Dicarbonylmolybdenum and tungsten complexes of α,β-unsaturated esters. Preparation, properties and application in the complexation of α,β-unsaturated ketones ☆

Th. Schmidt

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Abstract

Dicarbonylbis(1-oxa-1,3-diene) complexes of molybdenum and tungsten can be prepared from ethyl and methyl methacrylate by employing either $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ or $(CH_3CH_2CN)_3W(CO)_3$ in modified standard complexation reactions. The crystalline, air-sensitive compounds can be obtained in 61%–94% yield. Both NMR spectroscopic studies and the X-ray crystal structure of the tungsten methyl methacrylate complex $[H_2C=C(CH_3)C(O)OCH_3]_2W(CO)_2$ suggest that the bonding mode of the unsaturated ester ligands in these compounds differs from η^4 to some extent, i.e. the coordination of the carbonyl fragment is an intermediate between $\eta^2\text{-}\pi$ and η^1 at the carbonyl oxygen. The unsaturated ester ligands are labile with respect to exchange reactions, which allows other 1-oxa-1,3-dienes to replace them under very mild conditions. Most interestingly, in the case of the tungsten compounds, even complexes of temperature-sensitive α,β-unsaturated ketones can thus be easily obtained in excellent yield at room temperature.

Keywords: Molybdenum; Tungsten; α,β-Unsaturated esters; Ligand exchange; Crystal structure; NMR spectroscopy

1. Introduction

In contrast to the variety of well-known and well-examined diene complexes, heterodienes such as 1-oxa-1,3-dienes in the coordination sphere of transition metals other than iron have only recently attracted considerable interest [1]. From the structure of such complexes and the bonding situation of the ligands, their reactivity also turned out to be markedly different from that observed with diene complexes. Several stoichiometric [2] as well as catalytic applications [3] of oxadiene complexes have already been reported during the last few years. However, these investigations were limited to a special class of 1-oxadiene ligands, i.e. unsaturated ketones or aldehydes.

Only very few complexes of oxadienes bearing additional polar substituents are known. Among these are tetracarbonyl molybdenum and tungsten complexes of acrylic esters that have been prepared by Grevels et al. [4] using photochemically induced ligand displacement.

The unsaturated ester in these complexes is exclusively η^2-coordinated via the alkene fragment, leaving the ester fragment uncoordinated. In the course of our investigations directed towards the synthesis and reactivity studies of molybdenum and tungsten oxadiene complexes, we became specifically interested in the preparation of complexes where both alkene and ester fragments are bound to the metal. In this context, we recently reported that vinyl ketones as well as unsaturated esters and amides can be employed as ligands to form homoleptic tris(oxadiene) molybdenum complexes if the complexation reaction can take place under mild conditions [5]. In addition, we were looking for novel complexation reactions in order to obtain tungsten complexes under equally mild conditions. So far, standard complexations by ligand substitution using acetonitrile or propionitrile tungsten carbonyl complexes [1b,6] require a temperature of at least 50–60°C to proceed at a reasonable rate. When higher temperatures are necessary in some cases (e.g., see Ref. [3c]), the product yields are either unacceptably low or the corresponding oxadiene complexes were not accessible at all. Such problems arose especially in the case of β-unsubstituted α,β-unsaturated carbonyl compounds, which are easily

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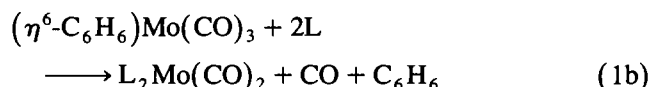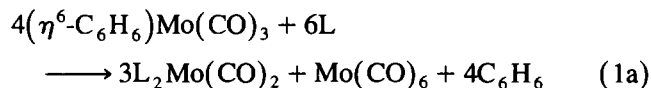☆ Dedicated to Professor W. Grimme on the occasion of his 65th birthday.

polymerisable at higher temperatures due to their pronounced Michael reactivity.

We now report the preparation and characterisation of novel dicarbonyl methacrylic ester complexes of molybdenum and tungsten. Most remarkably in the tungsten case, these compounds undergo ligand exchange with other oxadienes such as α,β-unsaturated ketones even at room temperature and thus allow access to the corresponding tungsten complexes for the first time in high yield.

2. Results and discussion

2.1. Synthesis and characterisation

Although standard complexation methodology can be employed in the preparation of the methacrylic ester complexes, some precautions (see Experimental details) are necessary, specifically in the case of the molybdenum complexes to prevent decomposition of the product. For example, methyl methacrylate complex 1 can be obtained cleanly in boiling n-hexane starting from η^6-benzenetricarbonylmolybdenum. It is remarkable that carbon monoxide is liberated during that complexation reaction and that only a small amount of hexacarbonyl molybdenum is formed during its course. Far less than the 0.25 mol equiv. that should be expected from the stoichiometry of a dismutation reaction as shown in Eq. (1a) can be isolated from the crude reaction product by sublimation. Additional support for a different reaction pathway comes from the product yield of 94% for complex 1, which is far above the 75% based on a molybdenum starting complex that should be expected as a maximum from a reaction that proceeds according to Eq. (1a). Thus, the major complexation pathway, at least in this special case, seems to be different from that observed in the majority of oxadiene complexation reactions we have investigated (e.g. Ref. [1b]). It is probably of the type shown in Eq. (1b). The reasons for the occurrence of such different reaction pathways are under investigation.

$$4(\eta^6\text{-}C_6H_6)Mo(CO)_3 + 6L$$

$$\longrightarrow 3L_2Mo(CO)_2 + Mo(CO)_6 + 4C_6H_6 \quad (1a)$$

$$(\eta^6\text{-}C_6H_6)Mo(CO)_3 + 2L$$

$$\longrightarrow L_2Mo(CO)_2 + CO + C_6H_6 \quad (1b)$$

$$(L = 1\text{-oxa-}1,3\text{-diene})$$

All attempts to prepare complex 1 from the in situ generated solvent complex $(THF)_3Mo(CO)_3$ [1b] failed due to the formation of extremely air-sensitive, yellow precipitates, which, according to their IR spectra, contain coordinated THF. This THF could neither be removed in vacuo nor replaced by other solvents such as

diethyl ether or acetone without complete decomposition of the product. Even preformed 1 was not stable in THF solution. The tolerance of 1 for benzene is just sufficient to allow its use as an NMR solvent at room temperature. In contrast, the ethyl methacrylate molybdenum complex 3 can readily be prepared from the THF solvent complex (Table 1). Another indication of the lability of complexes 1 and 3 comes from their behaviour on recrystallisation. Only in the presence of the appropriate alkyl methacrylate (about 5 mol%) can they be dissolved in n-pentane without undergoing extensive decomposition. It seems most likely that the excess ester shifts the dissociation equilibrium of the ligand towards the undissociated complex, thus stabilising it.

