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Ligand exchange processes between molybdenum and zinc additives in lubricants: evidence from NMR (^{1}H, ^{13}C, ^{31}P) and HPLC-MS analysis†

Yu Min Kiw,[ab] Philippe Schaeffer,[a] Pierre Adam,*[a] Benoît Thiébaut,[b] Chantal Boyer[b] and Géraldine Papin[b]

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The tribological performances of engine oils have been shown to be enhanced by the synergistic interactions between Mo dithiocarbamates ($Mo(DTC)_2$) with other additives, and notably Zn dithiophosphates ($Zn(DTP)_2$). Being two key components in formulated lubricants, a detailed understanding of the mechanisms involved between these two types of additives is needed to develop engine oils with enhanced friction reduction performances, and improved fuel economy. In this context, we report here the investigation at the molecular level of the interactions between Mo and Zn complexes with DTC and DTP ligands using laboratory experiments. Our analytical approach comprised NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) allowing direct investigation of both homoleptic and heteroleptic Mo and Zn complexes as well as a specifically-developed HPLC-MS method for the investigation of the different DTC species formed during lubricant ageing experiments. The results showed that ligand exchange reactions between $Mo(DTP)_2$ and $Zn(DTC)_2$ complexes strongly favor the migration of the DTC ligands from Zn to Mo, illustrating the higher affinity of Mo for DTC ligands. In the case of binary mixtures involving $Mo(DTC)_2$ and $Zn(DTP)_2$ – a combination of additives frequently used in formulated lubricants – the formation of mixed complexes (Mo(DTC)(DTP)) resulting from ligand exchange reactions could be directly evidenced for the first time by the analytical methods used. These species could account, at least to some extent, for the synergistic effect of $Mo(DTC)_2$ and $Zn(DTP)_2$ on the friction reducing properties of engine oils. However, they were formed in significantly lower proportions than those previously reported in the literature using indirect methods.

1. Introduction

With the latest introduction of new motor oil specifications, automotive manufacturers, transportation companies and lubricant industries are constantly searching for new lubricant formulations or additional engine oil characteristics to meet the needs of the new engine tests. Two general methods used to improve fuel economy are the reduction of lubricant viscosity and the incorporation of appropriate friction modifiers. Among the latter,[1] organomolybdenum compounds such as molybdenum dialkyldithiocarbamates ($Mo(DTC)_2$) are able to generate a thin film of molybdenum disulfide (MoS_2) with low shear strength between the rubbing surfaces as a result of chemical transformations,[2–4] and have also proved to be substantially effective in lowering boundary frictions.[5–7]

However, upon oil ageing, molybdenum additives undergo oxidative decomposition that leads to a significant drop in their tribological performances in the lubrication systems.[8–13] According to Jensen *et al.*[12] and Arai *et al.*,[13] the loss of $Mo(DTC)_2$ additives could be attributed to their thermo-oxidative degradation during oil oxidation upon engine functioning. Igarashi *et al.*[11] also suggested that the accumulation of oil oxidation products could inhibit the formation of the MoS_2 tribofilm, thus reducing the tribological performances of the oil. Given the presence of metallic parts in the engines which can act as effective oxidation catalysts, internal combustion engines can be considered as chemical reactors that are able to catalyze the oxidation processes. Therefore, engine oils are more prone to oxidation than lubricants used in other applications.

Since $Mo(DTC)_2$ complexes decompose easily and hence loose their functionality during engine oil oxidation over time, investigation of the mechanisms of action of $Mo(DTC)_2$ in the presence of other additives in oil, as well as the study of factors that can potentially increase their functional lifespan during engine operation are necessary in order to achieve substantial improvements of friction reduction and fuel economy of engine oils. Therefore, it is of importance to understand the nature of

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[a] *University of Strasbourg, CNRS, Institut de chimie de Strasbourg, UMR 7177, F-67000 Strasbourg, France. E-mail: padam@unistra.fr*

[b] *TOTAL Solaize Research Center, BP22-69360 Cedex, France*

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the interactions between molybdenum compounds and other additives, which can have either synergistic or antagonistic effects. Previous investigations have indeed shown the importance of adding other additives to the oil blend in order to reduce the loss rate of molybdenum compounds during ageing, thereby extending their useful life as efficient friction modifiers.[14,15] In this respect, Minami *et al.*[16] and Greene *et al.*[17] reported that the addition of sulfur-containing additives improved the friction reducing properties of molybdenum compounds, and interactions between molybdenum and zinc derivatives were notably found to be extremely important with regard to fuel efficiency improvement[15] and to lifespan extension of Mo(DTC)$_2$ additives.[3] Particularly, the combination of Mo(DTC)$_2$ and zinc dithiophosphates (Zn(DTP)$_2$) was proved to show synergistic effects on the friction reducing properties of engine oils.[18–25]

According to the literature, ligand exchange reactions occur when Mo(DTC)$_2$ and Zn(DTP)$_2$ are mixed, resulting in the formation of mixed molybdenum and zinc complexes with all possible combinations of dithiophosphate and dithiocarbamate ligands.[12,26–29] These reactions are believed to activate the transformation of Mo(DTC)$_2$ to form the MoS$_2$ tribofilm on the rubbing surfaces.[2,30,31] Other authors have, however, reported that Mo(DTC)$_2$ complexes demonstrate a better capacity than Mo(DTP)$_2$ complexes to generate MoS$_2$ at the tribocontact and thus showed a better friction reducing ability,[32] suggesting that enhanced capacity to form MoS$_2$ films using mixtures of Mo(DTC)$_2$ and Zn(DTP)$_2$ does not exclusively result from ligand exchange reactions between Mo and Zn complexes. Yagashita *et al.*[29] have investigated ligand exchange reactions between Mo(DTC)$_2$ and Zn(DTP)$_2$ and concluded that the equilibrium was strongly in favor of Mo(DTC)$_2$ and Zn(DTP)$_2$ and that Mo(DTP)$_2$, Zn(DTC)$_2$ and related complexes with mixed ligands were formed only to a very limited extent. Nevertheless, the method used to evaluate these ligand exchange reactions was not described with further details. Jensen *et al.*[12] have documented that the ligand exchange reactions between Mo(DTC)$_2$ and Zn(DTP)$_2$ lead to the formation of Mo(DTP)$_2$ and Zn(DTC)$_2$, the formation of mixed derivatives being favored at high temperatures (160 °C) and enhanced in lubricants which have undergone thermooxidative alteration. However, the methods used by these authors to evaluate these exchange reactions were circumstantial (see Discussion section). Important ligand exchanges between Mo(DTC)$_2$ and Zn(DTP)$_2$ were also reported to occur at lower temperatures (80 °C) and appeared to be very sensitive to the polarity of the solvent used according to Shea *et al.*[27]

In this context, we have re-investigated the possibility and extent of ligand exchange reactions between molybdenum and zinc complexes of dialkyldithiocarbamates and dialkyldithiophosphates (Fig. 1) using an analytical approach involving NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) and HPLC-MS analysis. Since molybdenum and zinc derivatives are both key components used in engine oils, investigation at the molecular level of the underlying mechanisms of interactions between these compounds will be beneficial for the future improvement of energy-conserving lubricant formulations.

2. Experimental section

2.1. Materials (base oil and additives)

The commercial mineral base oil used in this work was provided by Total Marketing & Services. The chemical structures of the Mo and Zn complexes used and/or discussed in this study are shown in Fig. 2. The additives Mo(DTC)$_2$ **2a–2c** (Sakuralube 525), Mo(DTC)$_2$ **2d** (Sakuralube 600) and Mo(DTP)$_2$ **1** (Sakuralube 400) were purchased from Adeka, whereas Zn(DTP)$_2$ **4a–4d** were purchased from Infineum. Sakuralube 525 comprises a mixture of Mo(DTC)$_2$ **2a–2c** whereas Sakuralube 600 is a pure compound corresponding to Mo(DTC)$_2$ **2d** (Fig. 2). Mo(DTP)$_2$ **1** (Sakuralube 400) and Zn(DTP)$_2$ **4a** correspond to primary dithiophosphate complexes with C$_8$ (ethylhexyl) alkyl chains. Secondary Zn(DTP)$_2$ additives were purchased as a mixture of compounds **4b–4d** with C$_3$ and C$_6$ alkyl chains. Purchased

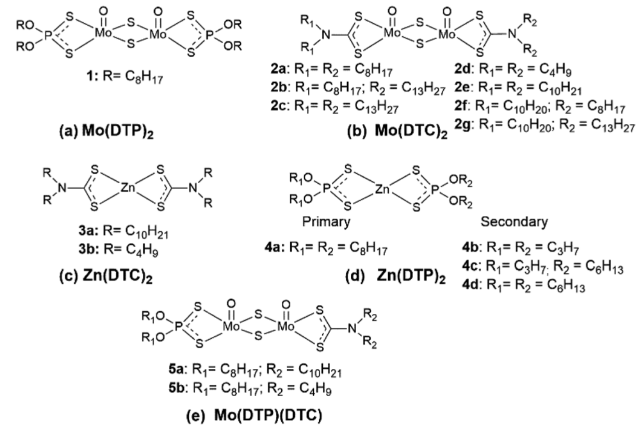

Fig. 2 Chemical structures of lubricant additives cited in this work. (a) Molybdenum dithiophosphates Mo(DTP)$_2$; (b) molybdenum dithiocarbamates Mo(DTC)$_2$; (c) zinc dithiocarbamates Zn(DTC)$_2$; (d) primary and secondary alkyl zinc dithiophosphates Zn(DTP)$_2$; (e) Mo complexes with mixed dithiophosphate and dithiocarbamate ligands Mo(DTP)(DTC).

