Synthesis and Hydrophosphorylation of π -Complexes of Esters of Unsaturated Carboxylic Acids with Chromium Subgroup Metals

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Received June 4, 2003

Abstract—Photochemical and thermochemical activation were used to prepare new π -complexes of chromium, molybdenum and tungsten containing η^2 - and η^4 -coordinated methyl acrylate, methyl cynnamate, and dimethyl fumarate molecules. Geometric, electronic, and energetic parameters of the coordinated ester molecules were found and factors governing η^2 - and η^4 -coordination of the oxodiene system were revealed by nonempirical calculations. Monocarboxylic acid esters incorporated in the π -complexes react with dialkyl hydrogen phosphites to give dialkyl acyl phosphites coordinated with the metal center and susceptible to oxidation the corresponding phosphates. In this case, the phosphorylation involves the OH-tautomer of dialkyl hydrogen phosphite. Coordinated dimethyl fumarate undergoes phosphorylation by two concurrent pathways, viz. transesterification or Pudovik reaction. In the latter case, fragmentation of the organometallic compound takes place.

One of the well-defined present-day trends in organic and organometallic synthesis is functionalization of unsaturated organic compounds, dienes or heterodienes inclusive, in the coordination sphere of a transition metal [1, 2]. The significant changes in the electronic and steric structure of an unsaturated molecule incorporated as ligand in the coordination sphere of a transition metal can not only affect the rate and regioselectivity of its functionalization, but also make feasible reactions atypical or impossible for the uncoordinated molecule. Despite the successful use of methods of organometallic chemistry in organic synthesis [3], there has been little work on chemical transformations of organometallic compounds in the coordination sphere of transition metals.

Recently we reported reactions of dialkyl hydrogen phosphites with α -enones [4, 5] and haloarenes [6] in the coordination sphere of carbonyl complexes of transition metals of the chromium subgroup. Here we present the results of theoretical and experimental investigations into the hydrophosphorylation reaction of unsaturated carboxylic acid esters in the coordination sphere of carbonyl π -complexes of Group VIB metals.

As follows from the known structures of π -complexes of unsaturated carboxylic acid esters with chromium subgroup metals bearing simultaneously carbonyl and phosphine [7] or phosphite [8] ligands, the oxodiene ligand can coordinate both by the η^2 and by the η^4 type. For one and the same ligand and complex-forming metal, both types of coordination can simultaneously occur [7]. We successfully synthesized π -complexes of acrylates, cynnamates, and diethyl fumarate with chromium subgroup metals bearing carbon monoxide molecules only. To this end, we made use of our previously developed procedure for preparing metal carbonyl π -complexes of oxodienes, based on ligand exchange under photochemical and thermal activation conditions [4, 5].

The photochemically activated reaction of unsaturated carboxylic acid esters with chromiun subgroup metal(0) hexacarbonyls gave complexes I and II containing the ligand η^2 -coordinated by the with C=C bond.

$$\begin{array}{c} O & O \\ \mathbb{R}-CH=CH-C-O-CH_3 + M(CO)_6 \xrightarrow{hv} \mathbb{R}-CH=CH-C-O-CH_3 \\ \downarrow \\ M(CO)_5 \\ \mathbf{Ia-Ic, IIa-IIc} \end{array}$$

M = Cr (I), W (II); R = H (a), Ph (b), C(O)OCH₃ (c).

