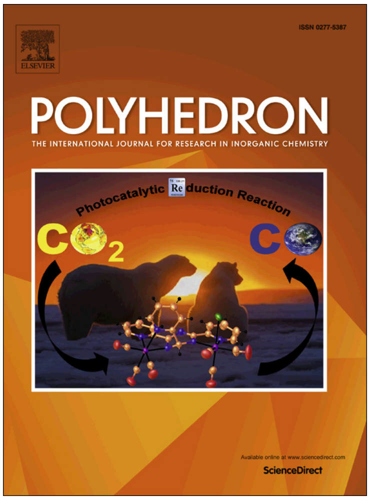

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Oxido- versus imido- transfer reactions in oxido-imido molybdenum(VI) complexes: a combined experimental and theoretical study

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ABSTRACT

The reaction of the oxido-imido molybdenum(VI) compounds [Mo(O)(Nmes)(S_2CNR_2)$_2$] (mes = 2,4,6-$C_6H_2Me_3$, R_2 = $^iPr_2$, **1a**; C_4H_4, **1b**) with an excess of PMe_3 was investigated. [Mo(Nmes)(S_2CNR_2)$_2$(PMe_3)] (R_2 = $^iPr_2$, **2a**; C_4H_4, **2b**) complexes and the corresponding phosphane oxide $OPMe_3$ were exclusively detected as reaction products, according to an oxygen atom transfer (OAT) reaction. No evidence of the possible imido transfer reaction was observed. In order to explain the selective OAT reaction in this system, DFT calculations were carried out with the model compound [Mo(O)(N-2,6-$Me_2C_6H_3$)(S_2CNMe_2)$_2$], **1c**, and PMe_3 as reactant. The two possible oxido transfer and imido transfer pathways were considered and the nucleophilic attack of the phosphane to the multiple bonded atom was the associative intermolecular processes modelled. The oxido transfer is thermodynamic and kinetically favoured with respect the imido one in agreement with the experimental results.

1. Introduction

A large number of compounds containing the oxido or the imido ligands are now known for the majority of the transition metals.[1] Both groups permit stabilization of high formal oxidation states and, in particular, for molybdenum the area of dioxido[2] and bis(imido)[3] complexes are very extensive. This situation contrasts with the relatively low number of mixed oxido-alkylimido or oxido-arylimido derivatives of this metal[4,5,6,7,8] and the relatively scarce data about their reactivity.[4c,k,5b,7b,8] Molybdenum catalysed oxygen atom transfer (OAT) reactions are of extraordinary interest in many processes at several levels: academic, industrial and biological.[9] For this reason, several research groups designed model molybdenum complexes and studied their OAT chemistry.[10,11,12] In marked contrast, the related imido transfer reaction is much less developed and the examples of molybdenum mediated imido transfer reactions are not abundant.[13,14]

A common model OAT reaction is the oxido-transfer to phosphanes and our research group investigated the oxido-transfer, and also the imido-transfer reaction, to PMe_3 by using dioxido and bis(imido) molybdenum(VI) compounds, respectively.[15,16] The ligand exchange reaction of dioxido and bis(imido) derivatives gave a straightforward synthetic route for the preparation of mixed oxido-imido complexes.[5b,17] This fact allowed the possibility of investigating the transfer of one or both groups to phosphane reagents. In fact, the reaction of phosphanes with oxido-*p*-tolylimido and oxido-*N*-tosylimido molybdenum(VI) complexes was early studied by Maatta[18] and Holm,[19] respectively. More recently, other research groups became interested in this reaction and, for example, oxido-tert-butylimido compounds with an unsymmetrical Schiff base ligand were analysed by Heinze[8] and oxido-tert-butylimido compounds with β-ketiminato or η^2-pyrazolato ligands were studied by Mösch-Zanetti.[7] Herein, as a continuation of our own work in the area of imido-molybdenum compounds,[20,21] we describe a combined experimental and theoretical study of the reactivity of oxido-imido complexes of molybdenum(VI) versus PMe_3 substrate.