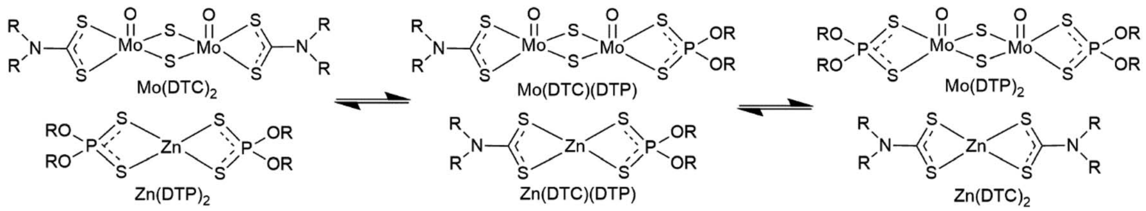

Fig. 1 Ligand exchange reactions between Mo(DTC)$_2$ and Zn(DTP)$_2$ (adapted from Jensen *et al.*[12]).

compounds were used without any further purification except for the compounds **1** and **4a** which were purified by chromatography on a silica gel column prior NMR measurements in order to remove the hydrocarbon base oil and polar constituents (see Section 2.2.). Zn bis(di-*n*-decyldithiocarbamate) **3a** was synthesized according to a published procedure (see Section 2.3.).[33]

2.2. Purification of compounds 1 and 4a

An aliquot of the commercial additive containing compound **1** (respectively compound **4a**) was fractionated on a silica gel column using CH_2Cl_2 as eluent yielding, respectively, fraction F1 (1.2 dead volumes) containing the hydrocarbon base oil and a more polar fraction F2 (2 dead volumes) containing compound **1** (respectively compound **4a**).

2.3. Synthesis of Zn bis(di-*n*-decyldithiocarbamate) 3a

An heterogeneous mixture containing didecylamine (4.00 g, 13.44 mmol) and sodium hydroxide (811 mg, 14.45 mmol) in 11 mL of water was stirred with a magnetic stirrer at 10 °C for 10 min. Carbon disulfide (1.30 mL, 1.64 g, 21.50 mmol) was then added dropwise at 30 °C during 1 h followed by addition of 16 mL of water. Stirring was continued for 2 h, after which a solution of zinc chloride (1.39 g, 10.20 mmol) in water (6 mL) was slowly added at 40 °C in the course of 1 h. After stirring for a further 3.5 h, the reaction mixture was cooled down to room temperature and filtered using a Büchner funnel to recover the solid material formed. The yellowish solid obtained was dried under vacuum for a few hours at room temperature and subsequently filtered through silica gel using dichloromethane as eluent to get rid of the salts formed during the reaction. After removal of the solvent under reduced pressure, Zn bis(di-*n*-decyldithiocarbamate) **3a** was obtained as a white solid in 58% yield (purity > 95%; see ^{1}H- and ^{13}C-NMR in ESI Fig. 5S†).

^{1}H-NMR (500 MHz; $CDCl_3$): 3.75 (t, $J = 7.8$ Hz, 8H), 1.80–1.70 (m, 8H), 1.34–1.22 (m, 56H), 0.88 (t, $J = 6.9$ Hz, 12H). ^{13}C-NMR (125 MHz; $CDCl_3$): 202.6, 55.1, 32.0, 29.7, 29.6, 29.4, 29.4, 27.0, 26.93, 22.8, 14.3. Probe-MS (EI, 70 eV): *m*/*z* (relative intensity) 812 (M^+, 9%), 810 (15), 808 (16), 775 (12), 436 (14), 372 (7), 340 (57), 308 (100).

2.4. Oil thermal ageing experiments

Thermal ageing experiments were carried out on lubricants using 50 g of hydrocarbon base oil samples containing molybdenum or/and zinc additives (1 weight%) at 135 °C under a stream of argon (100 mL min^{-1}) in a multi-necked round-bottomed flask for the following studies:

– Thermal stability of $Mo(DTC)_2$ **2a–2c** at 135 °C.

– Ligand exchange reactions between $Mo(DTC)_2$ **2a–2c** and $Zn(DTC)_2$ **3a**.

Oil samples (1 mL aliquots) were collected over a period of 16–18 hours at 1 h intervals through a septum using a syringe for HPLC-MS qualitative and quantitative analysis. The first sample (defined as $T = 0$ h) was collected when the oil-additive mixture reached 135 °C.

2.5. Investigation of ligand exchange reactions using HPLC-MS

Each sample from oil thermal ageing experiments was prepared as follows: 20 μL of internal standard (2,3-bis(*n*-octadecyloxy) propan-1-ol; 1.7 mg mL^{-1}) were added to an aliquot (20 mg) of each collected sample (1 mL) diluted in 1 mL of solvent (*n*-heptane/isopropanol: 95/5). The sample was then diluted by 10-fold in the same solvent before being analysed by HPLC-MS. Quantification of a given $Mo(DTC)_2$ homologue was performed by integrating the area of the peak on the sum of the mass chromatograms corresponding to the pseudo-molecular ions $[M + H]^+$ of the various Mo isotopologues of this compound (between ^{92}Mo and ^{100}Mo) (*cf.* ESI Fig. 1S† for the mass spectra and extracted ion chromatogram of **2a–2c**) and comparison with the area of the internal standard. Absolute response factors have not been determined for the different $Mo(DTC)_2$ complexes. Concentration calibration curves have been established for compounds **2a–2c** and were shown to be linear ($R^2 > 0.97$) in the range 0–2000 ng per injection (*cf.* ESI Fig. 2S†). Complexes with DTP ligands including $Mo(DTP)_2$ **1** and $Zn(DTP)_2$ **4a–4d** could not be detected with our HPLC-MS method.

2.6. Investigation of ligand exchange reactions using NMR

Ligand exchange reactions were performed in NMR glass tubes using $CDCl_3$ as solvent for the experiments at 25 °C, and D_8-toluene for the experiments at 105 °C. The full ^{1}H- and ^{13}C-NMR spectra at 25 °C of the 4 substrates **1**, **2d**, **3a** and **4a** used for these experiments are presented in ESI Fig. 3S–6S.† The partial ^{1}H-NMR spectra (3.0–5.0 ppm) at 105 °C of the 4 substrates **1**, **2d**, **3a** and **4a** are presented in ESI Fig. 7S† and the ^{31}P-NMR spectra at 25 °C of **1** and **4a** are shown in ESI Fig. 8S.† The conditions related to the different ligand exchange experiments performed are listed in Table 1.

2.7. High pressure liquid chromatography-mass spectrometry (HPLC-MS)

Samples were analysed by HPLC-MS using an Agilent HP 1100 series instrument equipped with an auto-injector, and connected to a Bruker Esquire 3000+ ion trap mass spectrometer. A Chemstation chromatography manager software (HPLC) and a Bruker Data Analysis software (MS) were used. Separations were achieved on a Zorbax SIL 5 μm column (Agilent, 4.6 × 250 mm) at 30 °C. The sample injection volume was set at 10 μL. Compounds were eluted with a flow rate of 0.4 mL min^{-1} in isocratic mode using *n*-heptane/isopropanol: 98.5 : 1.5 v/v as the mobile phase. The mass spectrometer was equipped with an atmospheric pressure photoionization source (APPI) used in the positive ion mode. Conditions for MS analyses were: nebulizer pressure 50 psi, APPI temperature 420 °C, drying temperature 350 °C, drying gas (N_2) flow 5 L min^{-1}, capillary voltage −2 kV, corona 4 μA, scan range *m*/*z* 400–2000. HPLC-MS analyses were performed in triplicate for each sample collected except for the experiment dealing with the investigation of the thermal

Table 1 Molar ratios of the different authentic additives and temperature conditions used for the NMR (^1H, ^{13}C, ^{31}P) investigation of ligand exchange reactions involving molybdenum and zinc DTP/DTC complexes

Substrates	Molar ratio	Temperature
$Zn(DTC)_2$ **3a**/$Zn(DTP)_2$ **4a**	1 : 1	−80 °C, −40 °C, −10 °C, 25 °C, 105 °C
$Mo(DTP)_2$ **1**/$Zn(DTC)_2$ **3a**	4 : 1	25 °C, 105 °C
	1 : 1	25 °C, 105 °C
$Mo(DTC)_2$ **2d**/$Zn(DTP)_2$ **4a**	1 : 4	25 °C, 105 °C
	2 : 1	25 °C, 105 °C

stability of $Mo(DTC)_2$ additives **2a–2c** at 135 °C under argon (see Section 3.2.1.).

