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Oxygen atom transfer photocatalyzed by molybdenum(VI) dioxodibromo-(4,4′-dicarboxylate-2,2′-bipyridine) anchored on TiO_2

Carlos A. Páez [a,1], Nelson J. Castellanos [a,1], Fernando Martínez O. [a], Fabio Ziarelli [b], Giuseppe Agrifoglio [c], Edgar A. Páez-Mozo [a,*], Henri Arzoumanian [d,*]

[a] Escuela de Química, Centro de Investigación en Catálisis (CICAT), Universidad Industrial de Santander, Km 2 vía El Refugio, Piedecuesta, Santander, Colombia
[b] FR1739 CNRS, Université Paul Cézanne, Faculté des Sciences, St Jérôme, Marseille, France
[c] IVIC, Caracas, Venezuela
[d] UMR 6180 CNRS, Chirotéchnologies: Catalyse et Biocatalyse, Université Paul Cézanne, Faculté des Sciences, St Jérôme, Marseille, France

Abstract

The molybdenum(VI) dioxodibromo-(4,4′-dicarboxylate-2,2′-bipyridine) complex was anchored on a TiO_2 solid matrix, fully characterized by ^{13}C and ^{15}N solid-state NMR spectroscopy and evaluated as an oxygen atom transfer agent under visible light ($\lambda > 420$ nm) irradiation. It was compared with the complex molybdenum(VI) dioxodibromo-(4,4′-dicarbomethoxy-2,2′-bipyridine) under homogeneous conditions. Two positive effects were observed: (1) an important reactivity increase due to the photogenerated electronic flux onto the molybdenum coordination sphere and (2) a catalyst life span amplification due to the isolation of the metallic centers allowing the catalytic system to be turned on and off in the presence or absence of O_2.

Keywords: Molybdenum(VI) complex; TiO_2 matrix; CPMAS NMR; Oxygen transfer

1. Introduction

In the important field of oxo-transfer chemistry, numerous molybdenum complexes have been studied, especially as models for the active site of oxo-transfer molybdoenzymes [1–4]. The first examples responded to two criteria, namely a sulfur environment and a large steric demand to avoid inactive μ-oxo dimer formation [5–8]. Later studies, however, showed that the sulfur environment, although favorable, was not necessary and the high steric requirement of ligands only postponed the irreversible μ-oxo dimer formation in a catalytic system [9–11].

In this context, we have reported several molybdenum oxo, dioxo and μ-oxo complexes bearing various ligands among which some exhibited exceptional oxygen atom transfer capability either under stoichiometric or catalytic conditions using different oxygen atom donors [11–14]. Interestingly, the substrates to be oxidized can be phosphanes but also alcohols, arylalcanes or olefins. Furthermore, in the majority of these complexes the ligand present in the coordination sphere were bipyridyl ligands and exhibited, as expected, a significant acceleration under UV irradiation.

This report concerns the anchoring on a semiconductor solid matrix such as anatase TiO_2, of a molybdenum complex with the endeavor, on one hand, to isolate the metallic centers to hamper any μ-oxo dimer formation, and on the other to favor the oxo-transfer process by a photogenerated electronic flux towards the Mo=O moiety.

2. Experimental

2.1. General

All materials were commercial and were used without further purification unless otherwise noted. All solvents were

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* Corresponding authors.
E-mail address: epaez@uis.edu.co (E.A. Páez-Mozo).

[1] On leave at Université Paul Cézanne Marseille.