The tungsten complexes 2 and 4 are less sensitive and could easily be obtained by standard methods (Table 1). The complexes can be dissolved in coordinating solvents such as benzene or THF without extensive decomposition. As the yields obtained are both below 75%, no definite conclusion regarding the complexation mechanism (vide supra) is possible. Nevertheless, as some evolution of carbon monoxide can be observed and the amount of hexacarbonyl tungsten produced is below 0.25 mol equiv. it is possible that in these cases also reactions similar to those in Eqs. (1a) and (1b) take place simultaneously.

$$R = CH_3, C_2H_5$$

A, C (M = Mo),
B, D (M = W)

M = Mo, W

$$(2)$$
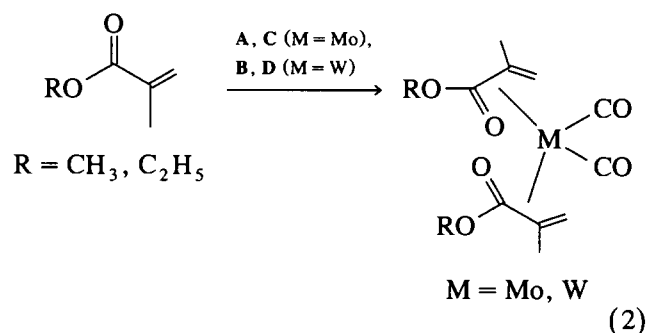
Only one diastereoisomer of the complexes was obtained from each of these reactions. This could either be
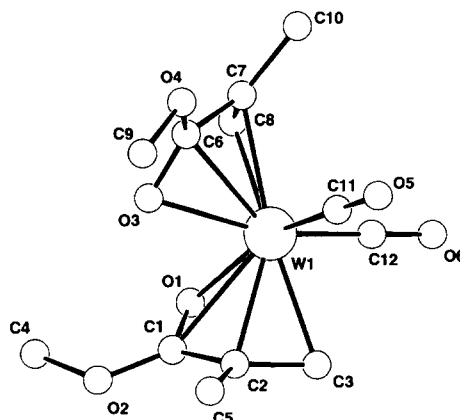
Fig. 1. Molecular structure of $[H_2C=C(CH_3)C(O)OCH_3]_2W(CO)_2$ (2).

Table 1
Preparation conditions and melting points of dicarbonylbis(alkyl methacrylate) complexes of molybdenum and tungsten

R	M	Product	Method [a]	Yield (%)	M.p. (°C)
CH_3	Mo	1	A	94	58–59 (dec.)
CH_3	W	2	B	61	54–55
C_2H_5	Mo	3	C	68	55–56 (dec.)
C_2H_5	W	4	D	72	60–61

[a] Preparation conditions: A: $(\eta^6\text{-}C_6H_6)Mo(CO)_3$, n-hexane, reflux; B: $(CH_3CH_2CN)_3W(CO)_3$, n-hexane, reflux; C: $(\eta^6\text{-}C_6H_6)Mo(CO)_3$, THF, 20°C; D: $(CH_3CH_2CN)_3W(CO)_3$, n-heptane, 90°C.

due to a high diastereoselectivity in the complexation reaction or, more likely because of the facile ligand dissociation in solution, due to rapid equilibration to yield the more stable diastereomer. The NMR spectra of all four complexes clearly indicate that the compounds exhibit C_1 symmetry. This is in accordance with previous findings [7] showing that prochiral unsaturated ketones selectively yield C_1 symmetric complexes where the different enantiotopic π-faces of the two ligands are coordinated to the metal. In contrast, we have so far only been able to obtain C_2 symmetrical compounds from chiral oxadienes. Most remarkably, in comparison to the ^{13}C NMR spectra to the free methacrylic esters, small downfield coordination shifts of 1–10 ppm are observed for the ester carbonyl carbons. Therefore, from these spectral data it cannot even be concluded that the ester fragments are coordinated to the metal at all. In contrast, the coordination shifts of the alkene fragments are all upfield and between 59 and 80 ppm for the α- and 63–80 ppm for the β-carbon atoms. These data are summarised in Table 2 in more detail. As an explanation for the small carbonyl-carbon coordination shift, one might assume that donation of electrons to the metal does not involve the carbonyl π-system but primarily the lone pair at the oxygen, leading to deshielding of the carbonyl-carbon atom as a result of the increased electron demand from the carbonyl oxygen.

Striking evidence for the coordination of both the

alkene and the ester fragment comes from the mass spectra which confirm compositions of the type $L_2M(CO)_2$ (L = 1-oxa-1,3-diene) for compounds 1 to 4. These are in accordance with coordinatively saturated 18-electron complexes only for the case of L acting as a 4e donor ligand. In addition, no intense signal could be observed in the 1750–1560 cm^{-1} region of the IR spectra, where a free ester carbonyl stretching vibration should be expected to appear. This latter result is also in contrast to the hypothesis of an exclusive lone-pair coordination of the ester, as in that case only a minor shift of the carbonyl stretching frequency of less than 100 cm^{-1} is to be expected [8]. However, a partial contribution of such a coordination mode might still be operative.

2.2. X-ray crystal structure of tungsten complex 2

In order to clarify the bonding situation of the ester ligands, single-crystals of the tungsten complex 2 obtained from n-hexane solutions were subjected to X-ray crystal structure analysis. The resulting molecular structure of 2 is shown in Fig. 1. The $L_2W(CO)_2$ composition of the complex as well as the coordination of both alkene and ester fragment is clearly confirmed.

