Synthesis, structure and properties of bisallyltris(trimethylphosphine)molybdenum(II) [1]
X-ray crystal structures of $[Mo(\eta^1:\eta^2\text{-}C_3H_5)_2(PMe_3)_3]$ and $PMe_4^+[MoCl_4(PMe_3)_2]^-$

Cornelia Borgmann, Christian Limberg *, Alexander Driess

*Universität Heidelberg, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

Abstract

Reaction of $[MoCl_2(PMe_3)_4]$ with two equivalents of allylmagnesiumbromide yields the highly reactive bisallylmolybdenum compound $[Mo(\eta^1:\eta^2\text{-}C_3H_5)_2(PMe_3)_3]$, (**1**). In addition to its X-ray structure analysis its structure in solution is determined NMR spectroscopically. The Mo–C bonds are very sensitive to attack by compounds with slightly polar E–H bonds. This is exemplified in the reaction of **1** with CH_2Cl_2 generating propene, $[MoCl_3(PMe_3)_3]$, and PMe_4Cl in the first steps. The latter two compounds further react to yield the phosphonium salt $PMe_4^+[MoCl_4(PMe_3)_2]^-$, (**2**). Treatment of **1** with two equivalents of CO results in C–C bond coupling so that 1,5-hexadiene in addition to $[cis\text{-}Mo(CO)_2(PMe_3)_4]$ can be isolated. © 1997 Elsevier Science S.A.

Keywords: X-ray crystal structures; Molybdenum oxo compounds

1. Introduction

Although molybdenum oxo compounds are used extensively as industrial catalysts, e.g. in the oxidation of propene (Eq. (1)), there is comparatively little information on the mechanisms governing their activity.

$$CH_2=CH-CH_3 + O_2 \xrightarrow{350\,°C,\ 2\,atm,\ MoO_3/Bi_2O_3} H_2C=CH-CH=O + H_2O \qquad (1)$$
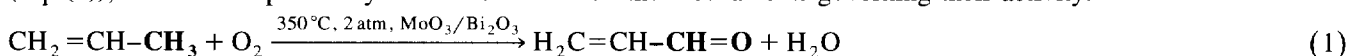
There is evidence [1] that Eq. (1) proceeds via the conversion of the molybdenum-bound propene to allyl by hydrogen shift as shown in Scheme 1, which justifies research concerning the oxo/Mo/allyl system. Recent research in our laboratory has been directed towards the preparation of such allyl complexes to serve as molecular models for species like **B**. However, if common synthetic routes established for the preparation of organometaloxides [2] are applied with the aim of synthesising compounds bearing the allylmolybdenum oxo fragment certain difficulties arise: in attempts to
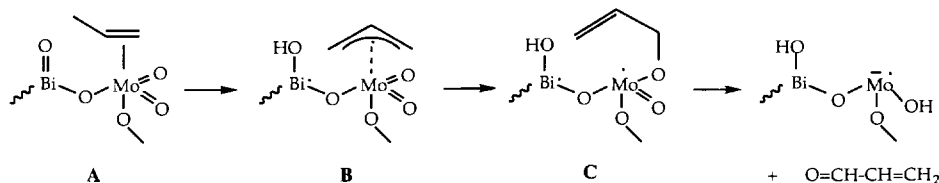
Scheme 1.

Scheme 2.
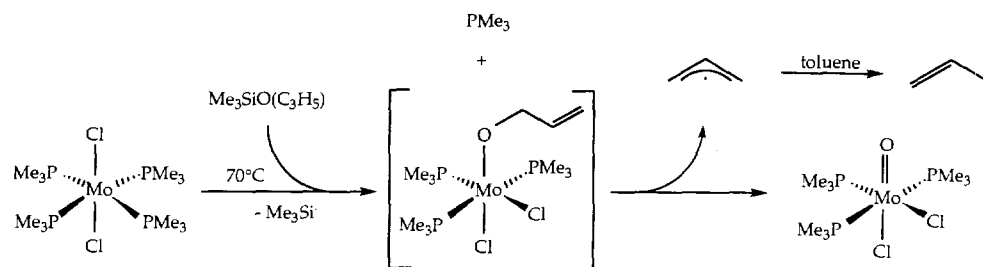
substitute leaving groups on molybdenum oxides via metathetical reactions the allylating reagents preferably attack the Mo=O bond while the oxidation of allylmolybdenum compounds generally supports the tendency of the allyl group to leave the molecule as a radical. The problems involved in the synthesis of allylmolybdenumoxides also become very obvious in the following findings: in 1992 the first allyltungsten oxide was synthesised by the reaction of $[WCl_2(PMe_3)_4]$ with $Me_3Si(OC_3H_5)$, yielding $[W(O)Cl(\eta_3\text{-}C_3H_5)(PMe_3)_2]$ and Me_3SiCl [3]. Hence, a Cl ligand has been substituted by an allyloxy group which then added oxidatively to the tungsten centre. Trying to apply this type of reaction to the corresponding molybdenum chloride we noticed that the $[MoCl_2(PMe_3)_4]/Me_3Si(OC_3H_5)$ system behaved completely different. Apparently no metathetical reaction rather than an oxo transfer from $Me_3Si(OC_3H_5)$ to the Mo centre occurs giving rise to the formation of $[Mo(O)Cl_2(PMe_3)_3]$ and propene. These results lead us to propose the reaction mechanism shown in Scheme 2 [4].