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thoroughly degassed prior to use. Dichloromethane and *n*-hexane were dried over molecular sieves, acetonitrile was distilled and kept under argon, and thionyl chloride was doubly distilled. Triphenylphosphine was recrystallized prior to use and checked by ^{31}P NMR for purity. Titanium oxide (Degussa-P25) with 50 m^2/g specific area and crystalline structure of 80% anatase and 20% rutile was dehydrated at 100 °C and 5×10^{-4} mbar for 48 h prior to use. IR spectra were recorded on a PerkinElmer 1720XFT spectrometer and UV–vis spectra were obtained on a HP 84 23 spectrophotometer. ^{1}H and ^{13}C NMR were performed on Bruker Avance 200 and 400 spectrometers. All solid-state CPMAS NMR spectra were obtained on a Bruker Avance 400 MHz NMR spectrometer operating at a ^{13}C and ^{15}N resonance frequency of 101.6 MHz and 40.6 MHz, respectively. ^{13}C and ^{15}N experiments were performed with a commercial Bruker Double-bearing probe with zirconium dioxide rotors of 4 mm outer diameter. The CP technique [15] was applied during magic angle spinning (MAS) of the rotor at 10 kHz. A ramped ^{1}H-pulse starting at 100% power and decreasing until 50% was used during contact time in order to circumvent Hartmann–Hahn mismatches [16,17], the contact time were 2 ms for ^{13}C CPMAS and 1.5 ms for ^{15}N CPMAS. To obtain a good signal-to-noise ratio in ^{13}C CPMAS experiment 2048 scans were accumulated using a delay of 2 s and to obtain an acceptable signal-to-noise ratio in ^{15}N CPMAS experiment 20,000 scans were accumulated using a delay of 5 s. The ^{13}C chemical shifts were referenced to tetramethylsilane and calibrated with glycine carbonyl signal, set at 176.5 ppm; the ^{15}N chemical shifts were referenced to neat nitromethane (CH_3NO_2) and ^{15}N signal set at 0 ppm [18].

2.2. Synthesis of the ligands

2.2.1. 2,2′-Bipyridine-4,4′-dicarboxylic acid [19] (**1**)

It was prepared according to a reported procedure from 4,4′-dimethyl-2,2′-bipyridine [20]. IR (cm^{-1}) KBr: ν 3441 (s), 2446 (s), 1729 (s), 1604 (s), 1461 (s), 1366 (s), 1290 (s), 1268 (s). ^{13}C NMR CPMAS (400 MHz): $\delta = 123.2$; 140.0; 150.3; 164.7.

2.2.2. 4,4′-Dicarbomethoxy-2,2′-bipyridine (**2**)

It was prepared according to a reported procedure via the acid chloride of the 2,2′-bipyridine-4,4′-dicarboxylic acid followed by its conversion to the dimethyl ester in methanol [21]. IR (cm^{-1}) KBr: 2967 (w), 1731 (s), 1437 (s), 1295 (s). ^{1}H NMR ($CDCl_3$) $\delta = 4.05$ (d, 3H); 8.16 (s, 1H); 9.05 (s, 1H); 9.26 (s, 1H). ^{13}C NMR CPMAS: $\delta = 53.4$; 55.0; 115.2; 120.1; 125.5; 130.3; 136.2; 142.7; 147.3; 149.8; 152.6; 160.8; 164.2.

2.2.3. 2,2′-Bipyridine-4,4′-dicarboxylate/TiO_2 (**3**)

The acid chloride obtained from the $SOCl_2$ treatment of 2,2′-bipyridine-4,4′-dicarboxylic acid (0.5 g, 0.2 mmol) was dissolved in 50 mL of dry CH_2Cl_2 and added to a CH_2Cl_2 (50 mL) suspension containing 1.0 g of anhydrous TiO_2. The mixture was vigorously stirred at 25 °C for 5 days and filtered under inert atmosphere to yield a brownish colored solid (1.09 g). IR (cm^{-1}) KBr: 3340 (s), 1731 (s), 1636 (m), 1596 (s), 1426 (s), 1394 (m), 1234 (s), 1210 (s), 1139 (w). ^{13}C NMR CPMAS: $\delta = 123.1$; 126.7; 131.4; 138.1; 140.2; 144.0; 147.7; 150.5; 153.5; 164.7 (t).

