Synthesis of Mesityl Oxide π-Complexes with Metals of Chromium Subgroup and with Iron. Theoretical and Experimental Investigation of the Ligand Dissociation Energy

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Abstract—At the use of photochemical and thermochemical activation new π-complexes of chromium, molybdenum, and tungsten were prepared containing in the coordination sphere η^2- and η^4-molecules of 4-methyl-3-penten-2-one. Nonempirical methods were applied to calculation of the energy parameters of the coordinated molecules, and the factors governing the η^2- and η^4-coordination of the oxodiene system were established. A thermochemical study was performed on the 4-methyl-3-penten-2-one η^4-coordination product with carbonyl metal core. A scheme of the thermal decomposition was suggested for the iron (0) η^4-(4-methyl-3-penten-2-one)tricarbonyl.

A development of new preparative procedures based on the chemo-, regio-, and stereoselective addition reactions is among the most prominent trends in the modern synthetic chemistry. The interest attracted by this field of the synthetic organic and organometallic chemistry originates from the "maximum atomic efficiency and atom-saving" [1] of the addition reactions, especially of those occurring strictly at the definite structural fragments of substrates.

We showed formerly that conjugated oxo- and aza-dienes located in the coordination sphere of the transition metals were involved in dialkyl phosphines addition at the carbon–heteroatom double bond irrespective of the type of heterodiene coordination with the metal center [2–6].
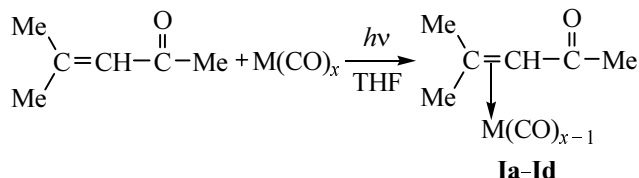
The equal reactivity of the coordinated heterodienes independent of hapticity of their bonding cannot be rationalized regarding the metal only as a protective group [3–6] since as we have established the bonding with the metal center results in significant changes in the geometry and electronic structure of the oxodiene ligand [7]. Obviously for successful intracomplex functionalizing of unsaturated molecules a detailed study is required on the factors governing the readiness of organometallic compounds formation and also on the thermal stability and reactivity of the unsaturated molecules within the coordination sphere of the transition metal.

In the present study we approached these problems by investigation of reactions between the 4-methyl-3-penten-2-one (mesityl oxide) and iron(0) pentacarbonyl and hexacarbonyls of metals of VIB group under both photochemical and thermochemical activation.

Under UV irradiation of a THF solution containing a homocarbonyl complex of a transition metal and mesityl oxide products were obtained of η^2-coordination of α-enone **Ia–Id**. The π-type coordination of the olefin ligand with the metal atom was confirmed by the appearance in the IR spectra of the reaction products of the absorption bands of the C=C bond coordinated to a metal center: 1560 (**Ia**), 1565 cm^{-1} (**Id**); in a free mesityl oxide the corresponding band was observed at 1640 cm^{-1}. In the region of the stretching vibrations of the C=O bond of the carbonyl ligands coordinated to the metal in the spectrum of compound **Ia** were observed four, and in the spectra of compounds **Ib–Id** five well resolved bands revealing that only one molecule of carbon monoxide was replaced in the coordination sphere of the metal at the π-complex formation. The frequency of the C=O group stretching vibrations belonging to the mesityl oxide did not substantially change in compounds **Ia–Ic** on complex formation compared to the free heterodiene [1720 (**Ia**), 1723 (**Ib**), 1718 (**Ic**), and 1725 cm^{-1} in the free mesityl oxide]. This fact and also the data of ^{13}C NMR spectroscopy given further suggest that the carbonyl group of the mesityl oxide is not involved into the coordination. The observed insignificant changes in the parameters of the IR spectra of the carbonyl group of ligands may be
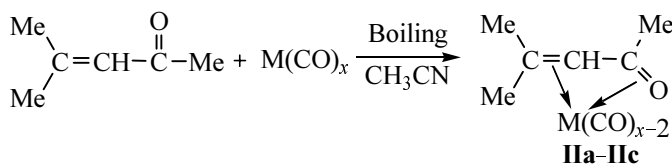
due to the structural transformations of the latter resulting from the coordination to the metal.

$$\underset{Me}{\overset{Me}{>}}C=CH-\overset{\overset{O}{\parallel}}{C}-Me + M(CO)_x \xrightarrow[THF]{h\nu} \underset{Me}{\overset{Me}{>}}C=CH-\overset{\overset{O}{\parallel}}{C}-Me$$
$$\downarrow$$
$$M(CO)_{x-1}$$

Ia–Id

M = Fe (**a**), $x = 5$; Cr (**b**), Mo (**c**), W (**d**), $x = 6$.