This radical mechanism corresponds well with the observation of Mayer et al. that $[W(O)Cl_2(PMe_3)_3]$ and bisbenzyl are formed on treatment of $[WCl_2(PMe_3)_4]$ with benzylalcohol [5]. Bisbenzyl should be the product of a radical recombination while in our case the allyl radical picked up a proton from the solvent (toluene). Apparently the oxophilic nature of tungsten and molybdenum in these systems is the driving force for the facile cleavage of C–O bonds in the alkoxides formed giving rise to the organic radicals. During the reaction of $[WCl_2(PMe_3)_4]$ with $Me_3Si(OC_3H_5)$ the W centre of the fragment resulting from the C–O bond cleavage is able to bind the allyl radical generated which is not possible in the Mo case (see Scheme 2). The most likely reasons for this finding are the lower electron densities at the Mo(IV) centres in the $[Mo(O)Cl_2(PMe_3)_2]$, or—if steric arguments are considered—even $[Mo(O)Cl_2(PMe_3)]$ fragments which are at the allyl groups disposal after C–O bond cleavage, as compared to the much softer W(III) centre in $[W(O)Cl(PMe_3)_2]$, the latter allowing sufficient backbonding for the stabilisation of an η^3-coordination mode.

We are therefore interested in the generation of allylmolybdenum compounds in which, bearing in mind the mechanism depicted in Scheme 1, the allyl groups are coordinated in an η^3-fashion and which possess a high electron density at the Mo centres stabilising this coordination mode for subsequent oxidation reactions.

2. Results and discussion

Since PMe_3 ligands are strong but soft σ-donors and weak π-acceptors they are ideally suited as co-ligands for the purpose mentioned above, so that the preparation of $Mo(C_3H_5)_x(PMe_3)_y$ systems seemed to be an attractive target.

2.1. Preparation of bisallyltris(trimethylphosphine)molybdenum(II) 1

As the starting material $[MoCl_2(PMe_3)_4]$ was chosen; this can be prepared in a four-step synthesis starting from $MoCl_5$ (the last step which includes the reduction of $[MoCl_4(PMe_3)_3]$ with Na/Hg [6] proceeded in our hands in an improved way when Zn was used). Reaction of this complex with two equivalents of allylmagnesiumbromide generated $[Mo(C_3H_5)_2(PMe_3)_3]$, (1), in good yield.

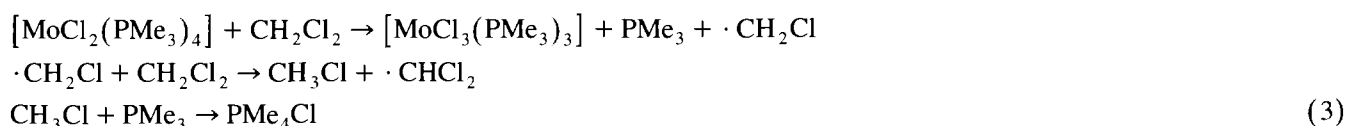$$Cl_2Mo(PMe_3)_4 + 2\,(C_3H_5)MgBr \longrightarrow \qquad + 2\,[MgClBr] + PMe_3 \qquad (2)$$
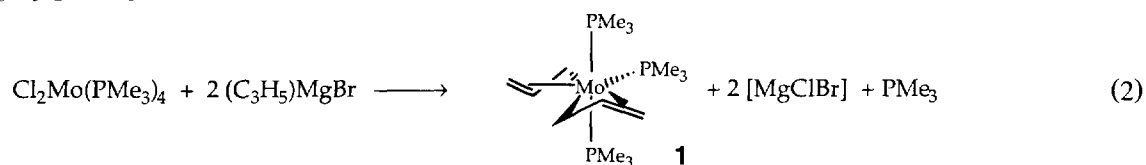
The existence of this compound had been suggested previously in reaction mixtures obtained by treatment of $[MoCl(C_3H_5)_3]$ with PMe_3 and Li [7] or $[Mo(C_2H_4)(C_3H_5)_2(PMe_3)_2]$ with PMe_3 [8] because of a ^{31}P NMR

