-C(20)	1.506(6)	1.518(7)	1.514(8)
C(20)=O	1.195(5)	1.188(6)	
C(20)-O	1.324(5)	1.312(6)	
O-C(21)	1.469(6)	1.496(6)	
C(21)-C(22)	1.442(10)	1.472(9)	
Phenyl cycles			
Mean deviation to the best (least squares plane) (Å)	±0.018	±0.015	±0.012
C-C mean (Å)	1.38±2	1.37±3	1.38±2
Dihedral angles (°)			
Ph(1)-Ph(2)	124	105	112
Ph(1)-Ph(3)	104	109	105
Ph(2)-Ph(3)	97	110	121

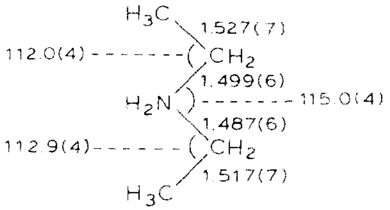


Fig. 4. Bond angles and bond distances found in $NH_2(CH_2CH_3)_2^+$.

contrast in the case of the dimesityldioxomolybdenum the by-products are mesitylene and dimesitylene, suggesting a one-electronic transfer process [*].

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[*] Preliminary ESR experiments have shown the presence of paramagnetic species to various extend. Further investigation of this aspect of the reaction is in progress.