

Preparation of an Oxoperoxocyanomolybdate(VI) Complex by Dioxygen Oxidation of an Oxocyanomolybdate(IV) Anion. Structure and Reactivity toward Phosphines and Olefins

Henri Arzoumanian,* Jean-François Pétrignani, Marcel Pierrot, Fouad Ridouane, and José Sanchez

Received January 8, 1988

Potassium oxopentacyanomolybdate(IV), $[\text{Mo}(\text{O})(\text{CN})_5]\text{K}_3 \cdot 2\text{H}_2\text{O}$, is prepared either through a disproportionation process of the molybdenum(V) cyano intermediate or by controlled hydrolysis of the octacyanomolybdate(IV). The tetraphenylphosphonium salt obtained under phase-transfer conditions reacts readily with dioxygen to give tetraphenylphosphonium oxoperoxotetra-cyanomolybdate(VI) $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_4][\text{PPh}_4]_2$, whose structure is determined by an X-ray analysis. The crystalline compound belongs to triclinic space group $P\bar{1}$ with $a = 10.951(2) \text{ \AA}$, $b = 22.597(6) \text{ \AA}$, $c = 10.283(2) \text{ \AA}$, $\alpha = 97.66(2)^\circ$, $\beta = 116.24(2)^\circ$, and $\gamma = 84.43(2)^\circ$. The volume of the unit cell is $2260(2) \text{ \AA}^3$ with $Z = 2$. The structure was refined to $R = 3.1\%$. The reactivity of the peroxy complex toward triphenylphosphine is studied and is shown to give 1.5 mol of phosphine oxide/mol of peroxy complex. This unusual stoichiometry is rationalized in terms of a classical oxidation of 1 mol of phosphine by the peroxy moiety followed by an oxo transfer involving 2 mol of the dioxomolybdenum(VI) intermediate. The plausible implications that such a process could have on the catalytic oxidation on metal oxide surfaces is given. The poor reactivity of the oxoperoxomolybdenum dianion toward olefins is dramatically increased in the presence of silver salts. A monoanionic species, stabilized by hexamethylphosphoramide, $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_3 \cdot \text{HMPA}][(\text{PhCH}_2)_3\text{P}]$, is isolated and characterized by an X-ray analysis. The crystalline compound belongs to monoclinic space group $P2_1/n$ with $a = 9.801(2) \text{ \AA}$, $b = 13.613(3) \text{ \AA}$, $c = 27.597(8) \text{ \AA}$, and $\beta = 90.56(2)^\circ$. The volume of the unit cell is $3682(2) \text{ \AA}^3$ with $Z = 4$. The structure was refined to $R = 7.12\%$.

Introduction

Cyano complexes of molybdenum are well-known and some, such as the octacyano ions, have been thoroughly studied.¹ Molybdenum cyano complexes bearing an oxo ligand, however, are more scarce, and few have been fully characterized. We have described² a bimetallic cyano complex containing an oxoperoxomolybdenum(VI) moiety, $[(\text{CN})_5\text{CoO}_2\text{Mo}(\text{O})(\text{CN})_5]^{5-}$, and its transformation into $[(\text{CN})_4\text{Mo}(\text{O})(\text{O}_2)]^{2-}$, but their full structural characterization had not been possible because of the lack of suitable monocrystals. Other oxo- or dioxocyanomolybdenum compounds have also been described, but none were reported as reacting with dioxygen.³

The synthesis under phase-transfer conditions of an oxomolybdenum(IV) cyano complex and its reactivity toward dioxygen, the full characterization of the resulting peroxy species, and the reactivity of the latter toward triphenylphosphine and olefins are the subject of this report.

Experimental Section

General Materials and Procedures. All materials were commercial products and were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use, and all reactions were carried out under argon. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. NMR spectra were recorded on a Bruker WH-100 spectrometer. IR spectra were recorded on a Nicolet MX5 spectrometer.

Crystal Structure Determination. Crystal data for compounds **5a** and **10**, together with details of the X-ray diffraction experiment, are reported in Table I. Cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range $20^\circ < 2\theta < 32^\circ$. Three intense reflections were recorded throughout the data collection every 10^3 s and showed no change of intensity for both crystals. Lorentz and polarization corrections were applied to the raw data since the values of μ are 3.97 and 4.75 for **5a** and **10**, respectively (Table I); absorption corrections were not necessary.

The positions of Mo and P atoms were determined by combining Patterson and Multan⁴ calculations. The remaining non-hydrogen atoms were located in successive difference Fourier syntheses. Hydrogen atoms were included in the structure factor calculation at idealized positions and were not refined. Scattering factors were taken from Cromer and Waber.⁵ Anomalous dispersion effects were included in F_o ; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.⁶

In the final cycle of refinement, all non-hydrogen atoms were refined anisotropically for compound **5a**; for compound **10**, only atoms of the anion $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_3 \cdot \text{HMPA}]^-$ and the P atom of the cation were refined anisotropically. The largest peaks in the final difference map were located near the Mo atoms.

All calculations were performed on a PDP 11/44 computer using SDP software.⁷ The final atomic coordinates for anion atoms may be found in Table II and IV; selected bond distances and angles are given in Tables III and V.