At first glance, the two ester ligands appear to be remarkably different in structure, most easily evident from the dihedral angles of the oxadiene moieties O(1)–

Table 2
^{13}C NMR chemical shifts δ (ppm) (solvent: benzene-d_6) and coordination shifts $\Delta\delta$ (ppm) for the metal coordinated carbon atoms [a] in the ester molybdenum (1 and 3) and tungsten complexes (2 and 4), and the corresponding atoms in the free methacrylic esters $H_2C=C(CH_3)=C(O)OR$ (boldface numbers)

	$\delta(^{13}C)$ (ppm)			$\Delta\delta(^{13}C)$ (ppm) [b]		
	C=O	C_α	C_β	C=O	C_α	C_β
R = CH_3	**167.26**	**136.73**	**124.97**	–	–	–
1	176.70	77.52	62.15	−9.44	59.21	62.82
	168.80	65.81	53.93	−1.54	70.92	71.04
2	176.82	69.53	53.88	−9.56	67.20	71.09
	168.31	57.36	45.27	−1.05	79.37	79.70
R = C_2H_5	**166.84**	**137.03**	**124.76**	–	–	–
3	176.86	76.60	62.15	−10.02	60.43	62.61
	169.34	65.56	53.92	−2.50	71.47	70.84
4	177.34	68.65	54.08	−10.50	68.38	70.68
	169.30	57.20	45.62	−2.46	79.83	79.14

[a] Connectivities of the atoms within ligands corresponding to the two sets of ligand signals have not yet been assigned.
[b] Definition: $\Delta\delta = \delta(\text{oxadiene}) - \delta(\text{complex})$.

Table 3
Selected interatomic distances (Å) and angles (°) for [H₂C=C(CH₃)C(O)OCH₃]₂W(CO)₂, (2)

Bond distances

W(1)–O(1)	2.256(4)	W(1)–O(3)	2.234(4)
W(1)–C(1)	2.508(6)	W(1)–C(6)	2.434(6)
W(1)–C(2)	2.231(5)	W(1)–C(7)	2.304(6)
W(1)–C(3)	2.241(6)	W(1)–C(8)	2.212(6)
W(1)–C(11)	1.940(6)	W(1)–C(12)	1.944(6)
O(5)–C(11)	1.172(8)	O(6)–C(12)	1.170(7)
O(1)–C(1)	1.245(7)	O(3)–C(6)	1.249(7)
C(1)–C(2)	1.465(8)	C(6)–C(7)	1.436(8)
C(2)–C(3)	1.421(8)	C(7)–C(8)	1.435(9)
O(2)–C(1)	1.314(7)	O(4)–C(6)	1.322(7)
O(2)–C(4)	1.451(9)	O(4)–C(9)	1.444(7)
C(2)–C(5)	1.512(8)	C(7)–C(10)	1.493(9)

Bond angles

C(1)–O(1)–W(1)	86.4(3)	C(6)–O(3)–W(1)	83.6(3)
C(2)–C(3)–W(1)	71.1(3)	C(7)–C(8)–W(1)	75.0(4)
O(5)–C(11)–W(1)	179.6(5)	O(6)–C(12)–W(1)	178.8(5)
C(2)–C(1)–O(1)	117.8(5)	C(7)–C(6)–O(3)	119.6(5)
C(2)–C(1)–O(2)	117.8(5)	C(7)–C(6)–O(4)	117.0(5)
C(3)–C(2)–C(1)	115.0(5)	C(8)–C(7)–C(6)	114.6(5)
O(2)–C(1)–O(1)	124.0(5)	O(4)–C(6)–O(3)	123.1(5)
C(4)–O(2)–C(1)	115.4(5)	C(9)–O(4)–C(6)	116.1(4)
C(5)–C(2)–C(1)	120.4(5)	C(10)–C(7)–C(6)	121.5(6)
C(5)–C(2)–C(3)	123.7(5)	C(10)–C(7)–C(8)	123.5(6)

Interligand bond angles

C(11)–W(1)–C(1)	132.2(2)	C(12)–W(1)–C(1)	115.2(2)
C(11)–W(1)–C(2)	98.6(2)	C(12)–W(1)–C(2)	109.6(2)
C(11)–W(1)–C(3)	89.2(2)	C(12)–W(1)–C(3)	73.5(2)
C(11)–W(1)–C(6)	77.9(2)	C(12)–W(1)–C(6)	138.0(2)
C(11)–W(1)–C(7)	79.8(2)	C(12)–W(1)–C(7)	103.9(2)
C(11)–W(1)–C(8)	112.8(2)	C(12)–W(1)–C(8)	88.8(2)
C(11)–W(1)–O(1)	160.9(2)	C(12)–W(1)–O(1)	98.2(2)
C(11)–W(1)–O(3)	98.0(2)	C(12)–W(1)–O(3)	163.0(2)
C(12)–W(1)–C(11)	87.3(2)	C(6)–W(1)–C(1)	103.6(2)
O(3)–W(1)–O(1)	82.1(1)	C(8)–W(1)–C(3)	151.4(2)
C(7)–W(1)–C(2)	146.4(2)		

C(1)–C(2)–C(3) and O(3)–C(6)–C(7)–C(8), which are −33.7° and 16.8°, respectively. Other than this discrepancy, however, corresponding intraligand as well as ligand-to-metal distances and angles are quite similar for both ligands, as deduced from the data given in Table 3. The alkene fragments are found in a distorted trans-orthogonal arrangement relative to each other. The angle at tungsten between the coordinated oxygen atoms is close to 90°, viz. O(1)–W(1)–O(3), 82.1(1)°. The latter structural feature in particular appears to be a critical requirement for the existence of stable oxadiene or oxapentadienyl complexes, since similar arrangements of the coordinated oxygens have been found in all oxadiene complexes we have investigated (see, for example, Refs. [1b,3c,5,9]). The distances between the tungsten atom and at least one of the alkene carbons of each ester ligand [W–C(2), W–C(3) and W–C(8)] are even shorter than the W–O distances for the same ligand, which is usually not the case for oxadiene

complexes and may be an indication of a pronounced π-coordination of these alkene fragments. In dicarbonylbis(η⁴-pulegone)tungsten, for example, the shortest distances are 2.376(8) Å [W–C] and 2.18(1) Å [W–O]. The dihedral angle O=C=C=C in that case amounts to 18.7° [1b].

