

# Use of phosphines as versatile molecular probes for studying the coordination states of molybdenum ions in Mo/SiO<sub>2</sub> catalysts by EPR

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Received 19 January 1996; accepted 26 April 1996

## Abstract

Adsorption of trimethyl-, triethyl- and tri(*t*-butyl)phosphine which have differing Tolman angles was used for the EPR characterization of the coordination sphere and spatial accessibility of Mo<sup>5+</sup> ions present on the surface of reduced supported Mo/SiO<sub>2</sub> catalysts. Due to the presence of <sup>31</sup>P nuclei a well resolved 1:2:1 ligand superhyperfine structure (ca. 3 mT) was observed even in the first derivative spectra showing that two phosphine molecules are directly bonded to exposed tetracoordinated Mo<sub>4c</sub><sup>5+</sup> species to form together with the remaining ligands a distorted octahedron with one distinct molybdenyl bond. This method detects tetracoordinated Mo species even when their EPR spectra are obscured by the simultaneous presence of the EPR signal of dominant hexacoordinated Mo<sub>6c</sub><sup>5+</sup> ions. The ligand arrangement in the tetracoordinated Mo<sub>4c</sub><sup>5+</sup> can be best explained in terms of a D<sub>2d</sub> pseudosymmetry giving rise to the resultant C<sub>s</sub> structure for this surface complex.

**Keywords:** EPR; Coordination state; SiO<sub>2</sub>; Mo<sup>5+</sup> ions; Phosphines; Molecular probes

## 1. Introduction

The problem of assessing the structure–reactivity relationship requires the knowledge of the molecular structure and the redox/acid–base functions of active centres. With the use of suitable probe molecules, EPR spectroscopy can detect the presence of adsorption sites [1], redox [2] and Lewis acid centres [3] as well as determine their number and strength, and reveal their oxidation and coordination state [4,5]. Recently,

MAS NMR spectroscopy has also been employed to evaluate the Brønsted and Lewis acidity of zeolites and other catalysts using trimethylphosphine as a probe [6]. Characterization of catalytic surfaces by means of probe molecules and the EPR technique has been reviewed by Che and Giamello [1] who give basic definitions and classification of probe molecules.

The properties of transition metal ions (TMI) which cause them to act as active sites in catalytic processes stem from their electronic structure, coordinative unsaturation and dispersion. This can be best illustrated by the reaction of CH<sub>3</sub>OH oxidation over various molybdenum

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based catalysts, which appear to be both dispersion and structure sensitive [7]. The determination of dispersion, oxidation and coordination states of active centres is therefore of great interest in relation to their adsorption and catalytic properties. This is not, however, a trivial task, because the heterogeneous nature of the solid surface, the lack of long range order (translational symmetry) of active sites along with their typically low concentration exclude application of many of the well established techniques conventionally employed in structural investigations.

The nature of information gained from EPR may vary from a simple confirmation of the presence of given paramagnetic active sites to the far more sophisticated and detailed analysis of the coordination sphere and molecular orbital structure of a particular transition metal ion located on the support surface [4]. However, direct interpretation of the EPR spectra often is impeded by the overlapping signals originating from the simultaneous presence of more than one centre. In such cases corroboration of the spectroscopic method by the use of probe molecules acquires a particular value.

EPR has proven to be a powerful tool for investigating surface coordination chemistry by means of probes having magnetic ( $I \neq 0$ ), and non magnetic ( $I = 0$ ) nuclei and which are able to fill up coordination vacancies producing characteristic changes in the EPR features. Typically used probe molecules are  $^{13}\text{C}$ O [4,8–10],  $\text{H}_2\text{O}$  [5,8],  $\text{CH}_3\text{OH}$  [4,10], which are coordinating predominantly via a  $\sigma$ -type bonding between the lone pair  $sp^n$  hybrid of the ligand and the 3d orbitals of the TMI of appropriate symmetry. While water and methanol probes can only provide information about the presence of coordinative unsaturation of the central cation, via the  $g$  tensor changes induced by the coordination [4,8], the  $^{13}\text{C}$ O molecule can reveal the number of coordination vacancies through the superhyperfine (shf) structure due to the interaction of nuclear spin  $I = 1/2$  of  $^{13}\text{C}$  with the unpaired electron [4,5,8–10]. The counting of

vacancies in transition metal ions with  $^{13}\text{C}$ O has been shown to be particularly suitable for TMI  $3d_\sigma$  orbitals carrying the unpaired electron, which have lobes pointing along the metal–ligand bonds (e.g. the  $d_{z^2}$  or  $d_{x^2-y^2}$  orbitals of  $\text{Ni}^+$  in  $\text{C}_{3v}$  or  $\text{C}_{2v}$  symmetry) that are able to make bonding with a  $\sigma$  donor CO probe [11]. The magnitude of coupling in such cases is usually sufficiently large (2.0–5.0 mT) to enable a straightforward analysis of the shf structure (Table 1). However, for ions with  $3d_\pi$  orbitals pointing between ligands, like  $d_{xy}$  of  $\text{Mo}^{5+}$  or  $\text{V}^{4+}$  in  $\text{C}_{4v}$  symmetry, the superhyperfine coupling constant between  $\text{Mo}^{5+}$  or  $\text{V}^{4+}$  and  $^{13}\text{C}$ O is significantly smaller (0.4–0.75 mT) due to the symmetry mismatch between the  $d_\pi(xy)$  and ligand  $\sigma$ -orbitals and remains usually unresolved in first derivative [5,8–10]. However, they can produce a considerable overlap with  $\pi$ -bonding ligands.

An approach has been then developed consisting in recording the first and third derivative EPR spectra after adsorption of  $^{13}\text{C}$ O [9]. The shf structure which is normally observed in third derivative permits determination of the number of CO molecules bonded to the metal centre. Since the resolution of spectra is crucial for reliable determination of the number of the shf lines the use of phosphorus-containing probes should offer considerable interest due to the large coupling constant of the  $^{31}\text{P}$  nucleus, its low nuclear spin value ( $I = 1/2$ ) and high natural abundance (100%). Replacing  $^{13}\text{C}$  carbon donor by  $^{31}\text{P}$  containing  $\sigma$ -donor with its much larger atomic hyperfine values ( $A_{\text{iso}} = 364$  mT and  $A_{\text{aniso}} = 20.6$  mT) in comparison to  $^{13}\text{C}$  ( $A_{\text{iso}} = 113$  mT and  $A_{\text{aniso}} = 6.6$  mT) should provide, therefore, a distinctly more sensitive probe for the determination of coordination unsaturation. All the above mentioned factors make the shf usually sufficiently well resolved, even in a first derivative presentation, for performing the straightforward vacancy counting.

