Bis(3,5-dimethylpyrazol-1-yl)acetate bound to titania and complexed to molybdenum dioxido as a bidentate N,N'-ligand. Direct comparison with a bipyridyl analog in a photocatalytic arylalkane oxidation by O₂

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Abstract *Bis*(3,5-dimethylpyrazol-1-yl)acetate, well known as a tridentate N,N,O ligand, was bound to MoO_2Cl_2 in a bidentate N,N manner by anchoring covalently, at first, the ligand onto a titanium oxide surface, followed by its complexation with the molybdenum dioxo entity. It was fully characterized by ¹³CPMAS NMR and FT-IR spectroscopy. The tethered complex was directly compared with an analogous bipyridyl species in the catalytic ethylbenzene oxidation by O_2 at room temperature, atmospheric pressure, and under visible light. The *bis*(pyrazol-1-yl) catalyst exhibited a significant initial higher oxygen atom transfer (OAT) capability, well in accord with its electron donating property. It was, unfortunately, hampered by a premature leaching phenomenon, totally absent in the comparable bipyridyl system.

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Introduction

Among the innumerable bidentate chelating ligands forming complexes with transition metals, the planar and fairly rigid 2,2'-bipyridine is certainly one of the most widely used. It has been studied with either low or high oxidation state metals [1-3]. We have, as many others, extensively used this ligand with complexes of molybdenum(VI) in catalytic oxidation reactions [4-6]. Closely related, and also frequently used, are (poly)pyrazolyl ligands. Since first reported by Trofimenko, over 40 years ago [7], either the (poly)pyrazolyl borates or the isoelectronic and isosteric methane analog have been studied, mainly with low oxidation state metals, for their distinct coordination behavior due to their flexibility and their different catalytic activity [8]. More recently, high oxidation state transition metals such as molybdenum(VI) dioxo complexes bearing these ligands have also been synthesized [8] and their catalytic activity measured in olefin epoxidation with tert-butyl hydroperoxide (TBHP) as oxidant [9]. When compared with other families of ligands such as diimine or bipyridine, its O-transfer ability was found to be in the middle range.

This O-transfer process is also possible with O_2 as the direct oxygen atom donor [10]; thus, we have reported, over the years, several molybdenum(VI) dioxo complexes, bearing mostly bipyridyl ligands and studied their catalytic activity in oxidation reactions with O_2 [11–19]. Recently, we significantly optimized their activity by anchoring them covalently on the semiconductor solid matrix TiO₂ and established that the mechanism of the catalytic O-transfer process is certainly different with a hydroperoxide or with dioxygen as the oxidant [20–22]. Likewise, the influence of a ligand in the coordination sphere can be expected to vary in their different O-transfer processes. When comparing

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bipyridyl and bis-pyrazolyl ligands, many features must be taken into account: the former has a rigid structure, whereas the latter has a significant flexional capacity [23], but what could be even more important in a catalytic process are the electron donor and acceptor properties of each one; the bipyridyl entity is an acceptor, whereas the bis-pyrazolyl ligand is a good donor [24]. We therefore, found opportune to compare directly TiO₂-covalently bound molybdenum dioxo complexes bearing bipyridyl and bis-pyrazolyl ligands in the O₂ catalytic oxidation of arylalkanes. We report here the covalent grafting of bis(3,5-dimethylpyrazol-1-yl)acetate on anatase TiO₂, its interaction with molybdenum(VI)dihalodioxido, as a bidentate ligand, its full characterization and its comparison with the bipyridyl analog in the O₂ oxidation of ethylbenzene, at room temperature and atmospheric pressure.