The assumed structure of **Ia–Id** complexes is also supported by the NMR data. The signal of the olefin proton in the ^{1}H NMR spectrum of the oxodiene shifts upfield: from 6.43 ppm in the free mesityl oxide to 3.86 in **Ia** and 4.03 ppm in **Id**. The position of methyl proton signals is virtually unchanged by coordination: they appear in the region 1.3–1.7 ppm. ^{13}C NMR spectra also indicate the η^2-coordination of the mesityl oxide to the metal center through the double carbon-carbon bond of the α-enone. The chemical shifts of carbons at the double bond of the mesityl oxide in compounds **Ib** and **Ic** are equal respectively to 85 and 80 (>$\underline{C}$=CH–), 63 and 68 ppm (>C=$\underline{C}$H–). In the noncoordinated molecule of the mesityl oxide these carbon signals appear at 147 (>$\underline{C}$=CH–) and 123 ppm (>C=$\underline{C}$H–). It is noteworthy that the position of the carbonyl carbon signal in the spectra of compounds **Ia–Id** did not notably change compared to its location in the spectrum of the free α-enone: 188 in compound **Ib** and 196 ppm in the free mesityl oxide. The latter fact suggests that in the complexes **Ia–Id** the π-bonding of the carbonyl group with the metal atom hardly exists. The observed insignificant changes in the chemical shifts of the carbonyl carbons of ligands may be due to the changes in the geometrical and electronic structure of the heterodiene ligand resulting from the coordination to the metal.

Heating at reflux of iron, chromium, and molybdenum carbonyls with the mesityl oxide in acetonitrile solution afforded the products of a η^4-coordination **IIa–IIc**.

$$\underset{Me}{\overset{Me}{>}}C=CH-\overset{\overset{O}{\parallel}}{C}-Me + M(CO)_x \xrightarrow[CH_3CN]{Boiling} \underset{Me}{\overset{Me}{>}}C=CH-C\overset{Me}{\underset{O}{<}}$$
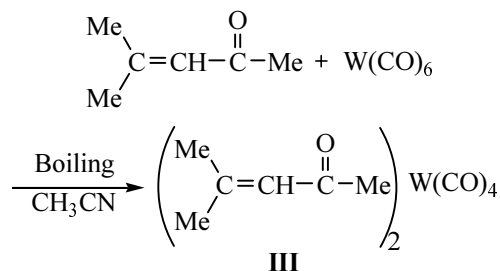$$\overset{\downarrow\nearrow}{M(CO)_{x-2}}$$

IIa–IIc

M = Fe (**a**), $x = 5$; Cr (**b**), Mo (**c**), $x = 6$.

This way of coordination is confirmed by appearance in the IR spectra of absorption bands belonging to the π-coordinated C=C bond [1575 (**IIa**), 1580 cm^{-1} (**IIc**)]

and by decreased by 30–40 cm^{-1} stretching vibrations frequency of C=O in α-enone as compared to free compound [1690 (**IIa**), 1688 (**IIb**), and 1695 cm^{-1} (**IIc**)]. The latter changes in the spectral characteristics are apparently caused by the coordination of the carbonyl group of the α-enone to the metal center. In the region of the stretching vibrations of the carbonyl ligands were observed well resolved bands, three for compound **IIa** and four for compounds **IIb** and **IIc** indicating the elimination of two CO molecules from the coordination sphere of iron, chromium, or molybdenum resulting in formation under thermochemical activation of metal complexes [(η^4-α-enone)M(CO)$_{x-2}$] (M = Fe, $x = 5$; M = Cr, Mo, $x = 6$). This conclusion is supported by the upfield shift of the olefin proton in the ^{1}H NMR spectra of compounds **IIa–IIc** [3.75 (**IIa**), 3.45 ppm (**IIc**)]. Similarly strong alteration in the chemical shifts in the ^{13}C NMR spectra were observed for all the three carbon atoms of the heterodiene system of compounds **IIa–IIc** [93(>$\underline{C}$=CH–), 75 (>C=$\underline{C}$H–), and 140 ppm (C=O)]. Analogously the synthesis conditions affected the structure of π-complexes we had previously prepared from chalcone and benzalacetone [3].