2.8. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were recorded on a Bruker Avance I 500 MHz spectrometer (500 MHz for ^1H; 125 MHz for ^{13}C; 202 MHz for ^{31}P) or on a Bruker Avance I 300 MHz spectrometer (121 MHz for ^{31}P) for NMR measurements at 25 °C and on a Bruker Avance III 400 MHz spectrometer (400 MHz for ^1H; 100 MHz for ^{13}C; 162 MHz for ^{31}P) for NMR measurements at 105 °C. The ^1H- and ^{13}C-chemical shifts are reported in ppm relative to tetramethylsilane with the residual protons and carbon atoms of the solvent used as internal standards ($CDCl_3$: δ^1H 7.26 ppm; $\delta^{13}C$ 77.2 ppm; D_8-toluene: δ^1H 7.09, 7.00, 6.98, 2.09 ppm; $\delta^{13}C$ 129.2, 128.3, 125.5, 20.4 ppm). The coupling constants (J) are expressed in Hertz (Hz). $CDCl_3$ and D_8-toluene were used for measuring NMR spectra at 25 °C and 105 °C, respectively, on 5–10 mg of molybdenum or zinc complexes diluted in *ca.* 0.8 mL solvent.

3. Results

3.1. ^1H, ^{13}C and ^{31}P NMR investigation of ligand exchange reactions between Mo and Zn dithiocarbamate and dithiophosphate complexes

DTC/DTP ligand exchange reactions between molybdenum and zinc complexes were investigated using ^1H, ^{13}C and ^{31}P NMR spectroscopy at 25 °C and 105 °C (Table 1). The authentic additives $Mo(DTP)_2$ **1**, $Mo(DTC)_2$ **2d**, $Zn(DTC)_2$ **3a** and $Zn(DTP)_2$ **4a** (Fig. 2) were used as substrates. Three types of experiments were performed, involving either a mixture containing $Zn(DTC)_2$ **3a** and $Zn(DTP)_2$ **4a**, a mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** or a mixture of $Mo(DTC)_2$ **2d** and $Zn(DTP)_2$ **4a** at different relative molar ratios (Table 1). In the experiments with **1** + **3a** or **2d** + **4a**, symmetrical complexes as well as related complexes with mixed dithiocarbamate and dithiophosphate ligands were expected to be formed (*cf.* Fig. 1).

The ^1H chemical shifts at 25 °C of the protons on methylene groups adjacent to the functional groups (α-OP or α-N) of the substrates are all in the 3.5–4.5 ppm range (Fig. 3) and clearly allow the various types of homoleptic complexes likely to occur during the ligand exchange reactions (*i.e.* $Mo(DTP)_2$, $Mo(DTC)_2$, $Zn(DTC)_2$ and $Zn(DTP)_2$) to be distinguished. For symmetry reasons, the 4 methylene groups adjacent to the functional groups of $Zn(DTC)_2$ **3a** (resp. $Zn(DTP)_2$ **4a**) have the same chemical shift and only 1 signal is observed for these protons at 3.75 ppm for **3a** (resp. 4.07 ppm for **4a**). In the case of $Mo(DTC)_2$ **2d**, a complex signal at 3.90 ppm is observed for the protons of the 4 methylene groups α to the functional groups due to the fact that the 2 protons at each methylene group are diastereotopic (related to the axial chirality of $Mo(DTC)_2$ complexes). In the case of $Mo(DTP)_2$ **1**, the two ligand alkyl chains are located below and above the "median plane" of the $Mo_2O_2S_6$ core of the molecule and are therefore not equivalent. Consequently, 2 signals at 3.78 and 4.49 ppm are observed for the methylene groups α to the functional groups.

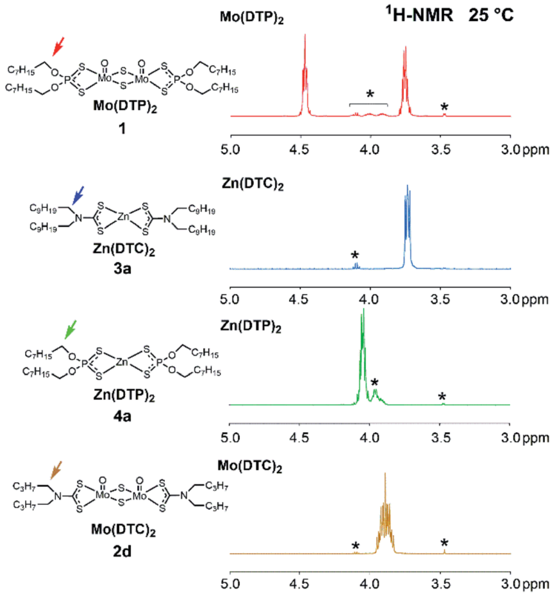

Fig. 3 Partial ^1H-NMR spectra (3.0–5.0 ppm, 500 MHz, $CDCl_3$, 25 °C) of the reference additives **1**, **2d**, **3a** and **4a** used to investigate DTC/DTP ligand exchange reactions. *: Impurities.

The NMR spectra of Mo and Zn complexes bearing mixed ligands (*i.e.*, Mo(DTC)(DTP) and Zn(DTC)(DTP)), which are potential intermediates formed in reactions involving Mo and Zn complexes, are however more difficult to obtain, since these compounds can probably not be isolated as pure compounds due to ligand exchange reactions (*i.e.*, equilibrium between all possible homoleptic and heteroleptic complexes). The ^1H, ^{13}C and ^{31}P chemical shifts of DTP ligands bound to Mo (resp. Zn) mixed complexes are expected to be very close to those of DTP ligands on $Mo(DTP)_2$ (resp. $Zn(DTP)_2$) complexes. However, small differences may affect, notably, the chemical shifts of the phosphorus atom, the methylene protons and the carbon atoms located α to the oxygen atom from DTP bound to a Mo complex, allowing DTP from homo- and heteroleptic Mo complexes to be distinguished. The same holds for the chemical shifts of ^{1}H and ^{13}C from DTC ligands from Mo and Zn complexes.

Therefore, in order to investigate specifically the ^{1}H, ^{13}C and ^{31}P chemical shifts of ligands from mixed complexes and to test whether the occurrence of these complexes can be detected and eventually quantified using NMR spectroscopy during ligand exchange reactions, experiments postulated to favour the formation of such mixed complexes were performed. To this aim, the evolution over time of a mixture of Zn(DTP)$_2$ **4a** and Zn(DTC)$_2$ **3a** in a 1 : 1 molar ratio postulated to lead to the formation of mixed Zn(DTC)(DTP) complexes was investigated by ^{1}H, ^{13}C and ^{31}P NMR in CDCl$_3$ at 25 °C. Similarly, an experiment likely to yield Mo(DTC)(DTP) complexes, for which Mo(DTP)$_2$ **1** and Zn(DTC)$_2$ **3a** were mixed in a 4 : 1 molar ratio, was carried out in CDCl$_3$ at 25 °C in order to detect the chemical shifts of the mixed complex formed. Since the affinity of DTC has been shown to be greater for Mo than for Zn (*e.g.* Yagashita and Igarashi[29]), transfer of the DTC ligands from Zn to Mo has been postulated to occur to a significant extent. However, in the latter experiment, the formation of the mixed Mo(DTP)(DTC) complex **5a** was anticipated along with the formation of Mo(DTC)$_2$ **2e**, since Mo(DTP)$_2$ **1** was present in a higher molar abundance.

