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Reactivity of bis(ethylene) complexes of molybdenum(0) versus α,β unsaturated carbonyl compounds. Crystal and molecular structure of $Mo(H_2C{=}CH{-}COOMe)_3(PMe_3)$

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Abstract

The interaction of *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ (**1**) with ester or amide reagents of formulation $H_2C{=}CH{-}C(O)R$ affords complexes $Mo[H_2C{=}CH{-}C(O)R]_3(PMe_3)$ (R = OMe, **2**; O^tBu, **3**; NMe_2, **4**). Conversely, the reaction of **1** with methyl vinyl ketone, $H_2C{=}CH{-}C(O)Me$, affords the compound $Mo[H_2C{=}CH{-}C(O)CH_3]_2(PMe_3)_2$ (**5**). Compounds **2**–**4** are obtained as ca. 9:1 mixture of two isomers. The major isomer of $Mo(H_2C{=}CHCOOMe)_3(PMe_3)$ **2** has been structurally characterized. Two of the methyl acrylate ester groups are bonded to the metal through the C=C and C=O double bonds as an 1-oxa-1,3-diene ligand, while the third is only ligated through the C=C double bond.

Keywords: Molybdenum; Olefin complexes; Unsaturated esters; Unsaturated amides; Methyl vinyl ketone

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1. Introduction

In the course of our studies of molybdenum and tungsten bis(ethylene) complexes [1] we have tried to systematically investigate the reactivity of the $M(C_2H_4)_2$ core (M = Mo and W) versus different type of reagents. For example, interestingly the interaction with carbon dioxide produces unique examples of carboxylation of ethylene at the transition metal center [2]. As a prolongation of our research on this compound, here we describe the reactivity of the *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ complex versus some α,β unsaturated carbonyl compounds, $H_2C{=}CH{-}C(O)R$. The interaction of **1** with this type of reagent produces complexes of general formulation $Mo[H_2C{=}CH{-}C(O)R]_3(PMe_3)$ (R = OMe, **2**; O^tBu, **3**; NMe_2, **4**). The molecular structure of the methyl ester derivative, **2**, has been determined by X-ray crystallography. Complex $Mo(H_2C{=}CHCOOMe)_3(PMe_3)$ shows two of the methyl acrylate groups bonded to the metal through the C=C and C=O double bonds as an 1-oxa-1,3-diene ligand, while the third is only ligated through the C=C double bond. The use of methyl vinyl ketone affords, conversely, the compound $Mo[H_2C{=}CH{-}C(O)CH_3]_2(PMe_3)_2$ (**5**). NMR studies are reported for compounds **2**–**5**. A related series of compounds have been recently reported by Schmidt and co-workers [3].

2. Experimental section

Microanalyses were by the Microanalytical Service of the University of Sevilla. IR spectra were recorded on Perkin-Elmer Model 883 spectrophotometer. ^1H, ^{13}C and ^{31}P-NMR spectra were run on Bruker AMX-300 and AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C-NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to

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$SiMe_4$. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The light petroleum used had a bp 40–60°C. The compound *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ (**1**) was prepared according to the published procedure ([1]a).