Scheme 3.
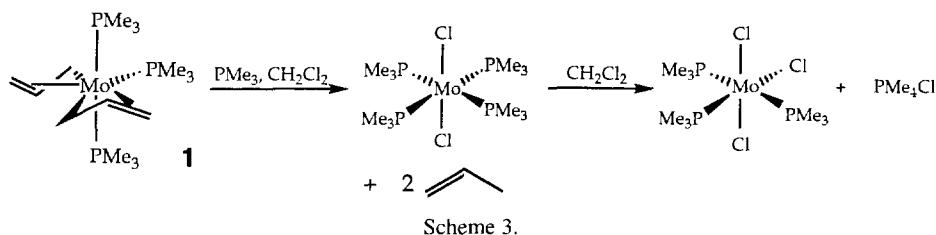
spectrum, but it had not been possible to isolate it in a pure state. It is not only thermally labile (dec.p.: 45 °C) but also very sensitive to reagents with slightly polar E–H bonds (E = element). Those are dissociated and the resulting proton is absorbed by the allyl groups yielding propene.

2.2. The reaction of 1 with CH_2Cl_2

The proton affinity of the allyl groups becomes very obvious in one of the solvolysis reactions of 1 we studied. 1 is soluble in toluene and petroleum ether but instantaneously reacts with CH_2Cl_2 initially forming the dichloride complex $[MoCl_2(PMe_3)_4]$, which was identified as an intermediate via its characteristic signal at $\delta = -8.95$ [6] in the ^1H NMR spectrum when the reaction was performed in CD_2Cl_2. After the reaction propene could be detected in the gas phase IR-spectroscopically, so that it can be formally viewed as a reaction of 1 with HCl, CH_2Cl_2 representing the source of the latter. However, since an additional PMe_3 ligand is needed, probably being provided by an alternative decomposition pathway of 1, the reaction cannot proceed quantitatively and the dichloride complex is just one intermediate in a complicated reaction sequence. Furthermore, this slowly reacts with dichloromethane as well to produce $[MoCl_3(PMe_3)_3]$ as shown in Scheme 3. The latter could also be shown independently by treating $[MoCl_2(PMe_3)_4]$ directly with CH_2Cl_2. In addition PMe_4Cl (identified by means of its ^1H and ^{31}P NMR spectra and its elemental analysis) precipitates which could be a product of the following reaction sequence:

$$[MoCl_2(PMe_3)_4] + CH_2Cl_2 \rightarrow [MoCl_3(PMe_3)_3] + PMe_3 + \cdot CH_2Cl$$
$$\cdot CH_2Cl + CH_2Cl_2 \rightarrow CH_3Cl + \cdot CHCl_2$$
$$CH_3Cl + PMe_3 \rightarrow PMe_4Cl \tag{3}$$

$$[MoCl_2(PMe_3)_4] + 2\,CH_2Cl_2 \rightarrow PMe_4Cl + [MoCl_3(PMe_3)_3] + \cdot CHCl_2$$

It has to be emphasised at this stage that these proposals are purely speculative and are just shown as one possible explanation for the formation of PMe_4Cl. Trying to employ radical traps in the reaction of $[MoCl_2(PMe_3)_4]$ with dichloromethane it was found that e.g. PhNO already reacts with the starting material in the absence of CH_2Cl_2 producing ESR-active species, so that attempts to trap radicals like $\cdot CH_2Cl$ and $\cdot CHCl_2$ and detect them via ESR spectroscopy were thwarted.

When the reaction of 1 with CH_2Cl_2 was performed in a flame-sealed vessel the PMe_4Cl formed according to Scheme 3 reacted further with $[MoCl_3(PMe_3)_3]$ to form $PMe_4^+[MoCl_4(PMe_3)_2]^-$, (2), so that the net equation must be formulated as