3.1.1. Ligand exchange experiments involving Zn(DTP)$_2$ and Zn(DTC)$_2$. If not kinetically inhibited, a mixture of Zn(DTC)$_2$ **3a** and Zn(DTP)$_2$ **4a** in a 1 : 1 molar ratio should result in the formation of the mixed Zn(DTC)(DTP) complex. The ^{1}H-NMR spectrum of the mixture after 1 h at 25 °C displayed the typical signals of the two substrates and, notably, the signal at 3.75 ppm and 4.07 ppm corresponding to the protons from the methylene groups adjacent to the functional groups (α-OP or α-N), respectively (Fig. 4a). No additional signals likely to correspond to methylene groups of DTC or DTP ligands from the mixed complex could be detected even after 24 h of reaction. Similarly, only one signal at 96.0 ppm could be detected in the ^{31}P-NMR spectrum of the mixture (Fig. 4b) whereas one would expect specific additional P signals related to the newly-formed mixed species to appear. The same experiment was also performed in D$_8$-toluene at 105 °C and, again, only the signals corresponding to the substrates in the ^{1}H- and ^{31}P-NMR spectra could be detected. These results could be explained by an extremely slow kinetic of the ligand exchange reaction, by the fact that the exchange is not thermodynamically favoured, or because the chemical shifts of ^{1}H and ^{31}P of the DTC and DTP ligands in the mixed complex have exactly the same values as in the symmetrical Zn complexes. Alternatively, in the ^{31}P- and ^{1}H-NMR spectra of the mixture, it can be envisaged that only 1 signal was observed for P and 1 signal for the ^{1}H from the methylene groups adjacent to N or O due to the fact that the ligand exchange reaction is a rapid process on the NMR time scale.

In this respect, it should be noted that Harrison *et al.*[34] have shown that Zn(DTP)$_2$ complexes in solution exist as a mixture of monomers and dimers in equilibrium (Fig. 5a), but these various types of DTP ligands cannot be resolved by NMR at room temperature because the exchange between the different forms of complexes is too rapid on the NMR time scale. These forms can, however, be revealed by ^{31}P-NMR measurements at low temperatures. A similar situation might occur with the mixture of Zn(DTC)$_2$ **3a** and Zn(DTP)$_2$ **4a** in which several complexes, comprising the monomer and dimer complexes related to Zn(DTP)$_2$ reported by Harrison *et al.*[34] likely co-exist, but also analogous structures for which DTP ligands are replaced by DTC ligands.

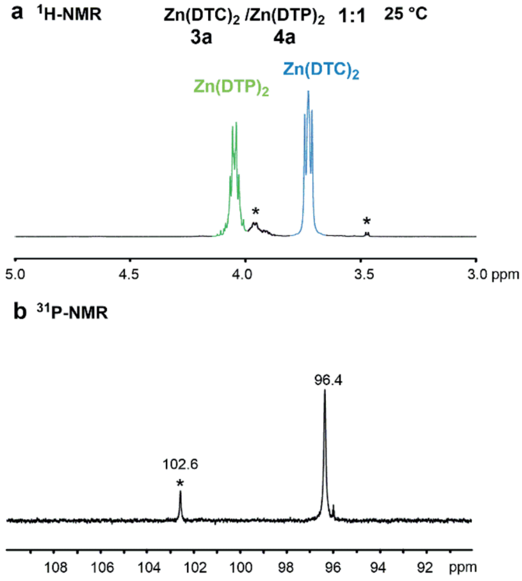

Fig. 4 Partial NMR spectra (CDCl$_3$, 25 °C) of a mixture of Zn(DTC)$_2$ **3a** and Zn(DTP)$_2$ **4a** in a 1 : 1 molar ratio after 1 h reaction. (a) ^{1}H-NMR spectrum (3.0–5.0 ppm, 500 MHz); (b) ^{31}P-NMR spectrum (90–110 ppm, 121 MHz). Green colour: Zn(DTP)$_2$, blue colour: Zn(DTC)$_2$ (*cf.* Fig. 3). *: Impurities.

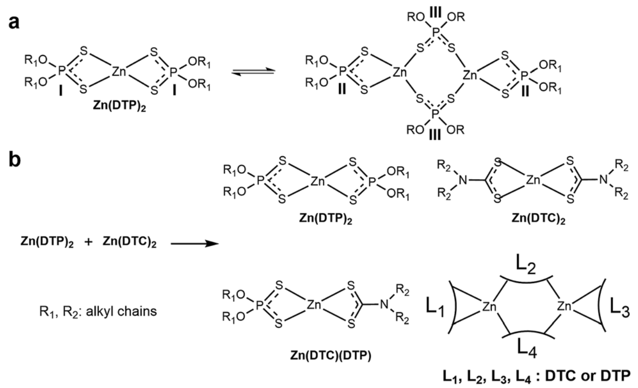

Fig. 5 (a) Monomeric and dimeric forms of Zn(DTP)$_2$ complexes in equilibrium in solution (adapted from Harrison *et al.*[34]); (b) various monomeric and dimeric complexes in equilibrium in solution formed by reaction of Zn(DTP)$_2$ with Zn(DTC)$_2$. For P atoms, at least 8 types of different chemical environments are potentially distinguishable by ^{31}P NMR. I, II, and III (a) correspond to P atoms with 3 different chemical environments distinguishable by ^{31}P-NMR at low temperature.

We have, therefore, performed temperature dependant ^{1}H- and ^{31}P-NMR measurements at −10 °C, −40 °C and −80 °C in D_8-toluene. At −80 °C, at least 6 ^{31}P-NMR signals (*vs.* 1 broad signal at *ca.* 97.4 ppm at 25 °C) were detected at 104.7, 104.4, 104.1, 103.9, 100.7, 100.3 ppm (Fig. 6), thus indicating that magnetically equivalent ^{31}P from DTP ligands at 25 °C are resolved at the low temperature of −80 °C.

The number of signals detected clearly indicates that they are not only related to the monomer and dimer complexes reported by Harrison *et al.*,[34] but most likely also comprise additional monomeric and dimeric structures for which DTP ligands are replaced by DTC ligands (Fig. 5b). Our ^{31}P-NMR investigation of the mixture of **3a** and **4a** thus clearly showed that ligand exchange reactions occur between both types of complexes at 25 °C, that both monomeric and dimeric structures exist (Fig. 5b and c) and that this exchange is a fast process on the NMR time scale.

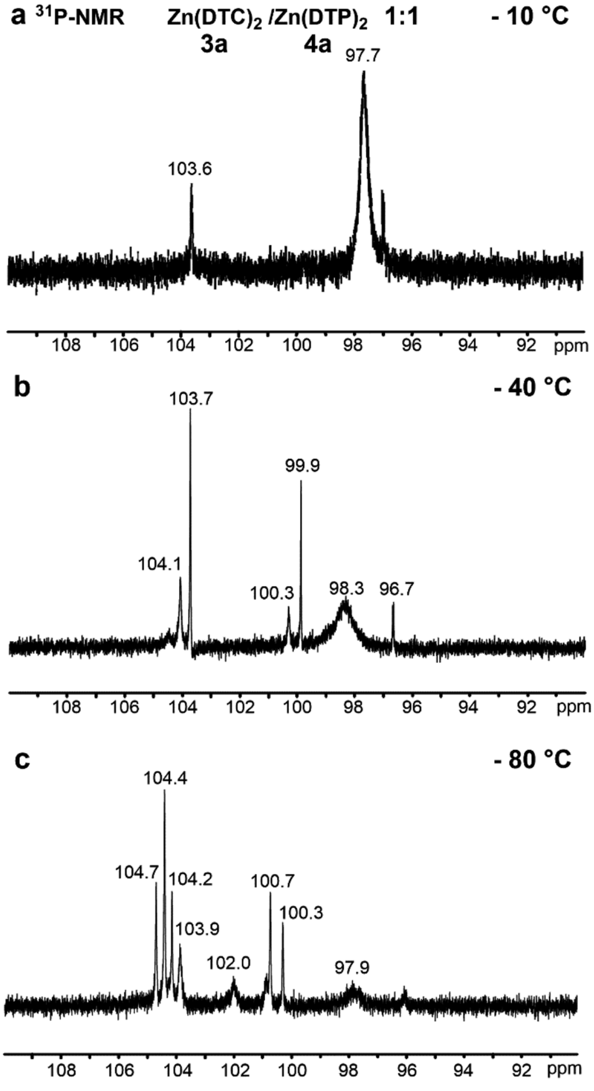

Fig. 6 Partial ^{31}P-NMR spectra (90–110 ppm, 243 MHz, D_8-toluene) of a mixture of Zn(DTC)$_2$ **3a** and Zn(DTP)$_2$ **4a** in a 1 : 1 molar ratio after 24 h at (a) −10 °C; (b) −40 °C; (c) −80 °C.

3.1.2. Ligand exchange experiments involving Mo(DTP)$_2$ and Zn(DTC)$_2$. To investigate DTC and DTP ligand exchange reactions between Mo and Zn complexes, experiments involving Mo(DTP)$_2$ **1** and Zn(DTC)$_2$ **3a** as substrates have been carried out. The substrates were mixed in a 4 : 1 and 1 : 1 molar ratio and the evolution of the two compound mixtures over time was followed by ^{1}H-, ^{13}C- and ^{31}P-NMR at 25 °C (in $CDCl_3$) and 105 °C (in D_8-toluene). Since the affinity of DTC has been suggested to be greater for Mo than for Zn (*e.g.* Yagashita and Igarashi[29]), transfer of the DTC ligands from Zn to Mo complexes was expected to occur to a significant extent. In particular, in the experiment for which **1** and **3a** were mixed in a 4 : 1 molar ratio, the formation of both Mo(DTP)(DTC) **5a** and Mo(DTC)$_2$ **2e** complexes in significant proportions along with Zn(DTP)$_2$ **4a** was anticipated.

