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Exchange of isonitrile ligands in the complex $[Mo(O)Cl(CNMe)_4]^+$ by the tetraphos ligand prP_4: Stereochemical influences on the reaction course

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ABSTRACT

Reaction of $[Mo(O)Cl(CNMe)_4]^+$ with the linear tetraphos ligand *meso* and *rac* prP_4 leads to a mixture of $[Mo(O)Cl(\kappa^4\text{-}meso\text{-}prP_4)]^+$ and $[Mo(O)Cl(CNMe)(\kappa^3\text{-}rac\text{-}prP_4)]^+$ which are identified by X-ray structural analysis and/or ^{31}P NMR spectroscopy. In the *meso* κ^4-product both of the phenyl groups of the central phosphorus atoms are oriented towards the oxo ligand whereas in the *rac* κ^3-product one of these phenyl groups is oriented to the oxo and the other to the chloro ligand. The origin of the different coordination modes lies in the different steric demands of the oxo and chloro ligands. The influences of the steric interactions are enhanced by the fact that exchange of the fourth isonitrile is difficult. This hypothesis is supported by the preparation of the complex $[Mo(O)Cl(CNMe)(dpepp)]PF_6$ whose isonitrile ligand is inert towards exchange by monophosphines, even under drastic conditions.

1. Introduction

Multiply bonded transition-metal complexes with d^2 configuration and phosphine coligands are of significant interest due to their relevance to synthesis, catalysis and biochemistry [1,2]. Against this background many complexes of the general formulae *trans*-$ME(PR_3)_4X$ or *trans*-$ME_2(PR_3)_4$ (M = transition metal, X = halide or pseudohalide, PR_3 = monodentate or ½ bidentate phosphine) have been prepared and investigated with respect to their electronic structures, spectroscopic properties and chemical reactivities [3–5]. A particularly attractive feature of the tetraphosphine platform present in these systems is the fact that it allows to accommodate and investigate a broad range of multiply bonded, axial ligands E such as oxide [2], nitride [2,6–8], imide [6–8], etc., under comparable geometric and electronic-structural conditions.

Due to the much better knowledge of the metal–O unit as compared to other metal–E moieties transition-metal oxo complexes doubtless constitute the prototypical examples for this class of compounds. With respect to Mo(IV) and W(IV) oxo complexes, several cationic complexes of the type *trans*-$[M(O)(X)(dppe)_2]^+$ (M = Mo and W) have been reported [9,10]: *trans*-$[Mo(O)(Cl)(dppe)_2]^+$ [11], *trans*-$[W(O)Cl(dppe)_2]^+$ [12], *trans*-$[Mo(O)(F)(dppe)_2]^+$ [13], and *trans*-$[Mo(O)(OCH_3)(dppe)_2]^+$ [14]. Remarkably, $[W(O)Cl(dppe)_2]^+$ and its molybdenum analog could be reduced by Na_x/Hg in the presence of phenol and N_2 to the dinitrogen complexes $[W(N_2)_2(dppe)_2]$ and $[Mo(N_2)_2(dppe)_2]$, respectively, thus establishing a link between M(IV)-oxo and M(0) dinitrogen chemistries (M = Mo, W) [15]. We applied this methodology to the synthesis of the complex $[Mo(N_2)_2(prP_4)]$ where prP_4 is a tetradentate phosphine ligand containing a central C_3 and two C_2 bridges [16]. The coordination of the linear tetraphos prP_4-ligand to mononuclear metal centers has been a goal of our group for a number of years [16–18]. In a first study, the prP_4 ligand was coordinated to *cis*- and *trans*-Fe(II)$(NCS)_2$ units and the stereochemistry of the resulting complexes was elucidated [17]. Preparation of the mentioned molybdenum bis(dinitrogen) complex $[Mo(N_2)_2(prP_4)]$ was achieved by electrochemical reduction of the oxo–iodo complex $[Mo(O)I(prP_4)]$, which in turn was synthesized starting from $[Mo(O)I_2(PMe_3)_2]$ [19]. The latter complex was obtained from $[Mo(O)Cl_2(PMe_3)_2]$ by halide exchange [16]. As this synthetic route involved several steps, we were seeking simpler ways to obtain a tetraphosphine-coordinated molybdenum oxo–halo complex.

An alternative potential precursor for the coordination of the tetraphos ligand prP_4 to mononuclear Mo(IV) centers is the tetrakis(isonitrile) molybdenum complex $[Mo(O)Cl(CNMe)_4]^+$ (**1**) whose isonitrile groups are subject to facile exchange by other ligands. In the first description of this complex by Novotny and Lippard, e.g., a high reactivity towards amines and thiols was reported [20,21]. Later on the complex was used by Donahue et al. for the syntheses of bis(dithiolate) complexes [22,23]. Herein exchange reactions of the complex $[Mo(O)Cl(CNMe)_4]^+$ with polydentate phosphines; i.e., tri- and tetraphosphines, are investigated. Besides characterizing the resulting products, the respective reaction courses are analyzed with the help of ^{31}P NMR spectroscopy. Particular emphasis is laid on elucidating the presence of mechanisms leading to

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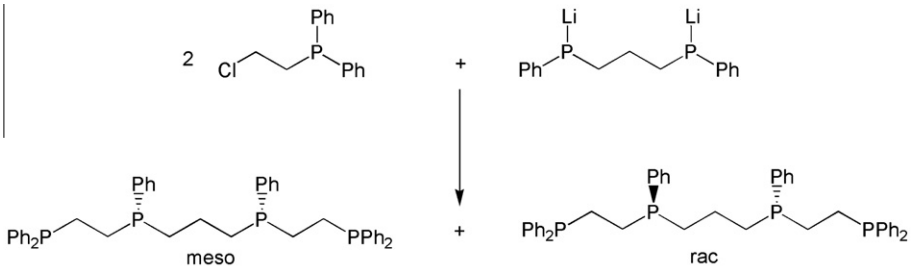


Scheme 1.