$$1 + 4\,CH_2Cl_2 \rightarrow 2\,C_3H_6 + \underset{\mathbf{2}}{PMe_4^+[MoCl_4(PMe_3)_2]^-} + [CHCl_2] + 2\,[CHCl] \tag{4}$$
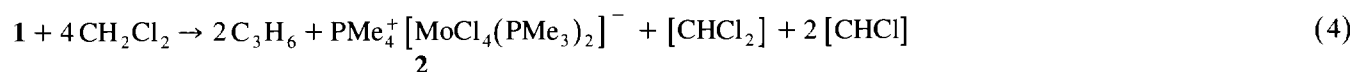
Unfortunately, the products which have their origin in the reactive fragments [CHCl] and [CHCl$_2$] could not be identified either by NMR spectroscopy or by GC/MS measurements. The reaction of PMe_4Cl with the trichloride yielding 2 is very slow so that crystals of 2 precipitate within 3 weeks from the original solution at room temperature. The geometry of the anion $[MoCl_4(PMe_3)_2]^-$, which has been mentioned previously [9a], as determined by X-ray crystallography is shown in Fig. 1. Table 1 lists relevant bond lengths and angles. The Mo atom displays pseudo-octahedral coordination, with a square-planar $MoCl_4$ unit and axial coordination of PMe_3. The idealised local symmetry of the Mo atom in the $MoCl_4P_2$ coordination is D_{4h}, with the C_4 axis passing through the P(1)–Mo–P(2) vector. The average Mo–Cl distance, 2.432(2) Å, is comparable to that observed for the Mo(III) complexes $PPh_4[MoCl_4(thf)_2]$ [9] and $C_{10}H_9N_2[MoCl_4(py)_2]$ [10].

2.3. The structure of 1

Although surface coordination of bisallylmolybdenum units produces effective heterogeneous catalysts, e.g. for olefin metathesis [11], molecular compounds with this fragment are very rare in the literature [7,8,12]. We were
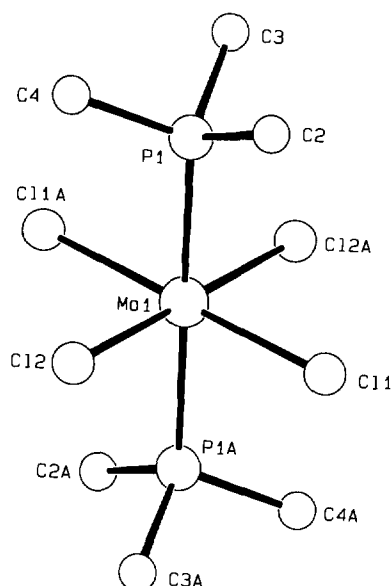
Fig. 1. The molecular structure of the anion of **2**.

Table 1
Selected bond lengths (Å) and bond angles (deg) in complex **2**

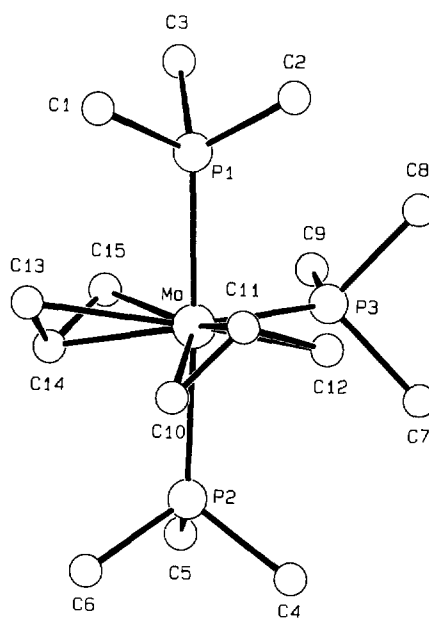| Mo–Cl(1)	2.432(2)	P(1)–C(2)	1.811(8)
Mo–Cl(2)	2.431(2)	P(1)–C(3)	1.798(8)
Mo–P(1)	2.540(2)	P(1)–C(4)	1.808(8)
Cl(1)–Mo–Cl(2)	89.40(8)	Cl(1)–Mo–P(1)	93.52(6)
Cl(1)–Mo–Cl(2A)	90.60(8)	Cl(2)–Mo–P(1)	88.47(7)

Fig. 2. The molecular structure of **1**.

Table 2
Selected bond lengths (Å) and bond angles (deg) in complex **1**

Mo–C(10)	2.359(8)	Mo–C(15)	2.313(3)
Mo–C(11)	2.246(6)	Mo–P(1)	2.467(2)
Mo–C(12)	2.311(6)	Mo–P(2)	2.447(2)
Mo–C(13)	2.362(1)	Mo–P(3)	2.461(1)
Mo–C(14)	2.251(7)		
P(1)–Mo–P(2)	177.54(4)	P(3)–Mo–C(14)	115.6(2)
P(1)–Mo–P(3)	91.55(5)	C(11)–Mo–C(14)	132.6(3)
P(2)–Mo–P(3)	90.83(5)	P(1)–Mo–C(11)	77.2(2)
P(3)–Mo–C(11)	111.7(2)	P(1)–Mo–C(14)	103.0(2)

therefore interested in the structure as well as the chemistry of **1**, not only with respect to the generation of allylmolybdenum oxides.