*Mixture of **1** and **3a** in a 4 : 1 molar ratio at 25 °C and 105 °C.* The results of the ^{1}H-NMR analyses carried out on the mixture of **1** and **3a** in a 4 : 1 molar ratio after 0.5 h, 18 h and 47 h at 25 °C, focusing on the methylene protons located α of the functional groups, are shown in Fig. 7. The formation of new

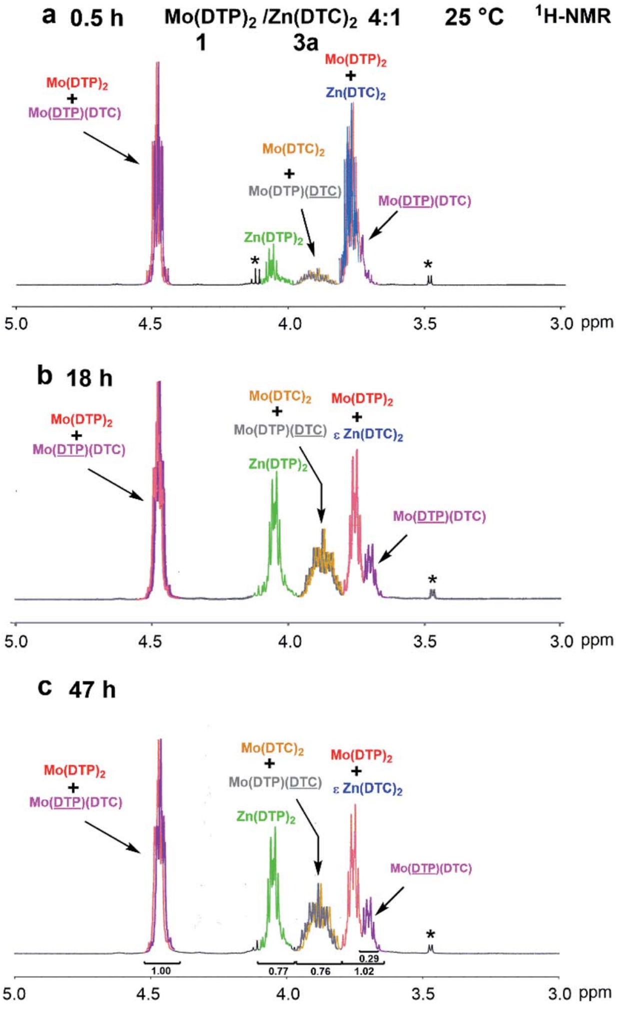

Fig. 7 Partial ^{1}H-NMR spectra (3.0–5.0 ppm, 500 MHz, $CDCl_3$, 25 °C) of a mixture of Mo(DTP)$_2$ **1** and Zn(DTC)$_2$ **3a** in a 4 : 1 molar ratio after (a) 0.5 h; (b) 18 h; (c) 47 h. *: Impurities.

compounds was already observed after 0.5 h of reaction (Fig. 7a), their relative amounts progressively increasing with time. The ^{1}H-NMR spectra obtained after 18 h and 47 h were almost identical (Fig. 7b and c), indicating that an equilibrium between the various complexes in solution was already reached after 18 h.

The formation of Mo complexes with DTC ligands comprising $Mo(DTC)_2$ **2e** and Mo(DTC)(DTP) **5a** was evidenced by the comparison between the chemical shifts of the ^{1}H-NMR spectra of the reaction mixture and of the reference compounds (Fig. 3 and ESI Fig. 3Sa–6Sa†). Indeed, the signal at 3.90 ppm (Fig. 7; orange colour) presents strong similarities (*i.e.*, comparable chemical shifts and coupling pattern) with that of the methylene groups adjacent to the nitrogen atoms of $Mo(DTC)_2$ **2d** bearing butyl alkyl chains (ESI Fig. 4Sa†).

As already mentioned, the chemical shifts of methylene protons located α to N-CS_2 bonds of DTC from homoleptic or heteroleptic Mo complexes are expected to be very close or even identical. In parallel, the formation of Zn complexes with DTP ligands was evidenced by the appearance of a signal at 4.07 ppm (Fig. 7; green colour) which is similar to that observed for protons of the methylenes adjacent to the O–P bond of the reference complex **4a** (Fig. 3 and ESI Fig. 6Sa†). Interestingly, the signals at 3.90 and 4.07 ppm have, as expected, the same integral value since to each DTP ligand on a Zn complex must correspond one DTC ligand transferred to a Mo complex. This further supports the hypothesis that protons from DTC of the mixed complex **5a** have chemical shifts almost identical to those of DTC in $Mo(DTC)_2$ **2e**. As shown by the measured integrals, this signal must indeed comprise the signals of all DTC ligands from both $Mo(DTC)_2$ **2e** and Mo(DTC)(DTP) **5a**.

The remaining signals in the ^{1}H-NMR spectrum of the mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** after 18 h and 47 h (Fig. 7b and c; red and purple colours) correspond most likely to protons located α to the O–P bonds in DTP from Mo complexes. The signals at 4.49 ppm and 3.78 ppm are identical to those detected for the $Mo(DTP)_2$ reference compound **1** (Fig. 3) and correspond to the alkyl chains of DTP ligands on both sides of the MoO_2S_6 core. The signal at 3.78 ppm (red colour) is, however, accompanied by a slightly shifted signal centred around 3.70 ppm (Fig. 7b and c; purple colour). Remarkably, the integral value of the signal at 4.49 ppm is almost identical to that corresponding to the sum of the signals at 3.78 and 3.70 ppm. On this basis, it can be proposed that the signals at 3.78 and 3.70 ppm correspond, respectively, to the protons of the methylenes adjacent to the O–P bond from the alkyl chain located below or above the "median plane" of the $Mo_2O_2S_6$ core from, respectively, $Mo(DTP)_2$ and Mo(DTP)(DTC) complexes **1** and **5a**, whereas the signal at 4.49 ppm corresponds to the superimposition of the signal from protons of the methylene groups located α to the O–P bonds from the alkyl chain located on the other side of the MoO_2S_6 core from both $Mo(DTP)_2$ and Mo(DTP)(DTC) complexes **1** and **5a**. This therefore indicates that mixed Mo complexes are indeed present in the reaction mixture and can be distinguished by ^{1}H-NMR spectroscopy. This is further supported by the interpretation of the ^{31}P-NMR spectrum which clearly showed the presence of two signals at 96.0 and 112.2 ppm corresponding to P from $Zn(DTP)_2$ and $Mo(DTP)_2$ complexes **4a** and **1**, respectively (*cf.* ^{31}P-NMR of standards, ESI Fig. 8S†), as well as a new signal at 112.8 ppm which can be ascribed to P from the mixed complex **5a** (Fig. 8a). The occurrence of the mixed Mo complex **5a** also appeared in the ^{13}C-NMR spectrum from the reaction mixture after 18 h and 47 h (Fig. 8b). Indeed, the signals corresponding to the C atoms from the methylene groups located α to the O–P bonds from $Mo(DTP)_2$ **1** (*cf.* ESI Fig. 3Sb†) on both side of the MoO_2S_6 core at 73.1 and 71.6 ppm are accompanied by two smaller signals at, respectively, 73.0 and 71.4 ppm which potentially correspond to the same carbon atoms of DTP ligands on mixed Mo(DTC)(DTP) complexes (Fig. 8b). Each signal appears as a doublet due to the presence of an asymmetric centre on the ethylhexyl alkyl chain. Our results thus clearly showed that mixed Mo(DTC)(DTP) complexes can be directly and unambiguously detected by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. Based on the values of the integrals measured for the methylene protons located α to the O–P bonds in Mo complexes, the relative proportion of $Mo(DTP)_2$ and Mo(DTP)(DTC) complexes **1** and **5a** corresponded to 55% and 45%, respectively, in the reaction mixture after 47 h.

