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Isolation and X-ray Crystal Structure of a Dimeric Molybdenum(V) Oxo Complex Containing a Bis(3,5-dimethylpyrazolyl)methane Ligand: An Unusual Case of Dioxygen Activation[†]

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Molybdenum(V) oxo complexes have been extensively studied in the context of molybdoenzymes.[1] The chemistry of this oxidation state is dominated by spin-paired dimeric compounds[2] rather than paramagnetic monomeric ones. Their structures are profoundly influenced by the chelating ligands as well as the method of synthesis.[3]

Of late, the polypyrazolylborate ligands[4] have been investigated in detail for their unique donor properties. Enemark[5] demonstrated that hydrotris(3,5-dimethylpyrazolyl)borate can provide stable monomeric Mo(V) oxo complexes of a large variety, since the sterically demanding ligand inhibits dimerization. Kochi[6] recently reported that oxidation of (hydrotris(pyrazolyl)borato)-tricarbonylmolybdenum(0) by dimethyldioxirane afforded dimeric and tetrameric Mo(V) oxo complexes which are structurally related to those obtained by Koch and Lincoln[7] as well as Trofimenko[8] earlier.

In this report, we describe the isolation and structural characterization of new, dimeric molybdenum(V) oxo complexes with a Mo_2O_4 core, which contain neutral, bidentate dipyrazolylmethane ligands. This is the first report of such compounds resulting from facile aerial oxidation of Mo(II) π-allyl complexes. Further, it has been possible to convert triphenylphosphine quantitatively into triphenylphosphine oxide in the presence of a catalytic amount of a Mo(II) π-allyl complex. To the best of our knowledge, this is the first instance where a Mo(II) center activates dioxygen.

Results and Discussion

Isolation of the Complexes. During our attempt to prepare the π-allyl complex **2a** by ligand exchange from the bis(acetonitrile) complex **1a** (Scheme I), we observed[9] the formation of a shiny brown crystalline product **3a** devoid of the π-allyl (^{1}H NMR) as well as the carbonyl groups (IR), instead of the desired organometallic product.[10] It was found that the same compound was also formed if a dichloromethane solution of complex **2b** was left overnight in air. Similarly, when complex **2c** was dissolved in dichloromethane solution and left overnight in air, dark brown shiny crystals of compound **3b** were obtained. These complexes were collected by filtration and dried in vacuo to provide analytical samples.

Structure of the Complexes. The X-ray crystal structure of compound **3a** was determined, and the ORTEP diagram is shown in Figure 1. The compound belongs to the general class of dimeric molybdenum(V) oxo complexes containing a Mo_2O_4 core. However, this structure is significant for it is the first compound to feature the neutral, bidentate bis(3,5-dimethylpyrazolyl)-methane ligand. The six-membered metallacycle exists in the boat conformation, which is typical for the complexes of this ligand.[11] The Mo–Mo distance of 2.56 Å is within the range of a metal–metal single bond, which would explain its diamagnetism at 25 °C. A distorted octahedral arrangement around the molybdenum and the presence of a molecular C_2 symmetry are common features of these complexes. The bond between molybdenum and a terminal oxygen atom (Table II) is shorter than that between a metal and a bridging oxygen atom, as would be expected.[3] Also, the Mo–N bond trans to the terminal oxo group is longer than the corresponding Mo–N bond cis to the terminal oxo group. The two bridging oxygens are slightly below the plane containing the two molybdenum atoms and the pair of equatorial ligands.

Mechanism of Formation. The Mo(V) complexes are generally prepared from Mo(VI) complexes by reduction.[12] Alternatively, low-valent molybdenum complexes are oxidized by use of various reagents.[6] The Mo(V) halides or oxyhalides are also used as starting materials. In contrast, the facile and clean aerial oxidation of Mo(II) compounds to Mo(V) dimers as observed in the present case is uncommon.[13]

The allyl radical released from the complex during oxidation forms a dimer as well. It was possible to isolate the dimer as a mixture of double-bond isomers (GC, mass) from the mother liquor which yielded complex **3b**. The stability of the allyl radical and the facility with which it can dimerize might render it particularly suitable for this reaction. We observed that the corresponding dibromo complex[14] (where the allyl group of the complex **2c** is replaced by bromine) did not undergo any chemical change upon exposure to air at room temperature for 2–3 days.

It would be premature to speculate on a mechanism for this oxidation. A peroxo intermediate could be involved, since its formation is feasible under these conditions, but we have no direct evidence so far to support its formulation (indirect evidence being oxygen transfer; vide infra).