2. Experimental section

2.1. General

All preparations and other operations were carried out under dry oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Solvents were dried and degassed before use. Infrared spectra were recorded on Perkin-Elmer Model 883 spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were run on Bruker AMX-300 and Bruker AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85 % H_3PO_4. ^{13}C NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. Compounds $[Mo(Nmes)(O)(S_2CNR_2)_2]$, **1a,b**, were prepared according to the literature procedure.[21]

*2.2. Reaction of [Mo(Nmes)(O)($S_2CN^iPr_2)_2$] with PMe_3: Formation of [Mo(Nmes)($S_2CN^iPr_2)_2(PMe_3)$] (**2a**)*

To a solution of [Mo(Nmes)(O)($S_2CN^iPr_2)_2$], **1a**, (0.06 g, 0.1 mmol) in THF (10 ml) was added an excess of PMe_3 (0.5 ml, 1 M solution in toluene). The colour of the mixture changed from red to violet. Within 10 minutes, the solution turned brown and the reaction was stirred overnight. Then, the volatiles were removed in vacuum. The resulting residue was a mixture of $OPMe_3$ and compound [Mo(Nmes)($S_2CN^iPr_2)_2(PMe_3)$], **2a**, which was characterized by NMR. Yield: quantitative (NMR), 86 % (isolated). Data for **2a**: ^1H NMR (500 MHz, C_6D_6): δ 6.58 (s, 2, CH, Ph), 2.49 (s, 6, *o*-CH_3), 1.97 (s, 3, *p*-CH_3), 1.42 (d, 7.5 Hz, 9, PMe_3), 1.2 (very br, 12, CH_3). The CH signals of ^{i}Pr groups were not discerned due to a dynamic process similar to that reported for complex **1a**.[21] $^{31}P\{^1H\}$ NMR (C_6D_6): δ 6.84 (s). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 220.4, 199.4 (s, S_2C), 154.9 (s, *ipso*-C), 134.9, 132.2 (s, *p*- and *o*-C), 128.5 (s, *m*-C), 50.9 (br, CH), 49.9 (br, CH), 21.0 (s, *p*-CH_3), 19.8 (s, *o*-CH_3), 19.5 (br, CH_3), 16.5 (d, J_{CP} = 13 Hz, PMe_3).

*2.3. Reaction of [Mo(Nmes)(O)($S_2CNC_4H_4)_2$] with PMe_3: Formation of [Mo(Nmes)($S_2CNC_4H_4)_2(PMe_3)$] (**2b**)*

The reaction of complex [Mo(Nmes)(O)($S_2CNC_4H_4)_2$], **1b**, with an excess of PMe_3 was carried out following a similar procedure. The resulting residue was again a mixture of $OPMe_3$ and compound [Mo(Nmes)($S_2CNC_4H_4)_2(PMe_3)$], **2b**. Yield: quantitative (NMR), 81 % (isolated). Compound **2b** was identified by comparison of its NMR data with those previously reported.[20] ^1H-NMR (300 MHz, $C_6D_5CD_3$): δ 7.63, 7.48 (pseudo t, J_{HH} = 2.3 Hz, 2H, NC_4H_4), 6.34 (s, 2H, C*H*, Ph), 6.04, 5.93 (pseudo t, J_{HH} = 2.3 Hz, 2H, NC_4H_4), 1.95 (s, 6H, *o*-CH_3), 1.86 (s, 3H, *p*-CH_3), 1.07 (d, J_{HP} = 9.2 Hz, 9H, PMe_3). $^{31}P\{^1H\}$-NMR ($C_6D_5CD_3$): δ -8.10 (s). $^{13}C\{^1H\}$-NMR (75 MHz, $C_6D_5CD_3$): δ 220.4, 206.7 (s, S_2C), 153.3 (s, *ipso*-C), 136.6, 135.4 (s, *p*-C and *o*-C), 128.5 (s, *m*-C), 121.1, 118.4, 114.3, 109.1 (s, NC_4H_4), 20.8 (s, *p*-CH_3), 19.3 (s, *o*-CH_3), 14.8 (d, J_{CP} = 28 Hz, PMe_3).