Synthesis of $[\text{Mo}(\text{O})(\text{CN})_5]\text{K}_3 \cdot 2\text{H}_2\text{O}$ (2) from MoCl_5 . To an open flask containing 60 mL of an aqueous solution of KCN (3.62 g, 55.7 mmol) was slowly added with stirring 1 g (3.7 mmol) of MoCl_5 . Addition of 150 mL of ethanol to the blue solution obtained after 3 h afforded a blue solid, which was twice redissolved and reprecipitated in ethanol-water, giving 1.44 g (48%) of $[\text{Mo}(\text{O})(\text{CN})_5]\text{K}_3 \cdot 2\text{H}_2\text{O}$ (mp 250°C). IR: $\nu(\text{Mo}=\text{O}) = 920 \text{ cm}^{-1}$, $\nu(\text{C}\equiv\text{N}) = 2100 \text{ cm}^{-1}$. Anal. Calcd for $\text{C}_5\text{H}_3\text{N}_3\text{K}_3\text{Mo}$: C, 15.3; H, 0.51; N, 17.8; K, 29.7; Mo, 24.5. Found: C, 16.2; H, 0.58; N, 17.9; K, 28.4; Mo, 26.4. Addition of 100 mL of tetrahydrofuran to the first filtrate precipitated a white solid, which was twice redissolved and reprecipitated from an acetone-water mixture, giving 1.70 g of a white solid exhibiting a wide IR absorption band at 820 cm^{-1} .

Synthesis of $[\text{Mo}(\text{O})(\text{CN})_5]\text{K}_3 \cdot 2\text{H}_2\text{O}$ (2) from $\text{MoCN}_8\text{K}_4 \cdot 2\text{H}_2\text{O}$ (4). A 50-mL aqueous solution of $[\text{Mo}(\text{CN})_8]\text{K}_4 \cdot 2\text{H}_2\text{O}$ ⁸ (1 g, 20 mmol) was irradiated under argon⁹ by UV light for 6 h to yield a blue solution. Addition of 200 mL of ethanol yielded 0.750 g of $[\text{Mo}(\text{O})(\text{CN})_5]\text{K}_3 \cdot 2\text{H}_2\text{O}$ (94%) as a blue solid. The infrared spectrum and the elemental analysis were identical with those of the product obtained from MoCl_5 .

Synthesis of $[\text{Mo}(\text{O})(\text{CN})_5]\text{PPh}_4$ (3). To a two-phase system of 30 mL of deoxygenated CH_2Cl_2 and 20 mL of H_2O containing $[\text{Mo}(\text{O})(\text{CN})_5]\text{K}_3 \cdot 2\text{H}_2\text{O}$ (1 g, 2.54 mmol) was added 2.95 g (7.61 mmol) of PPh_4Cl . After 5 min of stirring, the blue-green organic solvent was decanted and

- (1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 878.
- (2) Arzoumanian, H.; Lopez Alvarez, R.; Kovalak, A. D.; Metzger, J. J. *Am. Chem. Soc.* **1977**, *99*, 5175.
- (3) (a) Rosenheim, A.; Garfunkel, A.; Kohn, F. *Z. Anorg. Chem.* **1909**, *65*, 166. (b) Bucknall, W. R.; Wardlaw, W. *J. Chem. Soc.* **1927**, 2981. (c) Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* **1959**, 872. (d) Chadwick, B. M.; Sharpe, A. G. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 83. (e) Wiegardt, K.; Backes-Dahmann, G.; Haltzbach, W. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44. (f) Dudek, M.; Samotus, A. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 271. (g) Basson, S. S.; Leipoldt, J. G.; Potgieter, I. M. *Inorg. Chim. Acta* **1984**, *87*, 71. (h) Basson, S. S.; Leipoldt, J. G.; Potgieter, I. M. *Inorg. Chim. Acta* **1984**, *90*, 57.

- (4) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. N. "Multan 80, A System of Computer Programs for the Automatic Solution of the Crystal Structures from X-ray Diffraction Data"; Universities of York, England, and Louvain, Belgium, 1980.
- (5) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1979; Vol. IV, Table 2.2.3.
- (6) Cromer, D. T. Reference 5, Table 2.3.1.
- (7) Frenz, B. A. In *Computing in Crystallography*; Schenk, H.; Olthoff-Hazel Kamp, R.; Von Konigsfeld, H.; Bassi, B. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.
- (8) Furman, N. H.; Miller, C. O. *Inorg. Synth.* **1950**, *3*, 160.
- (9) Mac Diarmid, A. G.; Hall, N. F. *J. Am. Chem. Soc.* **1953**, *75*, 5204.