The thermochemical reaction of mesityl oxide with the tungsten(0) hexacarbonyl took another route: instead of tungsten(0) η^4-(4-methyl-3-penten-2-one)tetra-carbonyl we isolated a π-complex identified as tungsten(0) bis[η^2-(4-methyl-3-penten-2-one)]tetracarbonyl (**III**).

$$\underset{Me}{\overset{Me}{>}}C=CH-\overset{\overset{O}{\parallel}}{C}-Me + W(CO)_6$$
$$\xrightarrow[CH_3CN]{Boiling} \left(\underset{Me}{\overset{Me}{>}}C=CH-\overset{\overset{O}{\parallel}}{C}-Me\right)_2 W(CO)_4$$

III

Four well resolved bands belonging to four molecules of carbon monoxide (2010, 1970, 1920, 1880 cm^{-1}) coordinated to the tungsten atom, a significant reduction of the vibration frequency of the C=C bond to 1550 cm^{-1}, and unchanged position of the keto group absorption band belonging to mesityl oxide (1723 cm^{-1}) clearly show the π-coordination of the mesityl oxide molecule to the tungsten involving only C=C bond. In the ^{1}H NMR spectrum of compound **III** two considerably broadened signals are observed at 3.00–4.00 ppm corresponding to protons attached to the coordinated double bond of the ligand.

The spectrum of compound **III** is analogous to the ^{1}H NMR spectra of complexes of composition bis-(alkene)W(CO)$_4$ [8], and following the suggestion of this publication we assume that the appearance of two signals from the proton in the structure (>C=C$\underline{H}$–) is caused by the presence in the solution of compound **III** of two geometrical isomers, *trans*- **IIIa** and *cis*- **IIIb** tungsten(0) bis[η^2-(4-methyl-3-penten-2-one)]tetracarbonyl. The occurrence of two signals is due to rapidly established equilibrium between both isomers, and the broadening of the signals is caused by internal rotation of the ligand in the tungsten coordination sphere.
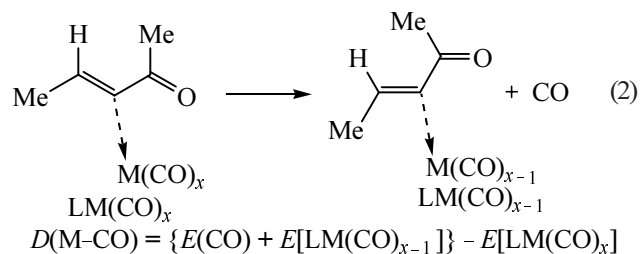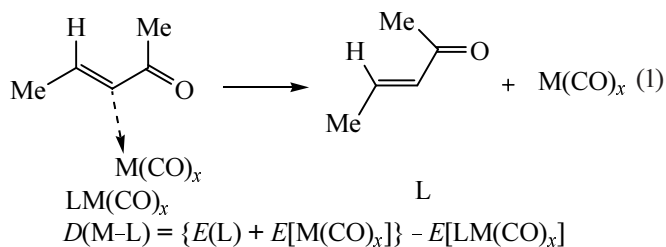
We presume that formation of complexes of composition tungsten(0) bis(η^2-enone)tetracarbonyl at the thermally activated reaction of tungsten(0) hexacarbonyl with mesityl oxide where we previously have obtained at the thermochemical activation complexes tungsten(0) (η^4-enone)tetracarbonyl with chalcone and benzalacetone [2, 3] is caused by smaller size of the mesityl oxide than that of chalcone and benzalacetone. Therefore at elimination of two carbon monoxide molecules in the coordination sphere of the bulky tungsted can be located two mesityl oxide molecules. At the same time the bulk of the chalcone and benzalacetone prevents their placement in these coordination vacancies. Thus the heterodiene molecule containing aromatic substituents is obliged to enter into the coordination of η^4-type.
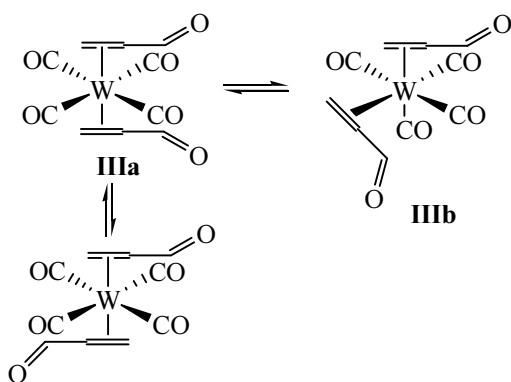
In order to gain an understanding of specific features we observed in formation of π-complexes with different coordination type we estimated the dissociation energies of metal–ligand bond in metal hexacarbonyls and in the π-complexes obtained therefrom, and also the enthalpy of reactions affording organometallic compounds of different hapticity.