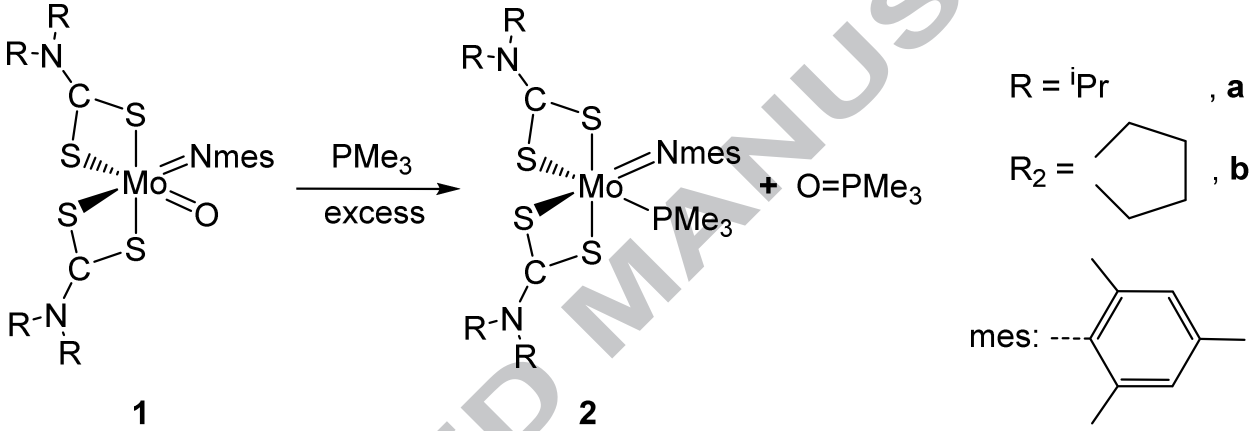
2.4. Computational details

The electronic structure and geometries of the model compounds were computed using density functional theory at the B3LYP level.[22] The Mo atom was described with the LANL2DZ basis set[23] while the 6-31G(d,p) basis set was used for all the remaining atoms. The optimized geometries of all the compounds were characterized as energy minima either by a nonexistence of imaginary frequencies (NImag = 0) or by very low vibrational frequencies (< 20 cm^{-1}) in the diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). These very low vibrational frequencies that do not lead to energy minimum optimisation have been reported in other cases, and it seems to be associated to numerical errors in the DFT integration grid. They could be eliminated by much more expensive calculation with a better grid.[24] Transition states were located using the quadratic synchronous transit (QST2) approach[25] and frequency calculations were performed in order to check the stationary states (NImag = 1). The DFT calculations were performed using the Gaussian 03 suite of programs.[26] Cartesian coordinates of all optimized compounds are collected in the Supporting Information.

3. Results and discussion

3.1. Reaction of oxido-imido molybdenum(VI) complexes with PMe$_3$

The dithiocarbamate derivatives [Mo(O)(Nmes)(S$_2$CNR$_2$)$_2$] (R$_2$ = ^{i}Pr$_2$, **1a**; C$_4$H$_4$,**1b**) were selected to investigate the possible competitive transfer of oxido and imido groups to tertiary phosphane PMe$_3$. Addition of an excess of PMe$_3$ to solutions of these complexes leads to formation of the compounds [Mo(Nmes)(S$_2$CNR$_2$)$_2$(PMe$_3$)] (R$_2$ = ^{i}Pr$_2$, **2a**; C$_4$H$_4$, **2b**) (Scheme 1). Both reactions were monitored by ^{31}P{^{1}H} NMR. The spectra showed signals due to the coordinated PMe$_3$ (δ 6.8, **2a**; -8.3, **2b**), one resonance due to the O=PMe$_3$ (around 30.8 ppm) and no evidence of the possible imido transfer reaction was observed. The structures shown in the Scheme 1 are easily deduced from their NMR data that reveal the presence of two non-equivalent dithiocarbamate ligands since, for instance, two singlets for the two S$_2$*C* groups are observed in the $^{13}C\{^1H\}$ NMR (at 220.4 and 199.4 ppm for **2a**). The formulation of the product **2b** was also confirmed by comparison of its NMR data with that of the same sample, reported previously by us, and obtained by treatment of $[Mo(Nmes)Cl_2(PMe_3)_3]$with two equivalents of $KS_2CNC_4H_4$.[20] Conversely to that observed by Holm in a related system,[19] in these reactions there was not signal of imido transfer and formation of mesN=PMe_3. Transfer of the oxido ligand to phosphane and reduction from molybdenum(VI) to molybdenum(IV) with coordination of PMe_3 takes place. This behaviour is similar to that observed by Heinze[8] and Mösch-Zanetti[7a,c] in related oxido-imido molybdenum(VI) complexes.



Scheme 1

3.2 Theoretical study of the reaction of model complex $[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$ with PMe_3: oxido versus imido transfer