The structure of products Ia-Ic and IIa-IIc is confirmed by IR and ¹H and ¹³C NMR spectroscopy. In the IR spectra of all the obtained compounds, a system of five well-resolved bands at 2100–1880 cm⁻¹ is observed. It was attributed to vibrations of carbonyls coordinated with the transition metal. The number of absorption bands in this case is equal to the number of carbon monoxide molecules coordinated with the metal center. The frequency of stretching vibrations of the coordinated double C=C bond decreases by 130–150 cm⁻¹ on average: 1700 cm⁻¹ in free methyl acrylate against 1550 cm⁻¹ in compound **Ha**, which is good agreement with published data [7]. In ¹H NMR spectrum, the signals of ethylene hydrogen atoms appear at 3.45-3.35 ppm against 6.00-6.04 ppm in free methyl acrylate. In ¹³C NMR spectra, the signals of ethylene carbon atoms appear at 45 (=CH) and at 49 ppm (= CH_2). The respective signals of free methyl acrylate are at δ_{C} 128.6 ppm and 130.1 ppm. The frequency of C=O stretching vibrations does not change considerably: 1695 cm⁻¹ in free methyl acrylate against 1680 cm^{-1} in complex IIa. Such an insignificant shift of the absorption band cannot be produced both by η^2 - and by η^4 -coordination of the carbonyl group on the transition metal atom and is evidently connected with attenuated conjugation between the C=C and C=O bonds because of their coordination with the metal. Similar changes in the

stretching vibration frequencies of multiple bonds located near a group involved coordination were observed previously [9]. We also came to the same conclusion on the basis of quantum-chemical calculations of oxodiene complexes of chromium subgroup metals [10].

The yield of tungsten π -complexes decreases in the η^2 -ligand series methyl cynnamate (53%), methyl acrylate (40%), and dimethyl fumarate (22%), under identical conditions of photochemical synthesis. This trend is probably associated with the decrease of the electron density on the ester olefin fragment in this series.

The thermochemically activated reaction of unsaturated carboxylic acid esters with metal(0) hexacarbonyls (boiling in acetonitrile solution) leads to formation of organometallic compounds of various structure. The way of coordination of the unsaturated ligand with the metal center in this case depends on the nature of substituents bound with the C=C-C=O system.

Methyl cynnamate reacts with chromium(0), tungsten(0), and molybdenum(0) hexacarbonyls to give π -complexes **IIIa**–**IIIc** formed by η^4 -coordination of the oxodiene with metal.

$$\begin{array}{c} \text{Ph-CH=CH-C-O-CH}_3 + M(\text{CO})_6 \xrightarrow[\text{CH}_3\text{CN}]{} \xrightarrow[\text{CH}_3\text{CN}]{} \text{Ph-CH=CH-C-O-CH}_3 \\ \downarrow \swarrow & \downarrow \swarrow \\ \text{O} \\ M(\text{CO})_4 \\ \hline \\ \text{IIIa-IIIc} \end{array}$$

M = Cr (a), Mo (b), W (c).

The purity of compounds **IIIa–IIIc** was established by TLC, and the structure was confirmed by IR and ¹H and ¹³C NMR spectroscopy. The IR spectra contain four well-resolved bands in the range 1880– 2100 cm⁻¹. They relate to vibrations of the four carbon monoxide molecules terminally coordinated with the metal. The frequency of C=C stretching vibrations of (η^4 -methyl cinnamate)metal(0) tetracarbonyls decreases by 140–150 cm⁻¹, from 1710 cm⁻¹ in uncoordinated methyl cinnamate to 1580 cm⁻¹ in complex **IIIc**, in agreement with published data [7]. Note that the v_{C=O} of methyl cinnamate changes more significantly in going to η^4 -complexes **IIIa–IIIc** compared to η^2 -complexes **Ia–Ic** and **IIa–IIc**. The coordination-induced decrease in v(C=O) of 70 cm⁻¹ (from 1670 cm⁻¹ in the starting ester to 1600 cm⁻¹ in compound **IIIc**) provides strong evidence in favor of η^1 -coordination of the ester carbonyl with the transition metal. In the ¹H NMR spectrum of compound **IIIc**, the signals of olefin hydrogen atoms are also shifted upfield as compared to the uncoordinated state and appear at 4.00–3.85 ppm. In the ¹³C NMR spectrum, the olefin carbon atoms are characterized by the signals at 43 (=*C*HC(O)OCH₃) and 51 ppm (Ph-*C*H=).