2.3. Synthesis of complexes

2.3.1. $Mo(O)_2Br_2[OP(C_6H_5)_3]_2$ (**4**)

To an HBr (45%) solution (6 mL) containing 1.0 g of $Na_2MoO_4 \cdot 2H_2O$ (4.15 mmol) was added 15 mL of diethyl ether and the mixture vigorously stirred for 5 min before the ether layer was separated, dried over anhydrous sodium sulfate. To the dried diethyl ether solution was added an acetone solution (60 mL) containing 1.9 g (7.4 mmol) of triphenylphosphine oxide. Stirring at room temperature for a few minutes resulted in the precipitation of a green solid which was filtered and recrystallized from CH_2Cl_2/Et_2O (1/1). IR (cm^{-1}) KBr: 3099 (w), 1702 (w), 1437 (s), 1174 (s), 1146 (s), 1121 (s), 1089 (s), 946 (s), 903 (s), 724 (s), 692 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.38$ (m, 2H); 7.53 (t, H); 7.76 (m, 2H). Anal. Calc. for $C_{36}H_{30}Br_2MoO_4P_2$: C, 51.21; H, 3.62. Found: C, 51.24; H, 3.58.

2.3.2. $Mo(O)_2Br_2$(4,4′-dicarbomethoxy-2,2′-bipyridine) (**5**)

To an HBr (45%) solution (3 mL) containing 0.2 g (0.8 mmol) of $Na_2MoO_4 \cdot 2H_2O$ was added 10 mL of diethyl ether. The mixture was stirred for 5 min and the organic layer separated, dried over anhydrous sodium sulfate and decanted. To the resulting dried solution was added a 60 mL acetone solution containing 0.2 g (0.8 mmol) of 4,4-dicarbomethoxy-2,2′-bipyridine. The yellow suspension obtained after stirring for 5 min was filtered and washed with Et_2O (100 mL). IR (cm^{-1}) KBr: 3082 (w), 2085 (w), 1733 (s), 1565 (m), 1437 (s), 1401 (s), 1333 (s), 1274 (s), 1233 (m), 946 (s), 913 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = 4.12$ (s, 3H); 8.29 (d, 1H); 8.92 (s, 1H); 9.78 (t, 1H). ^{13}C NMR CPMAS: $\delta = 53.5$; 54.3; 121.5; 122.3; 140.3; 141.2; 150.1; 152.0 (d); 161.5 (d).

2.3.3. $Mo(O)_2Br_2$(4,4′-dicarboxylate-2,2′-bipyridine)/TiO_2 (**6**)

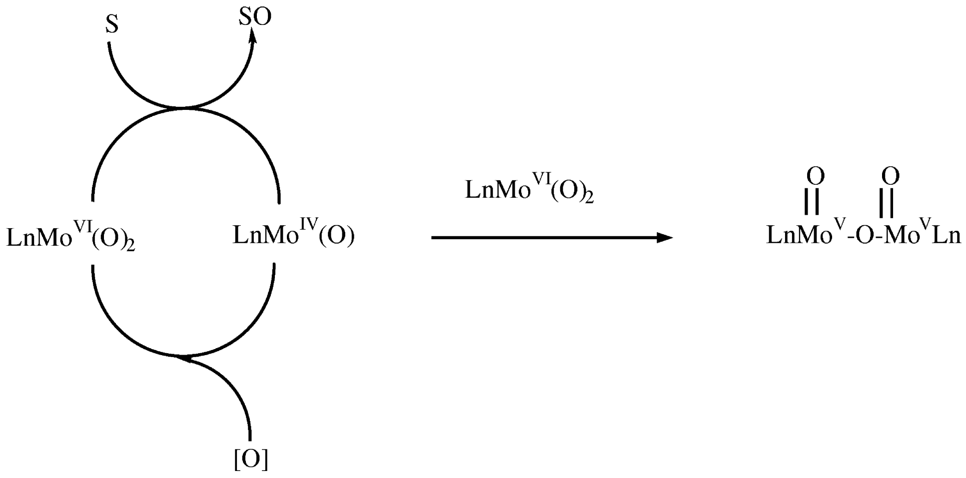
To a 50 mL CH_2Cl_2 suspension of freshly prepared 2,2′-bipyridine-4,4′-dicarboxylate/TiO_2 (0.5 g) was added a CH_2Cl_2 solution (50 mL) containing 0.35 g (0.41 mmol) of $Mo(O)_2Br_2[OP(C_6H_5)_3]_2$ (**4**). The mixture was vigorously stirred during 3 days at 25 °C and filtered under inert atmosphere to give 0.56 g of a light violet solid. IR (cm^{-1}) KBr: 1731 (s), 1603 (w), 1561 (w), 1395 (w), 1366 (s), 1291 (s), 1262 (s), 940 (s), 915 (s), 766 (m). ^{13}C NMR CPMAS: $\delta = 120.3$; 122.5; 126.0; 131.3; 137.6; 143.6; 147.2; 153.3; 162.9; 166.3.