After our experimental studies about the oxido-transfer reaction to PMe_3, we decided to investigate, using DFT at the B3LYP level,[27] the reaction of model complex $[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$, **1c**, with PMe_3, in order to give justification to our experimental observations. Although the nature of the N-substituents of dithiocarbamate ligand has a subtle effect on the OAT,[28] the modellization of dithiocarbamate with methyl substituents is adequate. As a proof of that, the calculated thermodynamic of the reaction of $[Mo(O)_2(S_2CNMe_2)_2]$ complex with PMe_3 ($\Delta H = -31.7$ kcal·mol^{-1}) compares well with the measured thermochemical data for $[Mo(O)_2(S_2CNEt_2)_2] + PPh_3$ ($\Delta H = -29.0 \pm 2.5$ kcal·mol^{-1}).[9e] The atom transfer reactions are associative intermolecular processes in which the nucleophilic attack proceeds by the approaching of the phosphane (or the substrate, in general) to the atom multiple bonded to the metal. For instance, previous theoretical studies, reported for the oxido transfer reaction in the system $[Mo(O)_2(NH_3)_2(SH)_2]$ + PMe_3, showed that the first step is the nucleophilic attack of PMe_3 on a π* Mo=O orbital perpendicular to the $[Mo(O)_2]$ unit and at a Mo-O-P angle of *ca.* 130º.[29] This affords a transition state with a weakened Mo-O bond and the phosphane bounded to one oxygen atom. Intermediates of this process, complexes $[Tp^{iPr}Mo(O)(OPh)(OPEt_3)]$,[30] $[Tp^*Mo(O)Cl(OPMe_2R)]$ (R = Me, Ph)[31] and $[Tp^*Mo(O)(SPh)(OPMe_3)]$,[32] were isolated and X-ray characterized showing Mo-O-P angles within the 130-144º range. The oxido transfer reaction in our system was modelled similarly and the reaction profile, as relative Gibbs free energy, the calculated structures of the transition state and intermediates are shown in Fig. 1. The energy reference was taken as the energy of the separate reagents ($[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$ + PMe_3). The optimised key intermediates and transition state structures appear in Fig. 2.

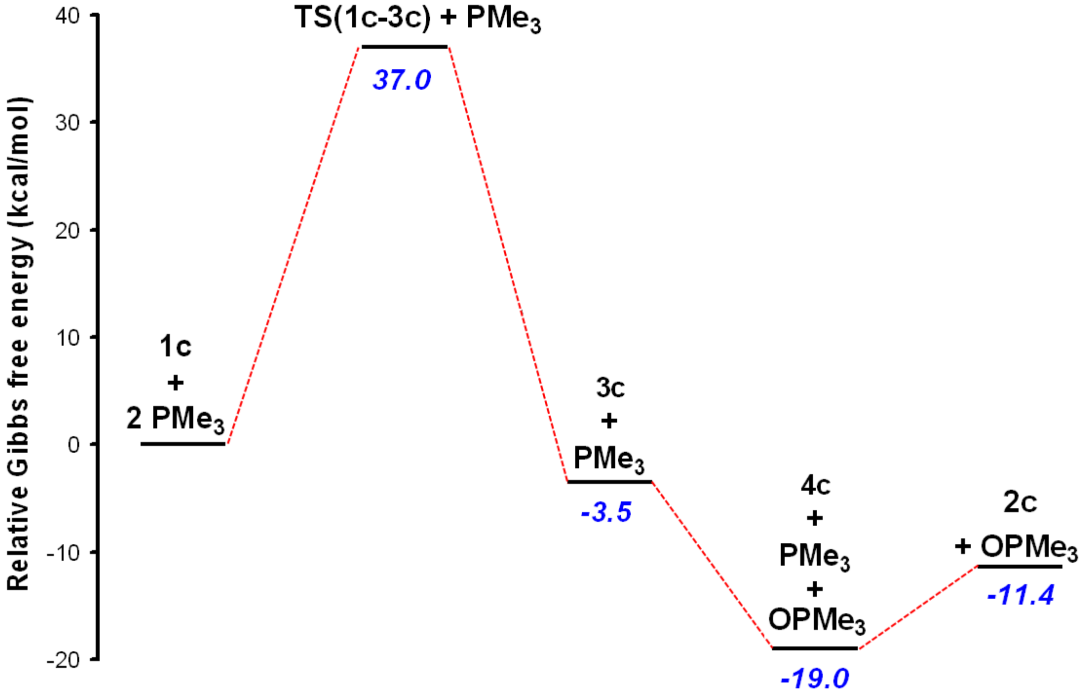
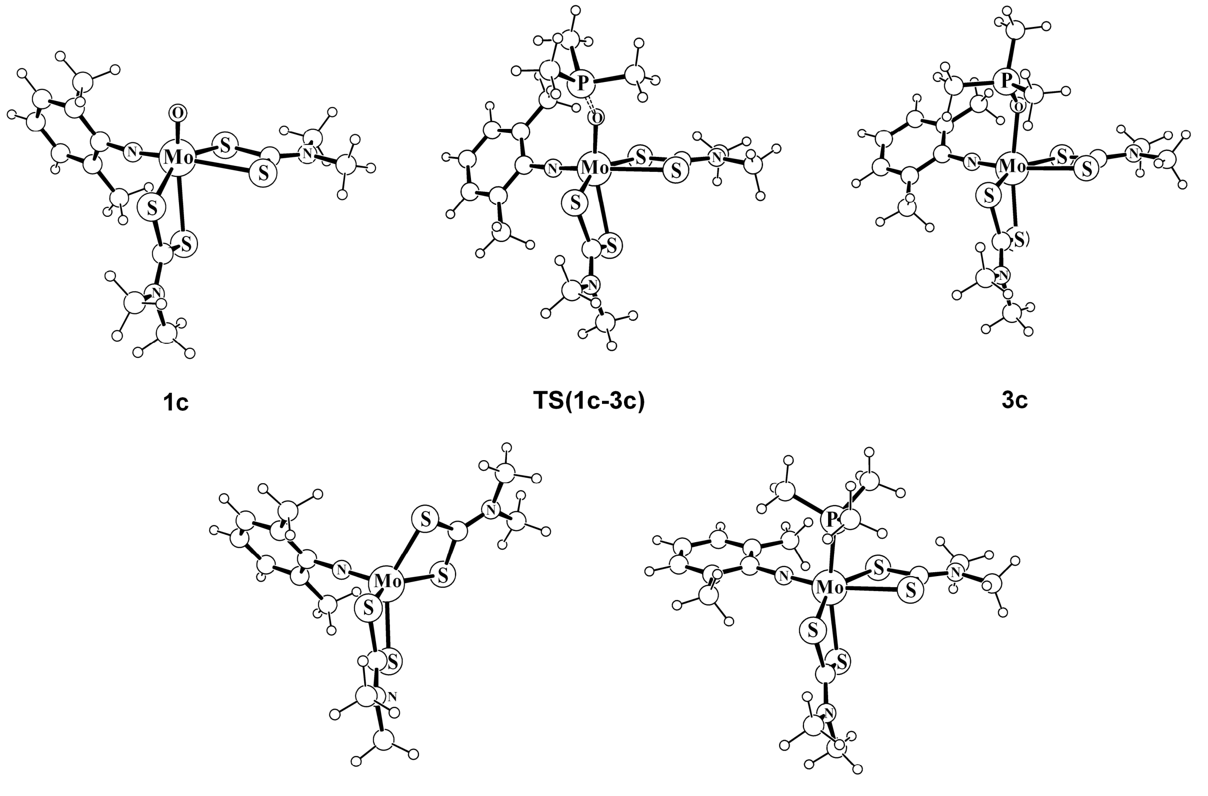