Metal(0) hexacarbonyls react with methyl acrylate and dimethyl fumarate under thermochemical activation to give products differing in structure from metal complexes **IIIa–IIIc**. In this case, substitution of two carbonyl ligands at the metal atom takes place, but the second coordination vacancy of the metal center is filled not by increase of capticity of ester-metal bonding, as with methyl cinnamate, but by coordination of one more acylate molecule by the double C=C bond.

$$\begin{array}{c} \text{R-CH=CH-C-O-CH}_{3} + \text{M(CO)}_{6} \xrightarrow[\text{CH}_{3}\text{CN}]{} \\ \text{O} \end{array} \qquad \begin{bmatrix} \text{O} \\ \parallel \\ \text{R-CH=CH-C-O-CH}_{3} \\ \downarrow \\ \text{M(CO)}_{4} \end{bmatrix}_{2} \\ \text{We We Ve Ve Ve} \end{array}$$

M = Cr (a), Mo (b), W (c); R = H (IV), $CH_3O(O)C$ (V).

The structur of $(\eta^2$ -methyl acrylate)₂- (**IVa–IVc**) and $(\eta^2$ -dimethylfumarate)₂metal(0)-tetracarbonyls (Va-Vc) were proposed on the basis of IR and ¹H NMR data. The system of four well-resolved bands in the range $1850-2050 \text{ cm}^{-1}$ in the IR spectra of these compounds relates to four carbonyl ligands. Here, too, the stretching vibration frequency of coordinated acylates is decreased by 150-170 cm⁻¹. These vibrations appear as two absorption bands. For example, in complex IVa, we assigned to them the bands at 1550 and 1530 cm⁻¹. Most probably, the appearance of such doublets arises from the possibility of formation of two stereoisomeric π -complexes, viz. cis- and $trans-(\eta^2-oxodiene)_2$ metal(0) tetracarbonyls. We did not make detailed assignments of each of the absorption bands to the *cis* or *trans* forms of organometallic compounds but presumed that the band at 1550 cm^{-1} belongs to the latter form, since a C=C bond coordinated with a transition metal exibits a stronger trans-effect than carbon monoxide [10]. Consequently, unsaturated *trans*-ligands feature weaker η^2 -bonding, which, in its turn, results in their weaker structural disturbance and smaller decrease in their $v_{C=C}$ values. The frequences of stretching vibrations of the ester C=O group in compound IVa-IVc and Va-Vc change insignificantly (by $10-20 \text{ cm}^{-1}$), similarly to what was observed with complexes Ia-Ic and IIa-IIc. Here, too, such changes in $v_{C=0}$ cannot be explained in terms of coordination of the carbonyl group with the transition metal and are probably associated coordination-induced changes in the geometric and electronic structure of the ligand. The broadening of the signal at 4.38–5.25 ppm in the ¹H NMR spectrum of compound IVa may be connected with stereochemical inhomogeneity of this compound and quickly establishing equilibrium between its *cis* and *trans* forms in solution. The same spectral picture has been observed for $(\eta^2$ -hexene)₂W(\overrightarrow{CO})₄ [11].

We previously showed that the photochemical synthesis of π -complexes of α -enones gives η^2 -coordinated products, and thermochemical activation of this reaction leads to η^4 -coordinated products. We interpret these results as follows. The η^2 -complexes are formed by a kinetically controlled reaction involving photochemical substitution of one carbon monoxide with heterodiene. The $\eta^4\mbox{-}complexes$ result from a thermodynamically controlled reaction and the formation of such products takes place under conditions of thermal synthesis of organometallic compounds [5]. As follows from our present resuts, under photochemical activation conditions, unsaturated carboxylic acid esters, too, substitute only one ligand in homocarbonyl derivatives of Group VIB metals, what provides η^2 -coordination by the C=C fragment. The thermochemical synthesis provides disubstitution products, yielding a η^4 -cinnamate complex and bisacylate compounds with η^2 -coordinated unsaturated ligands.