2.1. Synthesis of $Mo[H_2C{=}CH{-}C(O)OMe]_3(PMe_3)$ (2)

A solution of **1** (0.31 g, 0.68 mmol) in light petroleum (35 ml) was treated with three equivalents of $H_2C{=}CH{-}COOMe$ at r.t. Immediately, the color of the solution changed from yellow to dark red and, after stirring overnight, a yellow solid was formed. The colorless liquid was filtered off and the solid washed twice with light petroleum (10 ml). Recrystallization from saturated solutions of diethyl ether at −20°C afforded orange crystals of **2** in 86% yield. IR (Nujol): 1681, 1540, 1520 cm^{-1} (ν_{CO}). ^1H-NMR (300 MHz, C_6D_6): δ 0.83 (d, 9H, $^2J_{HP} = 8$ Hz, PMe_3), 0.86 (obscured m, 1H, $=CH_2$, B), (the three ester ligands have been labeled as A, B and C, respectively), 1.52 (ddd, 1H, $^3J_{HP} = 23.4$, $J_{HH} = 7.5$, 3.6 Hz, $=CH_2$, A), 2.08 (m, 1H, $=CH_2$, C), 2.13 (ddd, 1H, $^3J_{HP} = 8.6$, $J_{HH} = 8.6$, 3.1 Hz, $=CH_2$, B), 2.21 (t, 1H, $J_{HH} = 8.5$ Hz, $=CH-$, B), 2.51 (m, 1H, $=CH_2$, A), 2.70 (m, 1H, $=CH_2$, C), 2.71 (m, 1H, $=CH-$, C), 3.42 (s, 3H, CH_3), 3.43 (obscured m, 1H, $=CH-$, A), 3.49 (s, 3H, CH_3), 3.80 (s, 3H, CH_3). $^{31}P\{^1H\}$-NMR (81 MHz, C_6D_6): δ 33.2 (s). $^{13}C\{^1H\}$-NMR (50 MHz, C_6D_6): δ 13.6 (d, $J_{CP} = 29.3$ Hz, PMe_3), 44.7 (s, $=CH-$, B), 48.0 (d, $J_{CP} = 18$ Hz, $=CH_2$, B), 50.0 (s, CH_3), 52.0 (s, CH_3), 52.7 (s, CH_3), 55.9 (d, $J_{CP} = 11$ Hz, $=CH_2$, C), 56.3 (s, $=CH-$, A), 60.5 (d, $J_{CP} = 14$ Hz, $=CH_2$, A), 63.5 (s, $=CH-$, C), 172.3 (s, CO), 173.0 (s, CO), 177.4 (s, CO). Anal. Found: C, 41.76; H, 6.36. $C_{15}H_{27}O_6PMo$ requires: C, 41.86; H, 6.28. The $^1H\{^{31}P\}$, homonuclear COSY ^1H-^1H and heteronuclear $^{13}C\{^1H\}$-^1H spectra have been performed in order to corroborate the proposed assignments.

Selected data for the minor isomer: ^1H-NMR (300 MHz, C_6D_6): δ 1.05 (d, 9H, $^2J_{HP} = 8$ Hz, PMe_3), 3.29 (s, 3H, CH_3), 3.44 (s, 3H, CH_3), 3.47 (s, 3H, CH_3). $^{31}P\{^1H\}$-NMR (81 MHz, C_6D_6): δ 25.6 (s).

2.2. Synthesis of $Mo[H_2C{=}CH{-}C(O)R]_3(PMe_3)$ (O^tBu, 3; NMe_2, 4) complexes

To a solution of the compound **1** (0.2 g, 0.4 mmol) in light petroleum (60 ml) was added three equivalents of $H_2C{=}CH{-}C(O)O^tBu$. Immediately, the yellow solution turned red and, after 1 h, the color changed to orange. The reaction mixture was stirred overnight and the volatiles were then removed. The yellow residue was extracted with light petroleum (15 ml). Concentration of the solution and cooling at −20°C gave yellow crystals of the compound **3** in 75% yield. IR (Nujol): 1683, 1532 cm^{-1} (ν_{CO}). ^1H-NMR (500 MHz, C_6D_6): δ 1.39 (d, 9H, $^2J_{HP} = 5$ Hz, PMe_3), 1.44 (s, 9H, CH_3), 1.46 (s, 18H, CH_3), 1.63 (m, 1H, $=CH_2$), 1.82 (m, 1H, $=CH_2$), 1.85 (m, 1H, $=CH_2$), 2.01 (ddd, 1H, $^3J_{HP} = 8.9$, $J_{HH} = 2.6$, 1.4 Hz, $=CH_2$), 2.48 (t, 1H, $J_{HH} = 7.2$ Hz, $=CH$), 2.65 (ddd, 1H, $^3J_{HP} = 17.9$, $J_{HH} = 7.3$, 2.5 Hz, $=CH_2$), 3.24 (m, 1H, $=CH-$), 3.80 (t, 1H, $J_{HH} = 7.4$ Hz, $=CH-$), one $=CH_2$ signal is obscured. $^{31}P\{^1H\}$-NMR (202 MHz, C_6D_6): δ 24.6 (s). $^{13}C\{^1H\}$-NMR (125 MHz, C_6D_6): δ 14.3 (d, $J_{CP} = 26.5$ Hz, PMe_3), 28.3 (s, CH_3) 28.5 (s, CH_3), 28.6 (s, CH_3), 45.9 (s, $=CH-$), 49.3 (d, $J_{CP} = 11.6$ Hz, $=CH_2$), 50.9 (d, $J_{CP} = 10.6$ Hz, $=CH_2$), 54.4 (s, $=CH-$), 62.5 (d, $J_{CP} = 14.5$ Hz, $=CH_2$), 64.0 (s, $=CH-$), 76.9 (s, CMe_3), 80.4 (s, CMe_3), 81.5 (s, CMe_3), 172.0 (s, CO), 175.1 (s, CO), 176.1 (s, CO). Anal. Found: C, 51.79; H, 8.09. $C_{24}H_{45}O_6PMo$ requires: C, 51.72; H, 7.85. Selected data for the minor isomer: $^{31}P\{^1H\}$-NMR (202 MHz, C_6D_6): δ 23.9 (s).

