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Dioxygen ligand transfer from platinum to molybdenum. Isolation of a highly reactive molybdenum(VI) oxoperoxo dimer [1]

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Summary – The reaction of $Pt(O_2)(PPh_3)_2$ with $Mo(O)_2(mesityl)_2$ (mesityl = 2,4,6-$Me_3C_6H_2$) in pyridine results in the transfer of the dioxygen ligand from platinum to molybdenum giving, in the presence of PPh_4Cl, a molybdenum peroxo compound **1** in which all the organic moieties have been lost. This compound epoxidizes tetracyanoethylene at a rate estimated at 10^4 greater than the known oxodiperoxomolybdenum complex **2**. Furthermore, **1** exhibits a high selectivity for electron-poor olefins (TCNE/cyclooctene = 10^3). Elemental analysis, IR and ^{17}O NMR indicate that **1** is the tetraphenylphosphonium salt of an oxoperoxomolybdenum(VI) dimer.

dioxygen transfer / platinum peroxo / molybdenum oxoperoxo / epoxidation

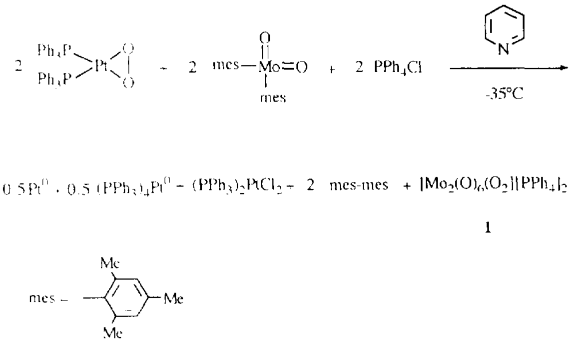
Introduction

Dioxygen activation in catalytic processes often involves bimetallic systems which imply the transfer of the dioxygen moiety from one type of metallic center to another [2]. Such bimetallic systems are most common in heterogeneous catalysis with molybdenum oxide 'doped' with a second metal, *eg*, Co, Ni or Bi [3, 4]. While investigating homogeneous bimetallic models such as Co/Mo [5] or Ni/Mo [6] we have shown that a transfer of the dioxygen ligand with formation of molybdenum peroxidic species could indeed be operative, allowing selective oxidation of organic substrates. However, the exact mechanism could not be established since no stable intermediate could be isolated.

Persuing our goal we studied the transfer of a dioxygen ligand from a platinum peroxo to a molybdenum(VI) dioxo complex and isolated a new oxoperoxomolybdenum compound exhibiting an unprecedented high reactivity towards olefins, which could be rationalized in terms of the electron-donating properties of neighboring metal-oxo groups. This new compound thus constituted a good model for metal oxide surface oxidations.

Results and discussion

The reaction between $Pt(O_2)(PPh_3)_2$ [7] and $MoO_2(mesityl)_2$ [8] in pyridine occurred readily at −35°C to give a red solution which rapidly became yellow. Upon warming to room temperature and addition of tetraphenylphosphonium chloride, we isolated two platinum-containing species: metallic platinum as a black precipitate and a divalent platinum complex characterized as $PtCl_2(PPh_3)_2$ [9]. From the remaining solution, bimesityl was isolated and characterized as the only organic product. Upon addition of *n*-pentane a cream-colored solid analyzing for $(Mo_2O_8)(PPh_4)_2$ **1** was obtained. This reaction can be schematized as follows [10].



Scheme 1

Compound **1** is fairly stable in the solid state but decomposes in room temperature solution with loss of O_2 and formation of a mixture of isopolymolybdate anions.

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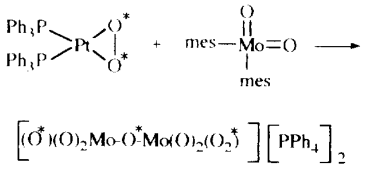
Table I. Olefin epoxidation with oxoperoxomolybdenum(VI) compounds[a].

Olefin	Peroxo complex	Products (%)[b]	Solvent	Reaction temperature	Reaction time[c]	Relative rate
TCNE	1	TCNE oxide (100%)	CH_2Cl_2	0°C	~ 2 min[d]	> 10^4
Cyclooctene	1	Cyclooctene Oxide (10%)	CH_2Cl_2	0°C	5 h	6
TCNE + Cyclooctene	1	TCNE oxide (100%) Cyclooctene oxide (0%)	CH_2Cl_2	0°C	~ 2 min[d]	–
TCNE + Cyclooctene	2	TCNE oxide (63%) Cyclooctene oxide (36%)	$C_2H_4Cl_2$	60°C	5 h	2 (TCNE) 1 (Cyclooctene)

[a] Stoichiometric ratio olefin/peroxo complex = 1. [b] Yields calculated by GPC with an internal standard. [c] Estimation based on yields and on reaction time and temperature. [d] Approximate time necessary to perform a product analysis.