From the coordination angles at oxygen, W(1)–O(1)–C(1) [86.4(3)°] and W(1)–O(3)–C(6) [83.6(3)°], it seems doubtful that lone-pair coordination is of primary importance in this compound, although recent studies have shown that the idealised position of a carbonyl oxygen lone pair forming an angle of 120° with the carbonyl bond might be an oversimplification [9], at least in some cases. As the long distances for W(1)–C(1) and W(1)–C(6) [2.508(6) and 2.434(6) Å] {compared to W(1)–O(1) [2.256(4) Å] and W(1)–O(3) [2.234(4) Å]} indicate, there is definitely a severe asymmetry in the metal coordination of the carbonyl fragment. The assumption of a decreased π-character for the coordination is supported by the observed carbonyl bond lengths [O(1)–C(1) 1.245(7) and O(3)–C(6) 1.249(7) Å], which are significantly shorter than those in the pulegone complex [1.34(1) and 1.35(1) Å] and thus indicate an increased double-bond character of these bonds.
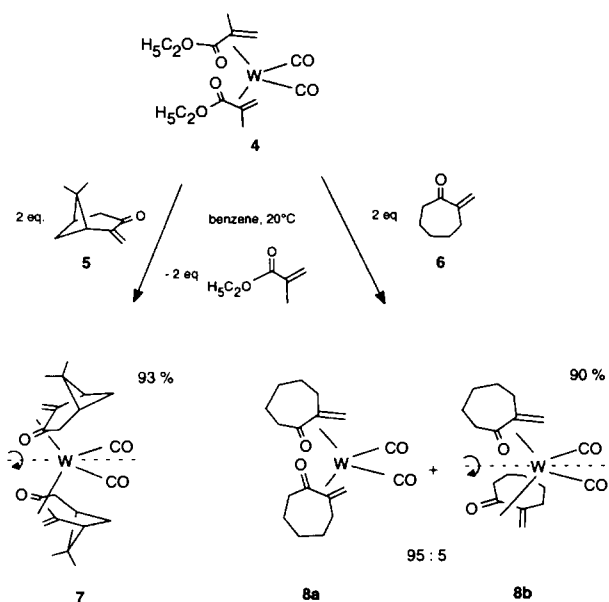
In conclusion, the data can be interpreted in terms of a strong π-type coordination of the alkene fragment. The bonding mode of the ester carbonyl group might be regarded as an intermediate between $\eta^2-\pi$ and a η^1-coordination involving either lone pair or σ-bonding of the carbonyl oxygen, as recently discussed in the case of homoleptic acrylic amide complexes [5b]. In line with this, a calculation of the distance difference Δd [Eq. (3)], which has already proven useful in the analysis of oxadiene bonding in other complexes [5], results in values of −0.12 and −0.15 for the two ester ligands, thus indicating some intermediacy between a η^4- and a η^2,σ^2-coordination.

$$\Delta d = 0.5\{d[\text{M-O}_{C=O}] + d[\text{M-C}_\beta]\}$$
$$- 0.5\{d[\text{M-C}_{C=O}] + d[\text{M-C}_\alpha]\} \quad (3)$$

2.3. Reactivity

The new ester complexes are relatively unstable towards ligand dissociation compared to dicarbonyl complexes of unsaturated ketones, as has already been pointed out. Developing the initial observation that addition of free methacrylic ester to a solution of the molybdenum complexes stabilises these compounds, we investigated the perspectives and possible applications of ligand displacement reactions in more detail.

The molybdenum complexes appear to be extremely reactive towards ligand-exchange reactions. Nevertheless, due to their instability, they are difficult to handle in coordinating solvents and tend to decompose when

H₅C₂O

CO
W
CO

H₅C₂O

4

2 eq.   benzene, 20°C   2 eq

5   - 2 eq   H₅C₂O   **6**

93 %   90 %

CO
W
CO

CO
W
CO +   CO
W
CO

95 : 5

7   **8a**   **8b**

Scheme 1.

dissolved in non-coordinating solvents such as saturated hydrocarbons. At present, they are not superior to the molybdenum solvent complexes already in use for complexation reactions.

In the tungsten complex series, the ethyl methacrylate complex **4** turns out to be a reasonable compromise between stability and reactivity. As summarised in Scheme 1, it cleanly reacts with a variety of α,β-unsaturated ketones to produce bis(oxadiene) tungsten complexes in high yield with liberation of the methacrylic ester. These reactions proceed reasonably rapidly even at room temperature. The methacrylic ester formed during the reaction can easily be removed in vacuo afterwards. For example, complexes of the methylene ketones (R)-(+)-pinocarvone (**5**) and 2-methylenecycloheptanone (**6**) can be obtained in 93% and 90% yield, respectively. No excess of ketone is necessary for the exchange reaction to go to completion, thus avoiding contamination of the product by oligomerisation products of the highly reactive β-unsubstituted α,β-unsaturated ketones.

The outcome of these reactions is in marked contrast to results of classical tungsten complexation reactions [11] employing the above-mentioned ketones. In the reaction of tricarbonyltris(propionitrile)tungsten with an excess of pinocarvone in boiling n-heptane, complex **7** could be obtained in only 37% yield due to thermally induced decomposition, i.e. oligomerisation, of the highly reactive Michael system. In the case of 2-methylenecycloheptanone (**6**), an analogous reaction in n-hexane at only 40°C gave rise to a 53% yield of the complexes **8a** and **8b**. The remarkable formation of both a major C₁- and a minor C₂-symmetric diastereomer, which, according to our experience, is highly unusual in the series of vinyl ketone complexes, will be

discussed together with other results in this respect in a forthcoming publication [12].

3. Experimental details

Preparation and handling of all the organometallic compounds were performed under an inert atmosphere of dried and purified argon using standard Schlenk techniques. The solvents were purified prior to use by standard procedures, usually employing Na[AlEt₄] as a drying agent for hydrocarbons and ethers, and subsequently saturated with argon. Melting points were determined in capillary tubes sealed under argon and are uncorrected.