By using the same experimental method the analogous complex $Mo[H_2C{=}CH{-}C(O)NMe_2]_3(PMe_3)$, **4**, was obtained as orange crystals from a saturated solution of light petroleum in 70% yield. IR (Nujol): 1600, 1556 cm^{-1} (ν_{CO}). ^1H-NMR (500 MHz, C_6D_6): δ 1.08 (d, 9H, $^2J_{HP} = 7.8$ Hz, PMe_3), 1.17 (td, 1H, $J = 9.4$, 2.4 Hz, $=CH_2$, A), 1.22 (ddd, 1H, $^3J_{HP} = 8.2$, $J_{HH} = 4.2$, 1.6 Hz, $=CH_2$, B), 1.50 (ddd, 1H; $^3J_{HP} = 12.3$, $J_{HH} = 8.7$, 2.5 Hz; $=CH_2$, A), 1.73 (t, 1H; $J = 9.2$ Hz; $=CH-$, A), 1.95 (ddd, 1H; $^3J_{HP} = 22$, $J_{HH} = 7.1$, 4.2 Hz, $=CH_2$, B), 2.21 (dt, 1H, $J = 6.9$, 3.3 Hz, $=CH_2$, C), 2.39 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 2.84 (s, 9H, 2 CH_3), 2.91 (m, 1H, $=CH_2$, C), 2.93 (t, 1H, $J = 6.9$ Hz, $=CH-$, C), 3.38 (t, 1H, $J = 7.8$ Hz, $=CH-$, B). $^{31}P\{^1H\}$-NMR (202 MHz, C_6D_6): δ 32.3 (s). $^{13}C\{^1H\}$-NMR (125 MHz, C_6D_6): δ 14.5 (d, $J_{CP} = 27.5$ Hz, PMe_3), 32.6 (s, CH_3) 35.0 (s, CH_3), 35.5 (s, CH_3), 36.1 (s, CH_3), 36.5 (s, CH_3), 37.0 (s, CH_3), 42.3 (s, $=CH-$, A), 46.2 (d, $J_{CP} = 20$ Hz, $=CH_2$, A), 54.4 (s, $=CH-$, B), 54.8 (s, $=CH-$, C), 56.6 (d, $J_{CP} = 12.5$ Hz, $=CH_2$, C), 59.9 (d, $J_{CP} = 16$ Hz, $=CH_2$, B), 171.3 (s, CO), 180.1 (s, CO), 181.5 (s, CO). Anal. Found: C, 46.23; H, 7.41; N, 8.57. $C_{18}H_{36}N_3O_3PMo$ requires: C, 46.05; H, 7.67; N, 8.95. Selected data for the minor isomer: $^{31}P\{^1H\}$-NMR (202 MHz, C_6D_6): δ 34.8 (s). ^1H-NMR (500 MHz, C_6D_6): δ 0.91 (m, 1H), 1.11 (d, 9H, $^2J_{HP} = 7.9$ Hz, PMe_3), 1.67 (m, 1H), 2.07 (m, 1H), 2.27 (m, 1H), 2.34 (s, 9H, CH_3), 2.40 (s, 9H, CH_3), 2.65 (s, 9H, CH_3), 2.71 (s, 9H, CH_3), 3.08 (m, 1H). $^{13}C\{^1H\}$-NMR (125 MHz, C_6D_6): δ 14.3 (d, $J_{CP} = 27$ Hz, PMe_3), 33.3 (s, CH_3) 34.9 (s, CH_3), 35.7 (s, CH_3), 36.3 (s, CH_3), 43.9 (s, $=CH-$), 47.6 (d, $J_{CP} = 19$ Hz, $=CH_2$), 58.4 (d, $J_{CP} = 11$ Hz, $=CH_2$), 58.9 (s, $=CH-$), 59.0 (d, $J_{CP} = 20$ Hz, $=CH_2$), 172.0 (s, CO), 178.1 (s, CO), 178.4 (s, CO).