Table I. Experimental Details of the Crystal Structure Determination

formula	[Mo(O)(O ₂)(CN) ₄][PPh ₄] ₂	[Mo(O)(O ₂)(CN) ₃ ·HMPA][(PhCH ₂)Ph ₃ P]
fw	926.8	754.62
space group	P1	P2 ₁ /n
a, Å	10.951 (2)	9.801 (2)
b, Å	22.597 (6)	13.613 (3)
c, Å	10.283 (2)	27.597 (8)
α, deg	97.66 (2)	
β, deg	116.24 (2)	960.56 (2)
γ, deg	84.43 (2)	
V, Å ³	2 260 (2)	3 682 (2)
Z	2	4
d _{calcd} , g/cm ³	1.362	1.361
cryst size, mm	0.2 × 0.3 × 0.3	0.5 × 0.3 × 0.6
μ(Mo Kα), cm ⁻¹	3.97	4.75
diffractometer		Enraf-Nonius CAD-4
radiation monochromated in incident beam (γ, Å)		Mo Kα (0.71073)
orientation reflns: no.; range (2θ), deg		25; 20–32
temp, °C		20 °C
scan method		ω-2θ
data colln range (2θ), deg	2–48 (±h, ±k, l)	2–46 (±h, k, l)
tot. no. of unique data; no. with F ² > 3σ(F ²)	7460; 4596	5148; 3355
no. of params refined	559	299
R, %	3.1	7.12
R _w , %	3.4	10.3
quality-of-fit indicator ^c	1.17	1.2
largest shift/esd, final cycle	0.05	0.10
largest peak, e/Å ³	0.35	0.40

$${}^a R = \sum (F_o - F_c) / \sum F_o. \quad {}^b R_w = [\sum w(F_o - F_c)^2]^{1/2}; w = 1/\sigma^2(F_o). \quad {}^c \text{Quality of fit} = \sum w(F_o - F_c)^2 / (\sum w F_o^2)^{1/2}.$$

dried over anhydrous MgSO₄. Recrystallization from an acetonitrile-diethyl ether mixture at -30 °C yielded **3** as green crystals, 2.56 g (80%) (mp 125 °C dec). IR: ν(Mo=O) = 920 cm⁻¹, ν(C≡N) = 2100 cm⁻¹, and absorption bands due to the PPh₄ cation (995, 1095, 1425 cm⁻¹). Anal. Calcd for C₇₇H₆₀N₃OP₃Mo: C, 73.4; H, 4.8; N, 5.5; P, 7.4; Mo, 7.6. Found: C, 70.9; H, 4.77; N, 5.38; P, 6.92; Mo, 7.6.

Syntheses of [Mo(O)(O₂)(CN)₄][PPh₄]₂ (5a**).** A CH₂Cl₂ solution (20 mL) of [Mo(O)(CN)₃][PPh₄]₃ (2.0 g, 1.58 mmol) was stirred under an oxygen atmosphere for 30 min. The green solution turned gradually orange-yellow (this oxygen absorption can be followed either volumetrically on a Topfler pump or spectrophotometrically by measuring the intensity of a band at 390 nm characteristic of **5a**). The product was precipitated from the CH₂Cl₂ solution by adding 15 mL of diethyl ether. Recrystallization from an acetonitrile-diethyl ether mixture yielded 1.18 g (80%) of orange-yellow crystals (mp 169 °C dec). IR: ν(Mo=O) = 915 cm⁻¹, ν(O—O) = 895 cm⁻¹. Anal. Calcd for C₅₂H₄₀N₄O₃P₂Mo: C, 67.4; H, 4.3; N, 6.1; P, 6.7; Mo, 10.4. Found: C, 65.2; H, 4.8; N, 6.0; P, 6.2; Mo, 10.6.

Synthesis of [Mo(O)(O₂)(CN)₄][AsPh₄]₂. By a procedure analogous to the synthesis of **3**, 0.5 g (1.3 mmol) of **2** was treated with 1.59 g (3.8 mmol) of tetraphenylarsonium chloride. The green CH₂Cl₂ solution (20 mL) was stirred for 30 min under an atmosphere of oxygen, yielding a yellow solution. Addition of diethyl ether (15 mL) precipitated a yellow solid, which was recrystallized from an acetonitrile-diethyl ether mixture to give 1.0 g (80%) of a yellow-orange crystalline solid (mp 198 °C dec). IR: ν(Mo=O) = 915 cm⁻¹, ν(O—O) = 895 cm⁻¹. Anal. Calcd for C₅₂H₄₀N₄O₃As₂Mo: C, 60.10; H, 3.95; N, 5.43; As, 14.0; Mo, 9.35. Found: C, 61.65; H, 4.00; N, 5.50; As, 14.8; Mo, 9.50.

Reaction of [Mo(O)(O₂)(CN)₄][PPh₄]₂ with PPh₃. The reaction was carried out in acetonitrile at 25 °C under argon with a ratio of **5a**/PPh₃ = 0.5. The formation of OPPh₃ was followed by ³¹P NMR spectroscopy, by comparison with standard solutions (see Figure 1). At the end of the reaction the mixture was filtered. The green solution upon evaporation yielded an oily product. IR: ν(Mo=O) = 920 cm⁻¹, ν(C≡N) = 2100 cm⁻¹, characteristic of **3**; ν(P—O) = 1190 cm⁻¹, characteristic of OPPh₃. The filtrate was an amorphous white solid exhibiting two wide absorption bands centered at 895 and 780 cm⁻¹ ([Mo₂O₇][PPh₄]₂ ν(Mo=O) = 880 cm⁻¹, ν(Mo—O—Mo) = 790 cm⁻¹; [Mo₃O₁₀][PPh₄]₄ ν(Mo=O) = 920–908 cm⁻¹, ν(Mo—O—Mo) = 808 cm⁻¹).¹⁰ The elemental analysis indicated the absence of cyano groups.