Fig. 1 Reaction profile for the oxido transfer reaction to PMe_3 of $[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$ complex and the following ligand substitution (relative Gibbs free energy in kcal·mol^{-1}).

The first step is the nucleophilic attack of PMe_3 to a molecular orbital π* Mo=O, roughly perpendicular to the moiety [Mo(O)(N-2,6-$Me_2C_6H_3$)]. The resulting transition state **TS(1c-3c)** shows an elongated Mo=O bond (1.863 versus 1.718 Å in **1c**) and the phosphane approaching to this oxygen atom (1.929 Å) (see Fig. S1 in supplementary data). Similar structural parameters were found in the calculations of the transition state for the [$Tp^{iPr}Mo(O)_2(OPh)$] + PMe_3 system.[33] The asymmetry of the O-P-C angles (155.6, 95.2 and 94.2º) is evident in **TS(1c-3c)** in agreement with other related calculations.[34] The barrier for the nucleophilic attack of PMe_3 is 37.0 kcal·mol^{-1}. This value is somewhat higher than the $\Delta G^{\#}_{298}$ experimentally observed for the formation of [$Tp^{iPr}Mo(O)(OPh)(OPR_3)$][35] or [$Tp^*Mo(O)Cl(OPR_3)$][36] intermediates in acetonitrile. The transition state **TS(1c-3c)** goes forward to the intermediate **3c** in which the Mo-O bond reaches 2.278 Å and the phosphane is definitively bonded to the oxygen atom (1.525 Å). In the intermediate **3c** the $OPMe_3$ ligand is now produced, as occurred in complex [$Tp^*Mo(O)Cl(OPMe_3)$],[31] with similar Mo-$OPMe_3$ and O-P distances. In particular, the Mo-O-P angle of 128.7º is analogous to the complex [$Tp^{iPr}Mo(O)(OPh)(OPEt_3)$] (experimental,[30b] 130.9º; calculated,[37] 128.5º). The formation of the final product is produced by substitution of the $OPMe_3$ ligand by PMe_3 in a stepwise process: dissociation of $OPMe_3$ ligand with formation of the intermediate [Mo(N-2,6-$Me_2C_6H_3$)(S_2CNMe_2)$_2$], **4c** and, then, PMe_3 coordination affording the product [Mo(N-2,6-$Me_2C_6H_3$)(S_2CNMe_2)$_2$(PMe_3)], **2c**, (Mo-P bond distance of 2.494 Å). Both, **4c** and **2c**, are Mo(IV) imido compounds in which the Mo-N bond distance is reduced (1.733 and 1.760 Å for **4c** and **2c**, respectively) in comparison with that found in **1c** for the same distance (1.780 Å). This is in agreement with the bond order increase produced by the involvement in **4c** and **2c** of an additional metal *d*-π orbital initially shared in **1c** with the oxido ligand. The overall oxido transfer reaction is exergonic (-11.4 kcal·mol^{-1}).