From ^{1}H-, ^{1}H{^{31}P}-, ^{31}P{^{1}H}-, ^{13}C{^{1}H}-DEPT- and ^{1}H-COSY-NMR spectra it can be deduced that in solution the MoP$_3$-unit of the molecule, in contrast to what has been suggested previously [7], is T-shaped and that the C$_3$H$_5$-groups are equivalent being η^3-, or more correctly η^1:η^2-coordinated. In all spectra all signals could be assigned unambiguously, so that a geometry as shown in Eq. (3) could be proposed.

Crystals of **1** could be grown when the synthesis of **1** was performed in a special passivated glass apparatus as described in Section 4. **1** crystallises in the triclinic space group $P\bar{1}$. The crystal structure is shown in Fig. 2 and the relevant bond lengths and angles are summarised in Table 2. If both allyl groups are considered as point charges the coordination sphere of **1** is reduced to a trigonal bipyramid. The allyl groups and one PMe$_3$ ligand are oriented roughly in a plane then, while the two residual PMe$_3$ groups lie perpendicular to this plane. The extension of the C(11)–Mo–C(14) angle from 120° to 132.6(3)° can be explained by a repulsive effect of the allyl groups bonded much closer to the Mo centre than the phosphine ligands. For the same reason the C(11)–Mo–P(3) and C(14)–Mo–P(3) angles are smaller than 120°. The allyl groups are η^1:η^2-coordinated with C(12) and C(15) representing the σ-bonded carbons, showing the shortest terminal Mo–C bond distances. Both the allyl groups and the PMe$_3$ ligands are disordered (conformationally and rotationally respectively). By comparison of the electron densities a probability of 65% can be assigned to the structure shown in Fig. 2, with an anti symmetrical orientation of the allyl groups and a non-crystallographical C_2-axis along the Mo–P(3) bond. An alternative way to describe the coordination sphere around the Mo centre in **1** is given by formal separation of the allyl groups into a σ- and a π-donor part yielding therefore a puckered pentagonal bipyramidal structure. However, both a trigonal and a pentagonal coordination sphere would account for the diamagnetism of **1** since an e$_1$ set of orbitals is generated as the HOMOs.

2.4. Reaction of 1 with CO

The reaction of **1** with CO was of interest since treatment of [Mo$_2$(C$_3$H$_5$)$_4$] with CO had lead to [Mo(CO)$_4$(CH$_2$=CH(CH$_2$)$_2$CH=CH$_2$)] in the past [13] and it seemed worth investigating whether the allyl groups in **1** could be caused to show C–C coupling reactions as well. Indeed the reaction of **1** with two equivalents of CO resulted in the formation of 1,5-hexadiene, [cis-Mo(CO)$_2$(PMe$_3$)$_4$] [14] and (probably under release of free PMe$_3$ needed in Scheme 4) to an unidentified highly labile Mo compound.

The close neighbourhood of the two allyl groups and the electronic conditions at the Mo centre therefore allow C–C bond formation and the product is released from the metal centre giving way to the stronger ligands PMe$_3$ and CO respectively.
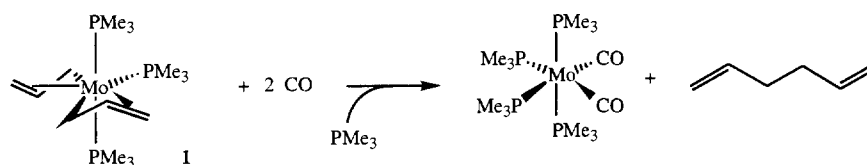
Scheme 4.

3. Prospects

The reaction of **1** with CH_2Cl_2 discussed above conveys an idea about the proton affinity of the allyl groups in **1** and suggests reactions making use of this sensitivity in order to introduce oxo ligands into this system at the same time. Currently, reactions of **1** with e.g. allylalcohol are under investigation.

With respect to subsequent oxidation reactions of **1**, cyclic voltammetric measurements with **1** were performed. In thf **1** shows a reversible step at $E_{1/2} = -600$ mV which corresponds to an oxidation as shown by recording of a polarogram, suggesting that **1** can be oxidised without decomposition of its principal framework. Further reactions concerning **1** will be reported in a subsequent publication.