Experimental

All materials were commercial and were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use. Acetonitrile was distilled and kept under argon. Titanium oxide (Degussa-P25) with 50 m^2/g specific area and crystalline structure of 80 % anatase and 20 % rutile was dehydrated at 60 $^{\circ}\mathrm{C}$ and 5×10^{-4} mbar for 48 h prior to use. FT-IR (KBr) spectra were recorded on a Perkin-Elmer 1720XFT. ¹H and ¹³C NMR were obtained 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 ¹³C resonance frequency of 101.6 MHz. The ¹³C experiments were performed with a commercial Bruker Double-bearing probe with zirconium dioxide rotors of 4-mm outer diameter. The CP technique [25] was applied during Magic Angle Spinning (MAS) of the rotor at 10 kHz. A ramped ¹H-pulse starting at 100 % power and decreasing until 50 % was used during contact time in order to circumvent Hartmann-Hahn mismatch [26, 27]. The contact time was 2 ms. To obtain a good signal-tonoise ratio in ¹³C CPMAS experiments, 2048 scans were accumulated using a delay of 2 s. The ¹³C chemical shifts were referenced to tetramethylsilane and calibrated with glycine carbonyl signal, set at 176.5 ppm. Thermogravimetric analysis was performed using a Micromeritics instrument which has a thermogravimetric analyzer TGA 2950 Hi-Re operating with a heating ramp of 10.00 °C/min in a range between 30.0° and 900 °C. Molybdenum elemental analysis was carried out with an atomic absorption spectrophotometer (AAS) Thermo S4. The samples were analyzed after acid digestion with previous calcination in a muffle furnace at 500 °C for 5 h. The detection limit of the AAS method is 0.230 mg/L. Gas chromatography (CG) analysis of the photo-oxidation products was performed with a HP-6890 equipped with a flame ionization detector and HP-INNOWAX column (30 m \times 0.32 mm \times 0.25 μ m). Benzene was used as internal standard.

Synthesis and characterization

Synthesis of bis(3,5-dimethylpyrazol-1-yl)acetic acid (1)

This compound was synthesized according to the literature procedure [28, 29] starting from dichloroacetic acid instead of dibromoacetic acid and with a reaction time of 72 h. FT-IR (KBr, cm⁻¹) 1,737 (COOH), 1,562 (C=N). ¹H NMR (CDCl₃, 200 MHz): δ 2.16 (s, 6H, CH₃), 2.23 (s, 6 H, CH₃), 5.89 (s, 2H, H_{pz}), 6.93 (s, 1H, CH). ¹³C NMR (CDCl₃, 62.5 MHz): δ 11.1 (CH₃), 13.3 (CH₃), 70.4 (CH), 107.8 (CH_{pz}), 141.9 (C_{pz}), 148.9 (C_{pz}), 165.1 (COOH). ¹³C RMN/CPMAS (400 MHz, solid, 23 °C) δ 165.3 (s, COOH), 150.4 (s, C_{pz}), 146.1(s, C_{pz}), 143.5 (s, C_{pz}), 142.3 (s, C_{pz}), 108.9 (s, CH_{pz}), 107.4 (s, CH_{pz}), 71.7 (s, CH_{met}), 13.6 (s, CH₃), 13.2 (s, CH₃), 12.1 (s, CH₃), 10.5 (s, CH₃). Elemental analysis: C₁₂H₁₆N₄O₂ Calc: C 58.1, H 6.5, N 22.6, Found C 59.4, H 7.0, N 22.2.

Trimethylsilylation of bis(3,5-dimethylpyrazol-1-yl)acetic acid

Bis(trimethylsilyl) urea (0.102 g, 0.5 mmol) was added to a benzene suspension (40 mL) containing *bis*(3,5-dimethylpyrazol-1-yl)acetic acid (1) (0.248 g, 1 mmol). The mixture was refluxed for 4 h, cooled to room temperature, and filtered. The filtrate was evaporated to yield the product trimethylsilyl ester of *bis*(3,5-dimethylpyrazol-1-yl)acetic acid (3) as a white solid. FT-IR (KBr, cm⁻¹) 1,750 cm⁻¹ (C=O), 1,561 (C=N), 836 (-Si–CH₃). ¹H NMR (CDCl₃, 200 MHz): δ 6.82 (s, 1H, CH), 5.90 (s, 2H, H_{pz}), 2.24 (s, 6H, CH₃), 2.20 (s, 6H, CH₃), 0.155 (s, 9 H, (Si–(CH₃₎₃). ¹³C NMR (CDCl₃, 200 MHz): δ 175.5 (C=O), 149.0 (C_{pz}), 141.6 (C_{pz}), 107.8 (C_{pz}), 42.4 (CH), 13.3 (CH₃), 11.1 (CH₃).