η⁶-Benzenetricarbonylmolybdenum(0) [13] and tricarbonyltris(propionitrile)tungsten(0) [6a] were prepared by modifications of published procedures. (R)-(+)-Pinocarvone was obtained from α-pinene via epoxidation, epoxide cleavage and oxidation of the resulting trans-pinocarveol [7] while 2-methylenecycloheptanone was prepared from cycloheptanone via Mannich reaction and pyrolysis of the Mannich base hydrochloride [11].

NMR spectra were recorded on a Bruker AM-200 instrument (200.1 MHz [¹H], 50.3 MHz [¹³C]); solvent signals were used as internal standards. Signal multiplicities obtained from DEPT experiments are given in brackets after the shift values. Mass spectra were obtained using a Varian 311A instrument (for metal-containing ions, signals corresponding to the major isotopes ⁹⁸Mo and ¹⁸⁴W are reported), IR spectra from a Nicolet 7199 FT-IR instrument, approximate intensity data are given by s(trong), m(edium), w(eak) and sh(oulder). Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim and der Ruhr.

3.1. Dicarbonylbis(methyl methacrylate) molybdenum (1)

A yellow suspension of 258 mg (1.0 mmol) (η⁶-C₆H₆)Mo(CO)₃ in n-hexane (30 ml) was heated to reflux with stirring. Freshly distilled methyl methacrylate (1.5 g, 15 mmol) was then added rapidly via syringe. Within 1 h a colour change to red could be observed, accompanied by weak evolution of carbon monoxide. Due to the sensitivity of the product complex, monitoring by TLC turned out to be impractical. Therefore, the reaction time was extended to 24 h at reflux temperature to ensure complete reaction. At that time a small amount of black tar had deposited on the glass walls of the reaction flask. The clear, dark red reaction mixture was filtered through a sintered glass first and the volatile components [solvent, methyl methacrylate and Mo(CO)₆] removed in vacuo (30 Pa, then 10⁻² Pa at room temperature). The resulting red

oil, which is also slightly volatile under high vacuum, could not, due to thermal sensitivity, be purified by sublimation. It already gave a correct elemental analysis. Recrystallisation from n-hexane was possible only in the presence of excess methyl methacrylate and reduced the yields dramatically to about 20%. On standing in a freezer for several months, the crude product finally solidified to form a yellow powder of 1.

Compound 1: Yield, 331 mg (94%, 0.94 mmol), m.p. 58–59°C (dec.). Anal. Found: C, 40.44; H, 4.65; Mo, 27.15%. $C_{12}H_{16}MoO_6$ (352.2) requires: C, 40.92; H, 4.58; Mo, 27.24%. IR (KBr pellet) $\tilde{v}$ (cm^{-1}); 2958 (m), 2910 (w), 2860 (w) (v_{CH}); 1949 (s), 1863 (s) $[v_{CO}, Mo(CO)_2]$; 1555 (sh), 1530 (m), 1460 (s), 1448 (s), 1431 (m), 1380 (m), 1339 (s), 1210 (s), 1175 (m), 991 (m), 760 (w), 705 (w). ^{1}H NMR (benzene-d_6) δ: 3.43 [d, 1H, =CH_2, ^2J(HH) = 4.0 Hz]; 3.28 (s, 3H, OCH_3); 3.27 [d, 1H, =CH_2, ^2J(HH) = 1.6 Hz]; 3.12 (s, 3H, OCH_3); 3.07 (d, 1H, =CH_2, 4.0 Hz); 2.32 (d, 1H, =CH_2, 1.6 Hz); 2.00 (s, 3H, H_3C-C=); 1.78 (s, 3H, H_3C-C=) ppm. ^{13}C NMR (benzene-d_6) δ: 229.00 [s, Mo(CO)$_2$]; 228.80 [s, Mo(CO)$_2$]; 176.70 (s, C=O ester); 168.80 (s, C=O ester); 77.52 [s, =C(CH$_3$)]; 65.81 [s, =C(CH$_3$)]; 62.15 (t, =CH_2); 53.93 (t, =CH_2); 53.42 (q, OCH_3); 53.12 (q, OCH_3); 18.86 (q, H_3C-C=); 17.65 (q, H_3C-C=) ppm. MS (EI, 70 eV) m/z [rel. int. (%)]; 354 (10, M$^+$); 326 (8, M$^+$- CO); 298 (9, M$^+$- 2CO); 200 (19); 100 (22, $C_5H_8O_2^+$); 69 (62); 41 (100, $C_3H_5^+$).

3.2. Dicarbonylbis(methyl methacrylate)tungsten (2)

Freshly distilled methyl methacrylate (3.0 g, 30 mmol) was added to a stirred suspension of 866 mg (2.0 mmol) tricarbonyltris(propionitrile)tungsten in n-hexane (30 ml) and the resulting mixture heated to reflux for 48 h. During this time, some CO was liberated and the mixture turned orange–red. After cooling, the supernatant liquid was filtered off and the residue extracted twice with hot n-hexane. The combined hexane solutions were concentrated in vacuo (10 Pa) and residues of methyl methacrylate and W(CO)$_6$ were then removed under high vacuum (10^{-2} Pa). The dark red, partly crystalline residue was recrystallised from n-hexane between 20°C and −78°C in the presence of some drops of methyl methacrylate. Dark red crystals of 2 were dried under high vacuum.

Compound 2: Yield, 540 mg (61%, 1.23 mmol), m.p. 54–55°C. Anal. Found: C, 32.52; H, 3.63; W, 41.73%. $C_{12}H_{16}O_6W$ (440.1) requires: C, 32.75; H, 3.66; W, 41.77%. IR (KBr pellet) $\tilde{v}$(cm^{-1}): 2978 (m) 2956 (m), 2925 (w), 2855 (w) (v_{CH}); 1939 (s), 1859 (s) $[v_{CO}, W(CO)_2]$; 1528 (m), 1459 (m), 1405 (m), 1380 (s), 1339 (s), 1195 (s), 1015 (m). ^{1}H NMR (benzene-d_6) δ: 3.32 (s, 3H, OCH_3); 3.28 [d, 1H, =CH_2, ^2J(HH) = 5.5 Hz]; 3.11 (s, 3H, OCH_3); 2.87 (d, 1H, =CH_2, 5.5 Hz);