4. Experimental section

All manipulations were carried out with a vacuum line (at a background pressure $< 10^{-4}$ mbar) or else, in a glove-box, or by means of Schlenk-type techniques involving the use of a dry argon atmosphere. CO gas was dried in a P_4O_{10} column and filled into a gas-tight syringe on a vacuum line. Dichlorotetrakis(trimethylphosphine)molybdenum(II) was prepared by slightly altering a literature procedure using $[MoCl_4(PMe_3)_3]$ as the Mo source [6] and Zn as the reducing agent. Solvents were dried according to standard procedures; microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg. IR spectra were recorded with a Bruker IFS 66 FTIR spectrometer. NMR spectra of solutions were recorded using a Bruker AC 200 instrument operating at 200 MHz. The deuterated solvents had been condensed into the NMR tubes previously before the tubes were flame-sealed. The X-ray diffraction measurement was made on single crystals on a Siemens P4 (Nicolet Syntex) R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). MS spectra were recorded with a Finnigan MAT 8230. The cyclic voltammetry measurement was performed on a Metrohm with NBu_4PF_6 (0.1 N) as the electrolyte and a Pt electrode against a calomel reference electrode. Because of the sensitivity of **1** a salt bridge had to be used.

4.1. Synthesis of bisallyltris(trimethylphosphine)molybdenum(II), (1)

Owing to the high sensitivity of the compound, not only to air but also to non-passivated glass walls, pure samples of **1** could only be obtained if its synthesis was performed in a glass-apparatus consisting of two Schlenk-tubes connected by a bridge and with an NMR-tube connected to one of the tubes. The whole apparatus was passivated with Me_3SiCl prior to use. 2.35 g (5.0 mmol) of dichlorotetrakis(trimethylphosphine)molybdenum(II) were introduced into the tube lacking the NMR-tube in the glove-box. 60 ml of diethyl ether were added and the resulting suspension treated with 10.1 ml (10.1 mmol) of a 1 M allylmagnesiumbromide solution. The yellow suspension turned dark orange and within 30 min a colourless solid precipitated. After a further 30 min of stirring at room temperature the solvent was removed in vacuo. The residue was extracted with ca. 40 ml of petroleum ether 40/60 and the solution decanted into the second tube. An aliquot of the solution was decanted into the NMR tube, all volatiles removed, d_8-toluene co-condensed and the NMR tube flame-sealed to check the purity of the compound. Afterwards petroleum ether 40/60 was distilled in vacuo into the vessel again and by cooling to $-80\,°C$ orange crystals of **1** were obtained in 90% yield. $C_{15}H_{36}MoP_3$ (405.32); dec.p.: 45 °C; IR (KBr): 3032w, 2966m, 2907m, 2808sh, 1459sh, 1420m, 1294m, 1278m, 1216w, 1153w, 1101w, 953vs, 867w, 843w, 692m, 647m cm^{-1}. MS (EI) m/e (rel. int. (%)): 408 (M$^+$, 5), 368 (M$^+$ − allyl, 2), 326 (M$^+$ − 2allyl, 22), 250 (M$^+$ − 2allyl − PMe$_3$, 24).
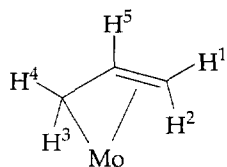
^{1}H NMR (d_8-toluene): δ 4.39 (m, 1 H, H^5), 1.74 (m, 1 H, H^2), 1.63 (m, 1 H, H^1), 1.07 (d, $^2J_{H-P} = 6.4$ Hz, 9 H, P(CH_3)$_3$), 0.94 (m, 18 H, P(CH_3)$_3$), 0.70 (m, 1 H, H^4), 0.44 (vq, $^2N_{H-P} = 6.9$ Hz, 1 H, H^3) ^{1}H{^{31}P} NMR (d_8-toluene): δ 4.39 (m, 1 H, H^5), 1.73 (dd, $^3J_{H^2-H^5} = 6.0$ Hz, $^2J_{H^2-H^1} = 3.9$ Hz, H^2), 1.61 (m, 1 H, H^1), 1.07 (s, 9 H,

Table 3
Crystal data and details of the structure determination of complexes **1** and **2**

	1	**2**
Formula	$C_{15}H_{37}MoP_3$	$C_{10}H_{30}Cl_4MoP_3$
Molecular weight	406.30	481.02
Crystal system	triclinic	monoclinc
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.016(4)	15.303(3)
b (Å)	9.702(4)	9.789(2)
c (Å)	13.284(5)	18.760(4)
α (deg)	90.01(2)	90
β (deg)	93.48(3)	112.600(10)
γ (deg)	104.52(3)	90
Cell volume (Å^3)	998.10	2594.5(9)
Z; D_{calc} (g m^{-3})	2; 1.352	4; 1.449
$F(000)$	428	1148
Crystal size (mm^3)	$0.20 \times 0.30 \times 0.40$	$0.20 \times 0.30 \times 0.30$
2θ range (deg)	4.3–48	2.9–48
h; k; l range	0 to 9; −11 to 10; −15 to 15	−11 to 17; −10 to 11; −21 to 19
μ (cm^{-1})	0.05	0.05
No. of collected reflections	3366	4244
No. of unique reflections	3118	4077
No. of reflections with $I > 2\sigma(I)$	2693	2614
No. of refined parameters	196	204
Final R, R_w	0.036, 0.092	0.051, 0.139
GOF	1.064	1.028
Min. max difference map (e$^-$ Å^{-3})	0.72	1.69