2.3. Synthesis of $Mo[H_2C{=}CH{-}C(O)Me]_2(PMe_3)_2$ (**5**)

A solution of **1** (0.18 g, 0.4 mmol) in light petroleum (30 ml) was treated with three equivalents of methyl vinyl ketone at r.t. The solution turned red and a brown solid was formed. After stirring overnight the reaction mixture was filtered, evaporated to dryness, and extracted with diethyl ether to give a red solution. Concentration and cooling at −30°C afforded red crystals of **5** in 30% yield. ^{1}H-NMR (300 MHz, 233 K, toluene-d_8) δ −0.08 (m, 1H, $=CH_2$, A), 0.26 (m, 1H, $=CH_2$, B), 0.88 (d, 9H, $^2J_{HP} = 7.8$ Hz, PMe_3), 0.9 (m obscured, 1H, $=CH_2$, A), 1.17 (d, 9H, $^2J_{HP} = 7.8$ Hz, PMe_3), 1.52 (m, 1H, $=CH_2$, B), 1.95 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 3.74 (t, 1H, $J = 7$ Hz, $=CH-$, A), 3.90 (t, 1H, $J = 6.5$ Hz, $=CH-$, B). $^{31}P\{^1H\}$-NMR (202 MHz, 293 K, C_6D_6): δ 7.09 (d, $^2J_{PP} = 4$ Hz, PMe3), 11.3 (d). $^{13}C\{^1H\}$-NMR (75 MHz, 233 K, toluene-d_8): δ 15.7 (d, $J_{CP} = 21$ Hz, PMe_3), 17.6 (d, $J_{CP} = 24$ Hz, PMe_3), 21.9 (s, CH_3), 40.4 (t, $J_{CP} = 30$ Hz, $=CH_2$), 51.3 (dd, $J_{CP} = 50$, 24 Hz, $=CH_2$), 68.8 (s, $=CH-$), 88.0 (s, $=CH-$), CO resonances were not observed. $^{13}C\{^1H\}$-NMR (125 MHz, 293 K, C_6D_6): δ 15.6 (d, $J_{CP} = 21$ Hz, PMe_3), 17.5 (d, $J_{CP} = 24$ Hz, PMe_3), 20.4 (br, CH_3), 21.5 (br, CH_3), 40.3 (br, $=CH_2$), 51.1 (br, $=CH_2$), 68.5 (br, $=CH-$), 88.2 (br, $=CH-$). Anal. Found: C, 43.16; H, 7.76. $C_{14}H_{30}O_2P_2Mo$ requires: C, 43.30; H, 7.73. Homonuclear COSY $^1H-^1H$ has been performed in order to corroborate the proposed assignments.

2.4. X-ray structural study of $Mo(H_2C{=}CHCOOMe)_3(PMe_3)$ (**2**)

A summary of the fundamental crystal data is given in Table 1. A prismatic orange crystal was epoxy resin coated and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo and P were taken from the International Tables for X-ray Crystallography [4]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [5] was applied at the end of the isotropic refinements.

A final refinement was undertaken with unit weights and anisotropic thermal motion for the non-hydrogen atoms. Hydrogen atoms were included with fixed isotropic contributions at their calculated positions. No trend in ΔF versus F_o or $(\sin\theta)/\lambda$ was observed. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-ray 80 System [6].

3. Results and discussion

3.1. Synthesis of $Mo[H_2C{=}CH{-}C(O)R]_3(PMe_3)$ ($R = OMe$, **2**; O^tBu, **3**; NMe_2, **4**) complexes

The interaction of *trans*-$Mo(C_2H_4)_2(PMe_3)_4$ (**1**) with α,β unsaturated carbonyl compounds, $H_2C{=}CH{-}C(O)R$, affords, after work up, complexes $Mo[H_2C{=}CH{-}C(O)R]_3(PMe_3)$ ($R = OMe$, **2**; O^tBu, **3**; NMe_2, **4**) (Eq. 1) in good yields. Compounds **2**–**4** are yellow or orange crystalline solids, soluble in common organic solvents.

$$Trans\text{-}Mo(C_2H_4)_2(PMe_3)_4 + H_2C{=}CH{-}C(O)R(\mathbf{1}) \Rightarrow Mo[H_2C{=}CH{-}C(O)R]_3(PMe_3) \qquad (1)$$

$R = OMe$, **2**, $R = O^tBu$, **3**, $R = NMe_2$, **4**.