Chlorodioxido(bis(3,5-dimethylpyrazol-1yl)acetate)molybdenum(VI) (4)

A benzene solution (40 mL) containing the trimethylsilyl ester of *bis*(3,5-dimethylpyrazol-1-yl)acetic acid (160.2 mg, 0.5 mmol) was added to a benzene suspension (20 mL) containing MoO₂Cl₂ (99.4 mg, 0.5 mmol). The mixture was stirred for 4 h at room temperature resulting in a clear solution. Evaporation of the solvent yielded a light green solid. FT-IR (KBr, cm⁻¹) 1,691, 1,300 (COO–), 1,558 (C=N), 942, 910 (MoO₂). ¹H NMR (CDCl₃, 200 MHz): δ

6.49 (s, 1H, CH), 6.12 (s, 1H, CH_{pz}), 6.06 (s, 1H, CH_{pz}), 2.69 (d, 6H, CH₃), 2.46 (d, 6H, CH₃). ¹H NMR (DMSO, 300 MHz): δ 7.12 (s, 1H, CH), 5.87 (s, 2H, CH_{pz}), 2.18 (s, 6H, CH₃), 2.08 (s, 6H, CH₃). ¹³C RMN/CPMAS (400 MHz, solid, 23 °C): δ 163.7 (s, COO), 155.7 (s, C_{pz}), 152.1 (s, C_{pz}), 144.5 (s, C_{pz}), 142.3 (s, C_{pz}), 111.8 (s, CH_{pz}), 107.7 (s, CH_{pz}), 66.5 (s, CH_{met}), 14.8 (s, CH₃), 14.0 (s, CH₃), 13.0 (s, CH₃), 9.8 (s, CH₃). Elemental Analysis C₁₂H₁₅ClMoN₄O₄ Calc: C 35.1, H 3.7, N 13.6, Found C 35.0, H 3.8, N 13.5.

Trimethylsilylation of TiO_2 (Degussa P-25) with hexamethyldisilazane

Hexamethyldisilazane (0.5 mL, 2.4 mmol) was added to a benzene suspension (40 mL) containing thoroughly dried (60 °C, 10^{-5} mbar, 24 h) TiO₂ (1 g, Degussa P-25, estimated 0.5 mmol of OH/g). The suspension was slowly stirred at room temperature for 24 h, and the resulting solid was filtered, washed thoroughly with benzene (2 × 25 mL), and dried under vacuum. ¹³C NMR/CPMAS: δ –1.4 ppm.

Reaction of bis(3,5-dimethylpyrazol-1-yl)acetic acid (1) with trimethylsilylated TiO_2

Bis(3,5-dimethylpyrazol-1-yl)acetic acid (1) (124 mg, 0.5 mmol) was added to a benzene suspension (50 mL) containing freshly prepared trimethylsilylated TiO₂, obtained from TiO₂ (1 g, Degussa P-25). The mixture was stirred for 24 h at 60 °C, and the resulting mixture was filtered. The solid (**5**) was thoroughly washed with benzene (3 × 25 min). FT-IR (KBr, cm⁻¹) 1,650 (C=O), 1,566 (C=N). ¹³C NMR/CPMAS (400 MHz, solid, 23 °C): δ 165.7 (s, COO), 149.5 (s, C_{pz}), 147.4 (s, C_{pz}), 142.0 (s, C_{pz}), 140.9 (s, C_{pz}), 108.7 (s, CH_{pz}), 107.7 (s, CH_{pz}), 72.7 (s, CH_{met}), 12.0 (s, 2CH₃), 10.2 (s, 2CH₃).