Synthesis of [Mo(O)(O₂)(CN)₄][(PhCH₂)Ph₃P]₂ (5b**).** By a procedure analogous to the synthesis of **3**, 0.5 g (1.3 mmol) of **2** was reacted with 1.48 g (3.8 mmol) of benzyltriphenylphosphonium chloride. The dried green organic solution was then stirred under O₂ for 30 min, and the yellow product was precipitated with diethyl ether. Recrystallization

from an acetonitrile-diethyl ether mixture (60/40) yielded yellow crystals. IR: ν(Mo=O) = 915 cm⁻¹, ν(O—O) = 895 cm⁻¹.

Synthesis of [Mo(O)(O₂)(CN)₃·HMPA][(PhCH₂)Ph₃P] (10**).** Under argon and at 0 °C, 2 g (2.14 mmol) of [Mo(O)(O₂)(CN)₄][(PhCH₂)Ph₃P]₂ was reacted with 1 g (5.14 mmol) of AgBF₄ in THF (30 mL). After 1 min a white solid precipitated while the solution became yellow. Hexamethylphosphoramide (HMPA) (4 mL, 22.3 mmol) was then added, and stirring was continued for 1 h to give upon filtration and evaporation at 0 °C a yellowish oil. Recrystallization from acetonitrile-diethyl ether-*n*-pentane (50/25/25) yielded orange crystals. IR: ν(Mo=O) = 960 cm⁻¹, ν(O—O) = 910 cm⁻¹. Anal. Calcd for C₃₄H₄₀N₆P₂MoO₄: C, 54.11; H, 5.31; N, 11.14; P, 8.22; Mo, 12.73. Found: C, 53.8; H, 5.32; N, 10.68; P, 8.30; Mo, 12.75.

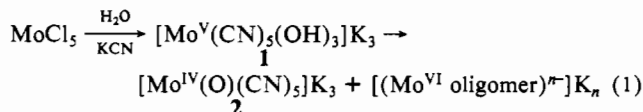
Reaction of [Mo(O)(O₂)(CN)₄][(PhCH₂)Ph₃P]₂ with Cyclooctene in the Presence of AgBF₄. Freshly distilled cyclooctene (1 mL, 7.68 mmol) in CH₂Cl₂ (6 mL) containing 0.5 mL of *o*-dichlorobenzene as internal standard was reacted under argon and at room temperature with 1 g (1.07 mmol) of [Mo(O)(O₂)(CN)₄][(PhCH₂)Ph₃P]₂ and 0.42 g (2.16 mmol) of AgBF₄. After 100 h, a gas chromatographic analysis indicated a 38% yield of cyclooctene oxide. No other products were detected.¹¹

Reaction of [Mo(O)(O₂)(CN)₃·HMPA][(PhCH₂)Ph₃P] with Cyclooctene in the Presence of AgBF₄. Freshly distilled cyclooctene (1 mL, 7.68 mmol) in degassed CH₂Cl₂ (6 mL) containing 0.5 mL of *o*-dichlorobenzene was reacted at -70 °C with 0.3 g (4.05 mmol) of **10** and 0.08 g (4.05 mmol) of AgBF₄. The yellow solution slowly became colorless while a white precipitate appeared. The temperature was slowly raised to 25 °C (10 h), and stirring was continued for 48 h. Gas chromatographic analysis of the resulting solution indicated a nearly quantitative yield (>98%) of cyclooctene oxide.¹¹

Results and Discussion

Two synthetic methods afforded the oxopentacyanomolybdate anion.

(a) **Synthesis from Mo^VCl₅.** Hydrolysis of molybdenum(V) pentachloride in the presence of potassium cyanide gives rise to a disproportionation reaction of a molybdenum(V) cyano intermediate (**1**), from which one can isolate by selective precipitation a Mo^{IV} compound as a blue solid (**2**) analyzing for Mo(O)(C₅N)₅·2H₂O and a mixture of Mo^{VI} anionic oligomers.¹²



(10) (a) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1976**, *98*, 8291. (b) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 6146.

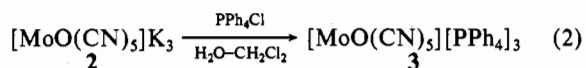
(11) Nearly identical results were obtained by using the tetraphenylphosphonium analogue, with norbornene as the substrate and AgNO₃ as the silver salt.

Table II. Positional Parameters and Their Estimated Standard Deviations in $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_4]^{2-}$ (Anion of **5a**)

atom	x	y	z	$B, \text{\AA}^2$
Mo	0.57141 (3)	0.27313 (2)	0.70713 (4)	3.587 (7)
O1	0.581 (3)	0.3585 (1)	0.7491 (4)	6.5 (1)
O2	0.620 (3)	0.3328 (1)	0.7213 (3)	6.05 (9)
O3	0.6428 (3)	0.2445 (1)	0.8701 (3)	5.63 (8)
C1	0.4611 (4)	0.1903 (2)	0.6114 (4)	3.56 (9)
N1	0.4071 (3)	0.1466 (2)	0.5670 (4)	5.03 (9)
C2	0.7035 (4)	0.2175 (2)	0.6288 (4)	3.9 (1)
N2	0.7749 (3)	0.1876 (2)	0.5914 (1)	5.3 (1)
C3	0.3719 (4)	0.2968 (2)	0.6992 (4)	5.2 (1)
N3	0.2664 (4)	0.3097 (2)	0.6910 (4)	7.9 (1)
C4	0.4535 (4)	0.2897 (2)	0.4667 (4)	3.73 (9)
N4	0.3923 (4)	0.2999 (2)	0.3493 (4)	5.7 (1)