The ^{1}H-NMR spectrum of **2** is typified, besides the PMe_3 resonance, by the presence of three different set of signals due to the three methyl acrylate ligands. The use of phosphorus decoupled-^{1}H-NMR spectrum simplifies the spectrum, but some signals are obscured by the Me resonances. A strong $^3J_{HP}$ coupling constant of 23.4 Hz was observed for a $=CHH$ resonance and tentatively assigned to the η^2-methyl acrylate ligand (labeled A, see Section 2, while the others as B and C fragments). This hydrogen atom occupies a pseudo-*trans* position (see the structural results ahead) with respect to the PMe_3 ligand. Homo- and hetero-nuclear two-dimensional NMR studies have been carried out with compound **2** allowing a complete assignment of the acrylate signals (see Section 2).

Table 1
Crystallographic data for $Mo(H_2C{=}CHCOOMe)_3(PMe_3)$ **2**

	$Mo(H_2C{=}CHCOOMe)_3$ (PMe_3) **2**
Empirical formula	$C_{15}H_{27}O_6PMo$
Formula weight	430.3
Crystal system	Monoclinic
Space group (cm^{-1})	$P2_{1/c}$
a (Å)	8.987(2)
b (Å)	17.611(3)
c (Å)	23.474(3)
β (°)	93.27(1)
V (Å^3)	3709(1)
Z	8
$D_{calc.}$ (g cm^{-3})	1.54
μ(Mo–K_α), cm^{-1}	7.98
Temperature (K)	295
λ(Mo–K_α), (Å) (graphite monochromated)	0.71069
R^a	0.035
Rw^b	0.041

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [b] $R_w = [\Sigma w\Delta^2F/\Sigma w|F_o|^2]^{1/2}$.

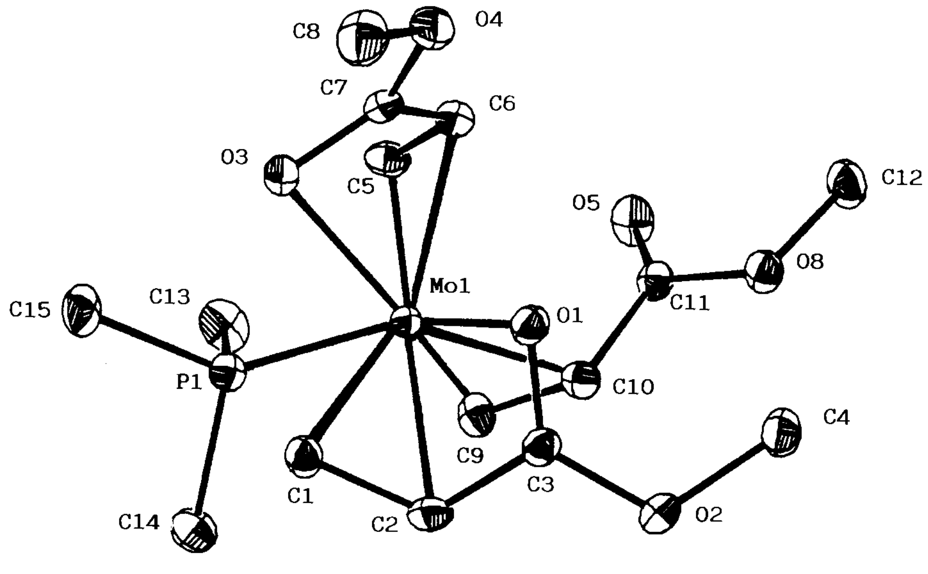


Fig. 1. Molecular structure of Mo(H_2C=CHCOOMe)$_3$(PMe$_3$) **2**.