In addition, the complex **3a** has apparently almost completely disappeared after 47 h. Indeed, the signal corresponding to the methylene protons adjacent to N–CS_2 bonds from DTC on Zn complexes (*cf.* ^{1}H-NMR spectrum of **3a**, Fig. 3) is normally superimposed with that of the signal at 3.78 ppm corresponding to the methylene protons located α to O–P bonds of DTP alkyl chains located on one side of $Mo(DTP)_2$ complexes. Since the value of the integrated signals at 3.78 and 3.70 ppm corresponding to DTP alkyl chains on the same side of the

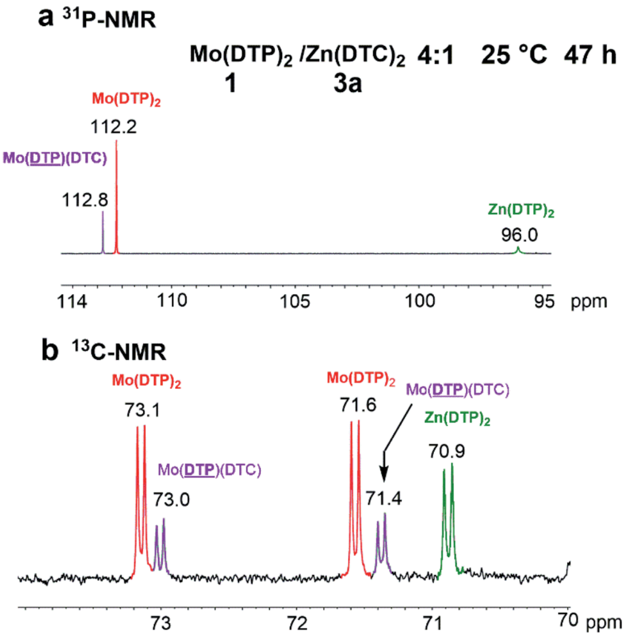

Fig. 8 Partial NMR spectra ($CDCl_3$, 25 °C) of a mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** in a 4 : 1 molar ratio after 47 h. (a) ^{31}P-NMR spectrum (94–115 ppm, 121 MHz); (b) ^{13}C-NMR spectrum (70–74 ppm, 125 MHz).

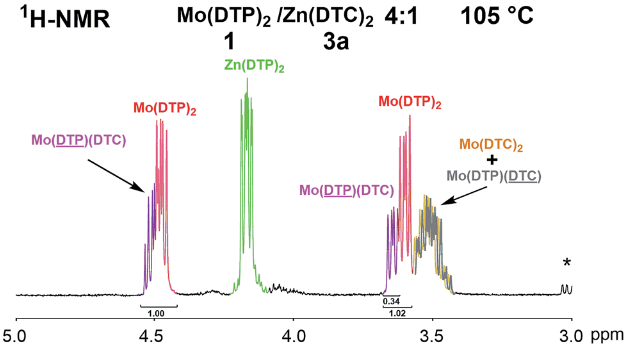

Fig. 9 Partial ^{1}H-NMR spectrum (3.0–5.0 ppm, 500 MHz, D_8-toluene, 105 °C) of a mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** in a 4 : 1 molar ratio after 15 min. *: Impurities.

MoO_2S_6 core from, respectively, $Mo(DTP)_2$ and Mo(DTP)(DTC) complexes **1** and **5a** ppm (Fig. 7b and c; red and purple colours) is identical to that of the DTP methylene protons at 4.49 ppm (Fig. 7b and c; red and purple colours) corresponding to DTP alkyl chains on the other side of the MoO_2S_6 core, it can be concluded that the contribution of protons from $Zn(DTC)_2$ to this signal is extremely small.

An experiment using the same mixture of **1** and **3a** in a 4 : 1 molar ratio was also performed in D_8-toluene at 105 °C. Fig. 9 shows the chemical shifts of the ^{1}H-NMR signals between 3.5–4.5 ppm from the reaction mixture. By comparison with the ^{1}H-NMR spectra of the reference compounds **1**, **2d**, **3a** and **4a** measured under the same conditions (ESI Fig. 7S†), it appeared that the ligand exchange reactions between $Mo(DTP)_2$ and $Zn(DTC)_2$ took place at a much faster rate at 105 °C (as compared to 25 °C) and that a very similar composition of the reaction mixture as that obtained at 25 °C was observed after only 15 minutes (*vs.* 18 h; see above). In particular, the specific signals corresponding to the methylene protons located α to O–P bonds of DTP from the mixed complex **5a** were observed for both types of DTP ligands alkyl chains (above and below the MoO_2S_6 core). The formation of the mixed complex **5a** could also be evidenced by ^{31}P-NMR spectroscopy (ESI Fig. 9S†). Interpretation of the integral values from the ^{1}H-NMR spectrum showed that the relative proportions of the different complexes in D_8-toluene at 105 °C were close to those observed in $CDCl_3$ at 25 °C and consequently, neither the nature of the solvent nor the temperature seem to have an important effect on the composition of the reaction mixture. A higher temperature seemed, however, to slightly favour the formation of the mixed complex.

Mixture of ***1*** *and* ***3a*** *in a 1 : 1 molar ratio at 25 °C and 105 °C.* Based on the interpretation of the ^{1}H-NMR spectra, the reaction between **1** and **3a** in solution in a 1 : 1 molar ratio led predominantly to the stoichiometric formation of $Mo(DTC)_2$ and $Zn(DTP)_2$ complexes **2e** and **4a** at 25 °C (ESI Fig. 10S†). The ligand exchange reaction between the two substrates was relatively fast, and ligand exchange products were already observed 1 h after mixing **1** and **3a**. The characteristic ^{1}H-NMR signals from **1** and **3a** decreased over time while those of $Mo(DTC)_2$ **2e** and $Zn(DTP)_2$ **4a** increased. After 95 h at 25 °C, **1** and **3a** had almost totally disappeared, leaving large amounts of **2e** and **4a** in the solution. The small signals at, respectively, 4.49 ppm and 3.70 ppm (ESI Fig. 10Sc;† purple colour) could be ascribed to minor DTP from Mo complexes, mainly as the mixed Mo(DTP)(DTC) complex **5a** (*cf.* Fig. 7). This was further confirmed by the presence of a signal at 112.8 ppm in the ^{31}P-NMR spectrum of the reaction mixture after 95 h (ESI Fig. 11S†) as well as by the small signals at 73.0 and 71.4 ppm in the ^{13}C-NMR spectrum (*cf.* Fig. 8b). Similar results were obtained when the reaction was performed in D_8-toluene at 105 °C.

3.1.3. Ligand exchange experiments involving $Mo(DTC)_2$ and $Zn(DTP)_2$. Ligand exchange reactions involving $Mo(DTC)_2$ and $Zn(DTP)_2$ complexes, the two types of additives widely used in combination in commercial lubricants, were also investigated by NMR spectroscopy. Laboratory exchange reactions using mixtures of **2d** and **4a** in a 1 : 4 and 2 : 1 molar ratios were performed at 25 °C ($CDCl_3$) and at 105 °C (D_8-toluene) and their evolution over time was followed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.

Mixture of ***2d*** *and* ***4a*** *in a 2 : 1 molar ratio at 25 °C.* ESI Fig. 12Sa† shows the partial ^{1}H NMR spectrum of the mixture of **2d** and **4a** in a 2 : 1 molar ratio after 24 h at 25 °C. Comparison with the reference spectra (Fig. 3) clearly showed that $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3b** were not formed within this frame of time. Formation of the related mixed Mo complex **5b** was not observed according to the ^{1}H-NMR spectrum, but traces of the typical signal at 112.8 ppm from the mixed complex **5b** was detected in the ^{31}P-NMR spectrum of the reaction mixture (ESI Fig. 12Sb†). Our results thus indicate that ligand exchange reactions between these two types of complexes did not take

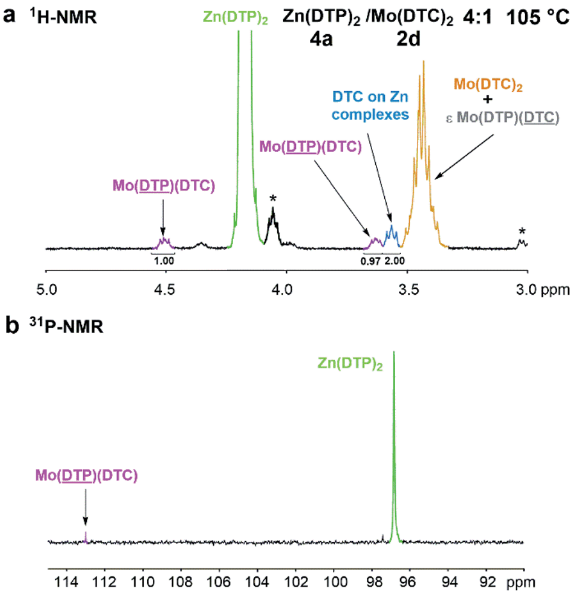

Fig. 10 Partial NMR spectra (D_8-toluene, 105 °C) of a mixture of $Zn(DTP)_2$ **4a** and $Mo(DTC)_2$ **2d** in a 4 : 1 molar ratio after 15 min. (a) ^{1}H-NMR spectrum (3.0–5.0 ppm, 500 MHz); (b) ^{31}P-NMR spectrum (90–115 ppm, 162 MHz). *: Impurities.

place to a significant extent and that the amounts of **5b** formed were extremely low under the conditions used. This likely reflects the stability of Mo complexes bearing dithiocarbamate ligands as already observed with the experiments involving Mo(DTP)$_2$ and Zn(DTC)$_2$. Our results might also be explained by the fact that the kinetic of ligand exchange reactions between **2d** and **4a** is extremely slow at 25 °C.