Oxygen-Transfer Reaction. The possibility of a metal peroxo intermediate in the reaction pathway prompted us to examine the feasibility of oxygen transfer to an oxygen acceptor molecule, thereby blocking the path leading to a Mo(V) dimer.[15] When 2 equiv of triphenylphosphine was added to a freshly prepared solution of 1 equiv of the allyl complex **2b** in acetonitrile (the rate

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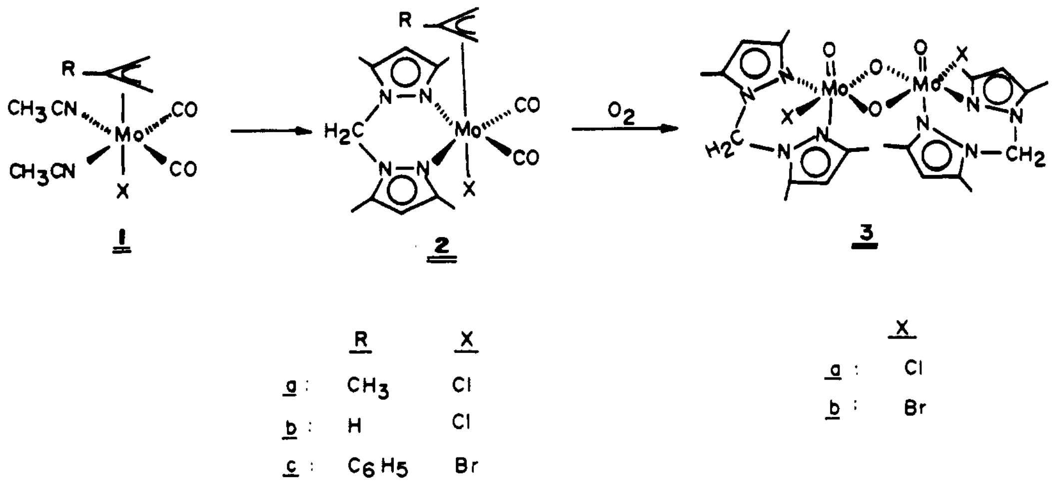
Scheme I



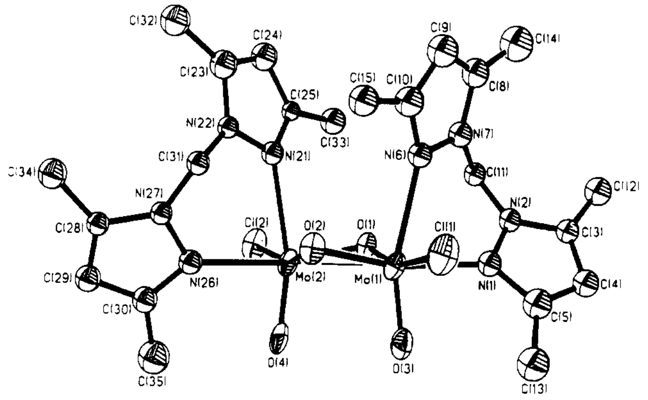


Figure 1.

Table I. Crystal Data and Structure Refinement Parameters

formula	$C_{22}H_{32}N_8O_4Cl_2Mo_2$
fw	735.3
space group	$I4_1/a$
a, Å	21.068(5)
b, Å	29.496(9)
V, Å^3	13092(6)
molecules/unit cell	16
ρ_{calcd}, g·cm^{-3}	1.49
μ_{calcd}, cm^{-1}	9.49
radiation	Mo Kα
cryst size, mm	0.05 × 0.15 × 0.30
temp, K	230
scan type	θ–2θ
scan width, deg	1.20 + Kα separation
2θ range, deg	3.0–40.0
std reflns	3 measd every 150 reflections
decay of stds	no
no. of reflns collcd	3387
no. of reflns obsd, $I \geq 3.0\sigma(I)$	1456
no. of params varied	193
GOF	1.51
R	0.055
R_w	0.067

Table II. Selected Bond Lengths (Å) and Bond Angles (deg)

Mo(1)–Mo(2)	2.559(3)	Mo(1)–Cl(1)	2.444(6)
Mo(1)–O(1)	1.939(12)	Mo(1)–O(2)	1.927(13)
Mo(1)–O(3)	1.650(14)	Mo(1)–N(1)	2.267(16)
Mo(1)–N(6)	2.418(16)	Mo(2)–Cl(2)	2.448(6)
Mo(2)–O(1)	1.930(12)	Mo(2)–O(2)	1.943(13)
Mo(2)–O(4)	1.687(14)	Mo(2)–N(21)	2.434(16)
Mo(2)–N(26)	2.275(16)		