The $^{31}P\{^1H\}$-NMR spectrum of **2** (and analogously those of **3** and **4**) display a singlet due to the coordinated PMe$_3$. Also, a minor resonance, in ca. 9:1 ratio, was detected in the spectrum and attributed to a geometrical isomer. This assumption was deduced due to the similar pattern of signals observed in the ^1H and $^{13}C\{^1H\}$ for the minor isomer, in comparison with the resonances of the major one. The minor isomer probably differs from the major one in the divergent orientation of the ester or amide fragments and selected data are collected in the Section 2. A similar geometrical isomer was found in some homoleptic amides and esters of molybdenum [7].

The $^{13}C\{^1H\}$-NMR spectrum of **2** shows three signals for the carbonyl carbons. The similar shifts (between 172 and 178 ppm) of these resonances (recall that there are two different coordination modes in the complex) and the small shift with respect to the free ligand are indicative of a small contribution of the π-carbonyl bonding [8] in agreement with the structural data found in the solid state.

The NMR data of compounds **3** and **4** are quite similar to those of **2** and will not be further commented.

3.2. Molecular structure of Mo(H_2C=CHCOOMe)$_3$(PMe$_3$) (2)

The crystal structure of Mo(H_2C=CHCOOMe)$_3$-(PMe$_3$) (**2**) has been determined. The asymmetric unit contains two independent molecules, completely equivalent from a chemical point of view and showing bond distances and angles quite similar. The molecular geometry of molecule 1 is shown in Fig. 1. Table 2 collects selected bond distances and angles for both molecules. Two methyl acrylate ligands are bonded to the molybdenum atom through the O=C and C=C bonds (η^4-1-oxa-1,3-diene form), meanwhile the third is only coordinated via the C=C double bond (the usual η^2-coordinated olefin). The sixth coordination position is occupied by a PMe$_3$ ligand. The three ester ligands are different in the complex. The oxadiene moieties have an average deviation of 0.071(5) Å for C1–C2–C3–O1 and 0.081(5) Å for C5–C6–C7–O3 from their respective molecular planes (molecule 1), being the other η^2-ester essentially planar. Similar values are found in molecule 2. The distances between the approximate oxadiene plane and the molybdenum atom are 1.782(1) and 1.774(1) Å (molecule 1), these are different from that found in the η^2-ester ligand (2.063(1) Å, molecule 1). The dihedral angles between the two oxadiene ligands are 69.0(3)° in molecule 1 and 68.5(2)° in molecule 2. The two alkene fragments of the oxadiene ligands are found in a distorted *trans*-orthogonal arrangement relative to each other, being the O1–Mo–O3 bond angle of 83.2(1)°, a disposition similar to that found in the compounds W(H_2C=CMeCOOMe)$_2$(CO)$_2$ [8], W(η^4-*R*-(+)-pulegone)$_2$(CO)$_2$ [9] and W(η^4-*R*-(+)-pinocarvone)$_2$(CO)$_2$ [10].

The Mo1–C3 and Mo1–C7 bond distances corresponding to the carbonyl carbon atoms of the oxadiene ligand (2.493(5) and 2.462(5) Å, respectively) are rather larger than the other Mo–C bond lengths (2.201–2.281 Å range). This fact is indicative of a lower π-character of the η^2-C=O bond in favour of a η^1-σ-coordination through the oxygen atom. Also the comparison of all C–C bond distances in the oxadiene ligands gives a narrow range of values (1.413(8)–1.429(8) Å), thus indicating a participation of η^2-σ^2-bonding coordina-

Table 2
Selected bond lengths (Å) and angles (°) for $Mo(H_2C{=}CHCOOMe)_3(PMe_3)$ **2**