*Mixture of **2d** and **4a** in a 1 : 4 molar ratio at 25 °C and 105 °C.* The same experiment at 25 °C ($CDCl_3$) using **2d** and **4a** in a 1 : 4 molar ratio led to similar results. However, when this experiment was performed at 105 °C (D_8-toluene), typical signals at 4.50 and 3.63 ppm corresponding to protons from methylenes adjacent to the oxygen atoms from DTP of Mo(DTP)(DTC) **5b** as well as a signal at 3.57 ppm potentially corresponding to methylene protons adjacent to the functionality from DTC on Zn complexes were detected after 15 min of reaction (Fig. 10a).

It is worth noting that the value corresponding to the sum of the integral of the proton signals corresponding to DTP methylenes on mixed Mo complexes was identical to that measured for the signal at 3.57 ppm from DTC on Zn complexes, since each DTP migrated from Zn to Mo must correspond to one DTC which has migrated from Mo to Zn complexes. Calculation based on the values of the integrals of the signals corresponding to DTP and DTC from Mo complexes allowed to evaluate that Mo(DTP)(DTC) **5b** represented *ca.* 16% and Mo(DTC)$_2$ **2d** 84% of the Mo complexes in the solution.

The formation in rather low amounts of the mixed Mo(DTP)(DTC) complex **5b** was further evidenced by ^{31}P-NMR as shown by the occurrence of the typical signal at 112.8 ppm (Fig. 10b). After heating at 105 °C, the mixture was cooled down to 25 °C, redissolved in $CDCl_3$ and the ^{1}H- and ^{31}P-NMR spectra re-measured. The typical signals of DTP from the mixed Mo(DTP)(DTC) complex **5b** and of DTC from Zn complexes were detected. Furthermore, the relative contribution of **5b** to the total Mo complexes was in the same range as that determined at 105 °C. It is therefore likely that the Mo(DTP)(DTC) **5b** detected at 25 °C correspond in fact to the complex formed at 105 °C and that reequilibration at low temperature did not occur for kinetic reasons.

3.2. Study of the interactions between Mo(DTC)$_2$ and zinc additives using HPLC-MS

A novel analytical method allowing detection and quantification of Mo(DTC)$_2$ additives by normal phase HPLC-MS was developed (see Section 2.7.). Ionization was achieved using an APPI source. Under the HPLC conditions used, Mo(DTC)$_2$ complexes with various alkyl chain lengths are partly separated and can be selectively detected based on their pseudo-molecular ions $[M + H]^+$. On the contrary, dithiophosphate complexes (*i.e.*, Mo(DTP)$_2$, Zn(DTP)$_2$) cannot be detected using this method.

3.2.1. Stability of Mo(DTC)$_2$ at 135 °C. The developed HPLC-MS method allowed the relative abundance of Mo(DTC)$_2$ additives to be followed over time and thus their thermal stability at 135 °C could be determined. For this purpose, a mixture of **2a–2c** in solution in a hydrocarbon base oil was heated at 135 °C under an atmosphere of argon for 6 h and samples were collected at one-hour intervals. No significant evolution of Mo(DTC)$_2$ relative concentrations was noticed over this period of time (Fig. 11), indicating that Mo(DTC)$_2$ complexes are thermally stable at 135 °C.

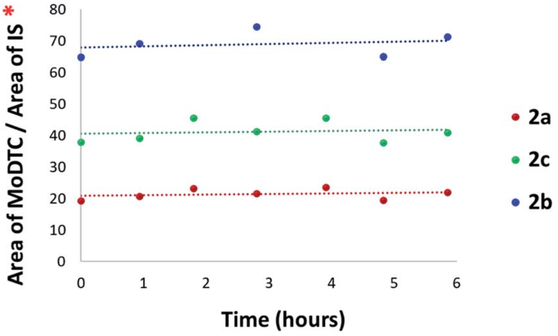

Fig. 11 Relative concentrations of Mo(DTC)$_2$ **2a–2c** in solution in a hydrocarbon base oil at 135 °C under an argon atmosphere over a 6 h time period as determined using HPLC-MS. IS: internal standard. **Y*-axis: arbitrary units.

3.2.2. Ligand exchange reactions between Mo(DTC)$_2$ and Zn(DTC)$_2$. In order to evaluate the exchange efficiency of ligands between Mo(DTC)$_2$ and Zn(DTC)$_2$, an experiment involving a mixture of Mo(DTC)$_2$ **2a–2c** and Zn(DTC)$_2$ **3a** (1 : 2 molar ratio) in a hydrocarbon base oil at 135 °C was carried out. The evolution of the composition of the reaction mixture was followed by HPLC-MS, all the substrates (**2a–2c** and **3a**) and the postulated DTC complexes formed by ligand exchange reactions being detectable using our analytical method. It could thus be determined that new Mo complexes were already formed at $T = 0$ h (*i.e.*, when the temperature of the reaction mixture just reached 135 °C). They comprised Mo(DTC)$_2$ with two DTC ligands based on di *n*-decylamine **2e** together with the asymmetric Mo complexes **2f** and **2g**.

HPLC-MS relative quantification of the various Mo(DTC)$_2$ homologues clearly showed a rapid decrease of the concentrations of the Mo(DTC)$_2$ substrates **2a–2c** (Fig. 12a) and the increase of the newly formed Mo(DTC)$_2$ **2e–2g** over time (Fig. 12b) (*cf.* ESI Fig. 13S† for the mass spectra of **2e–2g**). Since we have determined that Mo(DTC)$_2$ are thermally stable under our experimental conditions (*cf.* Section 3.2.1.), the decrease of the concentrations of the initial Mo(DTC)$_2$ most likely resulted from ligand exchange reactions. The rapid decrease of concentration of **2a–2c** mainly occurred during the 3 first hours of the experiment whereas that of compound **2e** progressively increased, clearly showing that this ligand exchange reaction is a rather fast process at 135 °C, though not instantaneous. After 3 h, the concentration of the various Mo(DTC)$_2$ homologues remained stable, suggesting that an equilibrium between the various Mo(DTC)$_2$ species has been reached.

The ligand exchange reactions between Mo(DTC)$_2$ **2a–2c** and Zn(DTC)$_2$ **3a** have also been evaluated at room temperature in cyclohexane. No ligand exchange products were formed during the first hour of the experiment. The mixture was then left at room temperature for another 6 h and was analysed again by HPLC-MS. This time, newly formed Mo(DTC)$_2$ **2e–2g** were

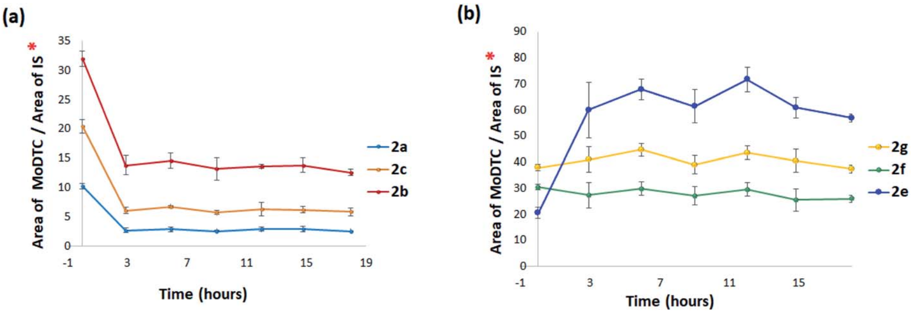

Fig. 12 Evolution of the relative concentrations of $Mo(DTC)_2$ species over time in the presence of $Zn(DTC)_2$ **3a** in lubricant base oil at 135 °C. (a) $Mo(DTC)_2$ substrates **2a–2c**; (b) $Mo(DTC)_2$ **2e–2g** newly formed by ligand exchange with $Zn(DTC)_2$ **3a**. The relative concentrations of $Mo(DTC)_2$ have been determined using HPLC-MS. IS: internal standard. **Y*-axis: arbitrary units.

detected, but in very small amounts. Afterwards, the amounts of **2e–2g** increased very slowly over a period of 18 h. Consequently, it appears that the ligand exchange reactions between $Mo(DTC)_2$ **2a–2c** and $Zn(DTC)_2$ **3a** also takes place, but the kinetic of this exchange is slow at room temperature.

