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Synthesis and Structure of Cyclopropenone π-Complexes with Pentacarbonyliron(0) and Hexacarbonyltungsten(0). Hydrophosphorylation of Cyclopropenone in the Transition Metal Coordination Sphere

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Abstract—New π-complexes of pentacarbonyliron(0) and hexacarbonyltungsten(0) containing η^2-coordinated cyclopropenone molecules were synthesized. The geometric, electronic structure, and energy parameters of the coordinated cyclic oxo diene were determined by nonempirical quantum-chemical methods. According to the theoretical and experimental (IR and NMR) data, the conjugation between the double carbon–carbon and carbon–oxygen bonds is broken as a result of coordination. The coordinated cyclopropenone reacts with dialkyl hydrogen phosphites to give the corresponding α-hydroxyphosphonate via addition at the carbonyl group, whereas hydrophosphorylation of the free ligand occurs at the double carbon–carbon bond.

The reactivity of polyene ligands coordinated to a transition metal has long been analyzed in terms of an approach according to which the metal is considered to act like a protecting group. This approach implies that the reactivity of a heteropolyene ligand changes to an appreciable extent upon formation of a π-complex with a transition metal when the degree of π-bonding with the metal is low [1, 2]. Here, the central metal ion is considered to be a protecting group which prevents one of the multiple bonds in the polyene from participating in chemical transformations. However, it was recently shown [3–5] that both η^2- and η^4-coordinated α-enones are capable of reacting with C- and P-centered nucleophiles to give functionalization products at the carbonyl group rather than at the double carbon–carbon bond. We presumed that the main reason for the observed variation in the reactivity of coordinated α-enones is not blocking of an «undesirable» reaction center by the metal but breaking of conjugation between the neighboring multiple bonds, which occurs when the ligand molecule enters metal coordination sphere. This assumption was confirmed by theoretical analysis of the structure of π-complexes derived from acyclic 1-oxo-1,3-dienes in terms of the Hartree–Fock theory [6]. The results of quantum-chemical calculations of the geometric and electronic structure parameters of coordinated α-enones indicate considerable distortion of bond lengths and bond angles in the coordinated molecule, which makes the C=C–C=O fragments in η^2- and η^4-coordinated unsaturated molecules essentially nonplanar.

With a view to obtain further support for the hypothesis implying rupture of conjugation in α-oxo dienes coordinated to a transition metal atom, as subjects for study we selected cyclic conjugated α-enones. Obviously, the probability for coordination with a metal through both conjugated multiple bonds is quite low. Therefore, we should be able to obtain organometallic compounds with a η^2-coordination mode (at one multiple bond) and hence to examine variation of spectral parameters of the other multiple bond which is not involved in the direct interaction with the metal.

For this puprpose, the best model seemed to be the simplest cyclic α-enone, cyclopropenone. Previously, Butenschon [7] studied reactions of cyclopropenone derivatives with electron-deficient cationic cobalt(II) and nickel(II) complexes, which followed two concurrent pathways. One of these led to formation of π-complexes containing η^2-cyclopropenone ligand coordinated at the C=C bond, and the other gave rise to metallacyclobutane structures via cleavage of the double carbon–carbon bond. We made an attempt to estimate the most probable ways for the reactions of cyclopropenone with pentacarbonyl-

Table 1. Calculated (RHF/SBK) enthalpies (kJ/mol) of model reactions of cyclopropenone with pentacarbonyliron(0) and hexacarbonyltungsten(0)

Reaction no.	$Fe(CO)_5$	$W(CO)_6$
1	2.3	8.4
2	13.5	18.4
3	–15.1	–7.3
4	73.8	85.6
5	8.6	23.4

iron(0) and hexacarbonyltungsten (0) by calculating the enthalpies of complex formation corresponding to reactions (1)–(5). The structure and energy parameters were calculated in terms of the Hartree–Fock theory with the use of the ECP basis set where inner-shell electrons are described by the Stevens–Basch–Krauss (SBK) model potential. Hydrogen atoms were treated using the 6-31G basis set, and valence shells of heavy atoms were simulated with the aid of quadruple and triple zeta basis sets for the *s*, *p* and *d* shells, respectively. *d*-Polarizing function was also used for heavy atoms. Full geometry optimization of the complexes was performed with that basis set [8].