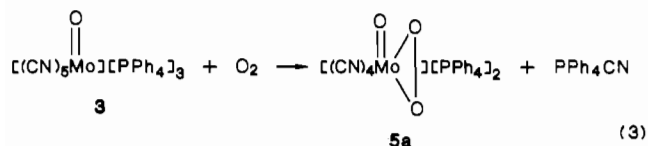
^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Compound **2**, exhibits an IR absorption band at 920 cm^{-1} characteristic of a $\text{Mo}=\text{O}$ vibration. Despite several successive recrystallizations, an adequate crystal for an X-ray analysis could not be obtained; however, a cation exchange with tetraphenylphosphonium chloride under phase-transfer conditions afforded the corresponding phosphonium salt as a light green crystalline solid (**3**).



(b) **Synthesis from $[\text{Mo}(\text{CN})_8]\text{K}_4$ (**4**).** Careful hydrolysis of **4** followed by precipitation with ethanol affords the blue solid **2** in high yield. This reaction is greatly accelerated by light and the presence of oxygen; the rapid and reversible loss of cyanide ion upon irradiation of **4** had indeed been reported by Hall.⁹ Compound **2** obtained by this method failed to yield adequate crystalline material for an X-ray analysis; it was thus transformed into the phosphonium salt **3** by cationic exchange (eq 2) under phase-transfer conditions as in section a. The reduction of sodium molybdate by methylhydroxylammonium chloride in the presence of sodium cyanide and cesium or ammonium chloride to give the corresponding aquopentacyanomolybdate(IV) has also been reported.^{3e} Its transformation by cationic exchange in an aqueous medium afforded the corresponding tetraphenylphosphonium heptaquopentacyanomolybdate analogous to **3**.

Reaction of **2 with Dioxygen.** Compound **2** is quite stable in air and does not react with oxygen even in solution, similar to all other analogues;³ on the other hand, **3** cleanly takes up 1 mol of dioxygen to give **5a**.¹³



This totally different behavior of **3** compared to that of the reported^{3e} analogous heptaquo compound prompted us to perform the X-ray analysis of **3**. The structure of the anion was found to be identical with the one reported except for the seven water molecules of crystallization.

The infrared spectrum of **5a** exhibits two absorption bands in the $900\text{--}850\text{-cm}^{-1}$ region, attributed to the oxo group (915 cm^{-1}) and the peroxy group (895 cm^{-1}). These values are very close to those of the analogous compound obtained from a Co–Mo

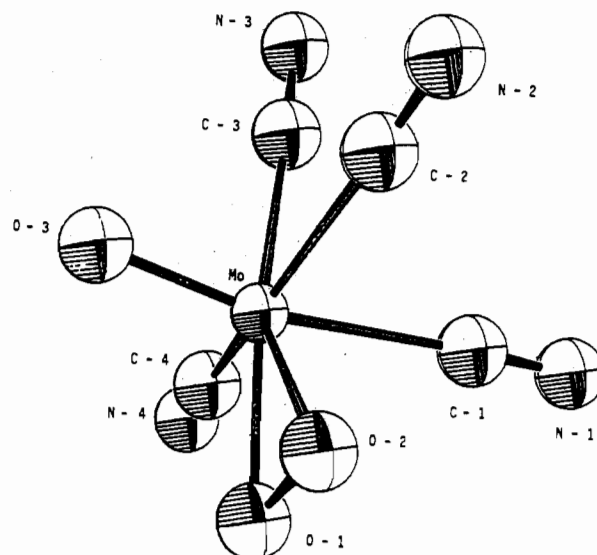
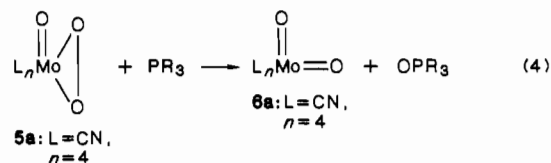


Figure 1. ORTEP view of the $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_4]^{2-}$ anion, showing the atom-labeling scheme. Atoms are represented by thermal ellipsoids of the 50% level.

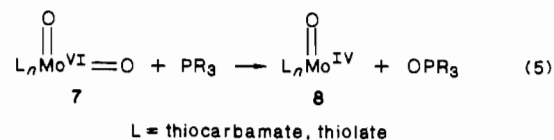
bimetallic system.² Its structure was confirmed by an X-ray analysis.

Structure of **5a.** The final atomic coordinates for atoms of the $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_4]^{2-}$ anion are given in Table II. A perspective drawing of **5a** is presented in Figure 1; selected bond distances and angles are given in Table III. The O2-O3 distance found in the peroxy group ($1.416 (5) \text{ \AA}$) compares well with the same distance given in the literature.¹⁴

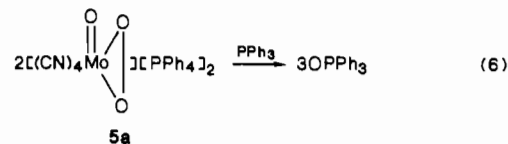
Reaction of **5a with Phosphines.** Compound **5a** exhibited an unusual reactivity toward phosphines. Molybdenum peroxy complexes are known to oxidize phosphines to phosphine oxides according to¹⁴



In addition, it has been shown that when L is a thiocarbamate ligand¹⁵ or a thiolate sulfur atom containing moiety, as recently described by Holm,¹⁶ the oxo group can also be transferred to a phosphine, reducing the molybdenum compound.