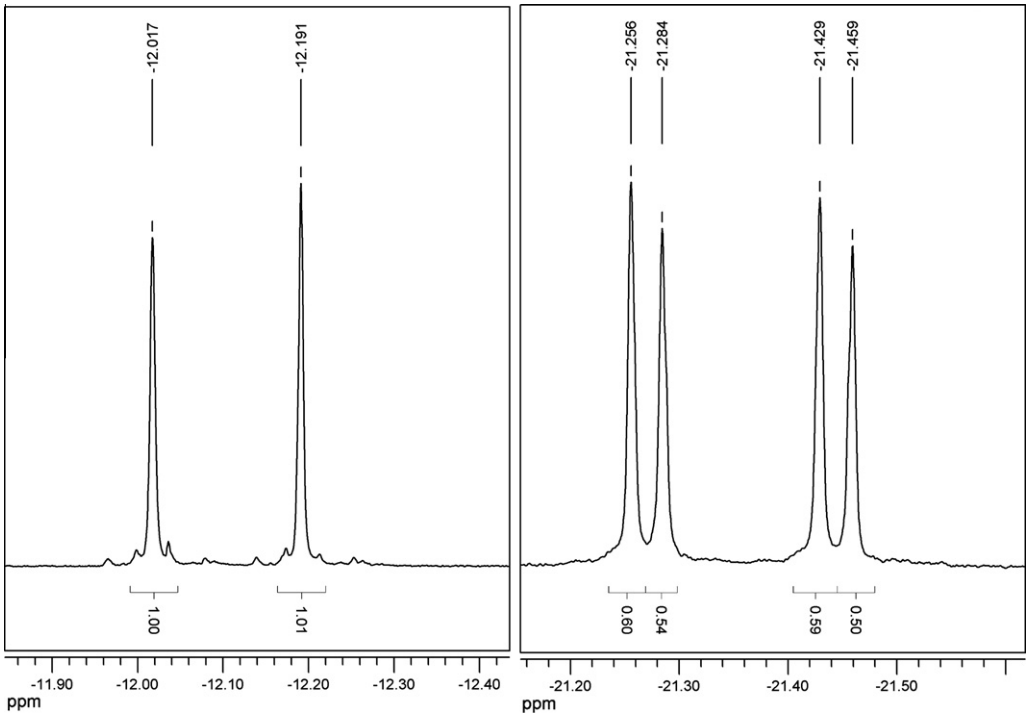


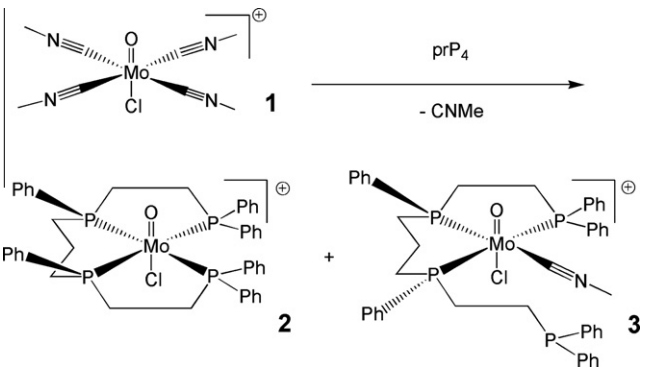
Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of the prP_4-ligand.

stereoselectivity. The general implications of the results with respect to the preparation of Mo complexes with tetraphosphine ligands are discussed.

2. Results and analysis

2.1. Synthesis of the precursors [21]

The preparation of $[Mo(O)Cl(CNMe)_4](PF_6)$ (**1a**) and $[Mo(O)Cl(CNMe)_4](BPh_4)$ (**1b**) was performed by dissolving $MoCl_5$ in



Scheme 2.

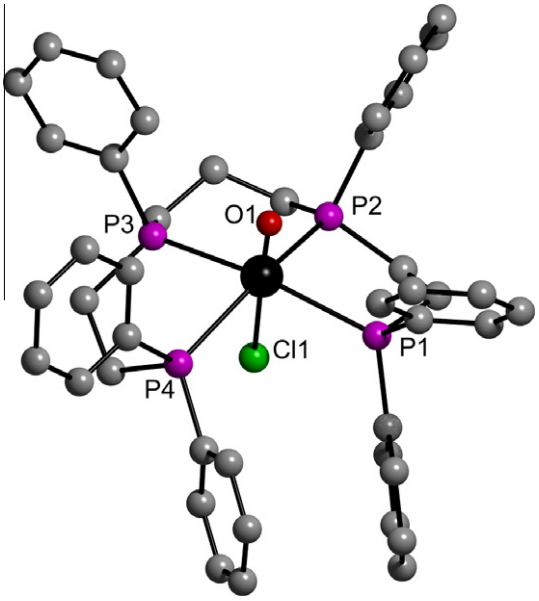


Fig. 2. Single crystal structure $[Mo(O)Cl(\kappa^4\text{-}meso\text{-}prP_4)]BPh_4$ (**2b**).