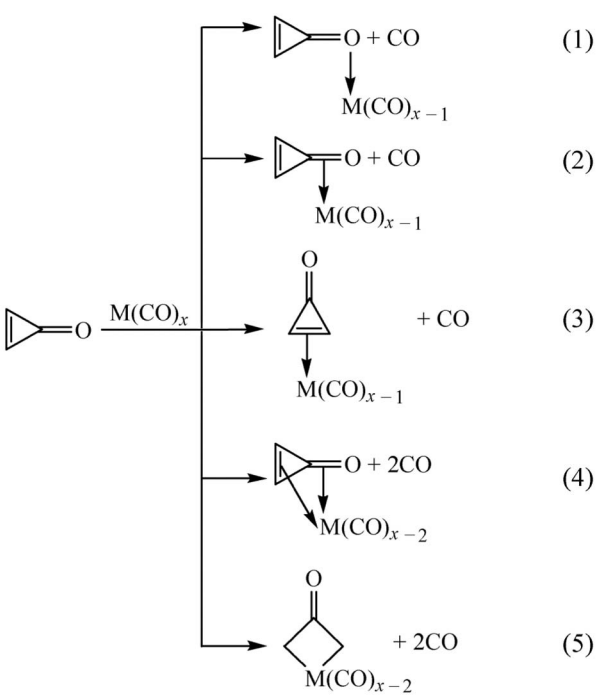


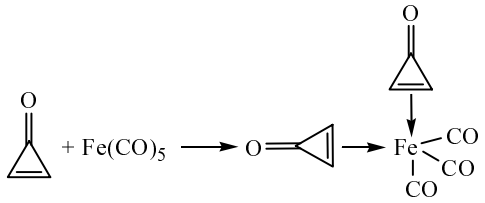
Table 1 contains the calculated enthalpies of model reactions (1)–(5). According to the enthalpy factor, the most favorable is formation of η^2-(cyclopropenone)-tetracarbonyliron(0) and η^2-(cyclopropenone)pentacarbonyltungsten(0) by reaction (3). A considerable endothermic character of reaction (4) may be due to the fact that bidentate coordination of cyclic α-enone should essentially change geometric structure of the oxo diene ligand, which destabilizes not only coordinated cyclopropenone molecule but also the resulting complex. The formation of a metallacyclobutane structure is thermodynamically unfavorable: reaction (5) is characterized by a large positive enthalpy due to very high energy of dissociation of the strong C=C and M–CO bonds, which could not be compensated by formation of two less strong metal–carbon σ-bonds. We can conclude that, though reactions (4) and (5) are more favorable than (1)–(3) from the viewpoint of entropy (they are accompanied by liberation of two CO molecules), the probability for these reactions to occur is very low.

The absolute preference for pathway (3) may be interpreted in terms of orbital control of complex formation between olefins and zero-valence metal carbonyl compounds: the process is characterized by a considerable contribution of π-dative interaction between the highest occupied molecular orbital (HOMO) of the metal and the lowest unoccupied molecular orbital (LUMO) of the olefin ligand [9]. According to the results of our calculations, the LUMO energy of cyclopropenone is negative (–0.11 eV), and its orbital density is localized on the double carbon–carbon bond. This may strongly favor formation of π-complexes by cyclopropenone via η^2-coordination at the C=C bond.

In order to elucidate structural variations in going from free cyclopentenone molecule to η^2-(cyclopropenone)-tetracarbonyliron(0) and η^2-(cyclopropenone)pentacarbonyltungsten (0), as well as to related pentacarbonyl metal(0) complexes, we calculated structural parameters of the corresponding π-complexes in terms of the Hartree–Fock theory using the effective shell potential method (Table 2). It is seen that these variations are significant: as a result of complex formation, the C=C bond becomes appreciably longer, the C=O bond shortens, and the ligand molecule becomes essentially nonplanar. Taking into account considerable reduction of the bond orders, the above data indicate breaking of conjugation between the C=C and C=O bonds in the cyclic oxo diene.

The results of our theoretical study are in a good agreement with the experimental data for the reactions of cycloprope-none with pentacarbonyliron(0) and hexacarbonyltung-sten(0). Pentacarbonyliron(0) reacts with cyclopropenone in acetonitrile at room temperature; mixing of the reactants is accompanied by vigorous gas

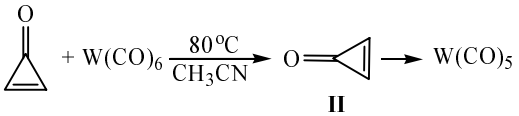
evolution, and the solution changes from orange [$Fe(CO)_5$] to dark violet. On the basis of the IR and ^1H and ^{13}C NMR spectra, the product was assigned the structure of bis[η^2-(cyclo-propenone)]tricarbonyliron(0) (**I**).