Molecule 1		Molecule 2	
Bond lengths (Å)			
Mo1–P1	2.436(1)	Mo2–P2	2.439(2)
Mo1–01	2.297(4)	Mo2–021	2.301(4)
Mo1–03	2.278(4)	Mo2–023	2.277(3)
Mo1–C1	2.201(7)	Mo2–C21	2.204(6)
Mo1–C2	2.281(5)	Mo2–C22	2.279(5)
Mo1–C3	2.493(5)	Mo2–C23	2.493(5)
Mo1–C5	2.240(6)	Mo2–C25	2.237(5)
Mo1–C6	2.230(5)	Mo2–C26	2.225(5)
Mo1–C7	2.462(5)	Mo2–C27	2.463(5)
Mo1–C9	2.244(6)	Mo2–C29	2.236(5)
Mo1–C10	2.262(5)	Mo2–C210	2.253(5)
O1–C3	1.251(6)	021–C23	1.259(6)
2–C3	1.335(6)	022–C23	1.346(6)
02–C4	1.454(7)	022–C24	1.454(7)
03–C7	1.256(7)	023–C27	1.250(6)
04–C7	1.331(7)	024–C27	1.346(6)
04–C8	1.438(8)	024–C28	1.442(9)
05–C11	1.202(7)	025–C211	1.208(7)
06–C11	1.353(7)	026–C211	1.364(7)
06–C12	1.434(8)	026–C212	1.434(7)
C1–C2	1.424(8)	C21–C22	1.424(8)
C2–C3	1.413(8)	C22–C23	1.399(8)
C5–C6	1.422(8)	C25–C26	1.435(7)
C6–C7	1.429(8)	C26–C27	1.412(8)
C9–C10	1.425(8)	C29–C210	1.418(8)
C10–C11	1.471(8)	C210–C211	1.462(7)
Bond angles (°)			
C9–Mo1–C10	36.9(2)	C29–Mo2–C210	36.8(2)
C6–Mo1–C10	92.9(2)	C26–Mo2–C210	92.2(2)
C6–Mo1–C9	109.0(2)	C26–Mo2–C29	109.3(2)
C5–Mo1–C10	92.2(2)	C25–Mo2–C210	91.0(2)
C5–Mo1–C9	86.6(2)	C25–Mo2–C29	86.3(2)
C5–Mo1–C6	37.1(2)	C25–Mo2–C26	37.5(2)
C2–Mo1–C10	83.9(2)	C22–Mo2–C210	84.3(2)
C2–Mo1–C9	87.7(2)	C22–Mo2–C29	87.0(2)
C2–Mo1–C6	147.1(2)	C22–Mo2–C26	147.4(2)
C2–Mo1–C5	174.2(2)	C22–Mo2–C25	173.1(2)
C1–Mo1–C10	120.3(2)	C21–Mo2–C210	120.7(2)
C1–Mo1–C9	112.6(2)	C21–Mo2–C29	111.5(2)
C1–Mo1–C6	138.3(2)	C21–Mo2–C26	139.2(2)
C1–Mo1–C5	145.9(2)	C21–Mo2–C25	146.4(2)
C1–Mo1–C2	37.0(2)	C21–Mo2–C22	37 0(2)
03–Mo1–C10	152.5(2)	023–Mo2–C210	151.6(2)
03–Mo1–C9	157.0(2)	023–Mo2–C29	157.2(2)
03–Mo1–C6	61.6(2)	023–Mo2–C26	61.3(2)
03–Mo1–C5	73.9(2)	023–Mo2–C25	74.2(2)
03–Mo1–C2	111.4(2)	023–Mo2–C22	112.1(2)
03–Mo1–C1	79.7(2)	023–Mo2–C21	80.8(2)
01–Mo1–C10	86.3(2)	021–Mo2–C210	86.6(2)
01–Mo1–C9	119.4(2)	021–Mo2–C29	119.1(2)
01–Mo1–C6	86.8(2)	021–Mo2–C26	87.2(2)
01–Mo1–C5	123.8(2)	021–Mo2–C25	124.5(2)
01–Mo1–C2	60.4(2)	021–Mo2–C22	60.3(2)
01–Mo1–C1	72.3(2)	021–Mo2–C21	72.7(2)
01–Mo1–03	82.3(1)	021–Mo2–023	82.5(1)
P1–Mo1–C10	111.8(2)	P2–Mo2–C210	112.4(1)
P1–Mo1–C9	75.0(2)	P2–Mo2–C29	75 7(2)
P1–Mo1–C6	112.3(2)	P2–Mo2–C26	111.8(1)
P1–Mo1–C5	78.3(2)	P2–Mo2–C25	77.8(1)
P1–Mo1–C2	99.2(2)	P2–Mo2–C22	99 4(1)
P1–Mo1–C1	80.0(2)	P2–Mo2–C21	79.3(2)
P1–Mo1–03	88.9(1)	P2–Mo2–023	88.4(1)
P1–Mo1–O1	152.0(1)	P2–Mo2–021	151.6(1)
C3–02–C4	116.2(4)	C23–022–C24	116.5(4)
C7–04–C8	115.8(5)	C27–024–C28	115.5(5)
Cll–06–C12	115.8(5)	C211–026–C212	115.4(4)
C1–C2–C3	113.9(5)	C21–C22–C23	114.9(5)
C5–C6–C7	116.3(5)	C25–C26–C27	116.7(5)
C9–C10–C11	119.9(5)	C29–C210–C211	120.3(5)