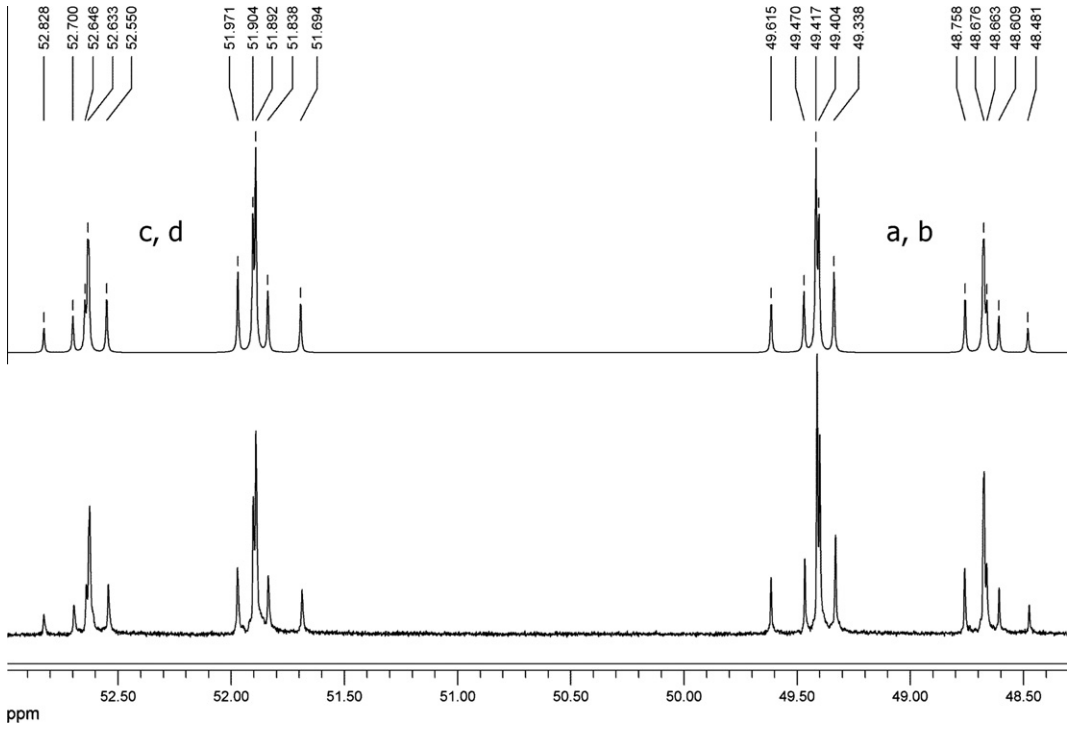


Fig. 3. $^{31}P\{^{1}H\}$ NMR AA′XX′-coupling scheme of $[Mo(O)Cl(\kappa^4\text{-}meso\text{-}prP_4)]^+$ (**2**) measured (bottom) and simulated (top).

methanol and adding methyl isonitrile. The chloride cation was exchanged against PF_6^- and BPh_4^- by addition of a methanolic solution of KPF_6 and $NaBPh_4$, respectively.

2.2. Synthesis and characterization of the tetradentate prP_4 ligand

prP_4 (1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane) was synthesized by reaction of two equivalents of (2-chloroethyl)-diphenylphosphane with one equivalent of 1,3-bis(lithiumphenylphosphido)propane (Scheme 1) [16]. Due to the existence of two asymmetric phosphorus atoms in the ligand two diastomeric forms of the product are possible. In *meso*-prP_4 both phenyl rings of the central phosphorus atoms are oriented to the same side whereas in *rac*-prP_4 one phenyl ring is oriented to the opposite side. As evident from ^{31}P NMR spectroscopy the preparation of the ligand generally leads to a mixture of *meso* and *rac* with varying proportions of both diastereomers [17].

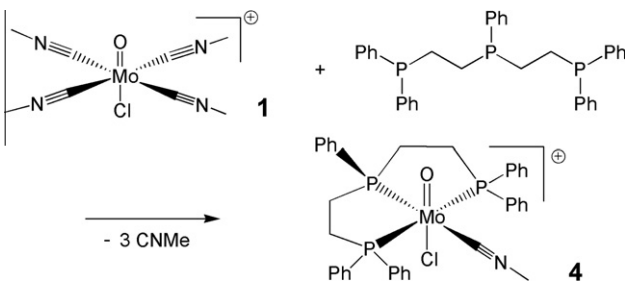
The ^{31}P NMR spectrum of the free prP_4 ligand shows three doublets corresponding to the two isomers (Fig. 1). Each isomer gives a four-line spectrum consisting of two doublets. Due to the higher shielding of the alkyl as compared to the phenyl groups, the signals at ~−21 ppm should belong to the asymmetric phosphorus atoms and the signals at −12.1 ppm to the terminal ones. This assignment is supported by the fact that the signals of the latter atoms have identical shifts in both isomers and therefore are superposed whereas the doublets of the asymmetric P atoms exhibit slightly different chemical shifts (−21.25 and −21.28 ppm), resulting in a four-line group. The pair of signals at lower field (higher intensity) belongs to the *meso* isomer of prP_4.

Table 1
Selected bond distances (Å) and angles (°) of $[Mo(O)Cl(\kappa^4\text{-}meso\text{-}prP_4)]BPh_4$ (**2b**).

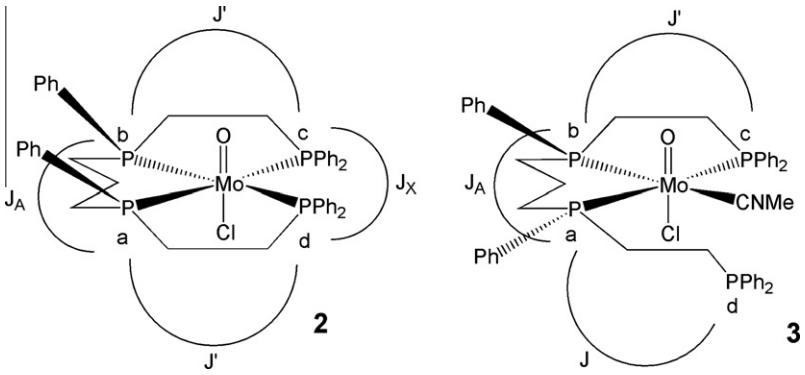
Bond distance (Å)			
Mo–O(1)	1.6771(14)	Mo–Cl(1)	2.5162(5)
Mo–P(1)	2.5432(5)	Mo–P(3)	2.4898(6))
Mo–P(2)	2.4934(5)	Mo–P(4)	2.5201(5)
Bond angle (°)			
P(1)–Mo–P(2)	80.391(18)	P(2)–Mo–P(3)	90.446(19)
P(1)–Mo–P(4)	102.683(17)	P(3)–Mo–P(4)	78.871(18)
O(1)–Mo–P(1)	96.73(5)	O(1)–Mo–P(3)	101.47(5)
O(1)–Mo–P(2)	102.67(5)	O(1)–Mo–P(4)	101.60(5)
Cl(1)–Mo–P(1)	81.564(19)	Cl(1)–Mo–P(3)	80.229(19)
Cl(1)–Mo–P(2)	77.099(18)	Cl(1)–Mo–P(4)	78.822(18)
O(1)–Mo–Cl(1)	178.29(5)		

Table 2
Comparison of $^{31}P\{^{1}H\}$ NMR coupling constants.