To find out the reason for such reaction pathways, we performed nonempirical quantum-chemical calculations of the geometric and electronic structure of metal hexacarbonyls and a series of π -complexes of unsaturated carboxylic acid esters using the method of effective shell potential with the SBK basis [12]. The applicability of this theoretical model for our purpose we substantiated previously [10]. Further evidence for the correct choice of the calculation basis comes from the data in Table 1. Analysis of the experimental [13, 14] and our calculated metal-carbon and carbon-oxygen distances in homoleptic complexes of metal(0) hexacarbonyls reveals their good agreement, especially for tungsten(0) hexacarbonyl. Therefore, in the present work we consider the calculation result for tungsten complexes only. The results for similar complexes of other metals will be reported in our further publications.

Basing on the results for tungsten complexes, we evaluated formation enthalpies for complexes $(\eta^2 \text{ ester})$.

W(CO)₅,
$$(\eta^2 \text{-ester})_2$$
W(CO)₄, and $(\eta^4 \text{-ester})$ W(CO)₄ by Eqs. (1)–(3). The resulting data are listed in Table 2.

$$\begin{array}{c} O & O \\ \parallel \\ R-CH=CH-C-O-CH_3 + W(CO)_6 \longrightarrow R-CH=CH-C-O-CH_3 + CO, \\ \downarrow \\ W(CO)_5 \end{array}$$
(1)

$$\begin{array}{ccc} R-CH=CH-C-O-CH_{3}+W(CO)_{6} \longrightarrow R-CH=CH-C-O-CH_{3}+2CO, & (2) \\ & & & \downarrow & \swarrow \\ O & & & & \downarrow & \swarrow \\ O & & & & W(CO)_{4} \end{array}$$

$$2R-CH=CH-C-O-CH_{3}+W(CO)_{6} \longrightarrow \left[\begin{array}{ccc} O \\ R-CH=CH-C-O-CH_{3} \\ W(CO)_{4} \end{array} \right]_{2} + 2CO. & (3) \\ & & & & & & & \\ \end{array}$$

Reactions (1)–(3) all are characterized by a slight exothermic effect and thus are fairly facile. Note that, according to the enthalpy factor, substitution of two carbon monoxide molecules is more favorable than $(\eta^2$ -ester)W(CO)₅ complex formation. It can be proposed that the entropy factor, too, will favor the former process, since the evolution of two CO molecules according to Eqs. (2) and (3) stronger increases the number of the degrees of freedom than the evolution of one CO molecule according to Eq. (1). Hence, it is safe to state that the substitution of two CO molecules in the reactions of tungsten hexacarbonyl with unsaturated acid esters is thermodynamically controlled.

At the same time, in the case of methyl acrylate and dimethyl fumarate, reaction (3) occurs to be more favorable according to the enthalpy factor, irrespective of whether the *cis* or *trans* form of the $(\eta^2 \text{-ester})_2$. W(CO)₄ complex is formed. In the case of methyl cynnamate, reaction (2), that is the formation of a product with increased hapticity of the acylate ligand, is preferred. Hence, with methyl cinnamate, the thermodymacally controlled products are tetracarbonyl-(η^4 -methyl cinnamate)metal(0) complexes **IIIa–IIIc**, while with methyl acrylate and dimethyl fumarate, bisacylate complexes **IVa–IVc** and **Va–Vc**, respectively, what agrees with our experimental data.

The reasons for the established regularity can be explained in terms structural changes induced in the molecule of unsaturated ester by its coordination with the metal center (Table 3). First of all note the elongation of the metal-coordinated double bond, as well as the loss of planarity of the C=C and C=O fragments at any type of coordination of the oxodiene system of the ligand. Note also the definite shortening of the C=O bond in η^2 -complexes, characteristic of the C=C-C=O system coordinated through only one carbon–carbon bond and the significant elongation of this bond in η^4 -coordinated esters. The described

Table 1. Experimental and calculated M–C and C–O distances (Å) in chromium subgroup metal hexacarbonyls

Complex	RHF–ECP/SBK calculation ^a		Experimental data	
$Cr(CO)_6$	1.915	1.149	1.914 ^b	1.140 ^b
Mo(CO)_6	2.079	1.149	2.063 ^c	1.145 ^c
W(CO)_6	2.068	1.151	2.058 ^c	1.148 ^c

^a Present results. ^b From single-crystal neutron diffraction [11].
 ^c From electron crystallography [14].