It oxidizes iodide ions readily indicating a strong peroxidic character in a stoichiometry estimated as ~ 1 peroxo/2 Mo. Its infrared spectrum exhibits two absorption bands at 790 and 880 cm^{-1} [11–13], suggesting the presence of μ-oxo and terminal oxo groups; however, numerous absorption peaks due to the tetraphenylphosphonium cation prevented the unambiguous assignment of the peroxidic function by IR.

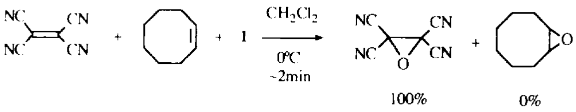
In order to observe the reaction by ^{17}O NMR, it was repeated using $Pt(^{17}O_2)(PPh_3)_2$. The ^{17}O NMR analysis of 1* exhibited three signals: a sharp line at 760 ppm (ν 1/2 = 120 Hz) from H_2O characteristic of a terminal oxomolybdenum group [14, 15]; one broad line at 70 ppm (ν 1/2 = 950 Hz) assigned to a linear μ-oxo group (comparable to a center oxygen atom in isopolymolybdates [16, 17]); and a very broad line centered at 290 ppm (ν 1/2 = 3 300 Hz) attributed to a peroxidic function [17]. The extreme broadness of the latter could be either indicative of a fluxional character of the ligand or due to the presence of more than one type of peroxo function. The analysis indicated, furthermore, that the transfer of the peroxidic moiety from platinum to molybdenum resulted in the labeling of only one terminal oxo, the μ-oxo and the peroxidic moiety excluding any $^1\eta$-$^1\eta$: Mo-O-O-Mo structure.



1*

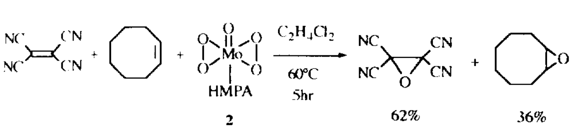
Scheme 2

Although the apparent dioxygen transfer from platinum to molybdenum was interesting since it confirmed the 'double jump' mechanism for O_2 activation by bimetallic systems, it is the unusual and unprecedented reactivity pattern of this complex which drew our attention. The results given in table I show that **1** reacts with cyclooctene about six times faster than the monomeric neutral oxodiperoxomolybdenum complex **2** [18]. What is even more noteworthy, is that **1** *epoxidizes tetracyanoethylene faster than cyclooctene by a factor greater than* 3 × 10^3. Thus, when 1 mol of tetracyanoethylene and 1 mol of cyclooctene are treated with 1 mol of **1**, only tetracyanoethylene oxide is obtained with no detectable amount of cyclooctene oxide.



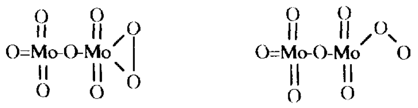
Scheme 3

This is strikingly different from complex **2**, which epoxidizes the same equimolar combination at a much slower rate (> 10^4 slower) to give a mixture of tetracyanoethylene oxide (oxiranetetracarbonitrile) and cyclooctene oxide (9-oxabicyclo[6.1.0]nonane).



Scheme 4

Such a high selectivity exhibited by **1** for electron-poor olefins implied the presence of a peroxidic function nucleophilic in character and somewhat different from the classical 'side-on' peroxo structure. Two plausible structural patterns could be envisaged for this peroxidic moiety: a $^2\eta$ 'side-on' peroxo **3** or a $^1\eta$ 'open-end' monodentate peroxo **4** ligand.



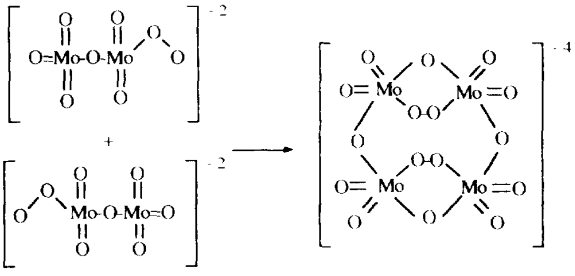
3 **4**

Scheme 5

The vast majority of molybdenum peroxo complexes characterized contain $^2\eta$ 'side-on' structures [19]; $^1\eta$-$^1\eta$ bridging peroxo ligands, although less common, are nevertheless well known and are usually found in polyoxoperoxomolybdate clusters [19]. On the other hand, $^1\eta$ monodentate peroxidic ligands are extremely rare and have been reported only as intermediates in molybdenum complexes bearing porphyrin rings [20-22].

The formation of an 'open-end' molybdenum peroxo complex was thus, *a priori*, unforeseen, but **1** must be present in such a form in order to rationalize its unprecedented nucleophilic character and unusually high affinity for an electron-poor olefin. Structure **4** complies with this.

Further support for structure **4** is provided by the argument that it could tentatively be considered as the precursor of the known tetramer **5** [23], which could be formed by simple coupling.



4 **5**

Scheme 6

Additional information could have been obtained from an X-ray analysis of **1**. Unfortunately, this was not totally successful since a very high thermal motion was present on the peroxo moiety of the molecule which made the positioning of the peroxidic oxygen atoms insignificant. It allowed, nevertheless, the exclusion, without any doubt, of a tetrameric structure **5** and confirmed the absence of any $^1\eta$-$^1\eta$ peroxo function [24].