The utility of phosphines as molecular probe is dictated by their ligand and redox properties. The bonding characteristics of these compounds

Table 1  
EPR parameters of selected transition metal complexes supported on SiO<sub>2</sub> surface with <sup>31</sup>P or <sup>13</sup>C containing probe molecules as ligands

Sample	Surface complex <sup>a</sup>	g tensor	<sup>31</sup> P shfs tensor (mT)	<sup>13</sup> C shfs tensor (mT)	Ground state	Ref.
V/SiO <sub>2</sub>	O=V <sup>IV</sup> (O <sub>L</sub> ) <sub>3</sub> (CO) <sub>2</sub>	g <sub>⊥</sub> = 1.985, g <sub>∥</sub> = 1.931		A <sub>⊥</sub> ≈ 0.7, A <sub>∥</sub> ≤ 0.7	d <sub>π</sub> (xy)	[9]
Mo/SiO <sub>2</sub>	O=Mo <sup>V</sup> (O <sub>L</sub> ) <sub>2</sub> OHCO	g <sub>1</sub> = 1.965, g <sub>2</sub> = 1.941, g <sub>3</sub> = 1.891		A <sub>1</sub> = 0.65	d <sub>π</sub> (xy)	[33]
Mo/SiO <sub>2</sub>	O=Mo <sup>V</sup> (O <sub>L</sub> ) <sub>3</sub> (CO) <sub>2</sub>	g <sub>1</sub> = 1.969, g <sub>2</sub> = 1.965, g <sub>3</sub> —		A <sub>1</sub> = 0.75, A <sub>2</sub> = 0.75, A <sub>3</sub> —	d <sub>π</sub> (xy)	[5,8]
Ni/SiO <sub>2</sub>	Ni <sup>I</sup> (O <sub>L</sub> ) <sub>2</sub> (CO) <sub>2</sub>	g <sub>1</sub> = 2.191, g <sub>2</sub> = 2.086, g <sub>3</sub> = 2.066		A <sub>1</sub> = 3.0, A <sub>2</sub> = 3.25, A <sub>3</sub> = 3.25	d <sub>σ</sub> (x <sup>2</sup> - y <sup>2</sup> )	[11]
Ni/SiO <sub>2</sub>	Ni <sup>I</sup> (O <sub>L</sub> ) <sub>2</sub> (CO) <sub>4</sub>	g <sub>⊥</sub> = 2.130, g <sub>∥</sub> = 2.009		A <sub>⊥</sub> = 5.15 <sup>a</sup> , A <sub>∥</sub> = 2.5 <sup>c</sup>	d <sub>σ</sub> (z <sup>2</sup> )	[11]
Ni/SiO <sub>2</sub>	Ni <sup>I</sup> (O <sub>L</sub> ) <sub>2</sub> (PEt <sub>3</sub> ) <sub>3</sub>	g <sub>⊥</sub> = 2.087, g <sub>∥</sub> = 2.280	A <sub>⊥</sub> = 5.0, A <sub>∥</sub> = 7.0	A <sub>∥</sub> = 5.5 <sup>a</sup> , A <sub>⊥</sub> = 5.5 <sup>c</sup>	d <sub>σ</sub> (x <sup>2</sup> - y <sup>2</sup> )	[11]
Ni/SiO <sub>2</sub>	Ni <sup>I</sup> (O <sub>L</sub> ) <sub>2</sub> (PEt <sub>3</sub> ) <sub>3</sub>	g <sub>⊥</sub> = 2.125, g <sub>∥</sub> = 2.013	A <sub>⊥</sub> = 7.0, A <sub>∥</sub> —		d <sub>σ</sub> (z <sup>2</sup> )	[23]
Mo/SiO <sub>2</sub>	O=Mo <sup>V</sup> (O <sub>L</sub> ) <sub>4</sub> (PEt <sub>3</sub> ) <sub>2</sub>	g <sub>∥</sub> = 1.925, g <sub>⊥</sub> = 1.960	A <sub>⊥</sub> = 2.5, A <sub>∥</sub> = 2.9		d <sub>π</sub> (xy)	this work

<sup>a</sup> Notation O<sub>L</sub> stands for lattice oxide ions located on the support surface.

<sup>b</sup> Shf splitting of axial ligand.

<sup>c</sup> Shf splitting of equatorial ligand.

to transition metal ions depend on a subtle blend of electronic ( $\sigma$  and  $\pi$ ) and steric (Tolman cone angle  $\theta$ ) effects, which can be separated quantitatively [12]. Interaction of phosphines with TMI centres in some cases is accompanied by reduction of transition metal even at ambient conditions [13].

In the present work, which corroborates earlier investigations from our laboratory [5,8–11], using various trialkylphosphine molecules as a probe we have studied the coordination and the spatial accessibility of  $\text{Mo}^{5+}$  species formed on the surface of the  $\text{Mo}/\text{SiO}_2$  catalyst. Although the steric characteristics of phosphines on various TMI are well known, no attempt has been made to apply this property for the study of surface supported transition metal ion centres.

## 2. Experimental

Grafted  $\text{Mo}/\text{SiO}_2$  catalysts have been prepared by reacting partially dehydrated silica (400  $\text{m}^2/\text{g}$ ) with molybdenum pentachloride in cyclohexane as described elsewhere [8] or by impregnation using ammonium heptamolybdate solution. Analysis of the grafted samples gave 0.15 and 0.33–0.31 wt% of molybdenum mainly in the isolated state [14]. The Mo content in impregnated samples was found to be 2 and 10 wt%. In the standard reduction catalysts were initially heated at 873 K in vacuum for 0.5 h and next heated under 200 Torr of oxygen for 2 h, then reduced under 200 Torr of hydrogen and finally outgassed for 0.5 h.

The gases  $\text{O}_2$  and  $\text{H}_2$  were supplied by l'Air Liquide and used without further purification. The  $(\text{CH}_3)_3\text{P}$ ,  $(\text{C}_2\text{H}_5)_3\text{P}$  and  $(t\text{-Bu})_3\text{P}$  phosphines (Strem) were adsorbed in the temperature range 77–295 K from the gas phase ( $(\text{CH}_3)_3\text{P}$ ,  $(\text{C}_2\text{H}_5)_3\text{P}$ ) or from solution in *n*-hexane ( $(t\text{-Bu})_3\text{P}$ ). Partial pressures of  $(\text{C}_2\text{H}_5)_3\text{P}$  at given temperature of adsorption were calculated using the following relationship:  $\log p = -2188/T + 8.42$ .

The EPR spectra were recorded at 77 K and room temperature on a Bruker (Model ESP 300) spectrometer working at 9.4 GHz (X-band) with 100 kHz field modulation. A Bruker variable temperature unit was used for recording the spectra at the temperature range 77–295 K. The third derivative spectrum was obtained by means of a subharmonic generator (Telmor) on a Varian E-3 spectrometer. All the data manipulation (subtraction, comparison and integration etc.) has been performed with the software provided by Bruker. Computer simulations of the spectra have been performed with a modified version of the SIM14A program [15].