1c TS(1c-3c) 3c

4c 2c

Fig. 2 Structures of the intermediates and the transition state in the oxido transfer reaction to PMe_3 of $[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$ complex.

Concerning the imido transfer pathway, the reaction profile and the calculated structures of the transition state and intermediates are shown in Fig. 3 and 4, respectively. The relative Gibbs free energy reference was taken as the energy of the separate reagents. Again the first step is the nucleophilic attack of PMe_3 to a molecular orbital π* $Mo{=}N\text{-}2,6\text{-}Me_2C_6H_3$. The transition state **TS(1c-5c)** shows an elongated Mo=N bond (1.906 versus 1.780 Å in **1c**) and the phosphane approaching to the nitrogen atom (2.244 Å) (see Fig. S2 in supplementary data). In this case, the nucleophilic attack of PMe_3 shows a barrier of 39.4 kcal·mol^{-1}. From this transition state is formed the intermediate **5c** that displayed the $Me_3P{=}N\text{-}2,6\text{-}Me_2C_6H_3$ ligand N-coordinated to the metal (2.229 Å). The dissociation of this ligand is exergonic affording the intermediate $[Mo(O)(S_2CNMe_2)_2]$, **6c**. The geometrical parameters of this intermediate are comparable to those found in structurally known $[Mo(O)(S_2CNR_2)_2]$ complexes.[38] Finally, the last part of the profile is the PMe_3 coordination that yields the product $[Mo(O)(S_2CNMe_2)_2(PMe_3)]$, **7c**, with a

Mo-P bond distance of 2.515 Å. The PMe_3 association, from **6c** to **7c**, is an endergonic step by 10.2 kcal·mol^{-1} (7.6 kcal·mol^{-1} for the related **4c** to **2c** transformation) and this theoretical result actually corroborates a related previous experimental observation. In fact, complex $[Mo(O)(S_2CNEt_2)_2(PMe_3)]$, reported by some of us,[39] readily loses PMe_3 in solution to give $[Mo(O)(S_2CNEt_2)_2]$ and the synthesis of the phosphane adduct requires the presence of an excess of PMe_3. The Mo(IV) oxido compounds, **6c** and **7c**, show Mo-O bond distances (1.680 and 1.696 Å for **6c** and **7c**, respectively) that are lower than that found in **1c** for the same distance (1.718 Å). As stated before for the imido-molybdenum(IV) complexes, this fact agrees with the bond order increase produced by the involvement in **6c** and **7c** of an additional metal *d*-π orbital, initially shared in **1c** with the imido ligand. The overall imido transfer reaction is slightly endergonic (1.2 kcal·mol^{-1}).