	$[Mo(O)I(prP_4)]^+$ [16]	$[Mo(O)Cl(\kappa^4\text{-}meso\text{-}prP_4)]^+$ (**2b**)
$^{2/4}J_{ab}$ (Hz)	−28.2	−27.4
$^{2}J_{cd}$ (Hz)	−18.4	−18.5
$^{2}J_{ac/bd}$ (Hz)	110.8	123.8
$\lvert^{2/3}J_{ad/bc}\rvert$ (Hz)	4.9	4.9
	$[Mo(O)Cl(CNMe)(\kappa^3\text{-}rac\text{-}prP_4)]^+$ (**3**)	
$^{2/4}J_{ab}$ (Hz)	−30.5	
$^{2}J_{cd}$	–	
$^{2}J_{ac}$ (Hz)	128.1	
$\lvert^{2/3}J_{bc}\rvert$ (Hz)	8.3	
$^{3}J_{ad}$ (Hz)	−28.2	



Scheme 3.



Scheme 4.

2.3. Synthesis and characterization of [Mo(O)Cl(κ⁴-prP₄)]BPh₄ (**2b**)

For the synthesis of the complex [Mo(O)Cl(κ⁴-prP₄)]BPh₄ (**2b**) on a preparative scale equimolar amounts of the tetrakis(isonitrile) complex [Mo(O)Cl(CNMe)₄]BPh₄ (**1b**) and the ligand prP₄ were suspended in acetone and reacted for 24 h at room temperature and about 14 h at 60 °C (cf. Section 4 and Scheme 2). The reaction leads to two products: the four times coordinated [Mo(O)Cl(κ⁴-prP₄)]⁺ (**2**) and the three times coordinated complex [Mo(O)Cl(CNMe)(κ³-prP₄)]⁺ (**3**), which is considered in Section 2.5. After reduction of the volume of the solution and cooling to −40 °C **2b** could be isolated as blue-violet solid. Violet crystals, suitable for an X-ray crystallographic characterization, could be obtained by slow evaporation of a CH_2Cl_2 solution.

The structure of the cation of **2b** shown in Fig. 2 reveals that the complex contains the *meso* and not the *rac* prP₄ ligand. The Mo–P distances are within the usual range (2.49–2.54 Å); the Mo=O and Mo–Cl bond lengths are 1.68 and 2.52 Å, respectively (cf. Table 1). The P–Mo–P angle between the terminal P-atoms is increased from 90° to 102° whereas the angle between the central P-atoms is about 90°. The angles between the central and the terminal P-atoms are ~80°, as known from Mo(0) complexes with dppe or depe ligands [24]. All O–Mo–P angles are larger than 90°, rendering the axial Mo=O/equatorial P coordination slightly pyramidal. With 178° the O–Mo–Cl angle is almost linear. The [Mo(O)I(prP₄)]⁺ cation which was crystallographically characterized as well exhibits a similar structure [16]. The main differences to the structure of **2b** are the longer Mo–I bond length of 2.95 Å as compared to the Mo–Cl bond of 2.52 Å and an increased angle between the terminal P-atoms (108° versus 102°).

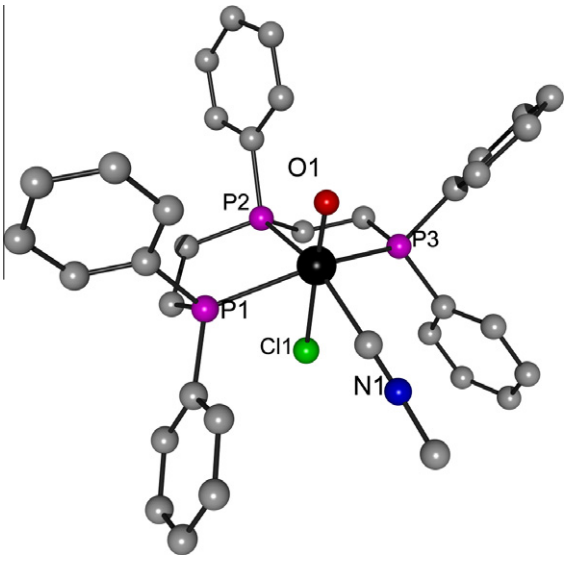


Fig. 4. Single crystal structure [Mo(O)Cl(CNMe)(dpepp)]PF₆ (**4**).

The ^{31}P NMR spectrum of **2b** is shown in Fig. 3, bottom. In contrast to the free prP₄ ligand which shows no coupling between the central phosphorus atoms, the spectrum now exhibits an AA′XX′ pattern (A = central, X = terminal P). The signal consists of two sets containing 10 lines each. The set at 52 ppm can be assigned to the terminal P atoms c, d and the set at 49 ppm to the internal P atoms a, b. The *trans* $^2J_{AX}$ coupling constant between the central P and the terminal P atoms is 123.8 Hz (cf. Table 2). The $^{2/4}J_A$ coupling constant among the inner P atoms is −27.5 Hz and the ^2J_X coupling constant between the terminal atoms is −18.5 Hz. Atoms b and c or a and d couple via the ethylene bridge and the metal which leads to a small resulting coupling constant of $|^{2/3}J'|$ = 4.9 Hz (Scheme 4, left). The AA′XX′ pattern of **2b** is related to the ^{31}P NMR spectrum of [Mo(O)I(prP₄)]BPh₄ [16]. The coupling constants in this complex were determined to $^{2/4}J_A$ = −27.4 Hz, $|^{2/3}J'|$ = 4.9 Hz, *trans* $^2J_{AX}$ = 110.8 Hz and ^2J_X = −18.4 Hz. Comparison with **2b** only reveals a major difference (13 Hz) for the *trans* $^2J_{AX}$ coupling constant. Moreover, due to the presence of different halide ligands in the two complexes different chemical shifts of the signals are observed. The signals of the chloro complex are centered at 50.6 ppm; for the iodo-complex they are shifted by 7.1–43.5 ppm. A similar chemical shift difference of 7.5 ppm was found by Bendix and Bgevig by comparing the complexes [Mo(O)I(dppe)₂]BF₄ and [Mo(O)Cl(dppe)₂]BF₄ [9].