The energy of metal–ligand bonds in metal complexes was estimated by calculation of the enthalpy of model

dissociation reactions of organometallic compounds (1) and (2).

$$D(\text{M–L}) = \{E(\text{L}) + E[\text{M(CO)}_x]\} - E[\text{LM(CO)}_x]$$

$$D(\text{M–CO}) = \{E(\text{CO}) + E[\text{LM(CO)}_{x-1}]\} - E[\text{LM(CO)}_x]$$

According to schemes (1) and (2) the heterodiene or carbonyl ligands at dissociation retained the electron pair of the respective bond, and the metal-containing fragment became a coordinatively unsaturated sixteen-electron species whose total optimization of geometry was also performed, and the bond energy was estimated as the energy of the reaction.

The calculated energies of ligand–metal bonds (Table 1) in the complexes studied show that the heterodiene bond to the metal is stronger than the metal–carbon monoxide bond. This situation leads to the heat evolution in the syntheses of the complexes under study and apparently to the thermodynamic feasibility of the formation of products with higher hapticity of the heterodiene coordination. The reliability of the calculated bond energies is confirmed by the agreement of the calculated values with the published data on the bond strength metal–carbon monoxide in the hexacarbonyl complexes of the chromium subgroup metals [9].

Table 1. Dissociation energies of metal–ligand bonds in oxodiene complexes calculated by RHF/SBK procedure and measured experimentally

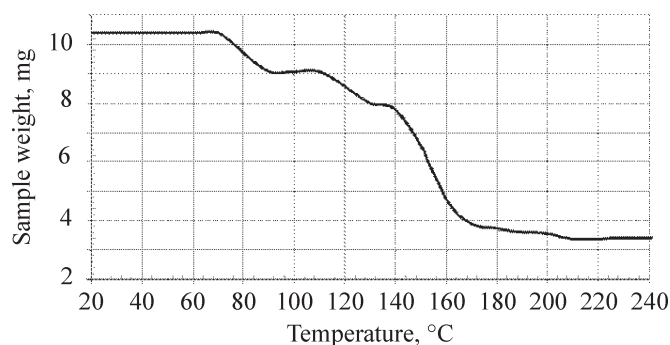| Bond	$D(\text{M–L})$, kJ mol^{-1}			
	Cr	Mo	W	Fe
(η^2-C=C)–M	296	200	168	304
(η^2-C=C, η^2-C=O)–M	495	355	350	507
(η^2-C=C, η^1-O)–M	350	300	326	376
(O≡C)–M	175	144	163	180
(O≡C)–M [9]	182 ± 12	157 ± 20	169 ± 12	190 ± 8

Fig. 1. Derivatogram of iron(0) η^4-(4-methyl-3-penten-2-one)-tricarbonyl (**IIa**) decomposition.

We performed a qualitative test of the validity of the energy values above by thermogravimetric analysis of compounds **IIa–IIc**. It was found that chromium(0) and molybdenum(0) η^4-(4-methyl-3-penten-2-one)tetra-carbonyl in the absence of oxygen were stable within a wide temperature range: According to the derivatograms the compounds were sublimed without decomposition in the range 100–150°C. The derivatograms of iron(0) η^4-(4-methyl-3-penten-2-one)tricarbonyl decomposition (Fig. 1) distinctly show the existence of three stages of the organometallic compound degradation: At 70–90°C (stage *1*) the first CO molecule is eliminated, the second carbonyl ligand is cleaved at 110–130°C (stage *2*), and at heating to 140–170°C (stage *3*) the elimination of mesityl oxide molecule is observed (see the scheme).

The further decomposition pattern becomes complicated due to the oxidation of the organometallic compound by the oxygen traces and defies interpretation; the final decomposition product consists of a mixture of iron(II) and iron(III) oxides.