4. Discussion

By combining our ^1H-, ^{13}C- and ^{31}P-NMR results, it clearly appears that the DTC/DTP ligand exchange reactions between molybdenum and zinc complexes goes strongly into favor of the migration of the DTC ligands from Zn complexes towards Mo complexes and of the formation of $Mo(DTC)_2$ and $Zn(DTP)_2$ complexes at 25 °C and 105 °C. Molybdenum showed indeed a greater affinity for dithiocarbamate *vs.* dithiophosphate ligands. It could also be determined that DTP and DTC ligands from Zn complexes are able to exchange rapidly at the NMR time scale. It is therefore not possible to detect specifically heteroleptic Zn complexes using NMR spectroscopy at room temperature.

On the other hand, based on the ligand exchange reactions involving $Mo(DTP)_2$ and $Zn(DTC)_2$, it could be established that Mo complexes bearing mixed DTP and DTC ligands were formed and could be detected using ^1H-, ^{13}C- and ^{31}P-NMR measurements. In the case of the reactions between $Mo(DTP)_2$ and $Zn(DTC)_2$, ligand exchange is a fast process, which is accelerated with increasing temperature (*i.e.*, within 18 h at 25 °C *vs.* 15 min at 105 °C), and goes to completion until all the DTC ligands from Zn complexes have migrated to Mo complexes (depending on the relative concentration of the substrates). $Mo(DTC)_2$ and $Zn(DTP)_2$ complexes are formed together with mixed Mo(DTC)(DTP) complexes, the latter even becoming a predominant species depending on the relative proportions of each substrate. Consequently, in the case of experiments involving both $Mo(DTC)_2$ and $Zn(DTP)_2$ -an association of additives frequently used in formulated lubricants-, the formation of $Mo(DTP)_2$ complexes was not observed regardless of the relative concentrations of the substrates. When a large excess of $Zn(DTP)_2$ relative to $Mo(DTC)_2$ species was used (4 : 1 molar ratio), the formation of the mixed Mo(DTC)(DTP) complex in D_8-toluene at 105 °C was unambiguously observed using ^1H- and ^{31}P-NMR measurements, the relative amounts of the mixed complex representing *ca.* 16% of all of the Mo complexes. This value is much lower than the proportions reported by Shea and Stipanovic[27] with up to 80% conversion of $Mo(DTC)_2$ obtained by reaction with $Zn(DTP)_2$ at 80 °C in toluene. However, in our experiments, we did not detect the formation of this mixed complex at a lower temperature (25 °C, in $CDCl_3$) even after 24 h of reaction, possibly due to the slow kinetics of the ligand exchange at this temperature, or because the equilibrium does not favor the formation of this compound at this temperature.

It should however be noted that the kinetics of the ligand exchange reactions might also depend on the nature of the solvent and could be significantly slower in a viscous medium such as a lubricant base oil. The kinetics of ligand exchange might also depend on the type of base oil or polarity of the solvent as proposed by Shea and Stipanovic[27] or on the occurrence of impurities such as dithiocarbamates or dithiophosphates of monovalent metals which might catalyse the exchange of ligands.

The possibility of ligand exchange reactions between $Mo(DTC)_2$ and $Zn(DTP)_2$, which were postulated to play a role in the synergetic enhancement of the tribological properties of lubricant containing both types of additives, has been investigated previously by several authors.[12,26–29,35] The present study, based on ^1H, ^{13}C and ^{31}P NMR detection of the different Mo and Zn complexes, indicates that ligand exchange between $Mo(DTC)_2$ and $Zn(DTP)_2$ complexes occurs to a rather limited extent at 105 °C, provided that $Zn(DTP)_2$ species are largely predominant. This contrasts with the findings from Jensen *et al.*[12,35] and Shea and Stipanovic,[27] in particular, which suggest that such exchanges might occur to an important rate, notably in lubricants which have undergone important oxidative alteration.

Jensen *et al.*[12,35] have indeed documented ligand exchange between $Mo(DTC)_2$ and $Zn(DTP)_2$ complexes based on laboratory experiments involving both types of complexes at a high temperature (160 °C) either under an inert atmosphere or under oxidative conditions. In these experiments, the substrates, molybdenum di(2-ethylhexyl)dithiocarbamate [$Mo(ehdtc)_2$] and zinc di(*n*-octyl)dithiophosphate [$Zn(odtp)_2$], were used in a 1 : 5.5 molar ratio. Quantification of Mo complexes with odtp ligands resulting from the ligand exchange reaction was however shown to be challenging since Mo(odtp)$_2$ and Mo(odtp)(ehdtc) could not be directly detected using the HPLC method developed by these authors. An indirect method was therefore developed based on the postulated efficient exchange between DTP and DTC ligands in the case of Mo complexes. To measure the concentrations of Mo(odtp)$_2$ and Mo(odtp)(ehdtc), an excess of zinc di(*n*-butyl) dithiocarbamate [Zn(bdtc)$_2$] was added into the reaction mixture at 160 °C, assuming a selective and quantitative exchange the odtp ligands from Mo complexes by di(*n*-butyl) dithiocarbamate ligands (bdtc) analyzable by HPLC. Thus, the resulting Mo(bdtc)$_2$ and Mo(bdtc)(ehdtc) species could indeed be identified and quantified, and were shown to represent up to *ca.* 20% of the Mo complexes at 160 °C under inert atmosphere. When carried out under oxidative conditions, the Mo derivatives with bdtc ligands represented even more than 90% of the Mo complexes after 4 h. However, the approach used by Jensen *et al.*[12] has two main flaws. Indeed, the ligand exchange step implies that this exchange must be selective and quantitative regarding the exchange between odtp ligands from Mo complexes by bdtc ligands. This assumption is of course questionable since ligand exchange reactions affecting Mo complexes and involving dithiocarbamates and dithiophosphates were precisely the processes investigated in the study. Furthermore, the addition of Zn(bdtc)$_2$ in a large excess into the reaction mixture likely induces ligand exchange with the unreacted Mo(ehdtc)$_2$ complex to form Mo(bdtc)$_2$ and Mo(bdtc)(ehdtc) species as unambiguously demonstrated in our study. Therefore, it is more than likely that the amounts of Mo(odtp)$_2$ and/or Mo(odtp)(ehdtc) complexes formed by ligand exchange reaction between Mo(DTC)$_2$ and Zn(DTP)$_2$ complexes and indirectly quantified by Jensen *et al.*[12] were at least overestimated.

5. Conclusions

Despite of being widely employed in commercial lubricants, a comprehensive description of Mo(DTC)$_2$ interactions with other additives at the molecular level is still lacking. Moreover, the introduction of new engine tests has led to a strong interest in understanding the molecular transformations of the additives from engine oils. In this context, our study was dedicated to the investigation of the interaction between molybdenum and zinc derivatives using an analytical approach involving NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) and a specifically-developed HPLC-MS method permitting the analysis of Mo complexes bearing DTC ligands. This approach allowed, notably, direct investigation of both homoleptic and heteroleptic Mo complexes formed in experiments involving DTC and DTP complexes of Mo and Zn at 25 °C, 105 °C and 135 °C.

Our results indicate that fast exchange of both DTC and DTP ligands between Zn complexes occur at room temperature and above, mixtures of DTP and DTC complexes of Zn most likely comprising homo- and heteroleptic complexes as well as dimeric structures. It could be shown also that ligand exchange reactions between Mo(DTP)$_2$ and Zn(DTC)$_2$ strongly favor the migration of DTC ligands from Zn to Mo, illustrating the higher affinity of Mo for DTC ligands at both 25 °C and 105 °C. The kinetic is, however, significantly faster at 105 °C. Mixed Mo(DTC)(DTP) complexes which can be specifically detected by ^{1}H-, ^{13}C- and ^{31}P-NMR can become predominant species in experiments with a high Mo(DTP)$_2$/Zn(DTC)$_2$ ratio. Ligand exchange between Mo(DTC)$_2$ and Zn(DTC)$_2$ was shown to be a relatively fast process, but not immediate, at 135 °C.

In the case of binary systems involving Mo(DTC)$_2$ and Zn(DTP)$_2$ additives frequently used in formulated lubricants, the formation of small amounts of Mo(DTC)(DTP) mixed complexes could be evidenced for the first time by direct analytical methods. The proportions observed were however significantly lower than those previously reported in the literature. These exchange reactions are operative at high temperature (105 °C) but seem to be inhibited at low temperatures (25 °C). It can be inferred from our results that these Mo(DTC)(DTP) mixed species can indeed be formed in engines and could account, at least to some extent, to synergistic effects of Mo(DTC)$_2$ and Zn(DTP)$_2$ on the friction reducing properties of engine oils.

Conflicts of interest

There are no conflicts to declare.

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