Complex **2b** was also characterized by vibrational spectroscopy. The infrared and Raman spectra are given in Supplementary Fig. S1. The Mo=O stretch is found at 955 cm^{-1}, the typical signals for aromatic phosphine ligands are located at 1443 and 1483 cm^{-1}.

2.4. Synthesis and characterization of [Mo(O)Cl(CNMe)(dpepp)]PF₆ (**4**)

For the preparation of the complex [Mo(O)Cl(CNMe)(dpepp)]PF₆ (**4**) equimolar amounts of the complex [Mo(O)Cl(CNMe)₄]PF₆ (**1a**) and the ligand bis(2-diphenylphosphinoethyl) phenylphosphane (dpepp) were suspended in acetone and reacted for 12 h at room temperature and 8 h at 60 °C (cf. Section 4 and Scheme 3). After reduction of the volume of the solution, extraction with THF and cooling of the THF solution to −40 °C a pale violet solid was isolated. Violet crystals, suitable for an X-ray crystallographic characterization, could be obtained by slow vapor diffusion of diethyl ether into a CH_2Cl_2 solution.

The structure of the complex cation of **4** is shown in Fig. 4. The dpepp ligand is bound in a meridional fashion in the equatorial plane, which in addition contains an isonitrile as a fourth ligand. The phenyl group of the central P-donor is oriented towards the

oxo ligand. The Mo–P distances are within the usual range (2.47–2.50 Å); the Mo=O and Mo–Cl bond lengths are 1.68 and 2.59 Å, respectively (cf. Table 3). Both P–Mo–P angles are around 80°, equal to those of the ethylene bridged P-atoms of the prP_4 complexes (*vide supra*). The Mo–C bond length of the isonitrile ligand is 2.150(3) Å, and its C–N bond length is 1.143(4) Å. This corresponds to a small shortening of the C–N bond as compared to the cation $[Mo(O)Cl(CNMe)_4]^+$ (C–N bond length 1.158(11) Å) [20].

Complex **4** was also characterized by vibrational spectroscopy. The infrared and Raman spectra are given in Supplementary Fig. S2. The spectrum shows the signal for the M=O vibration at 953 cm^{-1} and the isonitrile vibration at 2218 cm^{-1}. In comparison to the precursor **1** the isonitrile vibration is shifted about 17 cm^{-1} to smaller wavenumbers.

2.5. Exchange reaction of $[Mo(O)Cl(CNMe)_4]^+$ with prP_4: ^{31}P NMR monitoring

For an NMR-spectroscopic investigation of the exchange reaction of **1** with prP_4 the two components were suspended in equimolar amounts in dry acetone. After a short period of time the suspension cleared up to a violet solution. This happened much faster with the PF_6 salt **1a** than with the BPh_4 salt **1b**, probably due to the lower solubility of **1b**. The ^{31}P NMR spectrum of the reaction mixture (Fig. 5) showed several signals which could be assigned to two species (Scheme 2). As evident from a comparison with the spectrum of **2b** (*vide supra*) the AA′XX′ pattern at 52.8–48.5 ppm belongs to the κ^4 coordinated $[Mo(O)Cl(meso\text{-}prP_4)]^+$ complex **2**.

The other main signal set in the ^{31}P NMR spectrum consists of the signals at 56.8 ppm (c), 46.2 ppm (b), 21.6 ppm (a) and −12.3 ppm (d). This signal set can be attributed to a κ^3 coordinated complex $[Mo(O)Cl(CNMe)(\kappa^3\text{-}prP_4)]^+$ (**3**). The detailed assignment of the signals to the individual P atoms is shown in Scheme 4 (right). Atom a (ddd-signal) couples with atoms b, c and d; atoms b (dd-signal) and c (dd-signal) couple with each other and with atom a, and atom d (d-signal) only couples with atom a. Analysis of the signals leads to the following parameters: The *trans* ^2J coupling constant among atom a and the terminal atom c is 128.1 Hz. The coupling constant $|^{2/3}J'|$ among atoms b and c is 8.3 Hz; this coupling constant includes the *cis* coupling over the metal and the ^3J coupling over the ethylene bridge. The coupling constant $^{2/4}J_A$ among the two central P atoms is −30.5 Hz. The ^3J coupling among atom a and the uncoordinated atom d is 28.2 Hz, just as in the free ligand. The chemical shift of signal d is −12.3 ppm which is equal to the shift in the free prP_4 ligand as well.

Integrating the signals of the two components in the ^{31}P NMR spectrum shows that the κ^3 and κ^4 products are formed in about equal amounts. Importantly, the intensity ratio was found to be independent of the reaction conditions or the reaction time. It thus became clear that two reaction channels must exist, one leading to the κ^3- and the other to the κ^4-product. With respect to a structural assignment of the κ^3 complex, two possibilities exist; i.e., this complex can derive from the *meso* or the *rac* ligand. We believe that the second possibility applies, for the following reasons: (i) *meso* and *rac* prP_4 always form in comparable amounts. If the κ^4 *as well as*

Table 3
Selected bond distances (Å) and angles (°) of $[Mo(O)Cl(CNMe)(dpepp)]PF_6$ (**4**).

Bond distance (Å)			
Mo–O(1)	1.679(2)	Mo–Cl(1)	2.5852(7)
Mo–P(1)	2.5048(8)	Mo–P(3)	2.4980(8)
Mo–P(2)	2.4745(8)	Mo–C(61)	2.150(3)
C(61)–N(1)	1.143(4)		
Bond angle (°)			
P(1)–Mo–P(2)	79.52(3)	P(2)–Mo–P(3)	80.31(3)
P(1)–Mo–C(61)	95.59(8)	P(3)–Mo–C(61)	94.02(8)
O(1)–Mo–P(1)	105.17(8)	O(1)–Mo–P(3)	101.38(8)
O(1)–Mo–P(2)	102.25(8)	O(1)–Mo–C(61)	100.81(11)
Cl(1)–Mo–P(1)	76.43(2)	Cl(1)–Mo–P(3)	77.14(3)
Cl(1)–Mo–P(2)	78.21(3)	Cl(1)–Mo–C(61)	78.71(8)
O(1)–Mo–Cl(1)	178.38(8)		