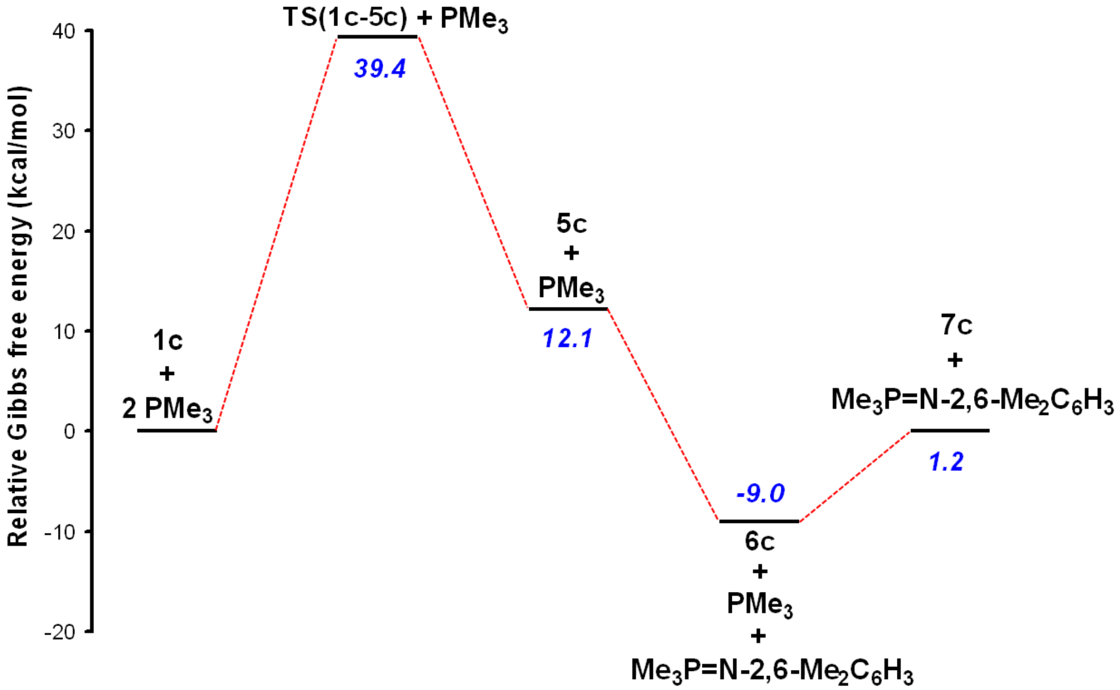
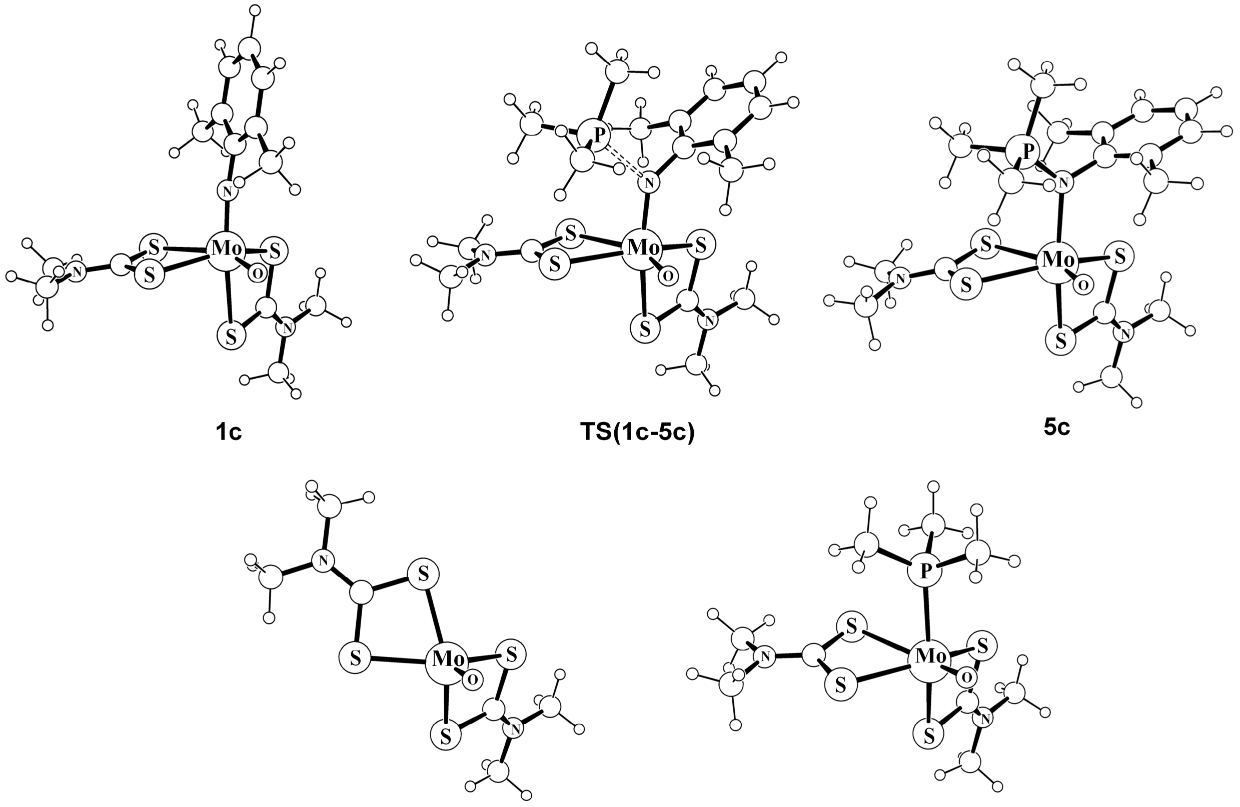


Fig. 3 Reaction profile for the imido transfer reaction to PMe_3 of $[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$ complex and the following ligand substitution (relative Gibbs free energy in kcal·mol^{-1}).