The results of the thermogravimetric analysis are qualitatively well consistent with the bond energies in the organometallic compounds estimated by quantum-chemical calculations. The analysis demonstrated a fairly high heat resistance of the products of the η^4-coordination of oxodienes to the transition metals. The organometallic compounds of the chromium subgroup proved to be especially stable.
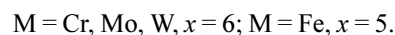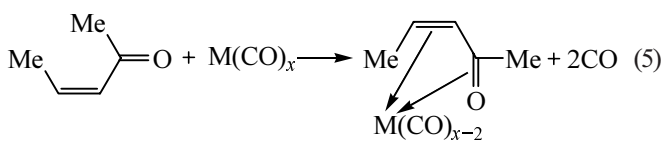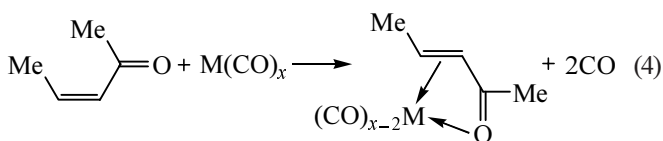
Table 2. Calculated enthalpy of formation for π-complexes of 3-penten-2-one of different hapticity

Reaction	ΔH of reaction, kJ mol^{-1}			
	Cr	Mo	W	Fe
(3)	−120	−56.7	−4.6	−123.7
(4)	+1.2	−12.4	+0.41	−16.1
(5)	−144.0	−67.4	−23.2	−146.5

Applying the calculated bond energies we evaluated by the additive scheme the enthalpy of formation for a series of heterodiene π-complexes with metal (Table 2); therewith we regarded the enthalpy factor as the principal, governing the thermodynamic preference of a certain complexing reaction.

$$\text{Me} \underset{\text{Me}}{\diagdown}\!\!=\!\!O + M(CO)_x \longrightarrow \text{complex} + CO \quad (3)$$
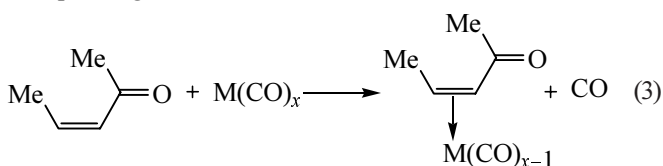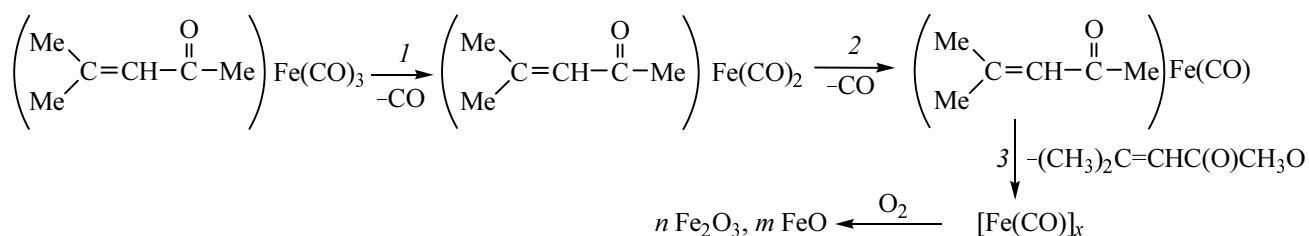
In the course of any among reactions (3–5) the number of degrees of freedom should increase due to the liberation of the gaseous carbon monoxide. Therefore the entropy factor should favor all reactions in question, although it cannot be directly estimated within the framework of the theoretical approach chosen.

$$\text{Me} \underset{\text{Me}}{\diagdown}\!\!=\!\!O + M(CO)_x \longrightarrow \text{complex} + 2CO \quad (4)$$

$$\text{Me} \underset{\text{Me}}{\diagdown}\!\!=\!\!O + M(CO)_x \longrightarrow \text{complex} + 2CO \quad (5)$$

$$M = Cr, Mo, W, x = 6; M = Fe, x = 5.$$

It is noteworthy that virtually all the reactions studied are exothermic, ant the enthalpy of formation of the

Scheme.

$$\left(\!\!\begin{array}{c}\text{Me}\\\text{Me}\end{array}\!\!\diagup\!\!C\!=\!CH\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!Me\right)\!Fe(CO)_3 \xrightarrow[-CO]{\textit{1}} \left(\!\!\begin{array}{c}\text{Me}\\\text{Me}\end{array}\!\!\diagup\!\!C\!=\!CH\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!Me\right)\!Fe(CO)_2 \xrightarrow[-CO]{\textit{2}} \left(\!\!\begin{array}{c}\text{Me}\\\text{Me}\end{array}\!\!\diagup\!\!C\!=\!CH\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!Me\right)\!Fe(CO)$$

$$\xrightarrow[\textit{3}]{} \; -(CH_3)_2C\!=\!CHC(O)CH_3O$$

$$n\,Fe_2O_3,\; m\,FeO \xleftarrow{\;O_2\;} [Fe(CO)]_x$$

η^4-complex (5) possesses more negative value than that of reaction (3) affording the η^2-coordinated product: Irrespective the nature of the chosen metal the products of the η^4-addition are more stable.