2.77 [d, 1H, =CH_2, ^2J(HH) = 2.8 Hz]; 2.15 (s, 3H, H_3C-C=); 1.80 (s, 3H, H_3C-C=); 1.55 (d, 1H, =CH_2, 2.8 Hz) ppm. ^{13}C NMR (benzene-d_6) δ: 220.60 [s, W(CO)$_2$]; 218.81 [s, W(CO)$_2$]; 176.82 (s, C=O ester); 168.31 (s, C=O ester); 69.53 [s, =C(CH$_3$)]; 57.36 [s, =C(CH$_3$), ^1J(WC) = 10.0 Hz]; 53.88 [t, =CH_2, ^1J(WC) = 9.6 Hz]; 53.19 (q, OCH_3); 53.18 (q, OCH_3); 45.27 [t, =CH_2, ^1J(WC) = 23.1 Hz]; 17.68 (q, H_3C-C=); 16.59 (q, H_3C-C=) ppm. MS (EI, 70 eV) m/z [rel. int (%)]: 440 (14, M$^+$); 412 (11, M$^+$- CO); 384 (21, M$^+$- 2CO); 286 (36); 69 (48); 41 (100, $C_3H_5^+$).

3.3. Crystal structure analysis of 2 [14]

Crystals were obtained from a filtered, concentrated solution in n-hexane by slowly cooling it to −78°C.

Molecular formula $C_{12}H_{16}O_6W$, molecular weight 440.1 g mol^{-1}; crystal size 0.39 × 0.60 × 0.39 mm, crystal colour red; $a = 9.674(2)$, $b = 10.796(2)$, $c = 13.904(4)$ Å, $\beta = 107.76(2)°$; $V = 1383.0$ Å^3; $T = 100$ K; $d_{calc} = 2.11$ g cm^{-1}; $\mu = 85.47$ cm^{-1}; $F(000) = 840$ e; $Z = 4$; monoclinic, space group $P2_1/c$ (No. 14); empirical absorption correction (min. transmission: 0.869, max.: 0.999); Enraf-Nonius CAD4 diffractometer, $\lambda = 0.71069$ Å, scan mode $\omega–2\theta$, 4394 measured data $(\pm h, +k, +l)$, $[(\sin \theta)/\lambda]_{max} = 0.70$ Å^{-1}, 4035 independent reflections, 3639 observed reflections $[I > 2\sigma(I)]$ for 172 refined parameters, structure solved by heavy atom method. All W, C and O atoms were refined anisotropically, H atoms were found and kept fixed $(U_{ISO} = 0.02$ Å$^2)$ during final refinement; $R = 0.033$, $R_w = 0.032$ $[w = 1/\sigma^2(F_o)]$, max. residual electron density 2.10 e Å^{-3}, the four most intense residual peaks are located at 0.87 Å to 0.94 Å distance around the tungsten atom. Selected bond distances and angles are given in Table 3; atomic positional parameters and equivalent isotropic thermal parameters in Table 4 [15].

3.4. Dicarbonylbis(ethyl methacrylate)molybdenum (3)

To a stirred, clear, yellow solution of 258 mg (1.0 mmol) of (η^6-C$_6$H$_6$)Mo(CO)$_3$ in 5 ml of THF, 1.14 g (10 mmol) of ethyl methacrylate were added rapidly at room temperature. Only a slight colour change to yellow–brown could be observed initially. After stirring at room temperature for 65 h, the clear solution was evaporated in vacuo and residues of the methacrylic ester and Mo(CO)$_6$ removed afterwards under high vacuum (10^{-2} Pa). The yellow–brown, solid residue was redissolved in diethyl ether, filtered and the solution evaporated to dryness. After washing with cold n-pentane (2 × 3 ml) the yellow–orange powder was dried under high vacuum. Recrystallisation from n-pentane was accompanied by significant decomposition and thus led to a severe reduction of the yield.

Table 4

Atomic fractional coordinates and equivalent isotropic thermal parameters ($\mathring{A}^2$) for [H$_2$C=C(CH$_3$)C(O)OCH$_3$]$_2$W(CO)$_2$ (2) with estimated standard deviations (e.s.ds) in parentheses [a]

Atom	x	y	z	U_{eq}
W(1)	0.7171(1)	0.1777(1)	0.1393(1)	0.012(1)
O(1)	0.5020(4)	0.2033(4)	0.0187(3)	0.019(2)
O(2)	0.3455(4)	0.2945(4)	0.0886(3)	0.024(2)
O(3)	0.6852(4)	0.3782(4)	0.1661(3)	0.018(2)
O(4)	0.8993(4)	0.4342(4)	0.2781(3)	0.019(2)
O(5)	0.9442(5)	0.1185(4)	0.3467(3)	0.027(2)
O(6)	0.8089(4)	−0.0680(4)	0.0587(3)	0.024(2)
C(1)	0.4487(6)	0.2152(6)	0.0891(4)	0.018(2)
C(2)	0.5159(6)	0.1465(5)	0.1825(4)	0.017(2)
C(3)	0.5738(6)	0.0291(5)	0.1692(4)	0.016(2)
C(4)	0.2977(7)	0.3727(6)	−0.0002(6)	0.036(4)
C(5)	0.4975(6)	0.1898(6)	0.2813(4)	0.023(3)
C(6)	0.8207(6)	0.3810(5)	0.1934(4)	0.015(3)
C(7)	0.8978(6)	0.3151(6)	0.1361(4)	0.019(3)
C(8)	0.8110(7)	0.2803(6)	0.0364(5)	0.023(3)
C(9)	0.8220(6)	0.4719(6)	0.3471(5)	0.023(3)
C(10)	1.0585(6)	0.2991(6)	0.1742(6)	0.031(4)
C(11)	0.8591(6)	0.1410(5)	0.2685(5)	0.018(3)
C(12)	0.7753(6)	0.0240(6)	0.0901(4)	0.019(3)
H(3a)	0.6064	−0.0242	0.2358	0.020
H(3b)	0.5388	−0.0182	0.1182	0.020
H(4a)	0.2442	0.3086	−0.0496	0.020
H(4b)	0.2208	0.4194	0.0012	0.020
H(4c)	0.3640	0.4181	−0.0105	0.020
H(5a)	0.5060	0.2758	0.2875	0.020
H(5b)	0.3903	0.1822	0.2846	0.020
H(5c)	0.5593	0.1608	0.3446	0.020
H(8a)	0.7366	0.3366	−0.0033	0.020
H(8b)	0.8621	0.2392	−0.0058	0.020
H(9a)	0.7643	0.3979	0.3625	0.020
H(9b)	0.9068	0.4973	0.4074	0.020
H(9c)	0.7595	0.5518	0.3200	0.020
H(10a)	1.1005	0.2869	0.2461	0.020
H(10b)	1.1015	0.3828	0.1667	0.020
H(10c)	1.0803	0.2298	0.1384	0.020

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$.