Table 2. Calculated formation enthalpies of π -complexes of tungsten with esters

Ester	Reaction	ΔH , kcal mol ⁻¹	
Methyl acrylate	(1)	-2.45	
	(2)	-5.58	
	(3)	$-9.87/-7.43^{a}$	
Methyl cynnamate	(1)	-1.13	
	(2)	-5.64	
	(3)	$-2.64/-1.67^{a}$	
Dimethyl fumarate	(1)	-0.98	
-	(2)	-4.38	
	(3)	-7.14/-6.63 ^a	

^a The first value relates to the *trans* form of $(\eta^2 \text{-ester})_2 W(CO)_4$ and the second, to the *cis* form of the same complex.

R	Coordination type	<i>l</i> (¹ C=O), Å	$l(^{2}C=^{3}C), Å$	\angle (³ C ³ C ¹ CO), deg	$\Delta \Delta H$, ^a kcal mol ⁻¹
CH ₃	\mathfrak{h}	1.217	1.330	0	0
	\mathfrak{h}^2	1.212	1.373	5.7	8.0
C ₆ H ₅	η^{4}	1.298	1.415	24.5	28.9
	b	1.218	1.345	0	0
	η^{2}	1.211	1.376	4.99	3.4
Dimethyl fumarate	η^4 b η^2 η^4	1.261 1.216 1.212 1.305	1.373 1.336 1.376 1.422	7.33 0 5.2 18.9	8.1 0 12.1 26.6

Table 3. Interatomic distances, torsion angles, and deformation energies of the coordination sphere^a of free and tungstencoordinated methyl acrylate, methyl cinnamate, and dimethyl fumarate, calculated by the RHF–ECP/SBK method

$$\begin{array}{c} O \\ R^{-3}CH^{=2}CH^{-1}C^{-}O^{-}CH^{-1} \end{array}$$

^a According to the Hoffman approach [15], the deformation energy of a ligand [$\Delta\Delta H$ (ligand)] in a coordination sphere is determined as a difference between the formation enthalpy of the ligand in a geometric state characteristic of the organometallic compound and the formation enthalpy of uncoordinated ligand. ^b Lacking.

structural changes in the ligand are better pronounced in η^4 - than in η^2 -complexes of unsaturated acid esters. This probably arises from the fact that tungsten has a fairly large atomic radius, and the heterodiene molecule must undergo considerable transformations to interact with it simultaneously by the π -systems of both the C=C and C=O groups. The deformation energy of the heterodiene ligand in the coordination sphere of the transition metal, too, is higher in the case of η^4 -coordination, what may be explained by a significant attenuation of the conjugation between the C=C and C=O bonds (the torsion angle between them may reach 25°).

At the same time, the above-mentioned changes are least characteristic of coordinated methyl cinnamate, as evidenced by its weakest geometry distortion and lowest deformation energy. This specific feature of methyl cinnamate may be explained by stronger stabilization of the heterodiene system due to its conjugation with the phenyl substituent. According to Table 3, methyl acrylate and dimethyl fumarate incorporated in η^4 -complexes undergo so significant geometric changes that it occurs thermodynamically more favorable to form organometallic compouns containing two η^2 -coordinated molecules in the coordination sphere (IVa–IVc and Va–Vc) than η^4 coordination products. The absence of significant changes in the geometric parameters of coordinated methyl cinnamate may be one of the reasons for the thermodynamically controlled formation of complexes **IIIa–IIIc.** Another reason for the difference between

the thermodynamically controlled products on the formation of metal complexes of methyl acrylate and dimethyl fumarate, on the one hand, and methyl cinnamate, on the other, is the larger volume of the latter. Apparently, the second methyl cinnamate molecule will destabilize the disubstitution product because of the steric hindrance arising from the neighborhood of two bulky ligands in the coordination sphere of the metal.