Cl(2)–Mo(2)–O(4)	92.8(5)	O(3)–Mo(1)–N(1)	86.1(6)
Cl(2)–Mo(2)–N(21)	79.4(4)	Cl(1)–Mo(1)–N(6)	79.3(4)
Mo(1)–Mo(2)–N(26)	134.1(4)	O(2)–Mo(1)–N(6)	90.4(5)
O(4)–Mo(2)–N(26)	85.9(6)	N(1)–Mo(1)–N(6)	76.6(6)
Mo(2)–Mo(1)–O(1)	48.4(4)	Mo(1)–Mo(2)–O(1)	48.7(4)
O(1)–Mo(1)–O(2)	92.9(5)	Mo(1)–Mo(2)–O(2)	48.3(4)
O(2)–Mo(1)–O(3)	106.3(6)	O(1)–Mo(2)–O(2)	92.7(5)
O(2)–Mo(1)–N(1)	166.5(6)	O(2)–Mo(2)–O(4)	105.4(6)
O(1)–Mo(1)–N(6)	81.1(5)	O(2)–Mo(2)–N(21)	81.5(5)
Mo(1)–Mo(2)–Cl(2)	136.8(2)	O(1)–Mo(2)–N(26)	168.1(6)
Cl(2)–Mo(2)–O(2)	160.8(4)	Mo(1)–O(1)–Mo(2)	82.8(5)
O(1)–Mo(2)–O(4)	105.6(6)	Mo(2)–Mo(1)–O(2)	48.9(4)
O(1)–Mo(2)–N(21)	87.8(5)	Cl(1)–Mo(1)–O(3)	93.8(5)
Cl(2)–Mo(2)–N(26)	88.6(4)	Cl(1)–Mo(1)–N(1)	87.0(4)
N(21)–Mo(2)–N(26)	80.4(6)	Mo(2)–Mo(1)–N(6)	100.2(4)
Mo(2)–Mo(1)–Cl(1)	135.6(2)	O(3)–Mo(1)–N(6)	161.6(6)
Cl(1)–Mo(1)–O(1)	160.3(4)	Cl(2)–Mo(2)–O(1)	88.1(4)
Cl(1)–Mo(1)–O(2)	86.8(4)	Mo(1)–Mo(2)–O(4)	96.4(5)
Mo(2)–Mo(1)–O(3)	96.6(5)	Mo(1)–Mo(2)–N(21)	98.6(4)
O(1)–Mo(1)–O(3)	105.1(6)	O(4)–Mo(2)–N(21)	164.3(6)
Mo(2)–Mo(1)–N(1)	136.6(4)	O(2)–Mo(2)–N(26)	86.7(6)
O(1)–Mo(1)–N(1)	89.0(6)		

of dimerization is slower in this solvent than in dichloromethane) and the solution was left in air for 2 days, triphenylphosphine was completely converted to triphenylphosphine oxide and the Mo(V) dimer **3a** was not formed. No perceptible oxidation of triphenylphosphine occurred in the absence of the metal complex. The experiment was repeated with a 10-fold excess of triphenylphosphine with respect to the metal complex, and a complete conversion to triphenylphosphine oxide after several days indicated the catalytic efficiency of the process.[16] Absence of dimeric Mo(V) oxo complex in the metallic residue suggests that the oxygen transfer to the phosphine could have occurred via a competing pathway.[17] It is interesting to note that the parent bis(acetonitrile) π-allyl complex **1a** does not transfer oxygen to triphenylphosphine under similar conditions. Also, the complex *cis*-$(PPh_3)_2(CO)_2ClMo(\pi\text{-allyl})$ was found to be inactive. Thus, it appears that pyrazole coordination favorably modifies the reactivity of the metal center for this reaction.

Oxygen transfer to triphenylphosphine has been intensively studied.[18] Particular interest in this transformation is related to oxomolybdoenzymes.[19] In all the cases studied so far, however, the oxidation is carried out by a Mo(VI) dioxo species which is converted to Mo(IV) by transferring the oxygen atom to the phosphine. For the present instance, it is not possible to formulate

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(16) The oxidation was allowed to proceed by simply exposing the solution to air. No attempt was made to optimize the conditions.

(17) However, possibility of a ligand-exchange reaction of complex **2b** with triphenylphosphine to afford a catalytically inactive species cannot be ruled out. Attempts to characterize the metallic residue are under way.

a Mo(VI) or Mo(IV) monomeric complex which features a neutral bidentate chelate and a halide ligand. Thus, we believe the pathway of this dioxygen activation and transfer is entirely different from those known to date, and extensive experimentation is required to gain an understanding of the steps involved.