Compound 3: Yield; 260 mg (68%, 0.68 mmol), m.p. 55–56°C (dec.). Anal. Found: C, 44.16; H, 5.31; Mo, 25.17%. C$_{14}$H$_{20}$MoO$_6$ (380.25) requires: C, 44.22; H, 5.30; Mo, 25.23%. IR (KBr pellet) $\tilde{\nu}$(cm^{-1}): 2980 (m), 2959 (m), 2925 (m), 2850 (m) (ν_{CH}); 1940 (s), 1861 (s) [ν_{CO}, Mo(CO)$_2$]; 1558 (m), 1531 (m), 1461 (m), 1402 (m), 1379 (s), 1340 (s), 1194 (s), 1015 (m), 760 (m), 708 (m). ^{1}H NMR (benzene-d_6) δ: 4.05–3.60 (m, 4H, OCH_2); 3.43 [d, 1H, =CH_2, ^2J(HH) = 3.9 Hz]; 3.26, [d, 1H, =CH_2, ^2J(HH) = 1.6 Hz]; 3.08 (d, 1H, =CH_2, 3.9 Hz); 2.32 (d, 1H, =CH_2, 1.6 Hz); 2.02 (s, 3H, H_3C–C=); 1.81 (s, 3H, H_3C–C=); 0.93 [t, 3H, OCH$_2$CH_3, ^3J(HH) = 7.1 Hz]; 0.90 [t, 3H, OCH$_2$CH_3, ^3J(HH) = 7.1 Hz] ppm. ^{13}C NMR (benzene-d_6) δ: 229.18 [s, Mo(CO)$_2$]; 229.07 [s, Mo(CO)$_2$]; 176.86 (s, C=O ester); 169.34 (s, C=O ester); 76.60 [s, =C(CH$_3$)]; 65.56 [s, =C(CH$_3$)]; 63.02 (t, OCH_2); 62.57 (t, OCH_2); 62.15 (t, =CH_2); 53.92 (t, =CH_2); 18.88 (q, H$_3$C–C=); 17.59 (q, H$_3$C–C=); 14.32 (q,

OCH$_2$CH_3); 14.13 (q, OCH$_2$CH_3) ppm. MS (EI, 70 eV) m/z [rel. int (%)]: 382 (21, M$^+$); 354 (11, M$^+$– CO); 326 (12, M$^+$– 2CO); 228 (30); 69 (81); 41 (100, C$_3$H$_5^+$).

3.5. Dicarbonylbis(ethyl methacrylate)tungsten (4)

To a suspension of 1.73 g (4.0 mmol) of (CH$_3$-CH$_2$CN)$_3$W(CO)$_3$ in n-heptane (30 ml) were added 1.14 g (10 mmol) of ethyl methacrylate (stabilised with 200 ppm of hydroquinone, used as received). The resulting mixture was heated to 90°C and kept at that temperature for 100 h, when a red clear reaction mixture was obtained. A small amount of black tar precipitated on the glass of the reaction flask. The liquid phase was filtered off and the residue extracted once with hot heptane and then discarded (**CAUTION**: Residue may be pyrophoric!). The combined heptane solutions were evaporated in vacuo to yield a brown–red oil. Traces of methacrylate ester and W(CO)$_6$ were removed under high vacuum (10^{-2} Pa). The crude product was then recrystallised by slowly cooling a solution in n-pentane (20 ml) to −78°C. Fine orange–red needles of the tungsten complex 4 were finally dried under high vacuum.

Compound 4: Yield, 1.35 g (72%, 2.88 mmol), m.p. 60–61°C. Anal, Found: C, 36.12; H, 4.32; W, 39.26%. C$_{14}$H$_{20}$O$_6$W (468.2) requires: C, 35.92; H, 4.31; W, 39.27%. IR (KBr pellet) $\tilde{\nu}$ (cm^{-1}): 2987 (sh), 2980 (m), 2958 (w), 2928 (w), 2855 (w) (ν_{CH}); 1941 (s), 1862 (s) [ν_{CO}, W(CO)$_2$]; 1520 (m), 1461 (m), 1405 (m), 1379 (s), 1195 (s), 1015 (m), 951 (w), 760 (w), 710 (w). ^{1}H NMR (benzene-d_6) δ: 3.98–3.50 (m, 4H, OCH_2); 3.38 [d, 1H, =CH_2, ^2J(HH) = 5.4 Hz]; 2.92 (d, 1H, =CH_2, 5.4 Hz); 2.78 [d, 1H, =CH$_2$, ^2J(HH) = 2.9 Hz]; 2.12 (s, 3H, H_3C–C=); 1.91 (s, 3H, H_3C–C=); 1.57 (d, 1H, =CH_2, 2.9 Hz); 0.93 [t, 3H, OCH$_2$CH_3, ^3J(HH) = 7.1 Hz]; 0.90 [t, 3H, OCH$_2$CH_3, ^3J(HH) = 7.1 Hz] ppm. ^{13}C NMR (benzene-d_6) δ: 221.50 [s, W(CO)$_2$]; 219.44 [s, W(CO)$_2$]; 177.34 (s, C=O ester); 169.30 (s, C=O ester); 68.65 (s, =C–CH$_3$); 63.42 (t, OCH_2); 63.08 (t, OCH_2); 57.20 (s, =C–CH$_3$); 54.08 [t, =CH$_2$, ^1J(WC) = 8.0 Hz]; 45.62 [t, =CH$_2$, ^1J(WC) = 22.1 Hz]; 18.04 (q, H$_3$C–C=); 16.88 (q, H$_3$C–C=); 14.54 (q, OCH$_2$CH_3); 14.24 (q, OCH$_2$CH_3) ppm. MS (EI, 70 eV) m/z [rel. int (%)]: 468 (6, M$^+$); 440 (5, M$^+$– CO); 412 (10, M$^+$– 2CO); 354 (9, M$^+$– C$_6$H$_{10}$O$_2$); 268 (15); 69 (95); 41 (100, C$_3$H$_5^+$).