## 3. Results and discussion

### 3.1. Phosphines as probes of the coordination number

Upon standard reduction all the  $\text{Mo}/\text{SiO}_2$  samples exhibit a complex EPR spectrum at 77 K (Fig. 1a) owing to the superimposed  $\text{Mo}^{5+}$  signals already discussed and assigned earlier [4,5,8]. The predominant one with  $g_{\perp} = 1.944$  and  $g_{\parallel} = 1.89$  corresponds to a hexacoordinated  $\text{Mo}_{6c}^{5+}$  ion, and the weaker signal to a pentacoordinated  $\text{Mo}_{5c}^{5+}$  ion ( $g_{\perp} = 1.957$ ,  $g_{\parallel} = 1.87$ ). Moreover an additional signal due to a tetraordinated  $\text{Mo}_{4c}^{5+}$  ion ( $g_{\perp} = 1.926$ ,  $g_{\parallel} = 1.76$ ) is also detected. All three types of  $\text{Mo}^{5+}$  cations possess a molybdenyl character, which is preserved upon adsorption [4,8]. When  $(\text{CH}_3)_3\text{P}$  or  $(\text{C}_2\text{H}_5)_3\text{P}$  is adsorbed, the EPR spectrum is dramatically changed (Fig. 1b, c). The features due to  $\text{Mo}_{4c}^{5+}$  species clearly disappear, while those of  $\text{Mo}_{5c}^{5+}$  and  $\text{Mo}_{6c}^{5+}$  are dominated by the superimposed new signal *A* of phosphine substituted molybdenum as can be judged from the appearance of hyperfine structure in the spectrum. The shape of the resultant complex spectrum is apparently associated with the amount of the tetrahedral  $\text{Mo}_{4c}^{5+}$  initially present on the surface after reduction since the ratio of the component signals varied correspondingly (Fig.

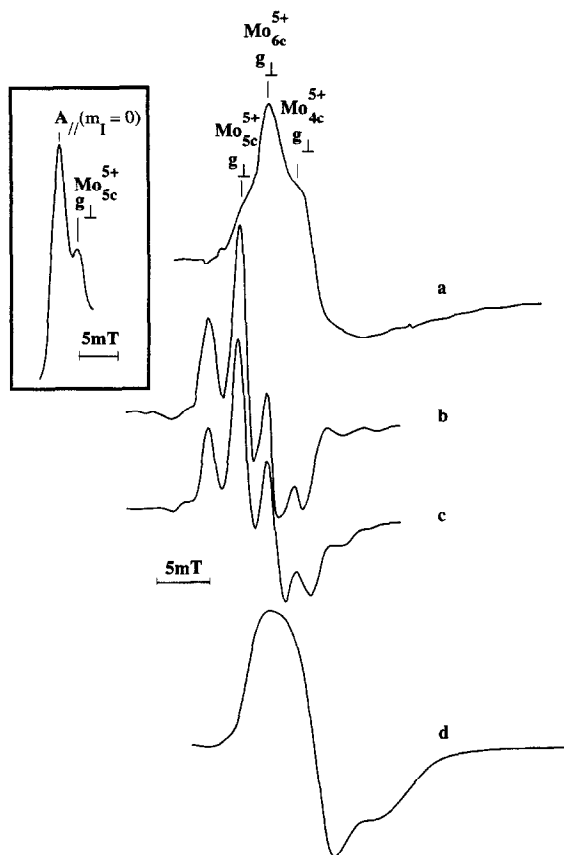


Fig. 1. EPR spectra (X band, 77 K) of reduced Mo/SiO<sub>2</sub> catalysts before (a) and after adsorption at room temperature of (b) (CH<sub>3</sub>)<sub>3</sub>P, (c) (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P, (d) *t*-Bu<sub>3</sub>P. In the insert a third derivative of the perpendicular line corresponding to  $m_l = 0$  (a component of the <sup>31</sup>P total spin  $I = I_1 + I_2 - 1/2 + 1/2 = 1$ ) of the bis(triethylphosphine) molybdenyl species is presented showing the presence of  $g_{\perp}$  (Mo<sub>5c</sub><sup>5+</sup>) features, due to pentacoordinated molybdenum, which are not affected by the adsorption.

2). The contribution of signal A is greatest for grafted 0.33 wt% sample (Fig. 2a) which has the highest relative concentration of Mo<sub>4c</sub><sup>5+</sup> species and considerably decreases in the case of impregnated 2 and 10 wt% samples (Fig. 2b, c) of progressively lower content of tetraordinated Mo species. In the latter case, the features due to the Mo<sub>4c</sub><sup>5+</sup> are practically undetectable in the initial spectrum. Its presence may be then revealed only via the application of the phosphine probe. These observations indicate that the signal A is formed at the expense of Mo<sub>4c</sub><sup>5+</sup>.

The signal A does not depend, except for its intensity, on the phosphine pressure in the entire

investigated range. This is clearly revealed in the in situ variable temperature adsorption experiment. The Mo/SiO<sub>2</sub> sample was initially cooled down to 77 K and next 12 Torr of triethylphosphine adsorbed. Then the temperature was gradually increased, with the sample kept inside the cavity. No change in the EPR spectrum was detected in the temperature range 77–180 K, indicating that under such conditions coordination does not occur. Obviously, the vapor pressure of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P is too low at these temperatures to enable formation of any surface complex with molybdenum centres. However, above 200 K, as the adsorption time steadily increases, the new lines of the diphosphine species appear in the spectrum (Fig. 3a), and after about 200–250 min the signal A of the phosphine complex practically reaches its maximal intensity. Fig. 3a shows the plot of the reaction progress with time at 200 K. The spectra recorded at 200 K correspond to the adsorption of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P at the threshold pressure  $p =$

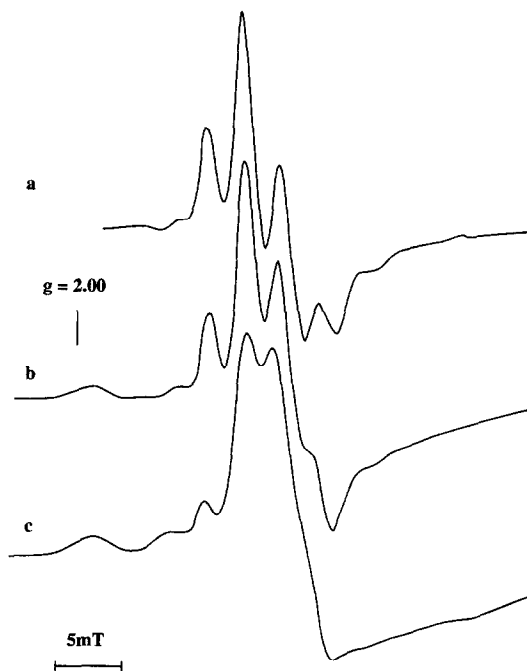


Fig. 2. EPR spectra (X band, 77 K) obtained after adsorption of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P onto reduced 0.33 wt% Mo/SiO<sub>2</sub> (a), 2 wt% Mo/SiO<sub>2</sub> (b), and 10 wt% Mo/SiO<sub>2</sub> (c).