$P(CH_3)_3$), 0.94 (s, 18 H, P(CH_3)$_3$), 0.70 (d, $^3J_{H^4-H^5} = 7.5$ Hz, 1 H, H^4), 0.44 (d, $^3J_{H^3-H^5} = 7.6$ Hz, 1 H, H^3); ^{31}P{^{1}H} NMR (d_8-toluene): δ 7.0 (d, $^2J_{P-P} = 34$ Hz, 2 P, PMe$_3$), 4.3 (t, $^2J_{P-P} = 34$ Hz, 1 P, PMe$_3$); ^{13}C{^{1}H} NMR 135°-DEPT (d_8-toluene): δ 77.6 (s, H$_2$C=CHCH$_2$), 38.9 (s, H$_2$C=CHCH$_2$), 36.7 (d, $^2J_{C-P} = 14.6$ Hz, H$_2$C=CHCH$_2$), 24.6 (d, $^2J_{C-P} = 20.3$ Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR 135°-DEPT (d_6-benzene): δ 77.6 (s, H$_2$C=CHCH$_2$), 39.1 (vq, $N_{C-P} = 2.8$ Hz, 3.7 Hz, H$_2$C=CHCH$_2$), 36.8 (dt, $^2J_{C-P} = 14.8$ Hz, $^2J_{C-P} = 2.8$ Hz, H$_2$C=CHCH$_2$), 24.6 (dt, $^1J_{C-P} = 19.4$ Hz, $^3J_{C-P} = 2.8$ Hz, P(CH_3)$_3$), 16.7 (vt, $^1N_{C-P} = 8.3$ Hz, 9.3 Hz, P(CH_3)$_3$). Anal. Found: C, 43.81; H, 9.02%; calc.: C, 44.34, H, 9.18%.

4.2. Crystal structure of bisallyltris(trimethylphosphine)molybdenum(II), (1)

A single crystal of **1** was obtained by performing the synthesis as described in Section 4.1 after cooling of the whole apparatus to −80 °C. The crystals were suspended in an oil in the glove box, quickly selected under the microscope and frozen to 200 K. Crystal data and refinement details are listed in Table 3. Atomic coordinates are listed in Table 4. Because of significant disordering only Mo, P and five C atoms (1, 6X, 9, 12, 15) were refined anisotropically.

4.3. Synthesis of tetramethylphosphonium[tetrachlorobis(trimethylphosphine)molybdate(III)], (2)

0.55 g (1.3 mmol) of **1** were introduced into a reaction vessel in a glove box and 2 ml of dichloromethane co-condensed on a vacuum line. After flame-sealing of the vessel and annealing, a vigorous reaction took place and the reaction mixture turned dark brown. Within 3 weeks slightly orange crystals of **2** separated which were isolated in ca. 80% yield by cracking of the seal of the vessel in an argon atmosphere followed by decanting of the overlaying solution and washing of the residue with dichloromethane. $C_{10}H_{30}Cl_4MoP_3$ (481.02); IR (KBr): 2964w, 2906w, 2297vw, 1413m, 1302m, 1261s, 1080br,vs, 1023br,vs, 983s, 946s, 864m, 801vs, 738m, 703m, 502w, 474w cm^{-1}. **2** is insoluble in most common organic solvents and water decomposes it immediately.

Unfortunately, after washing the crystals were still covered by a brown oil from which they could not be completely separated so that satisfactory elemental analyses could not be obtained.

4.4. Crystal structure of tetramethylphosphonium[tetrachlorobis(trimethylphosphine)molybdate(III)], (2)

A single crystal of **2** was obtained by performing the synthesis as described in Section 4.3. The crystals were suspended in an oil in the glove box, quickly selected under the microscope and frozen to 200 K. Crystal data and refinement details are listed in Table 3. Atomic coordinates are listed in Table 5.