tion. The value of 1.471(8) Å for the C10–C11 bond length found in the η^2-ester, higher than the other C–C distances, confirms this hypothesis. Following the Schmidt strategy [11] we have calculated the Δd parameter (Eq. 2), a qualitative measurement of the type of coordination, for the two oxadiene ligands.

$$\Delta d = 0.5\{d[\mathrm{M{-}O_{C=O}}] + d[\mathrm{M{-}C}_\beta]\} \\ -0.5\{d[\mathrm{M{-}C_{C=O}}] + d[\mathrm{M{-}C}_\alpha]\} \qquad (2)$$

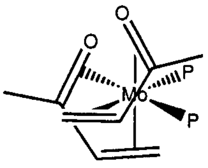
The values of -0.14 and -0.09 are closer to a η^2-σ^2-bonding scheme than an ideal π-η^4-ligand [11].

3.3. Synthesis of $Mo[H_2C{=}CH{-}C(O)Me]_2(PMe_3)_2$ *(**5**)*

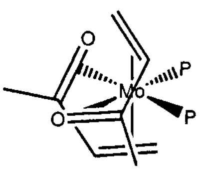
Conversely to that previously stated for the ester and amide reagents, the reaction of **1** with three equivalents of methyl vinyl ketone does not afford the expected $Mo[H_2C{=}CH{-}C(O)Me]_3(PMe_3)$, but the $Mo[H_2C{=}CH{-}C(O)Me]_2(PMe_3)_2$ (**5**) derivative (Eq. 3). Further substitution of an additional PMe_3 ligand by the methyl vinyl ketone does not occur.

$$\textit{Trans}\text{-}Mo(C_2H_4)_2(PMe_3)_4\ (\mathbf{1}) + H_2C{=}CH \\ {-}C(O)Me \Rightarrow Mo[H_2C{=}CH{-}C(O)Me]_2(PMe_3)_2\ (\mathbf{5}) \qquad (3)$$

Compound **5** is a red crystalline, air sensitive material, very soluble in Et_2O and hydrocarbon solvents. The formulation is consistent with the elemental analysis and NMR data collected. Related tris(methyl vinyl ketone) derivatives of molybdenum [12] and tungsten [13] are known and other dicarbonylbis(oxadiene) compounds of molybdenum and tungsten were reported previously [8,9]. In the IR spectrum no bands could be observed in the 1750–1500 cm^{-1} region (ν_{CO}) and, consequently, a lower wave number indicates a strong interaction between the π-carbonyl fragment and the metal center, in good agreement with a butadiene-like coordination fashion. Considering the no equivalence of the two phosphorus atoms and the two set of patterns for the ketone ligands, only two structures can be proposed for **5** (see **I** and **II**).



I



II

Complex **5** shows a fluxional behavior in solution and, in order to distinguish between structures **I** and **II**, we have performed a variable temperature NMR study. At 233 K the two vinyl ketone ligands are no equivalent, and each vinyl proton exhibit a different resonance in the ^{1}H-NMR spectrum. Upon increasing the temperature over 233 K, peak broadening is immediately significant, except for the PMe_3 ligands that remained invariable as two doublets. At 310 K, in the limit of the slow interchange, the =CH– resonances, at 3.74 (t) and 3.90 (t) ppm, collapse to a single signal. Similarly, the methyl groups of the vinyl ketone ligands, that appear as singlets at δ 1.95 and 2.79, collapse at 330 K. An ca. value of the $\Delta G^{\#} = 64$ KJ mol^{-1} is obtained at the coalescence temperature for the fluxional behavior. If the fluxional interchange process is attributed to a propeller rotation of the methyl vinyl ketone, structure **I** must be discarded because in this process exists an intermediate in which the two PMe_3 ligands become equivalent in opposition with the experimental NMR. In good agreement with the NMR data and the fluxional behavior, structure **II** was proposed for **5**.

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