Summary

We have reported a mild aerial oxidation of Mo(II) π-allyl complexes containing the bis(3,5-dimethylpyrazolyl)methane ligand to new Mo(V) dimeric oxo complexes, whose structures were determined by X-ray crystallography. It has been shown for the first time that these Mo(II) complexes can activate dioxygen and lead to catalytic oxidation of triphenylphosphine with high efficiency. The mechanism and the scope of this new reaction are being investigated in detail and will be reported in due course.

Experimental Section

General experimental conditions were the same as described earlier.[9] Elemental analyses were carried out by Dr. S. Y. Kulkarni and his group using a Carlo-Erba CHNS analyzer, Model EA-1108.

Preparation of 3a. Complex **1a** (207 mg, 0.64 mmol) was dissolved in dichloromethane (20 mL), and bis(3,5-dimethylpyrazolyl)methane (209 mg, 1.02 mmol) was added in one portion with stirring. After 5 min, the solution was allowed to stand at room temperature with a loose cotton plug. Brown crystals of compound **3a** separated from the solution after 48 h (148 mg, 63%).

Isolation of 3a from 2b. Compound **2b** (108 mg, 0.25 mmol) was dissolved in dichloromethane (15 mL), and the solution was left exposed to air for 48 h, during which time complex **3a** separated out as brown crystals. The crystals were collected by filtration and dried in air (54 mg, 59%). IR (Nujol): 1561, 1041, 963 cm^{-1}. Anal. Calcd for $C_{22}H_{32}N_8Cl_2O_4Mo_2$: C, 35.91; H, 4.35; N, 15.23. Found: C, 36.08; H, 4.43; N, 15.26.

X-ray Structure Analysis of Compound 3a. A single crystal of the compound was mounted on a Nicolet R3m/V diffractometer. Final unit cell parameters, given in Table I, were obtained by a least-squares fit of the angles of 24 accurately centered reflections ($16° < 2\theta < 27°$). Intensity data were collected in the range $3.5° \leq 2\theta \leq 40°$ at −43 °C using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A total of 3387 reflections were collected, 3074 unique, $R_{int} = 0.023$. Systematic absences were consistent with space group $I4_1/a$. Three standard reflections monitored after every 150 reflections did not show any significant change in intensity during the data collection. The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied. The minimum and maximum transition factors were 0.551 and 0.571, respectively. The structure was solved by heavy-atom methods with the SHELXTL-Plus package.[20] Full-matrix least-squares refinement was performed. Mo, Cl and O atoms were refined anisotropically; C and N atoms, isotropically. Scattering factors, with corrections for anomalous dispersion of heavy atoms, were taken from ref 21. Hydrogen atoms were placed at idealized positions with fixed isotropic temperature factors (U = 0.08 Å^2). The weight had the form $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ where $g = 0.0005$. Final cycles of refinement converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.055$, $R_w = [\sum\Omega(|F_o| - |F_c|)^2/\sigma(\Omega(F_o)^2)]^{1/2} = 0.067$, GOF = 1.51 for 1456 observed reflections [$I > 3.0\sigma(I)$]. Maximum and minimum residuals on final difference Fourier maps: 1.06 and −0.47 e/Å^3, respectively.

Isolation of 3b from 2c. Compound **2c** (50 mg, 0.09 mmol) was dissolved in dichloromethane (10 mL), and the solution was exposed to air for 48 h. The crystalline complex **3b** was isolated by filtration and dried under vacuum (29 mg, 78%). IR (Nujol): 1558, 1040, 963 cm^{-1}. Anal. Calcd for $C_{22}H_{32}N_8Br_2O_4Mo_2$: C, 32.03; H, 3.80; N, 13.59. Found: C, 31.93; H, 3.48; N, 13.18.

Oxidation of Triphenylphosphine. Complex **2b** (216 mg, 0.5 mmol) and triphenylphosphine (264 mg, 1 mmol) were dissolved in acetonitrile (20 mL), and the solution was allowed to stand in air. After 5 days, complete disappearance of triphenylphosphine was observed by TLC. The solvent was removed under reduced pressure, and the residue was treated with dichloromethane (10 mL). On addition of petroleum ether (10 mL) to this solution, precipitation of the metallic residue occurred as a green solid. After filtration and concentration of the filtrate, the residue was triturated with petroleum ether to obtain a pure sample of triphenylphosphine oxide as a white solid (268 mg, 94%). The experiment was repeated with the same quantity of complex **2b** and excess PPh_3 (1.32 g, 5 mmol). The complete conversion of the phosphine required 12 days, and the product phosphine oxide was isolated as before (1.18 g, 84%).

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Supplementary Material Available: Tables of bond lengths, bond angles, thermal parameters, and atomic coordinates (4 pages). Ordering information is given on any current masthead page.

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