When 2 mol of **5a** was reacted under inert atmosphere with triphenylphosphine, 3 mol of triphenylphosphine oxide was cleanly obtained.¹⁷



As is shown in Figure 2, a fast oxidation of 2 mol of phosphine occurs at first, followed by a relatively slower oxidation of a third

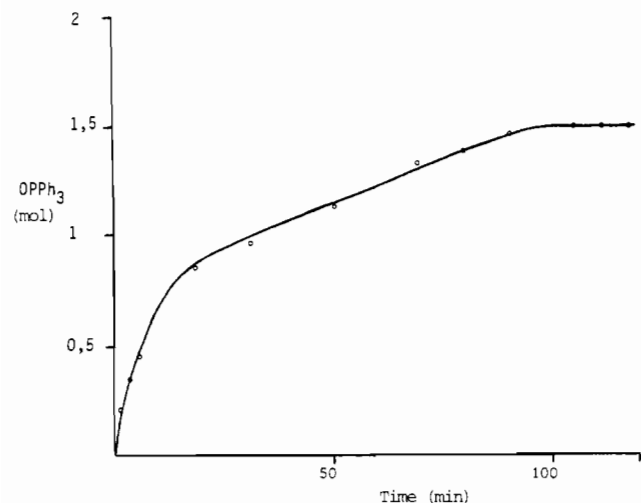
- (12) It was isolated as a white powder; its characterization was limited to the comparison of the infrared spectrum with those of authentic samples of ammonium isopolymolybdates.¹⁰ This indicated that the mixture could, in part, be made of $[\text{Mo}_2\text{O}_7]^{2-}$ and $[\text{Mo}_8\text{O}_{26}]^{4-}$.
- (13) When the reaction was performed in an ESR probe, a transient signal was observed which could be analyzed as overlapping spectra corresponding to two different molybdenum species, one centered at $g \approx 1.9734$ and the second at $g \approx 1.9899$. These species could be assigned to Mo^{V} peroxy or Mo^{IV} superoxy species.

- (14) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1.
- (15) Barral, R.; Bocard, C.; Séré de Roch, I.; Sajus, L. *Tetrahedron Lett.* **1972**, *17*, 1963.
- (16) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.
- (17) An analogous reaction was carried out with the tetraphenylarsonium salt in order to establish that the phosphine oxide did not arise from the oxidation of the cation. Identical results were obtained.

Table III. Selected Bond Distances and Angles for Compound **5a**^a

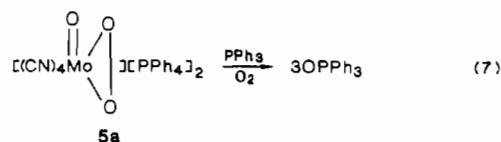
(a) Bond Distances (Å)					
Mo-O1	1.924 (3)	Mo-C2	2.175 (4)	C1-N1	1.134 (5)
Mo-O2	1.924 (3)	Mo-C3	2.167 (5)	C2-N2	1.144 (6)
Mo-O3	1.694 (3)	Mo-C4	2.291 (4)	C3-N3	1.132 (6)
Mo-C1	2.197 (4)	O1-O2	1.416 (5)	C4-N4	1.135 (5)
(b) Bond Angles (deg)					
O1-Mo-O2	43.2 (2)	O2-Mo-C3	121.8 (2)	C2-Mo-C3	150.7 (1)
O1-Mo-O3	106.5 (1)	O2-Mo-C4	86.3 (1)	C2-Mo-C4	82.9 (1)
O1-Mo-C1	153.4 (1)	O3-Mo-C1	88.2 (1)	C3-Mo-C4	80.5 (2)
O1-Mo-C2	123.5 (2)	O3-Mo-C2	92.7 (2)	Mo-O1-O2	68.4 (2)
O1-Mo-C3	79.5 (2)	O3-Mo-C3	97.7 (2)	Mo-O2-O1	68.4 (2)
O1-Mo-C4	86.7 (1)	O3-Mo-C4	166.3 (1)	Mo-C1-N1	177.3 (3)
O2-Mo-O3	105.9 (1)	C1-Mo-C2	76.5 (2)	Mo-C2-N2	178.1 (3)
O2-Mo-C1	153.8 (2)	C1-Mo-C3	76.6 (2)	Mo-C3-N3	178.0 (4)
O2-Mo-C2	80.8 (2)	C1-Mo-C4	78.2 (1)	Mo-C4-N4	177.1 (4)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

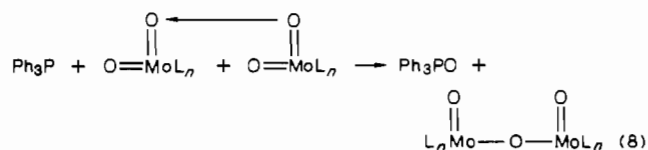
**Figure 2.** Number of moles of triphenylphosphine oxidized/mol of **5a**, under argon, as a function of time.

mole. Although this unusual stoichiometry indicates an initial oxidation according to reaction 4, the formation of the third mole of OPPh_3 can be explained by an oxo transfer analogous to reaction 5 only if 2 mol of the molybdenum dioxo complex **6** is involved in this transfer. The manner in which this transfer occurs is still speculative but could be rationalized by the intermediacy of a Mo^{V} μ -oxo dimer as previously reported¹⁵ in the case of (dialkylthiocarbamato)molybdenum complexes. The analogy could be extended further to the possibility of having the disproportionation of such a dimer into species of $\text{Mo}(\text{IV})$ and $\text{Mo}(\text{VI})$. Indeed, after reaction 6 was over, the molybdenum-containing residue when exposed to oxygen gave the peroxy compound **5a** in $\approx 50\%$ yield.