The least thermodynamically favorable are reactions of formation of products of oxodiene η^3-coordination through the π-system of the C=C bond and the unshared electron pair of oxygen; thus the formation of η^3-coordinated products is doubtful even as intermediates in reactions affording π-complexes. The data obtained support the previously published assumptions [3] that the complexes with η^4-coordination of oxodienes are the products of the thermodynamic control whereas the η^2-complexes are obtained under kinetic control of the reaction. This is in agreement with the experimental findings described above. The photochemical activation of the complexing reaction yielded predominantly η^2-(α-enone)M(CO)$_5$ complexes whereas the thermochemical activation afforded compounds η^4-(α-enone)M(CO)$_4$. Note also that according to the published data [10] the coordination of the metal center under study with a carbonyl group occurs as a rule at the expense of the π-system of the C=O bond and not through the electron pairs of oxygen.

The energy parameters not only permitted the prediction of the structure of the product formed by complexing but also allowed estimation whether the conjugation between the double bonds of the oxodiene involved in the coordination sphere of the transition metal would be retained. We estimated the enthalpy of hydration for the 3-penten-2-one in a free state and in the configuration that it took in the complexes under study. In keeping to the Hoffmann–Albright concept [11, 12] this energy parameter is evaluated as deformation energy of the ligand by the metal center. We found that the enthalpy of formation of the coordinated enone was higher than that of the free compound: the energy of deformation varied in the range 9–67 kJ mol^{-1} depending on the metal type and the way of the ligand coordination to the metal center. This result shows that the molecule loses the conjugation energy gain due to the disruption of the multiple bonds conjugation.

For the η^2-complexes of 3-penten-2-one the calculated destabilization energy is virtually linearly related to the electronegativity of the metal center (Fig. 2). Obviously the role of a π-dative component in formation of the organometallic compound is very significant for the less electronegative metals. Therewith the arising complex turns out to be more close to the metal-cyclopropane
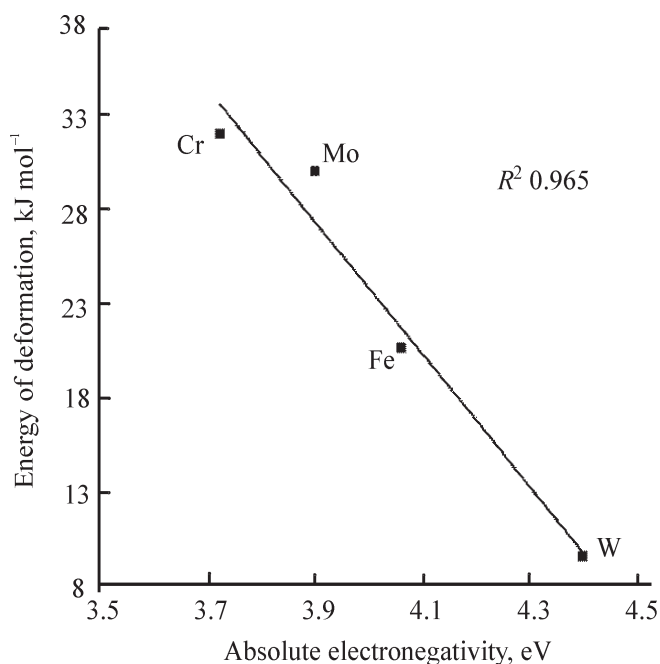

Fig. 2. Dependence of energy of deformation (kJ mol^{-1}) of coordinated 3-penten-2-one in complexes (η^2-enone)M(CO)$_x$ on the absolute negativity.
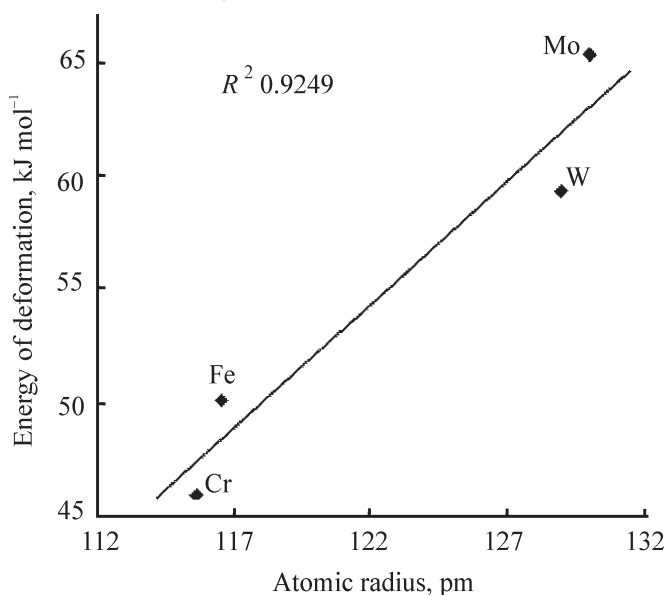