Reaction of anchored bis(3,5-dimethylpyrazol-1-yl)acetic acid on TiO_2 with MoO_2Cl_2

A THF solution freshly prepared containing MoO₂Cl₂(THF)₂ (0.10 g, 0.5 mmol) was added under inert atmosphere to a THF suspension (40 mL) containing freshly prepared *bis*(3,5-dimethylpyrazol-1-yl)acetic acid anchored on TiO₂, obtained from silylated TiO₂ (1 g). The mixture was stirred at room temperature for 24 h. The resulting yellow solid (**6**) was filtered off, washed with THF (4 × 25 mL), and dried under vacuum. FT-IR (KBr, cm⁻¹) 1,649 (C=O), 1,559 (C=N), 947, 905 (Mo=O). ¹³C NMR/CPMAS (400 MHz, solid, 23 °C): δ (ppm) 164.4 (s, COO), 154.5 (s, 2 C_{pz}), 144.2 (s, 2 C_{pz}), 108.2 (s, CH_{pz}), 103.5 (s, CH_{pz}), 69.4 (s, CH_{met}), 12.7 (s, 2CH₃), 11.1 (s, 2CH₃).

Synthesis of dichlorodioxido(4,4-dimethoxycarbonyl-2,2bipyridyl)molybdenum (VI) (7)

This compound was synthesized according to the literature procedure [16]. FT-IR (KBr, cm⁻¹) 1,727 (C=O), 1,566 (C=N), 944, 911 (Mo=O). ¹H-RMN (CDCl₃, 200 MHz), δ (ppm) 9.73 (d, 2H), 8.92 (s, 2H), 8.30 (d, 2H), 4.16 (t, 6H).

Catalysis: ethylbenzene photo-oxidation

The photocatalytic oxidation of the arylalkanes was carried out using a 10 mL batch micro-reactor (Ace-Glass model T-121 m) with immersion lamp (Phenix, 220 V). A 0.083 M solution of ethylbenzene in CH₃CN was thoroughly deoxygenated by bubbling N₂ gas for several hours at 5 °C before the addition of 0.045 g of either MoO_2/TiO_2 (6), a "mechanical" mixture of free molybdenum complex (4) and TiO_2 in the same proportion as (6), or pure TiO_2 . In all cases, the mixture was kept in the dark and under nitrogen for 1 h, to assure adsorption/desorption equilibrium, before visible light was turned on and kept for 4 h. Nitrogen was then replaced by O₂ in the dark. After a period of 2 h, the mixture was rendered, again, O₂-free by bubbling N₂ before the light was turned back on. The sequence was repeated as required. In a separate experiment, complex (6) was tested in the reaction of ethylbenzene following the same protocol. When the catalytic activity stopped after 660 min, the suspension was filtered and the solid (TiO₂) washed with THF $(3 \times 50 \text{ mL})$. The combined solutions were evaporated to give a solid. Its FT-IR spectrum was different from (4) and exhibited a strong absorption band at 751 cm⁻¹, characteristic of a Mo-O-Mo bonding, similar to the one obtained with the $bis(\mu$ -oxo) dimer previously reported [19].

Results and discussion

Synthesis and characterization

The ligand *bis*(3,5-dimethylpyrazol-1-yl)acetic acid (1) was chosen as starting material, since, as reported [20–22], through the carboxylate function it is possible to link covalently the ligand onto TiO₂, thus permitting a direct comparison with the 2,2'-bipyridyl-4,4'-dicarboxylic acid. This ligand can easily be prepared from 3,5-dimethylpyrazol and chloroacetic acid according to the literature procedure [28, 29]. However, and contrary to the bipyridyl analog, due to the presence of the carboxylate function, it has the potential of becoming a true tridentate N,N,O–ligand in the presence of various transition metal species giving rise to heteroscorpionate complexes (2) [30, 31] (Scheme 1).



Scheme 1 Synthetic route to obtain heteroscorpionate complexes

This otherwise interesting property becomes a hindrance if one wants to preserve the tethering ability of the carboxylate group. It was thus attempted to esterify the acid function with a trimethylsilyl group (**3**), followed by complexation with MoO_2Cl_2 and reaction with the Ti–OH entities on the surface of titania as reported for the bipyridyl analog [22] (Scheme 2).