According to this scheme, one should then be able to oxidize 3 mol of triphenylphosphine/mol of **5a** by running the reaction under oxygen. This was indeed observed.



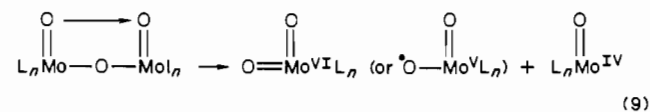
The necessary presence of 2 mol of the molybdenum dioxo complex **6** to achieve this oxo transfer can be rationalized if one considers one of the two molybdenum dioxo groups as an electron supplier:

**Table IV.** Positional Parameters and Their Estimated Standard Deviations in $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_3\text{-HMPA}]^-$ (Anion of **10**)

atom	x	y	z	$B_i^a \text{ \AA}^2$
Mo	0.27701 (8)	0.16119 (6)	0.10378 (3)	4.08 (2)
O1	0.1747 (7)	0.1666 (6)	0.0565 (3)	7.1 (2)
O2	0.4497 (7)	0.1284 (5)	0.0766 (3)	6.3 (2)
O3	0.3799 (8)	0.0443 (5)	0.0914 (3)	7.0 (2)
O4	0.3816 (6)	0.1710 (4)	0.1730 (2)	4.1 (1)
C1	0.3606 (9)	0.3061 (7)	0.0904 (3)	4.5 (2)
N1	0.410 (1)	0.3777 (7)	0.0804 (4)	7.1 (2)
C2	0.1465 (8)	0.2510 (6)	0.1131 (3)	4.0 (2)
N2	0.0700 (9)	0.2976 (8)	0.1665 (4)	7.3 (2)
C3	0.151 (1)	0.0518 (8)	0.1405 (4)	6.5 (3)
N3	0.087 (1)	-0.0036 (7)	0.1590 (4)	8.5 (3)
P1	0.4951 (2)	0.1677 (2)	0.20799 (8)	3.68 (5)
N4	0.6370 (9)	0.215 (1)	0.1899 (4)	9.5 (3)
C4	0.694 (1)	0.206 (2)	0.1466 (6)	12.2 (5)
C5	0.668 (2)	0.317 (1)	0.209 (1)	16.3 (8)
N5	0.532 (1)	0.0566 (6)	0.2212 (4)	7.9 (2)
C6	0.672 (2)	0.028 (1)	0.228 (1)	20 (1)
C7	0.142 (1)	-0.0241 (9)	0.2195 (6)	9.0 (4)
N6	0.4488 (9)	0.2209 (8)	0.2566 (3)	8.6 (3)
C8	0.511 (3)	0.195 (2)	0.3036 (7)	20.7 (9)
C9	0.351 (1)	0.2951 (9)	0.2614 (5)	7.3 (3)

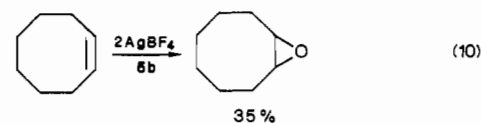
^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

This same role is then played in reverse during the disproportionation process



This reasoning can plausibly be compared to the high electronic density supplied by the sulfur-containing ligands;^{15,16,18} it can furthermore be extrapolated to the role of a metal oxide surface in heterogeneous catalytic oxidation processes.

Reaction with Olefins. The reactivity of **5a** or **5b** toward olefins is very poor, most probably due to both its anionic character and the difficulty to displace a cyano group. However, when an olefin (i.e. cyclooctene) was reacted with **5b** in the presence of 2 mol of AgBF_4 , in an attempt to neutralize the dianion, epoxidation occurred to 35% extent.



Isolation and characterization of the active intermediate (**9**), in the absence of an olefin failed since decomposition to give non

(18) Caradona, J. P.; Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 7856.