3.6. Oxadiene complexation reactions with tungsten complex 4

3.6.1. Using (R)-(+)-pinocarvone (5)

A mixture of 234 mg (0.5 mmol) of dicarbonylbis-(ethyl methacrylate)tungsten (4) and 150 mg (1.0 mmol)

of (R)-$(+)$-pinocarvone (5) in 3 ml of benzene was stirred at room temperature (20°C) under argon for 12 h. After removal of the volatile components in vacuo, the red–brown residue was recrystallised from n-pentane between 20°C and −78°C. After drying under high vacuum, red–brown crystals of dicarbonylbis[(R)-$(+)$-pinocarvone]tungsten (7) were obtained, identical in all respects to an authentic sample prepared by standard methods in 37% yield[11].

Compound 7: Yield, 251 mg (93%, 0.47 mmol), m.p. 157–158°C. Anal. Found: C, 48.96; H, 5.22; W, 33.96%. $C_{22}H_{28}O_4W$ (540.3) requires: C, 48.91; H, 5.23; W, 34.03%. IR (KBr pellet) $\tilde{\nu}$ (cm^{-1}): 2965 (w), 2922 (m), 2862 (w) (ν_{CH}); 1970 (s), 1961 (sh), 1880 (s), 1872 (s) [ν_{CO}, $W(CO)_2$]; 1465 (w), 1454 (w), 1405 (m), 1260 (w), 1095 (w), 802 (m), 575 (w). ^1H NMR (benzene-d_6) δ: 2.92–2.82 (m, 2H); 2.75 [d, 2H, $=CH_2$, ^2J(HH) = 2.9 Hz]; 2.71 (d, 2H, $=CH_2$, 2.9 Hz); 2.54–2.40 (m, 2H); 2.39–2.21 (m, 4H); 2.08–1.94 (m, 4H); 1.20 (s, 6H, C–CH_3); 0.83 (s, 6H, C–CH_3) ppm. ^{13}C NMR (benzene-d_6, all signals arising from two symmetry equivalent carbon atoms) δ: 220.47 [s, $W(CO)_2$]; 177.21 (s, C=O ketone); 93.89 (s, C=CH_2); 47.93 (t, H_2C=C); 45.03 (d); 41.98 [s, $C(CH_3)_2$]; 41.73 (d); 35.99 (t); 34.22 (t); 26.44 [q, $(H_3C)_2C$]; 21.52 [q, $(H_3C)_2C$] ppm. MS (EI, 70 eV) m/z [rel. int. (%)]: 540 (11, M^+); 512 (1, M^+− CO); 484 (100, M^+− 2CO); 91 (40); 53 (38); 41 (95).

3.6.2. Using 2-methylenecycloheptanone (6)

2-Methylenecycloheptanone (6) (49.6 mg, 0.4 mmol) was added under argon via a syringe to a solution of 93 mg (0.2 mmol) of dicarbonylbis(ethyl methacrylate)-tungsten (4) in 400 μl of benzene-d_6 placed in an NMR tube. After sealing, the tube was kept at room temperature (20°C) for 24 h. After that time none of the ester complex could be detected by NMR. The NMR tube was opened and all volatile components were removed from the reaction mixture in vacuo (5–10 Pa). The red, solid residue was then recrystallised from a small amount of n-pentane between 20°C and −78°C. After drying under high vacuum, analytically pure dicarbonylbis(2-methylenecycloheptanone)tungsten was obtained. The product (19 : 1 mixture of two diastereomers 8a and 8b of C_1 and C_2 symmetry, respectively) was identical in all respects to a sample obtained from a standard complexation reaction in 53% yield [11].

Compound 8: Yield, 88 mg (90%, 0.18 mmol), m.p. 93°C. Anal. Found: C, 44.30; H, 5.06; W, 37.60%. $C_{18}H_{24}O_4W$ (488.2) requires: C, 44.28; H, 4.95; W, 37.66%. IR (KBr pellet) $\tilde{\nu}$ (cm^{-1}) 2920 (m), 2843 (m) (ν_{CH}); 1977 (s), 1890 (s) [ν_{CO}, $W(CO)_2$]. ^1H NMR (benzene-d_6, major diastereomer) δ: 3.29 (m, 1H); 3.02 [d, 1H, $=CH_2$, ^2J(HH) = 4.8 Hz]; 2.81–2.65 (m, 1H); 2.69 (d, 1H, $=CH_2$, 4.8 Hz); 2.63 [d, 1H, $=CH_2$, ^2J(HH) = 1.6 Hz]; 1.90 (d, 1H, $=CH_2$, 1.6 Hz); 2.52–

1.05 (m, 18H) ppm. ^{13}C NMR (benzene-d_6, major diastereomer) δ: 217.24 [s, $W(CO)_2$]; 214.13 [s, $W(CO)_2$]; 194.43 (s, C=O ketone); 152.07 (s, C=O ketone); 99.53 (s, C=CH_2); 80.30 (s, C=CH_2); 53.60 (t, H_2C=C); 46.47 [t, H_2C=C, ^1J(WC) = 19.2 Hz]; 38.69 (t); 34.39 (t); 34.10 (t); 32.75 (t); 31.95 (t); 30.93 (t); 29.45 (t); 29.02 (t); 26.17 (t); 22.97 (t) ppm. ^{13}C NMR (benzene-d_6, minor diastereomer, from isomeric mixture) δ: 231.82 [s, $W(CO)_2$]; 183.91 (s, C=O ketone); 85.50 (s, C=CH_2); 52.77 (t, $=CH_2$); 38.84 (t); 33.19 (t); 30.81 (t); 29.22 (t); 23.29 (t) ppm. MS (EI, 70 eV) m/z [rel. int. (%)]: 488 (4, M^+); 460 (4, M^+− CO); 432 (90, M^+− 2CO); 91 (61); 79 (65); 67 (70); 41 (100, $C_3H_5^+$).

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[15] Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD 59114 and the journal citation.