This anticipated pathway, however, failed since the reaction of the trimethylsilyl ester with molybdenum dichloro dioxido resulted, nevertheless, in the quantitative formation of the heteroscorpionate complex (4). Apparently, (4) is rapidly formed when the ester is reacted with the molybdenum dioxo entity, and consequently, the carboxylate function is no longer available for reaction with the surface groups. One must point out that, under the reaction conditions, MoO_2Cl_2 does not remain attached to the matrix after washing.

The desired tethered bis(pyrazol-1-yl) complex on TiO₂ (6) was, however, obtained by modifying the procedure, namely by anchoring the bis(3,5-dimethylpyrazol-1-yl)acetic acid on a trimethylsilylated titania surface to give (5), prior to its treatment with MoO₂Cl₂ [22] (Scheme 3).

The loading of Mo complex bis(3,5-dimethylpyrazol-1-yl)acetate (6) was 0.0425 mmol/g of TiO₂ which is measurably lower than the value obtained with the bipyridyl analog [22]. A plausible explanation could be that the tethered complex (6), although much less prone than the

Scheme 2 Reaction of the trimethylsilyl ester with molybdenum dichloro dioxide.

Synthetic route failed to obtain

(6) covalently anchored on TiO_2

dioxomolybdeno(VI) complex

trimethylsilyl ester to be transformed into the heteroscorpionate complex (4) could partially undergo such a transformation under the reaction conditions during the complexation with MoO_2Cl_2 . Once the solvent and the compound (4) are removed, the solid matrix (6) is stable.

The assessment of the supported complex (6) according to that represented in scheme 3 was clearly established by 13 C CPMAS NMR. The comparison between the spectrum of a physical mixture of *bis*(3,5-dimethylpyrazol-1yl)acetic acid (1) with TiO₂ (Fig 1a) and the spectrum of the anchored ligand (Fig 1b), evidences an important shift of the signals attributed to the pyrazol rings, situated in the spectral region between 140 and 150 ppm. This confirms the covalent bond formed with the TiO₂ surface. Moreover, this new bond can be confirmed by the slight broadness of all the NMR signals (Fig. 1b), due to the reduced mobility of the anchored molecule.

A more important broadness of these signals is observed in (Fig 1c) where the complexation with Mo reduces drastically the mobility of the pyrazol ring. In addition, an important chemical shift variation is observed, in particular, for the signals of the pyrazol ring carbons close to Mo center (from 147.4–149.5 ppm to 154.5 ppm). Both the broadness of signals and the chemical shift variation shown in the spectrum (Fig. 1c) allow us to exclude the presence of a heteroscorpionate species (Fig. 1d) in (**6**).

The FT-IR spectral analysis of each intermediate leading to complexes (4) and (6) is depicted in Fig. 2 and corroborates the ¹³CMAS NMR results. The covalent anchoring of the free acid (1) (Fig. 2a) onto titania to give (5) (Fig. 2c) results, as expected, in a shift from 1,737 to 1,650 cm⁻¹ for the C=O stretching mode. The spectrum also indicates, as in the NMR analysis, the absence in (5) of either free acid (1) or any trimethylsilyl functionality. The heteroscorpionate complex (4) (Fig. 2b) exhibits absorption bands around









1,700 and 1,300 cm⁻¹ assigned tentatively to the symmetric and asymmetric stretching mode of a carboxylate structure [32]. The *cis*-MoO₂ stretching vibrations are observed at 940 and 908 cm⁻¹ [33]. Complex (6) (Fig. 2d) despite the low concentration bound on the matrix gave observable signals corresponding to the main vibrations of the complex anchored. The presence of a C=O stretching mode analogous to (5) is confirmed at 1,649 cm⁻¹, as well as two weak *cis*-MoO₂ dioxo bands at 947 and 905 cm⁻¹. More importantly, the FT-IR Spectrum of (6) excludes unequivocally any presence of either (1), (4) or (5) attached to the matrix.