The comparison of the profiles shown in Figs. 1 and 3 clearly demonstrates that the oxido transfer is kinetically (lower energy barrier for the transition state **TS(1c-3c)** with respect to **TS(1c-5c)**) and thermodynamically favoured (overall exergonic reaction for the formation of **2c**, -11.4 kcal·mol^{-1}, *versus* overall endergonic reaction for the formation of **7c**, 1.2 kcal·mol^{-1}) with respect the imido transfer, in agreement with the experimental results. Another point of interest is the specific contrast of the oxido and the imido transfer steps, namely the transformation of **1c** into **3c** or **5c**, respectively. For the oxido transfer the process for the formation of **3c** is exergonic, -3.5 kcal·mol^{-1}, whereas the imido transfer step that affords **5c** is significantly endergonic, 12.1 kcal·mol^{-1}. This may suggest an insufficient lifetime of the intermediate **5c**, which may prevent further chemical evolution to the final product **7c**. In fact, the reverse reaction, from **5c** to **1c**, would be exergonic by -12.1 kcal·mol^{-1} with a lower energy barrier of 27.3 kcal·mol^{-1}.



1c **TS(1c-5c)** **5c**

6c **7c**

Fig. 4 Structures of the intermediates and the transition state in the imido transfer reaction to PMe_3 of $[Mo(O)(N\text{-}2,6\text{-}Me_2C_6H_3)(S_2CNMe_2)_2]$ complex.

In order to elucidate if steric hindrance has importance in the imido transfer step, the profile shown in Fig. 3 was calculated again for the [Mo(O)(NPh)(S_2CNMe$_2$)$_2$] model complex, **1d**, with the phenyl imido substituent. For the imido transfer process, the results established a diminution of the energy barrier for the new transition state **TS(1d-3d)** of 1.4 kcal·mol^{-1} (see Fig. S3 in the supplementary data and Table S2), which confirmed the weight of steric features in the transfer reaction. Obviously, the most important difference between the isoelectronic oxido and imido functionalities is the diverse steric requirements. The phosphane entering group could have steric conflicts with the aryl substituent of the imido ligand and, consequently, the imido transfer reaction would be more impeded than the analogous oxido transfer from a steric point of view.

4. Conclusions

In summary, the reaction of [Mo(O)(Nmes)(S_2CNR$_2$)$_2$] complexes with PMe$_3$ occurs with a selective oxygen atom transfer reaction with formation of [Mo(Nmes)(S_2CNR$_2$)$_2$(PMe$_3$)] compounds and the corresponding phospane oxide OPMe$_3$. The oxido transfer is thermodynamic and kinetically favoured with respect the imido transfer according to DFT calculations carried out with the model compound [Mo(O)(N-2,6-Me$_2$C$_6$H$_3$)(S_2CNMe$_2$)$_2$] and PMe$_3$ as reactant. In this system in which both functionalities are simultaneously coordinated to the molybdenum center, the nucleophilic attack of PMe$_3$ to the multiple bonded atom is favoured for the oxido group with respect the imido ligand. The significance of the crowding of the metal surroundings in such a process is demonstrated by the calculations carried out with the model compound [Mo(O)(NPh)(S_2CNMe$_2$)$_2$] in which the imido ligand is less encumbered.

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Appendix A. Supplementary data

Major component of the imaginary frequencies found in the transition states, coordinates and structures of the optimised compounds. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/...

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Oxido- versus imido- transfer reactions in oxido-imido molybdenum(VI) complexes: a combined experimental and theoretical study

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GRAPHICAL ABSTRACT

Selective oxido transfer reaction to PMe_3 from oxido-imido molybdenum(VI) compounds $[Mo(O)(N\text{-}2,4,6\text{-}C_6H_2Me_3)(S_2CNR_2)_2]$ was observed without evidence of imido transfer. The oxido transfer was calculated to be thermodynamic and kinetically favoured with respect the imido one in agreement with the experimental results.