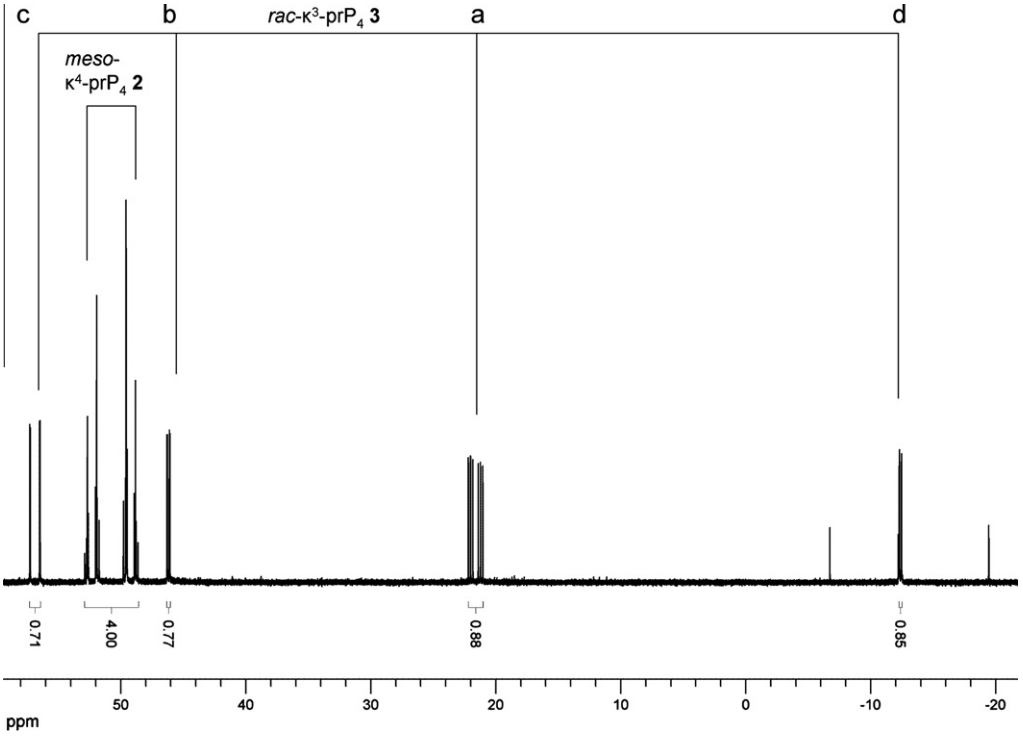
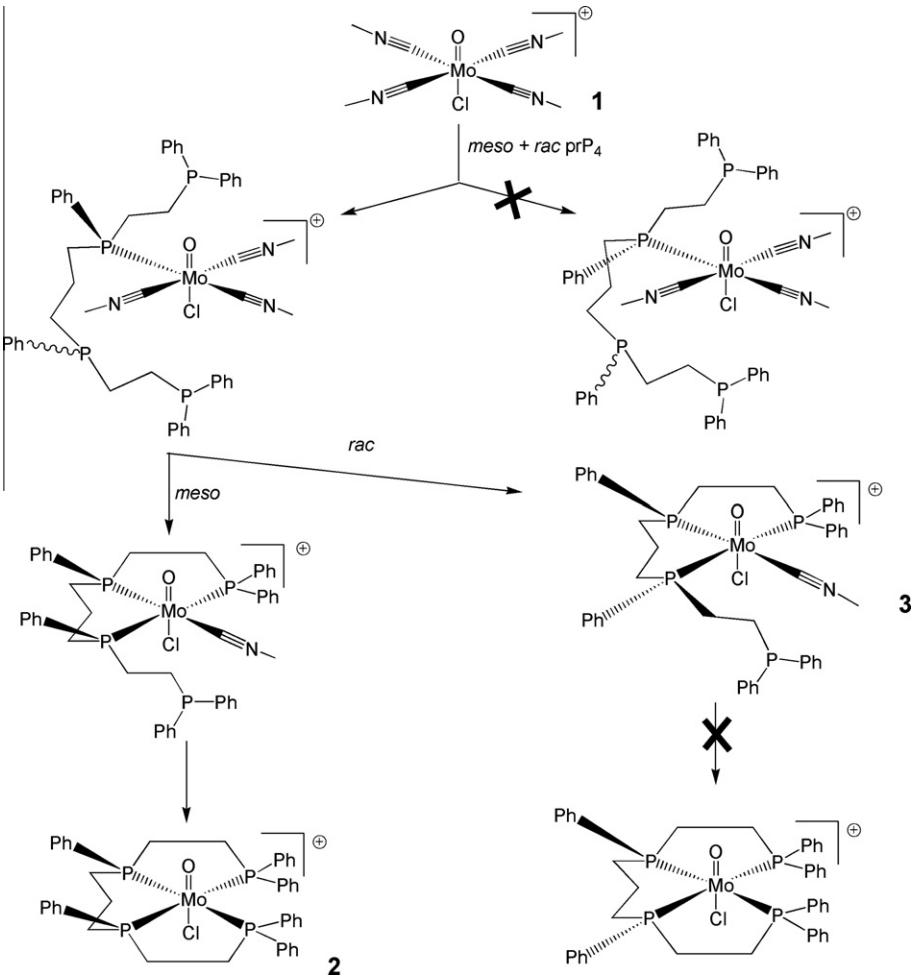


Fig. 5. $^{31}P\{^1H\}$ NMR spectrum of reaction mixture between **1** and prP_4.

the κ^3 complex derive from the *meso* ligand, the question arises as to where the *rac* ligand has gone. Moreover (ii), with increasing reaction time the κ^3 *meso* complex should convert to the κ^4 complex, which is not observed (*vide supra*). (iii) There is the possibility that the κ^3 species derives from a *meso* complex where one of the central phenyl groups is oriented to the chlorine ligand. This is sterically unfavorable and would imply that for a κ^4 coordination the second phenyl group is also oriented to the chlorine ligand (which is even more unfavorable). So this *meso* complex would "get stuck" in the κ^3 configuration. However, there is strong evidence that for steric reasons in a stable κ^3 Mo(IV) oxo–chloro tri- or tetraphos intermediate *not even one* phenyl group of a coordinated phosphine bridging two other coordinated phosphines can be oriented towards the chlorine ligand (see below). (iv) We thus conclude that the κ^3 complex does not derive from the *meso*, but from the *rac* ligand. Again, it is noteworthy that only one isomer is observed. From the rule established in (iii) that the complex does not tolerate a configuration in which one of the phenyl groups of the bridging, coordinated phosphines is oriented towards the chlorine ligand, we conclude that only the κ^3 complex with the *rac* ligand is formed where the central phenyl group is oriented towards the oxo ligand (Scheme 5, right). Starting from this complex the κ^4 complex cannot form as in this case one of the phenyl groups of the bridging phosphines would have to be oriented towards the chlorine ligand. If, in contrast, the phenyl group of the first bridging, coordinated phosphine is oriented towards the oxo ligand, the *meso* prP_4 ligand forms the κ^4 complex without problems (Scheme 5, left).