Reactivity

The comparative reactivity study between the bis(3,5-dimethylpyrazolyl)acetate and 2,2'-bipyridyl-4,4'dicarboxylate ligands bound to a molybdenum dioxo center, in the catalytic oxidation of ethylbenzene with O₂, was investigated both under homogeneous and TiO₂ bound heterogeneous conditions. An analogous comparison between *bis*-pyrazolyl and 2,2'-bipyridine ligands, lacking the carboxylate function, has been reported in an olefin epoxidation reaction catalyzed by a molybdenum dioxo complex and t-butylhydroperoxide as the oxidant [9]. The TOF obtained with the *bis*-pyrazolyl complex was shown to be slightly higher than for the bipyridyl analog.

When a carboxylic acid group is attached to these ligands, the species obtained upon complexation with the molybdenum dioxo entity differ. For the 2,2'-bipyridyl-4,4'dicarboxylic acid, it is necessary to methylate the acid function (7) in order to attain complexation [21]. Whereas the bis(3,5-dimethylpyrazolyl)acetic acid, upon reaction with MoO₂Cl₂, is immediately transformed into a N,N,Otridentate ligand, yielding quantitatively the heteroscorpionate (4) [8]. Although the molybdenum environment is slightly different in these two complexes (4, 7), a comparison was, nevertheless, made for the oxidation of ethylbenzene. The only observed product is acetophenone, as previously reported with various dioxomolybdenum complexes, arising from a four electron oxidation, via the alcohol intermediate [15]. It was followed, stepwise, in a sequence in which a stoichiometric O-transfer occurs under nitrogen, at room temperature and under visible light, followed by a period under dioxygen, in the dark, during which no O-transfer occurs but where the reduced Mo(IV) oxo species can be reoxidized to a Mo(VI) oxo-peroxo entity to complete the cycle [21, 22] (Scheme 4).

When a physical mixture of TiO_2 and complex (4) was reacted with ethylbenzene as a suspension, following the above protocol and compared with the corresponding dimethylester-bipyridyl molybdenum dioxo complex (7) (Fig. 3), the estimated rate of O-transfer to give acetophenone was shown to be higher for the complex bearing





the tridentate ligand by a factor of nearly two to three. This is in accord with a reported similar comparison made in the case of a TBHP phosphine oxidation with an analogous molybdenum heteroscorpionate complex [34]. The presence of greater electron density in the carbonyl function directly bonded to the metal center, apparently, accelerates the OAT significantly.

However, one other issue was revealed from this study, indeed, as shown in Fig. 3, the O-transfer process nearly stops for both systems after about 660 min. This propensity to give unreactive species, characterized as Mo(V) $bis(\mu - 0x0)$ dimers, under homogeneous conditions, has been reported by us and others [10, 16] when O₂ is the direct

oxidant. This inconvenience limited, therefore, the comparison between the two ligands to a stoichiometric OAT.

This handicap was eliminated with the titanium oxide surface bound molybdenum dioxo *bis*-pyrazolyl complex (6). Its reaction with ethylbenzene using the same reaction protocol was compared with the analogous TiO_2 bound bipyridyl system (8) previously reported [21, 22]. Here, the comparison is more direct than with the two homogeneous systems since the bidentate bonding mode is identical for both ligands.

The results depicted in Fig. 4 show a significantly higher initial rate of acetophenone formation which can be



light dark light dark light 0, 02 N₂ N₂ N₂ 400,0 (Mol Ketona/mol MoO2)*100 350,0 300,0 250,0 200,0 150,0 100,0 50.0 0,0 120 . 240 600 720 . 840 360 480 960 Time (min) - Δ- MoO2Cl2-Bis-pyrazolyl-COO/TiO2 (6) - MoO2Cl2-bipyridyl-COO/TiO2 (8)

Fig. 3 Evolution of [mol of ketone]/[mol of MOO_2] as a function of time for dioxomolybdenum(VI) complexes (4) and (7)

Fig. 4 Evolution of [mol of ketone]/[mol of MOO_2] as a function of time for TiO_2 modified with dioxomolybdenum(VI) complexes (6) and (8)



Fig. 5 Evolution of [mol of ketone]/[mol of MoO₂] as a function of time for physical mixture (4) + TiO₂ and anchored complex (6)

considered as the emanation of the real role of the ligand which is in accord with the electron donating property of the pyrazolyl ring. This result might also suggest that in the homogeneous system, the tridentate character, given as responsible for its higher activity, is not the only factor to be taken into account.