2.4. Photocatalytic triphenylphosphine oxidation

The photocatalytic oxidation of the triphenylphosphine was carried out using a 10 mL batch micro-reactor (Ace-Glass model T-121m) with immersion lamp (Phenix, 220 V). The light passes through a potassium dichromate solution (1 M) in order to remove UV radiation and to homogenize the light intensity distribution. The photon flux (I_O) per unit volume and unit time, was determined by chemical actinometry using Reinicke salt [22], with $\Phi = 0.231$ at $\lambda \geq 420$ nm. Measured $I_O = 3.47 \times 10^{-5}$ moles of photons/L s.

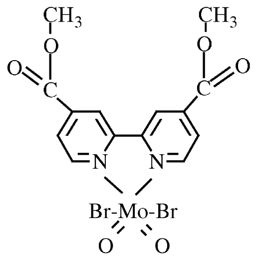
3. Results and discussion

In the oxo-transfer process from oxo-donors to various substrates, catalyzed by molybdenum(VI) dioxo complexes, one major problem lies in the irreversible formation of Mo(V)-μ-oxo species [7,23]. Indeed, when a Mo(VI) dioxo compound is reacted stoichiometrically with an oxo-acceptor such as a phosphine, a Mo(V)-oxo-μ-oxo compound is produced nearly quantitatively, plausibly via a metathetic Mo(VI)/Mo(IV) disproportionation reaction. This dimer is found to be totally inert towards most oxo-donors such as DMSO, N_2O or O_2. When the same Mo(VI) dioxo entity is reacted under catalytic conditions in the presence of an oxo-donor, the substrate (e.g. phosphine) is *catalytically* oxidized, indicating that an active reduced intermediate, capable of being reoxidized, is present and allows the catalytic cycle to remain alive. The life span of such cycle will depend directly on the rate at which the active intermediate will decay to the Mo(V)-oxo-μ-oxo inactive species.



In order to prevent or at least to delay the Mo(V)-μ-oxo dimer formation, sterically demanding and often sophisticated ligand systems have been introduced in the coordination sphere of the metal, but these often had a negative effect on the oxo-transfer capacity of the Mo(VI) dioxo species itself.

We thought another approach would be to anchor a Mo(VI) dioxo complex, otherwise known to be active in a homogeneous medium, on a solid matrix, isolate the metallic centers and thus avoid any dimer formation. Furthermore, using a semiconductor solid matrix such as TiO_2 or ZnO_2, the photogenerated electronic flux through a well-adapted ligand system could favor the oxo-transfer process. Indeed, recently TiO_2 has been used to support photo sensitizers such as metallic complexes of bipyridines [24–26], porphirines, phthalocyanines [22,27–29], viologens [30], and rodamine B, among others [31,32]. It has been shown that systems like photo sensitizers/TiO_2 are able to oxidize organic or inorganic substances, under irradiation with $\lambda \geq 420$ nm at room pressure and temperature [22]. For the present study we chose a molybdenum dioxodibromo-2,2′-bipyridine complex anchored on the solid matrix via a titanium carboxylate function on the 4,4′-position (**6**). For comparative purposes, the 4,4′-dicarbomethoxy ester complex was also synthesized (**5**).