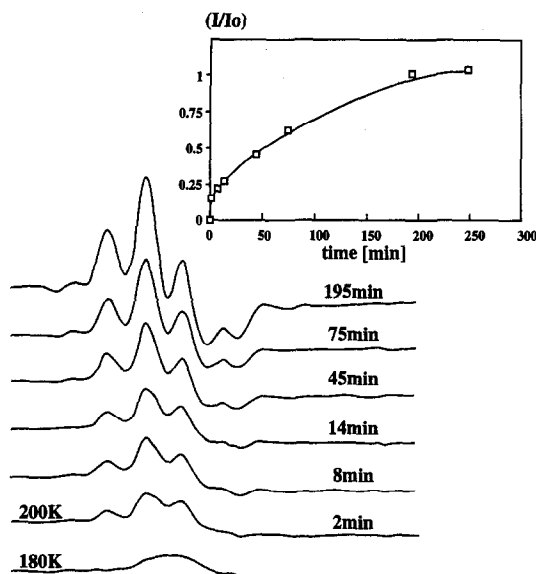


Fig. 3. Kinetics of the in situ adsorption of triethylphosphine onto 0.33 wt% Mo/SiO<sub>2</sub> catalyst at 200 K (evolution of the EPR signal). In the insert, a plot of the reaction progress with time is shown.

$3 \times 10^{-3}$  Torr where coordination occurs and which is the saturated vapor pressure of triethylphosphine at this temperature.

The new features of the spectrum (Fig. 1b) are assigned to phosphorus-containing species on the following basis. The 'perpendicular' part of the spectrum is better resolved, than the 'parallel' one, showing the appearance of new lines split by about 3.0 mT, absent in the initial spectrum. The latter obviously come from the superhyperfine (shf) coupling of the unpaired electron localized mainly on the molybdenum  $d_{xy}$  orbital [8] with the two equivalent <sup>31</sup>P nuclei of phosphine ligands. To a first approximation [16,17], the spectrum may be understood in terms of pseudo-axial  $g$  and hyperfine tensors with the 'parallel' hyperfine axis corresponding to one of the 'perpendicular'  $g$ -tensor axes. Thus the three low-field features correspond to  $g_{\perp}$  and  $A_{\parallel}$  components and the three high-field splittings then correspond to  $g_{\parallel}$  and  $A_{\perp}$ . Within these assumptions a computer simulation of the experimental spectrum of the molybdenum phosphine complex was performed and the result is shown in Fig. 4. The

general fit obtained is quite satisfactory explaining not only the gross features of the spectrum, but also reproducing correctly the intensities of the individual lines of the experimental EPR signal. Although rigorously it accounts only approximately for the real non-coincidence of the axes, since there is no reason that the angle separating  $g$  and  $A$  axes should be exactly 90°, the good fit obtained indicates that the angle must be close to this value. The detailed analysis of the spectrum as well as the molecular structure of the molybdenum diphosphine surface complex will be the subject of another paper [18]. Nevertheless, the conclusion that two phosphine ligands occupy equatorial sites in the complex is well accounted for by this analysis.

In principle, upon adsorption of phosphine ligands a splitting of the EPR lines due to the shf coupling with <sup>31</sup>P nuclei ( $I = 1/2$ ) as well as the shift of their positions, due to the change of both the coordination and the nature of coordinated ligand, is to be expected. This conclusion is based on the analysis of the theoretical expressions of  $g$  tensor components of Mo<sup>5+</sup> in axial symmetry [19]

$$g_{\perp} \cong 2.0023 - 2\lambda_M \beta_2 \epsilon / \Delta E_{(b_2 \rightarrow e)} \quad (1)$$

$$g_{\parallel} \cong 2.0023 - 4(2\lambda_M \beta_2 \beta_1 - \lambda_L \beta'_2 \beta'_1) / \Delta E_{(b_2 \rightarrow b_1)}$$

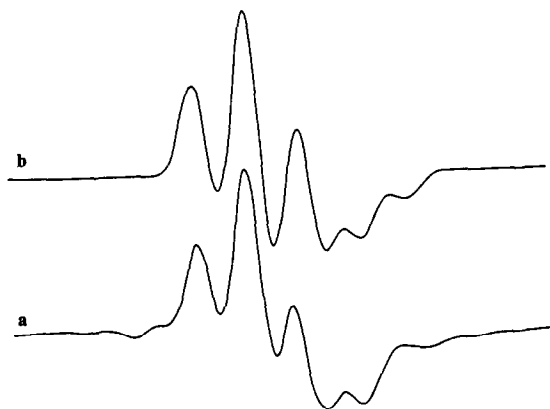


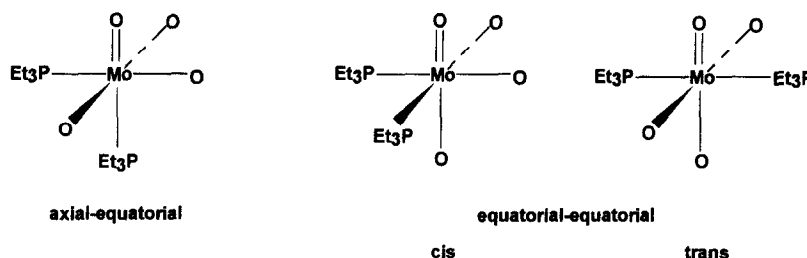
Fig. 4. EPR spectrum (X band, 77 K) of the molybdenyl bis(triethylphosphine) (a) experimental, (b) computer simulation assuming pseudo axial symmetry.

where  $\lambda_M$  and  $\lambda_L$  are the spin-orbit coupling constants of the central metal ion and the donor atom of the ligand respectively,  $\beta_2$ ,  $\beta_1$ ,  $\epsilon$ ,  $\beta'_1$  and  $\beta'_2$  are the coefficients of atomic orbitals of Mo and phosphine ligands constituting a singly occupied molecular orbital (SOMO), while  $\Delta E_{(b_2 \rightarrow e)}$  and  $\Delta E_{(b_2 \rightarrow b_1)}$  are the energy differences between the relevant molybdenum d orbitals labelled here within the axial  $C_{4v}$  point group symmetry. The minor terms containing overlap integrals are neglected. These equations show that especially  $g_{\parallel}$  and, to a lesser extent, also  $g_{\perp}$  depend on the nature of the ligands surrounding the central ion. Indeed, the larger value of spin-orbit coupling of  $^{31}\text{P}$  relative to O ( $\lambda_{\text{O}} = 152 \text{ cm}^{-1}$  and  $\lambda_{\text{P}} = 299 \text{ cm}^{-1}$ ) along with a stronger crystal field than that for oxygen (by a factor of about 2, [20]) created by  $(\text{C}_2\text{H}_5)_3\text{P}$  ligand cause a decrease of the shift of both  $g$  components ( $g_{\parallel} = 1.925$ ,  $g_{\perp} = 1.960$ ) from the free electron  $g_e = 2.0023$  value in comparison to those observed for hexacoordinated  $\text{Mo}_{6c}^{5+}$  ( $g_{\parallel} = 1.89$ ,  $g_{\perp} = 1.944$ ). The magnitude of the observed shf splittings  $A_{\perp} = 2.5 \text{ mT}$  and  $A_{\parallel} = 2.9 \text{ mT}$  is much higher than that obtained with  $^{13}\text{CO}$  adsorption on the same Mo/SiO<sub>2</sub> samples (0.75 mT for dicarbonyl and 0.4 mT for monocarbonyl complexes of  $\text{Mo}_{4c}^{5+}$  [8,10] and is comparable to that measured for  $\text{Ni}^+$  (ca. 3.0 mT) in Ni/SiO<sub>2</sub> [11] with  $d_{\sigma}$  ( $d_{z^2}$  or  $d_{x^2-y^2}$ ) ground state.