In order to check the above-mentioned sterical selection rule (which provides a consistent explanation of all experimental findings), the complex $[Mo(O)Cl(CNMe)(dpepp)]PF_6$ (**4**) was prepared by reaction of the tridentate phosphane dpepp (bis(2-diphenylphosphinoethyl)phenylphosphane) with the precursor **1a** (Scheme 3). In fact, the phenyl substituent of the central phosphine group was found to be oriented towards the oxo and not towards the chlorine ligand (*vide supra*). The C–N stretch of this complex was observed at 2218 cm^{-1} (Supplementary Fig. S2). In order to explore its reactivity compound **4** was treated with an excess of the monophosphine ligand dimethylphenylphosphine in CH_2Cl_2 under reflux. Moreover, this mixture was irradiated with UV light. In spite of these fairly drastic reaction conditions, only a very limited exchange of the isonitrile ligand was observed; i.e., the product still exhibited the CN-vibration of compound **4** at 2218 cm^{-1} (Supplementary Fig. S2). These findings demonstrate the general difficulty to exchange the fourth isonitrile ligand. Only if the steric conditions are favorable, i.e., only if the fourth P atom of the tetradentate prP_4 ligand is suitably arranged to coordinate in the position of the fourth isonitrile ligand, a successful exchange reaction (promoted by the chelate effect) occurs. If this is not the case, only three isonitrile ligands are exchanged, leading to the κ^3 complex.



Scheme 5.

3. Summary and conclusions

Reaction of the tetraisonitrile complex $[Mo(O)Cl(CNMe)_4]^+$ (**1**) with the tetraphos ligand prP_4 leads to a 1:1 mixture of two complexes, $[Mo(O)Cl(\kappa^4\text{-}meso\text{-}prP_4)]^+$ (**2**) and $[Mo(O)Cl(CNMe)(\kappa^3\text{-}rac\text{-}prP_4)]^+$ (**3**). The κ^4-product **2** has the two phenyl groups of the central phosphorus atoms oriented towards the oxo ligand whereas in the κ^3 product **3** one of these phenyl groups is oriented towards the oxo and the other towards the chlorine ligand. The origin of the different coordination modes lies in the different steric demands of the oxo and chloro ligands. The influences of the steric interactions are enhanced by the fact that exchange of the fourth isonitrile ligand is difficult. These hypotheses are supported by the preparation of the complex $[Mo(O)Cl(CNMe)(dpepp)]PF_6$ (**4**), where the phenyl group of the central P-atom is oriented towards the oxo ligand. Moreover, the isonitrile ligand of **4** is inert towards exchange by monophosphines, even under drastic conditions.

With the described isonitrile exchange reactions a general method for the coordination of tetraphos ligands to mononuclear molybdenum centers has been found. This complements our earlier studies on the coordination of the tetraphos ligand prP_4 to the molybdenum oxo complex $[Mo(O)I_2(PMe_3)_2]^+$, leading to the complex $[Mo(O)I(prP_4)]^+$ [16]. It has been shown that the steric demand of the axial halide ligand plays an important role in the reaction course, in particular with respect to a successful completion of the equatorial κ^4 coordination and a stereoselective formation of the κ^4-*meso* complex.

4. Experimental

4.1. Material and methods

All synthetic reactions were performed under an inert gas atmosphere using Schlenk techniques. The solvents were dried and distilled under argon atmosphere. The precursor $[Mo(O)Cl(CNMe)_4]^+$ (**1**) and the required methyl isonitrile [25] were prepared using the literature procedure [21]. The ligand prP_4 was prepared the reaction of $(C_6H_5)_2P\text{–}(CH_2)_2Cl$ [26] with 1,3-bis(lithiumphenylphosphido)propane [17].

IR spectra were obtained from KBr pellets using a Bruker IFS v66/S FT-IR-Spectrometer. Raman spectra were recorded on a Bruker IFS 66 RA 106 (laser wavelength 1064 nm). Elemental analyses were performed using a Euro Vector CHNS-O-element analyzer (Euro EA 3000). Samples were burned in sealed tin containers by a stream of oxygen. NMR spectra were recorded on a Bruker Avance 400 pulse Fourier transform spectrometer operating at a ^1H frequency of 400.13 MHz (^{31}P: 161.975 MHz) using a 5 mm inverse triple-resonance probe head with z-gradient. Reference as substitutive standard: H_3PO_4 85% pure, $\delta(^{31}P) = 0$ ppm.

4.1.1. X-ray single crystal structure analysis

Intensity data were collected using an STOE imaging plate diffraction system (IPDS-1) with Mo Kα radiation. Details of the structure analysis are collected in Table 4. The structure was solved with direct methods using SHELXS-97 and refinement was performed against F^2 using SHELXL-97 [27]. All non-hydrogens were refined anisotropic. The C–H H atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined using a riding model. For **2b** a numerical absorption correction was performed ($T_{min/max}$: 0.7653/0.9589). The asymmetric unit of **2b** and **4** contain additional dichloromethane solvent molecules which are completely disordered and for which no reasonable split model can be found. Therefore, the data were corrected for disordered solvent using the Squeeze option in Platon and the content of solvent was considered in the calculation of the molecular weight.