Table V. Selected Bond Distances and Angles for Compound 10^a

(a) Bond Distances (Å)					
Mo-O1	1.638 (7)	Mo-C1	2.173 (9)	O4-P1	1.468 (6)
Mo-O2	1.911 (7)	Mo-C2	2.082 (8)	C1-N1	1.123 (13)
Mo-O3	1.917 (7)	Mo-C3	2.190 (11)	C2-N2	1.179 (13)
Mo-O4	2.162 (6)	O2-O3	1.397 (10)	C3-N3	1.111 (14)
(b) Bond Angles (deg)					
O1-Mo-O2	103.7 (3)	O2-Mo-C2	153.2 (3)	C1-Mo-C2	77.8 (3)
O1-Mo-O3	102.4 (4)	O2-Mo-C3	121.9 (4)	C1-Mo-C3	155.9 (4)
O1-Mo-O4	168.8 (3)	O3-Mo-O4	87.9 (3)	C2-Mo-C3	78.8 (4)
O1-Mo-C1	93.0 (4)	O3-Mo-C1	121.7 (3)	Mo-O2-O3	68.8 (4)
O1-Mo-C2	90.8 (4)	O3-Mo-C2	155.2 (3)	Mo-O3-O2	68.4 (4)
O1-Mo-C3	93.2 (4)	O3-Mo-C3	79.5 (4)	Mo-O4-P1	158.3 (4)
O2-Mo-O3	42.8 (3)	O4-Mo-C1	85.3 (3)	Mo-C1-N1	173.9 (9)
O2-Mo-O4	86.9 (3)	O4-Mo-C2	78.0 (3)	Mo-C2-N2	176.5 (8)
O2-Mo-C1	79.0 (3)	O4-Mo-C3	84.1 (3)	Mo-C3-N3	180 (1)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

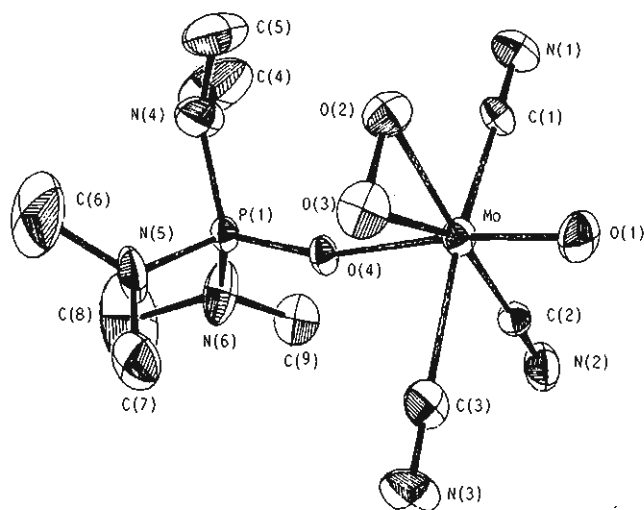
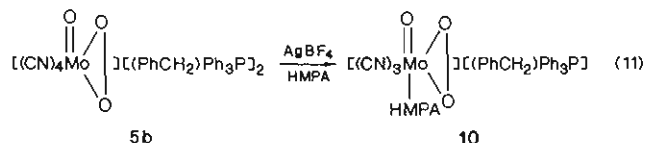


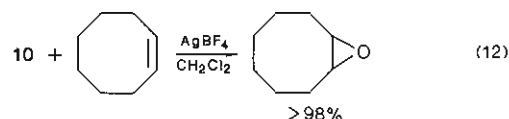
Figure 3. ORTEP view of the $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_3 \cdot \text{HMPA}]^-$ anion, showing the atom-labeling scheme. Atoms are represented with thermal ellipsoids at 20% electron probability for clarity.

peroxidic oligomers was faster than the crystallization process. Stabilizing the complex with HMPA and replacing the tetraphenylphosphonium cationic moiety by benzyltriphenylphosphonium ion yielded on the other hand the desired product under a crystalline form (**10**). The infrared spectrum of the orange solid exhibits two absorption bands at 960 cm^{-1} and 910 cm^{-1} attributed respectively to an oxo and a peroxy group. Elemental analysis indicated that the compound was a monoanion rather than the expected neutral species.



Its structure was confirmed by an X-ray analysis. Final atomic coordinates (Table IV) and selected bond distances and angles (Table V) as well as an ORTEP drawing (Figure 3) of **10** are given. The O-O distance ($1.397 (10) \text{ \AA}$) is comparable with that of **5b** ($1.416 (3) \text{ \AA}$), in agreement with literature values.¹⁴ An abnormally high thermal factor was obtained for the HMPA ligand. This has been previously reported for a diperoxo-molybdenum complex.¹⁹ The important bond length differences in this part of the molecule have, however, no influence on the oxoperoxo-molybdenum moiety.

The tendency of compound **5b** to oligomerize upon standing in solution is apparently diminished by the presence of HMPA. This could significantly lower the extent of decomposition during the oxidation process and thus increase the yield of epoxidation. This was indeed observed when **10** was reacted with cyclooctene in the presence of AgBF_4 : cyclooctene oxide was obtained nearly quantitatively



Acknowledgment. J.S. acknowledges the CEPET of Venezuela for a scholarship.

Registry No. 2, 115436-94-7; 3, 86568-26-5; 4, 17456-18-7; **5a**, 115509-89-2; **10**, 115436-97-0; $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_4][\text{AsPh}_4]_2$, 115509-90-5; PPh_3 , 603-35-0; OPPh_3 , 791-28-6; $[\text{Mo}_2\text{O}_7][\text{PPh}_4]_2$, 115436-95-8; $[\text{Mo}_8\text{O}_{26}][\text{PPh}_4]_4$, 67168-41-6; $[\text{Mo}(\text{O})(\text{O}_2)(\text{CN})_4][(\text{PhCH}_2)(\text{Ph})_3\text{P}]_2$, 115509-91-6; cyclooctene, 931-88-4; cyclooctene oxide, 286-62-4.

Supplementary Material Available: Tables of full thermal and positional data and further distances and angles for **5a** and **10** (14 pages); listings of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.

(19) Le Carpentier, J. M.; Schlupp, R.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1972, B28, 1278.