The number of phosphine molecules that fill up the vacancies within the inner sphere of molybdenum ions is directly deduced from the number  $N$  of the shf lines  $N = 2nI + 1$ , where

$n$  is the number of equivalent  $^{31}\text{P}$ -containing species. In principle, three different cases (shown in Scheme 1) with the same degree of saturation of the coordination sphere but with different arrangements of the phosphine ligands may be distinguished (i) a molecule of phosphine probe is coordinated in vertical while the second one in a planar position giving rise to *axial-equatorial* isomer of disubstituted  $\text{Mo}_{4c}^{5+}$ , (ii) two phosphines associate with the  $\text{Mo}_{4c}^{5+}$  forming a *cis*- (of  $C_s$  symmetry) or (iii) *trans*-diphosphine complex (of  $C_{2v}$  symmetry) producing a pseudooctahedral molybdenyl bis(triethylphosphine) complex with phosphine molecules coordinated in the horizontal plane of the symmetry.

Case (i) can be easily excluded since the shf structure observed upon adsorption clearly reveals the 1:2:1 pattern expected for two equivalent  $^{31}\text{P}$  nuclei (Fig. 4a) while for the *axial-equatorial* isomer a distinct shf pattern (consisting of doublet of doublets) due to the nonequivalent phosphines is expected [21]. In fact, it is known that an axial ligand (*trans* to M=O bond) has a longer and weaker M–L bond than a similar equatorial ligand (in a *cis* to M=O bond position), which makes delocalization of the odd electron density onto the axial ligand less favorable. As a result, hyperfine splittings due to the axially-coordinated P-containing species are considerably smaller than those coming from the equatorial ligands. For example, in the case of *mer*-O=WCl<sub>3</sub>(R<sub>3</sub>P)<sub>2</sub> complex the value of the  $a_{\text{iso}}$  of  $^{31}\text{P}$  for the phosphorus atoms in the *cis* to the W=O bonding



Scheme 1.

(equatorial) position amounts to 3.5 mT, while that corresponding to *trans* to the W=O (axial) ligand is less than 1.5 mT [21].

From the two possible (ii) geometries, the *trans*-structure can be rejected on the basis of steric arguments. Indeed in such symmetry, in order to preserve two previously existing bonds with surface oxygens and maintain the equivalency of the  $^{31}\text{P}$  nuclei, the only possible situation of the  $(\text{C}_2\text{H}_5)_3\text{P}$  ligands is in the horizontal plane of the octahedron formed upon coordination of these two molecules. However, estimation of steric requirements in this position (see below) indicates that such molecules cannot be accommodated owing to the too large value of their Tolman angles.

Following earlier studies of the coordination sphere of molybdenum in  $\text{Mo}/\text{SiO}_2$  using  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  as probe molecules [4,8,10] we can expect that  $\text{Mo}_{5c}^{5+}$  species should, in principle, also be able to coordinate one phosphine molecule and exhibit corresponding shf structure due to the one  $^{31}\text{P}$  nucleus in the spectrum. The analysis of this problem is complicated by the fact that one of the perpendicular lines of diphosphine occurs at the same position as the  $\text{Mo}_{5c}^{5+}$  perpendicular features. We found, however, no direct experimental evidence that this actually takes place since in the third derivative EPR spectra the resolution is sufficiently improved showing that upon adsorption of phosphines the perpendicular features of  $\text{Mo}_{5c}$  species remain unaffected (Fig. 1 insert). Furthermore computer simulation revealed that the observed experimental spectrum can be satisfactorily reproduced by assumption of the presence of only one species with two nearly equivalent phosphines associated with the  $\text{Mo}_{4c}^{5+}$  coordination sphere (Fig. 4b). The above results remain in analogy with the data obtained for  $^{13}\text{CO}$  adsorption, where it was stated that carbon monoxide molecules are adsorbed exclusively by tetracoordinated species [8]. This indicates that  $\text{Mo}_{4c}^{5+}$  contains two vacancies in the coordination sphere. Upon adsorption of two molecules of  $\text{P}(\text{C}_2\text{H}_5)_3$  these vacancies are filled and the

coordination sphere of  $\text{Mo}_{4c}^{5+}$  species completed. Therefore, the earlier attribution of  $\text{Mo}_{4c}^{5+}$  to tetracoordinated species has been confirmed. However, the use of the phosphine probe enabled detection of tetracoordinated molybdenum even in the cases where the parent EPR signal of  $\text{Mo}_{4c}^{5+}$  centres was too weak to be resolved in the simultaneous presence of the overwhelming signal of the dominant, in the impregnated catalyst,  $\text{Mo}_{6c}^{5+}$  species.

Under the conditions used in the present study, phosphines apparently act as probe molecules and interact exclusively with  $\text{Mo}_{4c}^{5+}$  species which have the highest coordination unsaturation. This, however, does not exclude the possibility that phosphines may affect to some extent also  $\text{Mo}_{6c}^{5+}$  or  $\text{Mo}_{5c}^{5+}$ , for instance via a slow ligand substitution reaction. Since it would require replacement of surface oxygen ligands by bulky  $\text{PEt}_3$ , this process is likely to be sterically hindered.

Perhaps the most intriguing feature of the present EPR study of the  $\text{Mo}_{4c}^{5+}$  interaction with phosphine molecules is that the molybdenum diphosphine species is readily formed while the molybdenum monophosphine is not. No lines other than those of the disubstituted complex are observed in the EPR spectrum. The diphosphine complexes, in contrast to those formed upon CO [10] or methanol adsorption [4,10] are formed not via the stepwise transformation of the monophosphine (for instance formed first at lower pressures) into diphosphine species (emerging at higher pressures by accepting the second molecule of  $(\text{C}_2\text{H}_5)_3\text{P}$ ). Instead, from the very beginning of the adsorption process both  $(\text{C}_2\text{H}_5)_3\text{P}$  molecules appear simultaneously within the coordination sphere and the prolonged contact time or increasing the pressure of the adsorbate (by rising the temperature) results just in the increase of the concentration of the molybdenyl bis(triethylphosphine) complex formed. Similar coordination behaviour was previously stated by Kasai and Jones in the case of bis(carbonyl)aluminium(0) generated in argon matrices by condensation of Al atoms and



CO molecules [22], where no evidence of monocarbonyl species was observed in the EPR spectra. The bis(carbonyl)aluminium(0) species is formed as the result of  $\sigma$ -type dative interaction between the lone-pair electrons of CO and the vacant  $sp^2_{x,y}$  hybridized orbitals of Al and  $\pi$ -type back-donation of the unpaired electron from the Al  $p_z$  orbital into the vacant antibonding  $\pi^*$  orbitals of CO. Synergism between the two types of interactions is crucial and Al monocarbonyl does not appear to have a bound state [22].