4.2. $[Mo(O)Cl(\kappa^4\text{-}prP_4)]BPh_4$ (**2b**)

0.40 g (0.70 mmol) $[Mo(O)Cl(CNMe)_4]BPh_4$ and 0.48 g (0.70 mmol) prP_4 were suspended in 70 ml of acetone. After 3 h the cloudy suspension turned into a clear violet solution. The solution was refluxed for 14 h and stirred at room temperature for further 24 h. Afterwards the solution was reduced in vacuum to 5 ml and was allowed to stand at −40° C. After 4 days a solid blue-violet precipitate was collected, washed with toluene and dried in vacuum.

Violet crystals, suitable for X-ray diffraction studies, could be obtained by slow evaporation of a CH_2Cl_2 solution.

Yield: 100 mg (12%). Elemental *Anal.* Calc. for $C_{67}H_{64}BClMoOP_4$: C, 69.90; H, 5.60. Found: C, 69.38; H, 5.55%.

IR (KBr): $\tilde{\nu}$ = 1483 (P-CH_2), 1435 (P-Ph), 955 (Mo=O) cm^{-1}.

$^{31}P\{^1H\}$ NMR (161.975 MHz, CD_2Cl_2): δ = 52.25 ($^{2/4}J_{ab}$ = −27.4 Hz, $^2J_{cd}$ = −18.5 Hz, $^2J_{ac/bd}$ = 123.8 Hz, $|^{2/3}J_{ad/bc}|$ = 4.9 Hz, 2P, $P_{c,d}$), 49.03 ($^{2/4}J_{ab}$ = −27.4 Hz, $^2J_{cd}$ = −18.5 Hz, $^2J_{ac/bd}$ = 123.8 Hz, $|^{2/3}J_{ad/bc}|$ = 4.9 Hz, 2P, $P_{a,b}$) ppm.

4.3. Reaction mixture of $[Mo(O)Cl(\kappa^3\text{-}prP_4)]PF_6$ and $[Mo(O)Cl(\kappa^4\text{-}prP_4)]PF_6$

An equimolar mixture of the precursor $[Mo(O)Cl(CNMe)_4]BPh_4/PF_6$ and the prP_4-ligand was refluxed in acetone for different periods of time from 6 h to several days. The solvent was removed in vacuum and the residue was characterized by NMR and vibrational spectroscopy.

Table 4
Crystallographic data of compounds **2b** and **4**.

Compound	$[Mo(O)Cl(\kappa^4\text{-}prP_4)]BPh_4$ (**2b**)	$[Mo(O)Cl(CNMe)(dpepp)]PF_6$ (**4**)
Empirical formula	$C_{68.50}H_{62}BCl_4Mo(O)P_4$	$C_{36}H_{36}ClF_6MoNOP_4$
Formula weight	1273.61	867.93
T (K)	293(2)	170(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
A (Å)	13.576(1)	18.647(2)
B (Å)	15.084(1)	12.374(1)
C (Å)	18.299(1)	18.446(2)
α (°)	88.16(1)	90
β (°)	70.49(1)	92.52(1)
γ (°)	65.65(1)	90
V (Å^3)	3193.7(2)	4252.1(5)
Z	2	4
D_{calc} (mg/m^3)	1.324	1.356
μ (mm^{-1})	0.515	0.575
θ (°)	1.49–28.00	2.29–27.94
Index ranges	h: −17/17 k: −19/19 l: −24/24	h: −24/24 k: −16/16 l: −24/24
Reflections collected	49 752	47 835
R_{int}	0.0302	0.0689
Independent reflections	15 247	10 158
Reflections with $I > 3\sigma(I)$	12 622	7894
Parameters	676	453
Goodness-of-fit	1.016	1.021
R_1 [$I > 2\sigma(I)$]	0.0363	0.0479
wR_2 (all data)	0.0990	0.1204
δF (e/Å^3)	0.326/−0.456	0.879/−1.033

4.4. [Mo(O)Cl(CNMe)(dpepp)]PF_6 (**4**)

A mixture of 300 mg (660 mmol) $[Mo(O)Cl(CNMe)_4]PF_6$ and 350 mg (660 mmol) of bis(2-diphenylphosphinoethyl)phenylphosphane was suspended in 40 ml acetone. After 10 min the cloudy suspension turned into a clear violet solution. The solution was refluxed for 8 h in acetone and was stirred for further 12 h at room temperature. Afterwards the solution was reduced in vacuum and the residue was extracted with 10 ml THF. A pale violet product could be obtained by cooling to −40 °C for 12 h. The product was dissolved in CH_2Cl_2, filtered over celite and again precipitated by adding THF. A small amount of the solid was solved in CH_2Cl_2 and was crystallized by slow vapor diffusion of diethyl ether. The obtained violet crystals were suitable for X-ray diffraction studies.

Yield: 250 mg (43%). Elemental *Anal.* Calc. for $C_{36}H_{36}ClF_6MoNOP_4$: C, 49.82; H, 4.18; N, 1.61. Found: C, 48.58; H, 4.27; N, 1.67%.

IR (KBr): $\tilde{\nu}$ = 2218 (CN), 1485 (P-CH_2), 1436 (P-Ph), 956 (Mo=O) cm^{-1}.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.975 MHz): δ = 95.42 (t, J = 2.5 Hz, 1P, inner P-Ph), 46.73 (d, J = 2.6 Hz, 2P, outer P-Ph_2) ppm.

^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.69–7.36 (m, 25H, phenyl), 3.69 (s, 3H, $CNCH_3$), 3.57–3.39 (m, 2H, CH_2), 3.05–2.80 (m, 4H, CH_2), 2.77–2.63 (m, 2H, CH_2) ppm.

4.5. Exchange reactions of 4 with monophosphines

200 mg of (23.0 mmol) $[Mo(O)Cl(CNMe)(dpepp)]PF_6$ and 90.0 mg (65.0 mmol) Me_2PhP were refluxed in 20 ml CH_2Cl_2 for 10 min by irradiation with a UV lamp. The mixture was reduced in vacuum and 20 ml of diethylether were added. After 12 h at −20 °C a violet resin could be isolated and was dried.

IR (KBr): $\tilde{\nu}$ = 2218 (CN), 1485 (P-CH_2), 1436 (P-Ph), 956 (Mo=O) cm^{-1}.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.044.

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