It is also interesting to compare the reaction pattern obtained with the physical mixture $(4)/\text{TiO}_2$ with the anchored complex (6). As depicted in Fig. 5, a higher rate is clearly observed with the tethered species which can be attributed to the direct interaction between the semiconductor and the organometallic entity in the OAT process.

Continuing the catalytic cycle (Fig 4), one observes that after a period under O_2 in the dark, during which the Mo(IV) is reoxidized, the formation of acetophenone proceeds as expected at a rate comparable with the bipyridyl system. However, after a second period under O₂, contrary to the bipyridyl system, the catalysis abruptly stops. A plausible explanation of this reaction pattern is a progressive formation of an inactive dimer which could arise from the transformation of (5) into the heteroscorpionate (4), which is soluble in the medium and, as shown earlier, prone to be dimerized rapidly. This hypothesis was verified in a separate experiment, in which the suspension, when the catalytic activity ends after 660 min, was filtered and evaporated to dryness yielding a solid. Its FT-IR spectral analysis (Fig. 6) is different from (4) and exhibits a strong absorption band at 797 cm⁻¹ characteristic of a Mo–O–Mo bonding mode and similar to the $bis(\mu$ -oxo) dimers previously characterized and reported as being inert to reoxidation [17, 35–37]. Further evidence was given by a TGA analysis of the matrix before and after reaction (Fig. 7), showing clearly that no significant amount of complex remains attached to the surface thus justifying the lack of



Fig. 6 FT-IR (KBr) spectra of solid obtained after ethylbenzene catalytic oxidation reaction using (6)



Fig. 7 TG analysis for as-made and used TiO_2 matrix modified with dioxomolybdenum(VI) complex (6)

oxidation. An additional plausible factor for the higher stability of (8) compared to (6) could be the slow reoxidation of the *bis*-pyrazolyl Mo(IV) entity by O_2 in the dark leaving more time for the heteroscorpionate (4) to be formed. This lower rate could be rationalized, also, by the poor π -acceptor property of the pyrazolyl ring.

Conclusion

Bis(pyrazolyl)acetate compounds are known to give rise to N,N,O-tridentate ligands in the presence of several transition metals [8, 9]. Compound (1) was, nevertheless, maintained as a bidentate N,N-ligand with MoO_2Cl_2 via the prior esterification onto a titanium oxide surface to give the tethered complex (6). This was fully characterized by ¹³CMAS NMR spectroscopy, and its reactivity directly

compared with the analogous TiO₂-bound bipyridyl [21, 22] species in the O_2 oxidation of ethylbenzene at room temperature and atmospheric pressure. The initial OAT rate of acetophenone formation seems to be significantly higher with complex (6), which is well in accord with the electron donating property of the pyrazolyl ring [24]. This behavior, however, rapidly deteriorates, most probably due to the leaching of the *bis*(pyrazolyl) moiety to give the soluble heteroscorpionate complex (4) which in turn is quickly transformed into an inactive dimer, stopping any catalytic activity. This leaching phenomenon is certainly due to the intrinsic instability of (5) in the presence of solvent, but it could plausibly be, also, assisted by a slow reoxidation step [Mo(IV) to Mo(VI)] under O_2 due to the poor electron accepting character of the pyrazolyl species, leaving more time for the detachment process to occur.

From a practical point of view, this study showed a significantly higher OAT capability for the *bis*(pyrazolyl) bound complex compared to its bipyridyl analog, as long as it remains catalytically active. This was also observed in a comparable homogeneous system. It also emphasized the importance of choosing the correct balance of electron donation and abstraction of the ligand system in a catalytic oxidation by O_2 . Apparently, the *bis*(pyrazolyl) complex (**6**) is a good OAT agent due to its electron donating property but a poor system for activating O_2 . A better balance seems to be attained by the bipyridyl ligand.

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