A possible transformation of molybdenum diphosphine surface complexes during thermal desorption at 373 K was further investigated by EPR (Fig. 5). The samples were progressively evacuated at this temperature and the shape of their spectra was analyzed. After 5 min of outgassing the intensity of the signal decreased twice and evacuation for 30 min completely

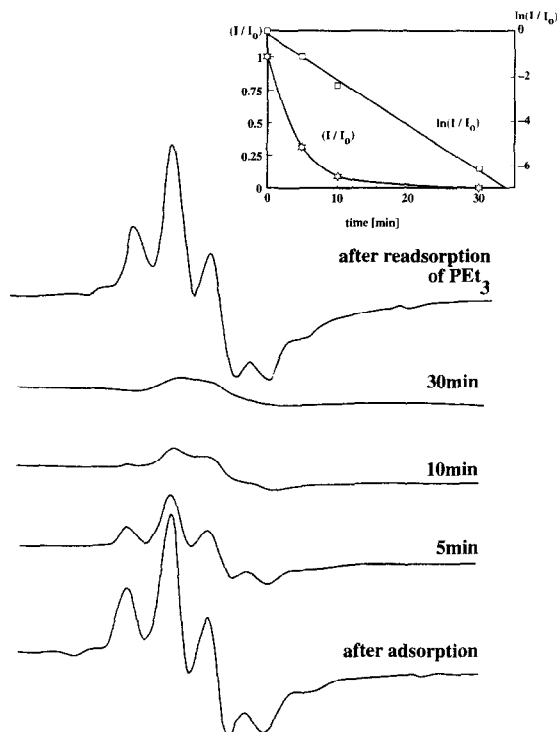


Fig. 5. Thermal decomposition of the molybdenyl bis(triethylphosphine) complex formed on the surface of 0.33 wt% Mo/SiO<sub>2</sub> catalyst under continuous evacuation at 373 K. In the insert associated kinetic curves are shown.

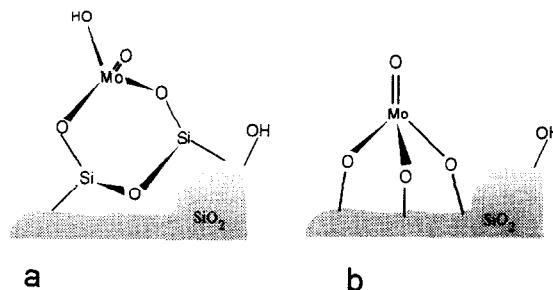
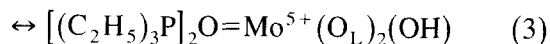
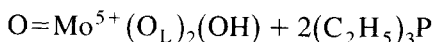


Fig. 6. Possible structures of Mo<sub>5+</sub> species grafted on the silica surface, which can give rise to nearly axial EPR spectrum (a) D<sub>2d</sub> pseudosymmetry (C<sub>s</sub>); (b) C<sub>3v</sub> structure.

destroyed the features attributable to <sup>31</sup>P shfs, indicating that practically all phosphine ligands under these conditions are desorbed. Fig. 6 shows the decay of molybdenyl bis(triethylphosphine) complex under vacuum at 373 K. The semi-logarithmic plot of decay (Fig. 5 insert) indicates a first order reaction with the rate constant value equal to  $k = 0.20 \text{ min}^{-1}$ . The equation describing this process can be then expressed as follows

$$[\text{Et}_3\text{PMo}]_t = [\text{Et}_3\text{PMo}]_{t=0} e^{-0.20t} \quad (2)$$

where  $[\text{Et}_3\text{PMo}]_t$  and  $[\text{Et}_3\text{PMo}]_{t=0}$  are current and initial concentration of the diphosphine complex respectively. During this reaction no other species were detected. We may therefore conclude that the molybdenyl bis(triethylphosphine) surface complexes are completely decomposed by outgassing at 373 K, releasing in concert two molecules of (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P, and without formation of any intermediate species like monophosphine complex. However, by subsequent readsorption of the phosphine at room temperature the initial diphosphine complex is restored (Fig. 5).



where O<sub>L</sub> stands for lattice oxygen O<sup>2-</sup> species located on the surface. The reversibility of the process has been therefore revealed.

Collation of the results obtained from variable temperature adsorption and thermal desorp-

tion clearly indicates that upon interaction of  $(C_2H_5)_3P$  with the tetracoordinated molybdenum centres only one type of the complex, containing exclusively two phosphine molecules, is formed. Thus adsorption of the phosphine probe results in filling of the previously existing coordination vacancies and does not provoke any change in the polydentate character of the bonding with the surface. This contrasts with the case of  $Ni^+/SiO_2$  catalysts where upon adsorption of ethylphosphine a series of various complexes of different coordination number and containing from one to four molecules of phosphine have been detected depending on the experimental conditions [23]. An interesting feature of these complexes is a mutable number of links (one for the tetra- and triphosphine species and two links for the bi- and monophosphine species) the  $Ni^+$  ion forms with the surface of the silica support.

The results of the present work show that there is no evidence for the generation of any other than diphosphine complexes in the entire investigated range of the applied conditions. The  $Ni^+$  ions are prone to change the number of links with the surface but the  $Mo^{5+}$  ions resist similar changes. This is most probably caused by the higher positive charge of the latter species which, owing to the electrical neutrality of the  $(C_2H_5)_3P$ , can be compensated exclusively by negative surface oxygens. On the other hand, the low electric charge of  $Ni^+$  makes the bonding with the surface more flexible. The same type of different behavior has also been observed in the case of the coordination of carbon monoxide by  $Ni^+/SiO_2$  and  $Mo^{5+}/SiO_2$  surface complexes [8,10,11].

### 3.2. Probing spatial accessibility of $Mo^{5+}$ ions using phosphines with various Tolman angles

The properties of metal-coordination compounds are to a large extent determined by the nature of the bound ligands. The latter can be factored into electronic and steric properties which are characteristic for each ligand. The

electronic properties refer to the extent of charge transfer or orbital overlap of the metal–ligand bond. The steric properties are the measure not merely of the ligand size, but also its spatial requirements in the coordination environment. The most widely employed measure of the amount of space occupied by a ligand is the cone angle  $\theta$ , first proposed by Tolman [24]. This angle is specified as the apex angle of a cylindrical cone with its origin 0.228 nm away from the centre of the phosphorus atom, whose sides just touch the van der Waals surfaces of the outermost atoms of the organic substituents.