The calculation results allow us, on the one hand, to explain the facile formation of homoleptic heterodiene complexes, previously noted by Schmidt [1], and, on the other, to predict the structure of a thermodynamically controlled organometallic reaction product.

We involved the thermodynamically controlled products, metal complexes **IIc**, **IVc**, and **Vc**, in reaction with dialkyl hydrogen phosphites. The choice of the organometallic substrates for the phosphorylation reaction was stipulated by their higher yields and resistance to oxidation compared to products **I** and **II** obtained under photochemical activation conditions. The convenience of tungsten as complex-forming metal is connected with the presence of a magnetically active isotope ¹⁸³W in the isotopic mixture of this element, and following changes in the ³¹P-¹⁸³W and ¹H-¹⁸³W coupling constants facilitates interpretation of spectral data.

The reaction of π -complexes **IIIc** and **IVc** with dialkyl hydrogen phosphites leads to formation of

mixed anhydrides of corresponding carboxylic and dialkylphosphoric acids **VIa–VIc** and **VIIa–VIIc** coordinated with the tungsten atom by the C=C bond of the unsaturated acid and the phosphoryl group.



R = Me (a), Et (b), *i*-Pr (c); R' = H (VI), Ph (VII).

Basing on the IR and ¹H and ³¹P NMR spectra, we proposed for products **VI** and **VII** the (η^3 -dialkyl-3-phenylprop-2-enoylphosphato)tetracarbonyltungsten(0) structure. The IR spectra of these compounds show bands at 2010, 1970, 1950, and 1910 cm⁻¹ assignable to four CO molecules terminally coordinated with the chromium subgroup metal. The band

at 1580 cm⁻¹ relates to the C=C bond coordinated with the metal, and the band at 1680 cm⁻¹ belongs to the ester carbonyl group not involved in coordination. The broadened band at 1300 cm⁻¹ belongs to the metal-coordinated phosphoryl group. The ³¹P NMR spectrum contains a signal at δ_P 0.29 ppm, i.e. in a range characteristic of a phosphite phosphorus atom, and the coupling constant equal to 34 Hz (measured by the ³¹P-¹⁸³W satellite splitting). Such a phosphorus-tungsten coupling constant suggests indirect contact of the phosphorus and tungsten atoms.

The reaction of fumarate complex Vc with dialkyl hydrogen phosphites under the same conditions leads to a mixture of products, the major products being adducts of dialkyl hydrogen phosphates and dimethyl fumarate, dimethyl 2-(dialkoxyphosphoryl)succinates **IXa–IXc**. They were identified by the agreement of the spectral picture with published data [16]. Complexes **VIIIa–VIIIc** whose spectral characteristics are close to those of compounds **VI** and **VII**, are minor phosphorylation products.



According to ³¹P NMR spectra, the ratio of products **VIII** and **IX** in the reaction mixture is 1:4. The formation of phosphonates IXa-IXc is accompanied by decomposition of the organometallic complexes. The crystalline products isolated from these reaction mixtures are formed by destruction of the carbonyl metal complexes, that evidently proceeds with increase of their nuclearity. The IR spectra of these compounds contain only ill-resolved bands at 1900–2100 cm^{-1} . The fact that the main reaction pathway in this case is phosphite addition may be connected with the significant electron-acceptor power of the two ester groups. The high electrophilicity of the unsaturated substrate makes possible the Pudovik reaction even by the double bond blocked by the metal center.

Analysis of the ³¹P NMR spectra of the reaction mixtures forming anhydride complexes **VIa–VIc** and **VIIIa–VIIIc** suggests that dialkyl acyl phosphates are formed via organometallic intermediate \mathbf{X} in which the dialkyl hydrogen phosphite is present in the OH-tautomeric form coordinated with the transition metal by the lone electron pair of phosphorus. We found compound \mathbf{X} both in the reaction mixture containing starting acylate complexes **III**–**V** and dialkyl hydrogen phosphites and as resulting from direct reaction between hexacarbonyltungsten(0) and dialkyl hydrogen phosphite in solution.

$$L_2W(CO)_4 + (RO)_2POH \xrightarrow{RO} P_OH \\ RO \downarrow WL_2(CO)_3 \\ Xa - Xc$$

$$R = Me$$
 (a), Et (b), *i*-Pr (c).