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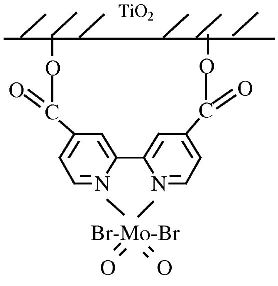
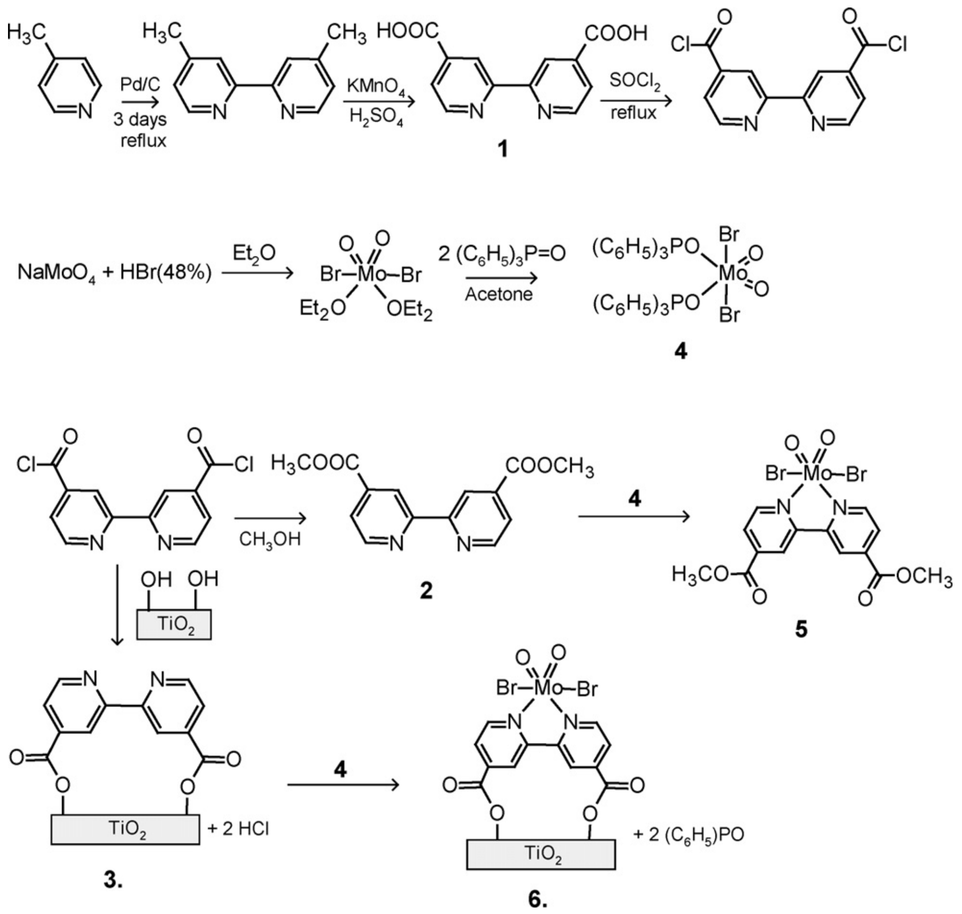


6

The synthetic route for the preparation of **5** and **6** is depicted above. The dimethyl ester complex (**5**) was obtained via a procedure reported for analogous complexes and was fully characterized by IR and ^1H NMR spectroscopy. The synthetic route chosen for complex **6** consisted of anchoring the bipyridyl moiety onto the solid TiO_2 matrix, via the 2,2′-bipyridyl-4,4′-dicarboxylic acid chloride, followed by the complexation of the anchored bipyridine on the molybdenum(VI) dioxodibromo complex **4**.



The characterization of **6** was done by IR spectroscopy and more thoroughly by solid-state ^{13}C and ^{15}N NMR spectroscopy. For comparative purposes the compounds **2**, **5**, and **6** were all analyzed by solid-state ^{13}C and ^{15}N NMR spectroscopy. ^{13}C spectrum of **2** (Fig. 1A) shows a doublet for each resonance, this is explained by the presence in the solid state of a mixture of *cis* and *trans* conformers. The ^{13}C spectrum of **5** (Fig. 1B), on the other hand exhibits as expected, only singlet resonances since the complex with the molybdenum moiety can be attained only with the *cis* conformation. Moreover, the chemical shift observed in the ^{15}N NMR solid state (Fig. 2A and B) confirms this binding through the nitrogen atoms. It is reflected as expected, by an important highfield shift (−105.4 ppm).