Quantitative measurements of relative ligand steric requirements are useful in a variety of assessments such as interpretations and predictions of changes in coordination number, rough comparative equilibrium constants or reaction rates. Such relationships have a predictive power and may provide the basis for a deeper understanding of experimental data [25]. Since cone angles are reasonably accurate measures of the relative three-dimensional space-filling properties, it is appealing to use this property for gauging of steric requirements around the Mo tetracoordinated species with the aim of distinguishing between possible geometric structures. In fact, this idea arises from the studies of steric effects in metal cluster compounds which based on assessing the space requirements of bulky ligands from the values of their cone angles [26]. Since the steric effects are approximately additive, the tabulated cluster cone angles can then be used to estimate the maximal number of ligands that can be coordinated at given centre, in terms of the steric saturation principle [26]. The crude assessments of the relative steric constraints introduced by some common ligands found in cluster chemistry give rise to reasonably accurate descriptions of the possible limiting cluster stoichiometries [27]. Therefore it is tempting to extend this method to study the structure of heterogeneous surfaces. Our approach differs from that generally used in the chemistry of homogeneous complexes since we try to use bulky phosphine ligands of various

values of the Tolman angle for probing the spatial accessibility and geometry of  $\text{Mo}^{5+}$  centres grafted on the surface of the silica support.

The tetracoordinated  $\text{Mo}_{4c}^{5+}$  species producing axial EPR signals can exist in two basic geometries which differ in the symmetry of the ligand arrangement and the number of bonds the molybdenum complex is making with the surface. The two possible limiting structures are typified by  $D_{2d}$  pseudo-symmetry (in fact the actual symmetry of this species is reduced to  $C_s$  and the label  $D_{2d}$  is used to denote the type of approximate geometrical arrangement of the ligands rather than the rigorous symmetry label for this species) and a  $C_{3v}$  structure, which are schematically shown in Fig. 6. Precedents can be found for these structures elsewhere [28]. In the following we will show that by adsorption of phosphines of various Tolman angle a distinction can be made between these geometries basing on the different spatial accessibility of the coordination sphere for each particular structure. As the space-filling probe we have used  $(\text{CH}_3)_3\text{P}$ ,  $(\text{C}_2\text{H}_5)_3\text{P}$  and  $(t\text{-Bu})_3\text{P}$  phosphines having the Tolman angle of  $118^\circ$ ,  $132^\circ$  and  $182^\circ$  respectively [25], which define the ligand steric demand. The EPR signals obtained after adsorption at room temperature are shown in Fig. 1b–d. While in the case of methyl- and ethylphosphine the presence of the characteristic triplet pattern clearly shows coordination of

these molecules to paramagnetic  $\text{Mo}_{4c}^{5+}$  and formation of disubstituted complex, for  $(t\text{-Bu})_3\text{P}$  only a slight broadening of the perpendicular part of the  $\text{Mo}^{5+}$  EPR spectrum was observed. This is caused apparently by the proton dipolar interaction owing to the contact with *n*-hexane solvent.

The size of the phosphine ligand that can be accommodated around the molybdenum polyhedron will be influenced primarily by the cone angle that is subtended at the Mo centre by molybdenyl  $\text{Mo}=\text{O}$  bonding and  $\text{Mo}-\text{O}_L$  links made with the surface. An EXAFS investigation of the Mo complexes attached to silica revealed that the  $\text{Mo}=\text{O}$  bond length is equal to ca. 0.17 nm and a greater distance from Mo to surface oxygen, which amounts to  $\text{Mo}-\text{O}_L = 0.21$  nm [29]. Extension of a model initially proposed for silica supported  $\text{Nb}_2\text{O}_5$  to molybdenum species suggest that these oxygens attached to surface Si atoms may project outside the surface of the support. Therefore the maximal distance from Mo to surface should be increased, but probably no more than to about 0.33 nm [29]. The estimates of the semicone angles are then performed for the limiting structures of Mo surface complex basing on the method of calculation of the maximum semicone angles  $\theta/2$  from the X-ray and van der Waals radii data, developed by Ferguson et al. [30]. Such values are for the most part in good agreement with those pre-

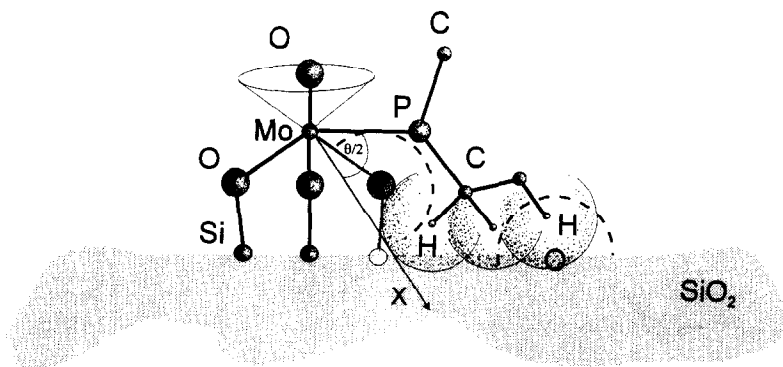


Fig. 7. Details of the graphical estimation of the maximum semicone angle  $\theta/2$  and the steric strain produced by coordination of ethylphosphine ligand in equatorial plane. The semicircles and cones indicate the size of van der Waals radii of phosphine hydrogen and surface oxygen atoms.

dicted by Tolman therefore may be mutually compared. Details of the calculation of the semicone angle  $\theta/2$  are explained in Fig. 7. The point of the contact of the cone generating vector  $\text{Mo} \rightarrow \text{X}$  from the metal, with the van der Waals sphere of the hydrogen atom, is taken as coplanar with the  $\text{Mo-P-H}$  atoms [30]. In the calculation the following averaged bond lengths have been used:  $d_{\text{Mo-P}} = 0.25 \text{ nm}$  [31],  $d_{\text{P-C}} = 0.183 \text{ nm}$  [32],  $d_{\text{C-C}} = 0.142 \text{ nm}$ ,  $d_{\text{C-H}} = 0.108 \text{ nm}$  [26] in conjunction with van der Waals radii of hydrogen and oxygen equal to  $0.12 \text{ nm}$  and  $0.14 \text{ nm}$  respectively [26]. The coordination about phosphorus and carbon was assumed to be essentially tetrahedral with angles averaging  $110^\circ$ . In the  $\text{C}_{3v}$  geometry, since the axial position is blocked by  $\text{Mo=O}$  bonding and owing to the rigid links with surface, we can reasonably assume that the equatorial sites are the only potential centres apt for coordination. As implied in the Fig. 7 in this case the steric requirements gauged by the graphic model preclude the coordination of phosphines, even if some favorable distortions of the  $\text{C}_{3v}$   $\text{Mo}_{4c}^{5+}$  structure is assumed. On the contrary, in the case of  $\text{D}_{2d}$  pseudosymmetry ( $\text{C}_s$ ) there is enough space for coordination of two methyl- or ethylphosphine molecules providing that they will project out-