Phosphite complex Xb is characterized by a signal

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at δ_P 167 ppm [¹J(³¹P-¹⁸³W) 310 Hz]. It is involved in intracomplex transesterification to form anhydride **XI** with a σ^3 -P atom. It was also detected by ³¹P NMR spectroscopy [$\delta_{\rm P}$ 127 ppm, ${}^{1}J({}^{31}{\rm P}{}^{-183}{\rm W})$ 310 Hz]. During isolation it oxidized to give final products containing a phosphate phosphorus atom.



The proposed phosphorylation scheme, in particular, can explain the absence of the catalytic effect on the formation of dialkyl acyl phosphites **XI** and dialkyl acyl phosphates, as well as Pudovik reaction products **IXa–IXc**. Here, evidently, amine competes with dialkyl hydrogen phosphite to occupy a place in the coordination sphere of the metal and complicates formation of compound **X**, not being involved in transesterification and addition reactions. Note that direct reaction of phosphite complex **X** with esters does not lead to transesterification. From these results it follows that for successful formation of dialkyl acyl phosphites and phosphates prerequisite is the coordination of both the ester and dialkyl hydrogen phosphite with the transition metal.

Hence, our present results provide evidence for a significant change in the reactivity of classical participants of the Pudovik reaction, produced by their coordination with transition metals. It is well known [16] that these substances in the uncoordinated state enter nucleophilic addition by the C=C bond, while in the coordination sphere of a metal they are capable of other reactions that are made possible due to a considerable structural and electronic modification of both molecules, induced by coordination.

EXPERIMENTAL

The IR spectra were obtained on a Specord M-80 spectrometer in mineral oil. The ¹H NMR spectra were measured on Varian UNITY 300 (299.94 MHz),

Brucker 100 (100 MHz), and Brucker Gemini 200 instruments (199.827 MHz) at 25°C in benzene- d_6 , chloroform- d_1 , and methanol- d_4 . The chemical shifts were measured against residual proton signals of the deuterated solvents. The concentrations of the solutions were 0.7–1.5 wt%. The ¹³C NMR spectra were recorded on a Varian UNITY 300 (75.4 MHz) against chloroform- d_1 signals.

Quantum-chemical calculations were carried out using the Gamess 98 program [17]. The structural and energetic parameters were calculated in the ECP (SBK) basis in which internal shell electrons are described by a model potential. This method makes use of the 6-31 G basis set for hydrogen and quadroand three-zeta basis sets for valence shells of heavy nuclei for the *s*, *p*, and *d* shells, respectively. For heavy metals, the *d*-polarization function is used.

Thin-layer chromatography was carried out on Silufol plates, eluent isopropanol-benzene (3:1), developer iodine vapor. All experiments were carried out under argon.

Pentacarbonyl(η^2 -methyl acrylate)tungsten(0) (IIa). Tungsten hexacarbonyl (0.400 g) in 20 ml of anhydrous degassed THF was irradiated in a quartz flask with a full UV light of a high-pressure mercury light for 40 min under argon with continuous stirring. If a glass flask was used, the irradiation time was increased to 2 h. A solution of 0.250 g of methyl acrylate in 2.0 ml of THF was added, and the resulting mixture was irradiated with continuous stirring for 2.5 h and then treated with hexane. The precipitate was filtered off on a glass frit to obtain a light yellow fine crystalline powder, yield 40%, decomp. point 111–113°C. IR spectrum, v, cm⁻¹: 1550 (coordinated C=C), 1680 (C=O of free methyl acrylate), 2100, 2020, 1940, 1900, 1880 (carbonyl ligands on tungsten). ¹H NMR spectrum, δ , ppm: 3.45-3.35 m (coordinated CH₂=CH). ¹³C NMR spectrum, $\delta_{\rm C}$, ppm: 45 s (coordinated =CH), 49 s (coordinated CH₂=).