Fig. 3. Dependence of energy of deformation (kJ mol^{-1}) of coordinated 3-penten-2-one in complexes (η^2-enone)M(CO)$_x$ on the atomic radius.

boundary structure of Dewar–Chatt–Duncanson suggesting a high degree of the coordinated molecule deformation. In the complexes of highly electronegative metals the dominant part in the bonding belongs to the electron transfer from the ligand π-orbitals to the unoccupied d-orbitals of the metal; the contribution from the π-dative

component is virtually lacking, and the ligand deformation is thus less pronounced [13].

In the η^4-complexes the destabilization grows with the increasing radius of the metal center (Fig. 3).Here apparenyly the main role belongs to the steric factors. In coordination of a heterodiene with a metal of a large atomic radius the greater ligand deformation is required and consequently the conjugation is hampered and the stability is reduced. The calculation results suggest that the strongest change in the reactivity of the coordinated heterodiene should occur in the η^2-complexes of transition metals with a low electronegativity, and for η^4-complexes of transition metals from the further periods. The most pronounced change in the reactivity of the heterodiene among the complexes we studied should be expected in the molybdenum derivatives. Thus presumably both η^2- and η^4-coordinated molecules can be brought into similar reactions, but the results may be different from those obtained with the free molecules.

EXPERIMENTAL

Commercial reagents and solvents: pentane, hexane, benzene, toluene, acetone, acetonitrile, tetrahydrofuran, ethanol, and triethylamine were used in the experiments after purification by standard procedures [13]. The initial organometallic compounds: tungsten(0) hexacarbonyl, molybdenum(0) hexacarbonyl, and chromium(0) hexacarbonyl were purified by sublimation in a vacuum of the roughing pump (5×10^{-2} mm Hg) at 60–80°C. Mesityl oxide was prepared and purified according to published procedures [14]. The π-complexes obtained were purified by reprecipitation with hexane or pentane from benzene solutions or by recrystallization from hexane or pentane.

Ir spectra were recorded on spectrophotometer Specord M-80 from samples as mulls in the mineral oil or as films in the wave number range 400–4000 cm^1 and on Fourier spectrometer Bruker Vector 2-2 with a resolution of 1 cm^{-1} and 64 scans accumulation from samples pelletized with KBr in the wave number range 200–4000 cm^{-1}. ^{1}H NMR spectra were registered on spectrometers Varian UNITY 300 (299.94 MHz), Brucker 100 (100 MHz), and Brucker Gemini 200 (199.827 MHz) at 25°C in deuterobenzene-d_6, deuterochloroform-d_1, deutero-acetone-d_6, and deuteromethanol-d_4, chemical shifts were measured from the signals of residual protons in the deuterated solvents, concentration of the analyzed solutions was 0.7–1.5 wt%. ^{13}C NMR spectra were taken on Varian UNITY 300 instrument (75.4 MHz) at 25°C

in deuterobenzene-d_6, deuterochloroform-d_1, deutero-acetone-d_6, and deuteromethanol-d_4, chemical shifts were measured from the signals of deuterated solvents. ^{31}P NMR spectra were recorded on spectrometers Varian UNITY 300 (121.4 MHz) and RYa 2303 (8MHz), 85% water solution of H_3PO_4 was used as external standard.

Thermal stability of the complexes in the temperature range from 25 to 300°C was measured by thermo-gravimetry using a microthermoanalyzer MGDTD 17C (Setaram). Average sample weight of complex was 10 mg, heating rate 10 deg/min.

Calculations by the GAMESS 98 program [15] were carried out on PC Intel Pentium II-450/128 Mb and Intel Celeron 733/256 Mb. In the calcu;ations of the structural and energy parameters of the objects under investigation we chose the basis SBK where the electrons of the internal shells were described by a model potential. In this method basic 6-31 G was applied to hydrogen, for the valence shells of the heavy nuclei were used quadro- and tri-z basis sets corresponding to s-, p-, and d-shells respectively.