side the surface being located on both sides of the symmetry plane. The paramagnetic complex of such a structure can account for the observed shfs originating from two equivalent equatorial  $^{31}\text{P}$  nuclei, and the steric window is sufficient for  $(\text{CH}_3)_3\text{P}$  and  $(\text{C}_2\text{H}_5)_3\text{P}$  but is too small for accommodation of the bulky  $(t\text{-Bu})_3\text{P}$  ligand. This is adequately accounted for by the lack of the relevant shf structure in the EPR spectrum in the latter case (Fig. 1d). The following pictorial model of the coordination of phosphine ligands to  $\text{Mo}_{4c}^{5+}$  surface species is then proposed (Fig. 8).

From the arguments developed above it is apparent that the experimental results can be best explained by the  $\text{D}_{2d}$  pseudosymmetry ( $\text{C}_s$ ) of the tetracoordinated surface complex of  $\text{Mo}^{5+}$ . This conclusion is corroborated by the analysis of the  $g$  tensor of the  $\text{Mo}_{4c}^{5+}$  species. The relevant expressions for the  $g$  factors for various symmetries for  $d^1(d^9)$  configuration were reported by Hathaway and Billing [34]. For a given ground state the  $g$  value shifts will depend on which states are coupled to it through spin-orbit interaction, and therefore on any degeneracy or symmetry relationships within the excited state. The observed large anisotropy ( $g_{\parallel} = 1.76$ ,  $g_{\perp} = 1.926$ ) of the Zeeman term can

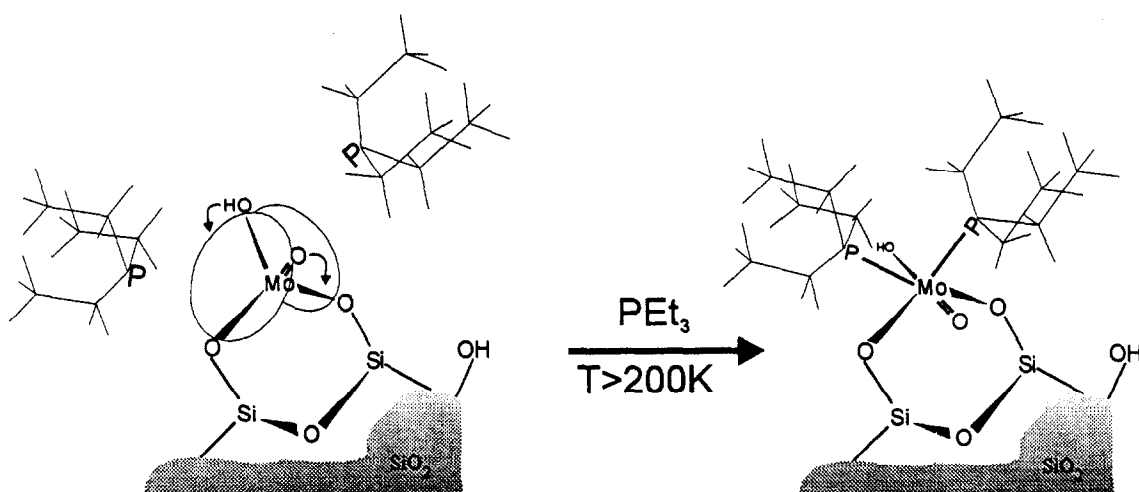


Fig. 8. Schematic picture of the transformation occurring upon coordination of the ethylphosphine ligands to  $\text{Mo}_{4c}^{5+}$  surface species of pseudo  $\text{D}_{2d}$  symmetry ( $\text{C}_s$ ). The ellipses symbolize the size of the cone angles subtended by the appropriate  $\text{Mo-O}$  bondings.

be reasonably accounted for by the theoretical expressions for  $g_{\parallel} = g_e - 8\lambda_{\text{Mo}}/\Delta E_1$  and  $g_{\perp} = g_e - 2\lambda/\Delta E_2$  [8], valid for  $D_{2d}$  symmetry and  $d_x^2 - d_y^2$  ground state. In the case of  $C_{3v}$  symmetry the  $d_z^2$  orbital belongs to the  $A_1$  representation whereas all other d orbitals span symmetry species E which provides a basis for their mutual mixing. This leads to an essential modification of the  $g$  parameters. In the particular case of compressed trigonally distorted tetrahedron Kazansky et al. [35] have shown that the  $g_{\parallel}$  component lies close to the free electron value ( $g_{\parallel} = 2.0$ ) while  $g_{\perp} = 2 - 6\lambda[\alpha^2/\Delta(A_1E^-) + \beta^2/\Delta(A_1E^+)]$ , where  $\alpha$  and  $\beta$  account for the mixing coefficients of relevant orbitals and  $\Delta$  stands for the energy difference between the levels of  $A_1$  and E symmetry. The analysis of the  $g$  tensor values predicted for  $C_{3v}$  structure ( $g_{\parallel} > g_{\perp}$ ) revealed that they cannot be accommodated by the experimental  $g$  tensor of  $\text{Mo}_{4c}^{5+}$  species with  $g_{\parallel} < g_{\perp}$ , providing additional argument against  $C_{3v}$  symmetry.

#### 4. Conclusions

$\text{P}(\text{C}_2\text{H}_5)_3$  proved superior to  $^{13}\text{CO}$  for the characterization of the coordination sphere of molybdenum centres. The presence of the exposed tetracoordinated Mo species has been detected by the well resolved shf structure of  $^{31}\text{P}$  exhibiting a characteristic 1:2:1 triplet. Application of the  $\text{P}(\text{C}_2\text{H}_5)_3$  probe enables detection of  $\text{Mo}_{4c}^{5+}$  of very low abundance in the simultaneous presence of dominant  $\text{Mo}_{6c}^{5+}$  species which otherwise cannot be detected because of the overlap of the corresponding spectra. Adsorption of a number of phosphines of different Tolman angle help to determine the spatial accessibility of this species and to distinguish between two possible geometries. The structure of tetracoordinated surface molybdenum complexes is better explained by  $D_{2d}$  pseudosymmetry ( $C_s$ ) than by  $C_{3v}$  geometry. Two phosphine molecules are directly bonded to a molybdenum

ion and this number does not change for lower adsorbate pressures.

#### Acknowledgements

Z.S. is grateful to the Ministère de l'Enseignement Supérieur et de la Recherche and the Université P. et M. Curie for an invited Professorship (PAST program). Strem Chemicals Inc. (France) is greatly acknowledged for providing the curve of the temperature dependence of triethylphosphine partial pressure.

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