Pentacarbonyl(η^2 -methyl acrylate)chromium(0), pentacarbonyl(η^2 -methyl cinnamate)tungsten(0), pentacarbonyl(η^2 -methyl cinnamate)chromium(0), pentacarbonyl(η^2 -dimethyl fumarate)chromium, and pentacarbonyl(η^2 -dimethyl fumarate)tungsten(0) were obtained by the same procedure. The yield of the organometallic products decreases in the series methyl cinnamate, methyl acrylate, and dimethyl fumarate.

Tetracarbonyl(η^4 -methyl cinnamate)tungsten(0) (IIIc). A solution of 0.5 g of hexacarbonyltungsten(0) in 20 ml of acetonitrile was refluxed under argon. Methyl cinnamate, 0.260 g, was then added, and the resulting mixture was refluxed for 14 h. The solvent was removed in a water-jet-pump vacuum without heating to concentrate the reaction mixture 4-5 times. The light green crystals that formed were filtered off under argon. A fine crystalline light green powder was obtained, yield 45%, decomp. point 138-141°C. IR spectrum, v, cm⁻¹: 1580 (coordinated C=C), 1600 (coordinated methyl cinnamate C=O), 2100, 2020, 1900, 1880 (carbonyl ligands on tungsten). ¹H NMR spectrum, δ, ppm: 4.00-3.85 m (coordinated CH=CH). ¹³C NMR spectrum, δ_C , ppm: 43 s (=*C*H-COCH₃), 49 s (coordinated Ph-CH=).

Tetracarbonyl(η^4 -methyl cinnamate)chromium(0) and tetracarbonyl(η^4 -methyl cinnamate)molybdenum(0) were obtained analogously.

Bis(η^2 -methyl acrylate)tetracarbonyltungsten(0) (IVc). A solution of 0.5 g of hexacarbonyltungsten(0) in 20 ml of acetonitrile was refluxed for 40 min under argon. Methyl acrylate, 0.260 g, was then added, and the resulting mixture was refluxed for 14 h. The solvent was removed in a water-jet-pump vacuum without heating to concentrate the reaction mixture 4–5 times. The light green crystals that formed were filtered off under argon to obtain a fine crystalline powder, yield 45%, decomp. point 138–141°C. IR spectrum, v, cm⁻¹: 1550, 1530 (coordinated C=C); 1675 (free methyl acrylate C=O), 2100, 2020, 1900, 1880 (carbonyl ligands on tungsten). ¹H NMR spectrum, δ , ppm: 5.25–4.38 (coordinated CH₂=CH).

Tetracarbonyl[η^3 -(diethyl 3-phenylprop-2-

enoylphosphate)]tungsten(0) (VIIb). Tetracarbonyl-(η^4 -methyl cinnamate)tungsten(0), 0.15 g, was dissolved in 5.0 ml of absolute degassed benzene, and 0.2 ml of diethyl hydrogen phosphite was added. The reaction mixture was kept for 24 h at room tempera-ture under argon and then its ³¹P NMR spectrum was measured. The solvent was removed in a water-jetpump vacuum to concentrate 4-5 times. The light green crystals that formed were filtered off under argon to obtain white fine crystals, yield 15%, decomp. point 88–94°C. IR spectrum, v, cm⁻¹: 1580 (coordinated C=C), 1680 (free ester C=O), 2010, 1970, 1950, 1910 (carbonyl ligands on tungsten), 1300 br (coordinated P=O). ¹H NMR spectrum, δ, ppm: 4.00-3.85 m (coordinated CH=CH). ³¹P NMR spectrum, $\delta_{\rm P}$, ppm: 0.29 ($J_{\rm PW}$ 34 Hz). ³¹P NMR spectrum of the reaction mixture also contained a signal at δ_P 127 ppm (J_{PW} 310 Hz). During isolation, this signal fully disappeared and quantitatively converted to a signal at $\delta_{\rm P}$ 0.29 ppm.

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