^{13}C spectrum of **6** (Fig. 1C) shows new resonances, that can be attributed to complex **6** contaminated with some anchored but uncomplexed bipyridyl residue. In addition ^{15}N spectrum (Fig. 2C) shows a slightly greater highfield shift, compared to compound **5**, probably due to the combined effect of both Ti and Mo atoms. This is well in accord with a molybdenum species bonded to a bipyridyl moiety anchored on the TiO_2 surface.

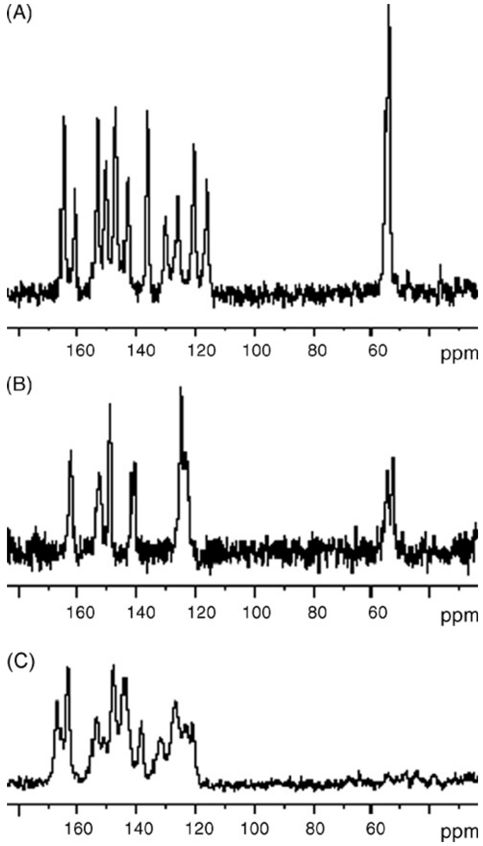


Fig. 1. ^{13}C CPMAS NMR of compounds **2** (A), **5** (B) and **6** (C).

3.1. Triphenylphosphine oxidation

The catalytic oxygen atom transfer process was examined with the anchored complex **6** using triphenylphosphine as the O-acceptor and dioxygen as the O-donor. To detect clearly the improvement brought by this system, it was compared with the

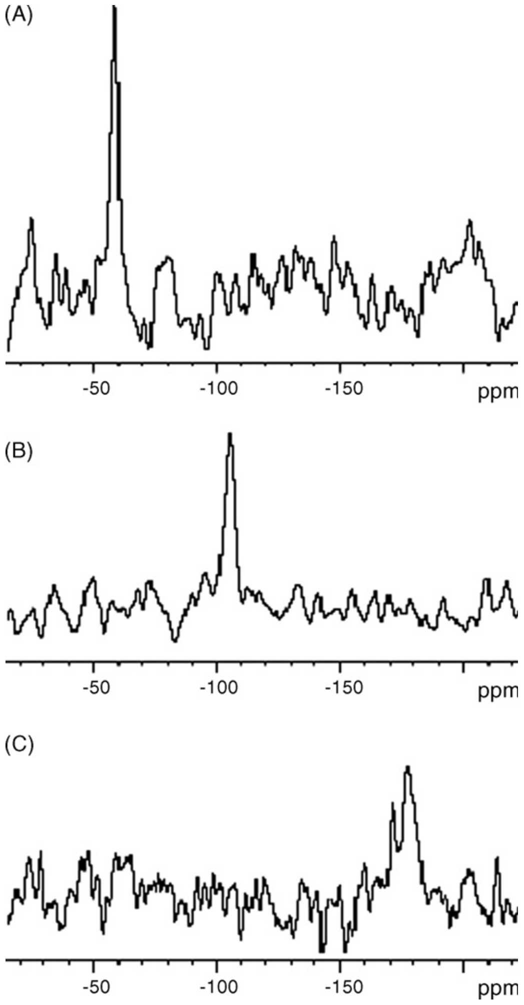


Fig. 2. ^{15}N CPMAS NMR of compounds **2** (A), **5** (B) and **6** (C).

analogous complex **5** under homogeneous conditions, but also with blank experiments: one composed of a mixture of complex **5** and TiO_2 and the other of pure TiO_2. Each experiment was run under identical conditions at room temperature, under O_2 both in the presence and absence of light (Figs. 3 and 4).