Cromium(0) η^2-(4-methyl-3-penten-2-one)penta-carbonyl (Ib). To a solution of 0.56 g of 4-methyl-3-penten-2-one in 7 ml of THF was added 1 g of chromium(0) hexacarbonyl. The mixture was subjected to UV irradiation from a high pressure mercury lamp for 8 h. The separated precipitate of colorless reaction product was filtered off and recrystallized from hexane; the colorless crystals were washed on the filter with two portions of cold hexane. Yield 35%, mp 172–176°C (decomp.). IR spectrum (mineral oil), ν_{max}, cm^{-1}: 1560 (coordinated bond C=C), 1723 (C=O); 1990, 1970, 1940, 1920, 1900 [Cr(CO)$_5$]. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm: 3.86 (C=C<u>H</u>). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm: 63 (C=<u>C</u>H), 85 (<u>C</u>=CH), 188 (<u>C</u>=O), 191, 200 [Cr(<u>CO</u>)$_5$].

Molybdenum(0) η^2-(4-methyl-3-penten-2-one)-pentacarbonyl (Ic) was prepared similarly to compound **Ib**. Light yellow crystals. Yield 45%, mp168–171°C (decomp.). IR spectrum (mineral oil), ν_{max}, cm^{-1}: 1555 (coordinated bond C=C), 1718 (C=O); 1995, 1980, 1960, 1930, 1910 [Mo(CO)$_5$]. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm: 3.74 (C=C<u>H</u>). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm: 68(C=<u>C</u>H), 80 (<u>C</u>=CH), 192 (C=O); 195, 207 [Mo(CO)$_5$].

Tungsten(0) η^2-(4-methyl-3-penten-2-one)-pentacarbonyl) (Id) was prepared similarly to compound **Ib**. Colorless crystals. Yield 32%, mp 175–177°C (decomp.). IR spectrum (mineral oil), ν_{max}, cm^{-1}: 1565 (coordinated bond C=C), 1720 (C=O); 1995, 1988, 1964,

1920, 1910 [W(CO)$_5$]. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm: 4.03 (C=C$\underline{H}$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm: 75 (C=$\underline{C}$H), 88 ($\underline{C}$=CH); 188, 212 [W(CO)$_5$], 194 (C=O).

Cromium(0) η^4-**(4-methyl-3-penten-2-one)tetra-carbonyl (IIb).** To a solution of 1 g of chromium(0) hexacarbonyl in 6 ml of acetonitrile was added 0.56 ml of 4-methyl-3-penten-2-one, and the mixture was heated at reflux in an argon atmosphere for 2 h. The crystalline light-yellow precipitate obtained was filtered off, recrystallized from hexane, and washed on the filter with cold hexane. Yield 68%, mp 173–177°C (decomp.). IR spectrum (mineral oil), ν$_{max}$, cm^{-1}: 1572 (coordinated bond C=C), 1688 (C=O coordinated to metal); 2005, 1980, 1950, 1910 [Cr(CO)$_4$]. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm: 3.52 (C=C$\underline{H}$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm: 74 (C=$\underline{C}$H), 92 ($\underline{C}$=CH), ($\underline{C}$=O), 192 [Cr(CO)$_4$].

Molybdenum(0) η^4-**(4-methyl-3-penten-2-one)-tetracarbonyl (IIc)** was prepared similarly to compound **IIb**. Colorless crystals. Yield 68%, mp 173–177°C (decomp.). IR spectrum (mineral oil), ν$_{max}$, cm^{-1}: 1580 (coordinated bond C=C), 1695 (C=O coordinated to metal); 2010, 1975, 1940, 1905 [MO(CO)$_4$]. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm: 3.45 (C=C$\underline{H}$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm: 75 ($\underline{C}$=CH), 93 (C=$\underline{C}$H), 140 ($\underline{C}$=O), 192 [MO(CO)$_4$].

Tungsten(0) bis[η^2-**(4-methyl-3-penten-2-one)]-tetracarbonyl (III)** was prepared in the same way as compound **IIb**. Colorless crystals. Yield 42%, mp 172°C (decomp.). IR spectrum (mineral oil), ν$_{max}$, cm^{-1}: 1550 (coordinated bond C=C), 1723 (C=O); 2010, 1970, 1920, 1880 [W(CO)$_4$]. ^{1}H NMR spectrum (C$_6$D$_6$), δ, ppm: 3.2, 3.9 (C=C$\underline{H}$). ^{13}C NMR spectrum (C$_6$D$_6$), δ, ppm: 79 (C=$\underline{C}$H), 101 ($\underline{C}$=CH), 194 (C=O), 188 [W(CO)$_4$].

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