Table 4
Atomic coordinates and U_{eq} of **1**

Atom	x	y	z	U_{eq}
Mo	1284(1)	3293(1)	2821(1)	18(1)
P(1)	3230(1)	5708(1)	2825(1)	25(1)
P(2)	−718(1)	934(1)	2871(1)	25(1)
P(3)	2447(1)	2630(1)	1271(1)	24(1)
C(1)	3001(37)	6968(25)	3826(22)	42(6)
C(2)	5570(15)	5979(12)	3021(10)	23(3)
C(3)	3111(16)	6798(13)	1659(9)	34(3)
C(1X)	3210(43)	6872(32)	3904(23)	44(7)
C(2X)	5595(18)	6006(15)	2802(11)	37(4)
C(3X)	2937(16)	6962(13)	1871(9)	35(3)
C(4)	34(15)	−688(12)	2922(10)	36(4)
C(5)	−2095(14)	273(11)	1714(8)	39(3)
C(6)	−2437(21)	623(21)	3750(12)	29(4)
C(4X)	113(12)	−658(10)	3203(8)	22(3)
C(5X)	−2427(19)	354(15)	1858(11)	28(4)
C(6X)	−2102(20)	610(17)	3964(11)	31(3)
C(7)	2696(34)	803(26)	1154(17)	31(7)
C(8)	4747(19)	3429(16)	1054(12)	36(5)
C(9)	1601(26)	2949(22)	14(13)	33(3)
C(7X)	2529(47)	790(35)	1059(21)	49(13)
C(8X)	4570(19)	3589(16)	929(11)	34(4)
C(9X)	1204(27)	2694(25)	50(18)	38(6)
C(10)	1477(9)	2738(7)	4547(5)	31(1)
C(11)	3092(8)	3285(7)	4179(5)	30(1)
C(10X)	2161(16)	3621(14)	4519(9)	33(3)
C(11X)	2312(15)	2360(13)	4149(8)	26(2)
C(12)	3568(5)	2409(4)	3427(3)	30(1)
C(13)	−575(10)	4577(9)	3458(5)	31(2)
C(14)	−1357(9)	3707(7)	2630(5)	33(2)
C(13X)	−1148(16)	3938(15)	3332(10)	38(3)
C(14X)	−480(15)	4764(12)	2549(8)	27(3)
C(15)	−587(5)	4023(5)	1669(3)	35(1)

Table 5
Atomic coordinates and U_{eq} of **2**

Atom	x	y	z	U_{eq}
Mo(1)	5000	5000	0	23(1)
Mo(2)	0	5000	5000	28(1)
Cl(1)	6073(1)	6923(2)	192(1)	41(1)
Cl(2)	6354(1)	3469(2)	455(1)	45(1)
Cl(3)	186(1)	3999(3)	6241(1)	53(1)
Cl(4)	−74(2)	2746(2)	4444(1)	53(1)
Cl(5)	4853(2)	5214(2)	6205(1)	51(1)
Cl(6)	6897(2)	4834(3)	6866(1)	72(1)
P(1)	5061(1)	5097(2)	1372(1)	30(1)
P(2)	−1794(1)	5099(2)	4552(1)	36(1)
P(3)	−912(2)	4792(2)	1520(1)	41(1)
C(1)	5865(6)	4843(9)	6006(4)	45(2)
C(2)	5956(6)	6197(9)	2037(4)	49(2)
C(3)	3973(6)	5646(11)	1438(5)	62(3)
C(4)	5291(6)	3464(8)	1859(4)	48(2)
C(5)	−2411(6)	3916(10)	3789(5)	58(3)
C(6)	−2270(6)	4750(12)	5281(5)	68(3)
C(7)	−2316(6)	6725(10)	4167(5)	56(3)
C(8)	−1430(7)	6356(10)	1625(5)	63(3)
C(10)	−1286(7)	3445(10)	1973(5)	65(3)
C(11)	−1238(4)	4440(9)	505(3)	50(2)
C(12)	364(4)	4944(11)	1986(3)	72(3)

4.5. Reaction of 1 with CO

0.58 g (1.4 mmol) of **1** were dissolved in 30 ml of petroleum ether 40/60 and treated with two equivalents of CO by means of a gas-tight syringe. After stirring for 4 h the initial dark orange solution decolorised to pale yellow and a brown solid precipitated. Filtering of the solution and cooling to $-80\,°C$ lead to the formation of 0.30 g (0.6 mmol) of brown crystals which were identified as *cis*-Mo(CO)$_2$(PMe$_3$)$_4$ by their ^{1}H- and ^{31}P-NMR spectra as well as by their MS and IR spectra [14]. By performing the reaction in d_8-toluene and investigation of the resulting reaction mixture by ^{1}H NMR spectroscopy 1,5-hexadiene could be identified as the major organic product.

5. Supplementary material available

Tables of bond lengths and angles, calculated hydrogen positions and anisotropic thermal parameters for both structures are available from C.L.

Acknowledgements

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