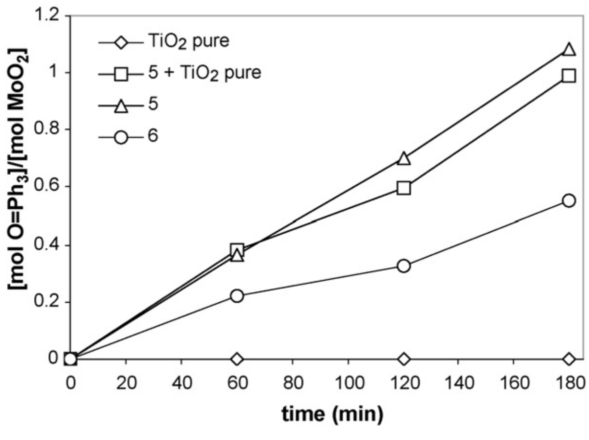


Fig. 3. Time evolution of the [mol. O=Ph_3]/[mol. MoO_2] as a function of time in the dark.

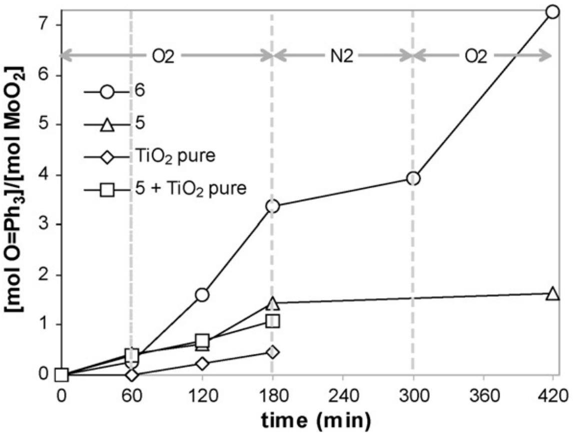


Fig. 4. Time evolution of the [mol. O=Ph_3]/[mol. MoO_2] as a function of time in the visible light. The suspensions were stirred in the dark for the first 60 min to assure adsorption/desorption equilibrium of PPh_3 [22].

The suspension of pure TiO_2 under O_2 atmosphere is totally inert in the absence of light, it can, however, oxidize partially PPh_3 when irradiated by visible light. The oxidation of PPh_3 in the homogeneous system with complex **5** either in the dark or under visible light is the result of a stoichiometric oxygen atom transfer from the Mo(VI) dioxo entity to the PPh_3. The same result is observed with the mechanical solid mixture made of complex **5** and TiO_2. On the other hand complex **6**, although less performant than the homogeneous system in the dark, exhibits a very important catalytic reactivity increase when irradiated with visible light. This is clearly indicative of a net synergic effect due to the photogenerated electronic flux, via the TiO_2 matrix onto the coordination sphere of molybdenum. Furthermore, the anchored system, by isolating each metallic center prevents the formation of Mo(V)-μ-oxo dimer and thus keeps the catalytic system alive. This is clearly shown in an experiment in which, after visible light irradiation under O_2 for 2 h, the system is evacuated and placed under inert gas for two additional hours (Fig. 4). The PPh_3 oxidation observed during this period corresponds to the stoichiometric reduction of Mo(VI) dioxo present in the reaction medium. When O_2 is reintroduced, the catalytic activity returns as performant as before. On the contrary, the homogeneous system, under the same conditions shows an analogous stoichiometric reduction under inert atmosphere but remains inactive when O_2 is reintroduced, probably due to Mo(V)-μ-oxo formation.

4. Conclusions

The anchoring of the molybdenum(VI) dioxodibromo-(4,4′-dicarboxylate-2,2′-bipyridine) complex on a TiO_2 solid matrix (**6**) brought two important improvements to the oxygen atom transfer catalytic system. On one hand, it increased significantly the O-transfer capability, via the photogenerated flux onto the molybdenum coordination sphere, and on the other, by isolating the metallic centers, it prevented the formation of inactive Mo(V)-μ-oxo dimers and thus lengthened the catalyst life span.

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