Experimental section

General

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. 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. Dioxodimesityl molybdenum [8], bis(triphenylphosphine) peroxo platinum [7] and oxodiperoxomolybdenum (HMPA) [15] were prepared according to previously described procedures. Labeled oxygen bis (triphenylphosphine) peroxo platinum was synthesized using labeled oxygen (32.9% ^{16}O, 21.2% ^{17}O, 45.9 ^{18}O) and by slightly modifying the procedure reported in order to avoid unnecessary loss of labeled reactant. Oxygen gas evolution during the decomposition of **1** was measured with a Toepler pump. NMR spectra were recorded on Bruker WH-200 or Bruker WH-100 spectrometers. The chemical shifts (ppm) were determined relative to tetramethyl silane (^{13}C, ^1H), phosphoric acid (^{31}P) and water (^{17}O). IR spectra were recorded on a Nicolet MX5 spectrometer. Gas chromatographic analyses were done using a SE 30 capillary column and 1,2-dichlorobenzene as the internal standard. Elemental analysis were carried out by the Service central d'analyse du CNRS, 69390 Vernaison, France.

Synthesis of [Mo_2O_8] [PPh_4]$_2$ **1**

A pyridine solution (10 mL) containing recrystallized $MoO_2(mesityl)_2$ (0.536 g, 1.5 mmol) was slowly added under argon to a precooled (−40°C) solution of $Pt(O_2)(PPh_3)_2$ (1.13 g, 1.5 mmol) in pyridine (20 mL). The suspension obtained was slowly warmed, while stirring. At −35°C, the solid started dissolving with the appearance of a red color which rapidly turned orange and then yellow. The solution was allowed to reach room temperature within 1 h, before PPh_4Cl (0.56 g, 1.5 mmol) in CH_2Cl_2 (10 mL) was added. Upon addition of *n*-pentane (1 mL) and standing, a black precipitate (metallic platinum) and white crystalline needles were obtained, characterized as $PtCl_2(PPh_3)_2$ by comparison with an authentic sample. (No yields were determined.) Upon longer standing at 6°C, 0.380 g (56%) of **1** was obtained as beige-colored cubic crystals.

Anal calc for $C_{48}H_{40}O_8Mo_2P_2$: C, 57.7; H, 4.0; Mo, 19.2; P, 6.2. Found: C, 58.3; H, 4.1; Mo, 20.4; P, 5.8.

The tetraphenylarsonium analog of **1** was synthesized by replacing PPh_4Cl by $AsPh_4Cl$. The quality of the monocrystal was not improved.

The synthesis of **1** was attempted by the peroxidation of [Mo_2O_7][PPh_4]$_2$ with H_2O_2. The presence of water, even when H_2O_2/urea was used, prevented the isolation of **1**.

Reaction of **1** *with tetracyanoethylene and cyclooctene*

To 0.8 g (0.8 mmol) of **1** was added at 0°C a 10 mL CH_2Cl_2 solution containing 0.10 g (0.8 mmol) of tetracyanoethylene, 0.088 g (0.8 mmol) of cyclooctene and 0.1 mL (0.13 g, 0.8 mmol) of 1,2-dichlorobenzene as an internal standard. The solution, which became instantly red, was analyzed immediately by GPC on an SE 30 capillary column. The yield of tetracyanoethylene oxide was 100%; no cyclooctene oxide was detected. When the same reaction was done in the absence of tetracyanoethylene, the reaction was run at 0°C for 5 h yielding (GPC): cyclooctene oxide (10%), cyclooct-2-en-1-ol (1%) and cyclooctanol (2%). The results obtained with the tetraphenylarsonium salt were identical.

Reaction of **2** *with tetracyanoethylene and cyclooctene*

To 0.15 g (0.4 mmol) of **2** was added a 10 mL dichloroethane solution containing the same mixture as above and the temperature was brought to 60°C. After 30 min the solution started to turn red. The evolution of the products was followed by GPC, which showed after 5 h the presence of tetracyanoethylene oxide (63%) and cyclooctene oxide (36%).

Conclusions

The reaction of a platinum peroxo complex with a molybdenum(VI) dioxo compound results in the transfer of the peroxo function from one metal to the other, corroborating the 'double jump' mechanism in dioxygen activation catalyzed by heterobimetallic systems. The dimeric molybdenum species **1** obtained exhibits exceptional reactivity towards electron-poor olefins ($\sim 10^4$ higher than known $^2\eta$ molybdenum peroxo complexes) suggesting the presence of a peroxidic function with high nucleophilic character. The dimer with only oxygen atoms might also be considered a good model for molybdenum oxide surfaces and thus be expected to have implications in catalytic oxidation processes on such surfaces.

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24 It depicted one molydenum atom surrounded by three terminal oxo oxygen atoms and a nearly linear (176°) μ-oxo group linked to the second molybdenum atom on which the thermal motion was observed. Attempts to obtain a better quality crystal by varying the solvent system or the nature of the countercation were unsuccessful