I

In the IR spectrum of complex **I** we observed well-resolved absorption bands at 2100, 2000, and 1950 cm^{-1}, which indicate the presence in the coordination sphere of iron(0) of three carbon(II) oxide molecules bound to the metal through the carbon atom. The C=C stretching vibration frequency decreases from 1650 cm^{-1} for the free enone to 1535 cm^{-1} in the complex. Such reduction of vibration frequency is characteristic of π-coordination of an olefinic double bond to a metal [10]. Rupture of conjugation between the double bonds leads to increase of the carbonyl vibration frequency from 1710 cm^{-1} in free cyclopropenone to 1730 cm^{-1} in complex **I**. Participation of the double C=C bond in π-coordination with the metal also follows from the upfield shift of the ^1H NMR signals of complex **I** to δ 5.3 ppm relative to 7.44 ppm in the spectrum of noncoordinated cyclopropenone [10]. An analogous upfield shift of signals from olefinic carbon atoms is also observed in the ^{13}C NMR spectra (δ_C 155 and 122 ppm for free cyclopentenone and complex **I**, respectively). The chemical shift of the carbonyl carbon atom also changes from δ_C 190 ppm (cyclo-pentenone) to 200 ppm (complex **I**).

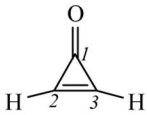
Unlike pentacarbonyliron(0), hexacarbonyltungsten(0) did not react with cyclopropenone spontaneously. By heating the reactants in acetonitrile we obtained compound **II** which was identified as η^2-(cyclopropenone)pentacarbonyltungsten(0).

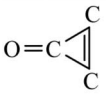
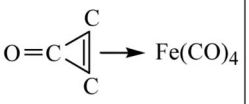
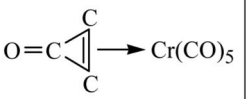
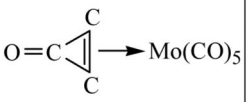
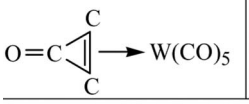


II

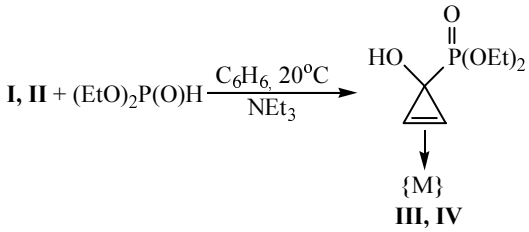
The IR spectrum of complex **II** contains five absorption bands belonging to five coordinated carbon(II) oxide molecules at 1820, 1850, 1900, 2000, and 2110 cm^{-1}. As with compound **I**, the C=C stretching vibration frequency of complex **II** is lower than that of the free ligand and is 1550 cm^{-1}. Also, the carbonyl stretching vibration frequency increases to 1720 cm^{-1}. These findings, as well as the upfield shift of the olefinic proton signal in the ^1H NMR spectrum (δ 5.8 ppm), may be explained best in terms of weakening of conjugation between the double carbon–carbon and carbon–oxygen bonds in cyclopropenone as a result of complex formation.

Table 2. Interatomic distances (Å) and C=C–C=O torsion angles (deg) in the free and coordinated cyclopropenone molecule



Molecule	$l(C^2=C^3)$	$l(C^1–C^2)$	$l(C^1=O)$	∠(C=C–C=O)
	1.360	1.426	1.280	0
	1.611	1.500	1.230	111.8
	1.604	1.498	1.230	116.1
	1.598	1.495	1.230	109.3
	1.617	1.502	1.230	103.1

We also examined hydrophosphorylation of metal complexes **I** and **II** with diethyl hydrogen phosphite in the presence of triethylamine. ^{31}P NMR and IR study of the reaction mixtures led us to conclude that the addition of phosphorus-containing reagent occurred at the carbonyl group of coordinated cyclopropenone to afford α-hydroxy phosphonates **III** and **IV** in which the three-membered ring is retained.

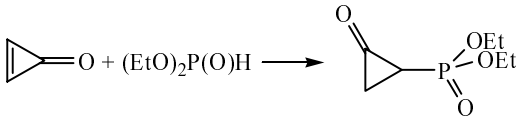


III, IV

III, M = Fe; **IV**, M = W; {M} is the corresponding carbonylmetal moiety.

The phosphorus atoms in compounds **III** and **IV** give rise to signals at δ_P 15.3 and 16.2 ppm, respectively, in the ^{31}P NMR spectra. These signals are located in a

weaker field relative to the corresponding signal of initial diethyl hydrogen phosphite. By analogy with published data [11], products **III** and **IV** were assigned the structure of α-hydroxy phosphonates formed via addition at the carbonyl group of cyclopropenone (inner-sphere Abramov reaction). Under analogous conditions, noncoordinated cyclopropenone reacted with diethyl hydrogen phosphate to give phosphonate **V** via addition at the double carbon–carbon bond. In the ^{31}P NMR spectrum we observed a singlet at δ_P 27.1 ppm.



V

Our attempts to isolate compounds **III**–**V** from the reaction mixtures by complete removal of the solvent (by distillation) resulted in their decomposition and formation of poorly soluble phosphorus-containing tars. In order to get more information on the structure of adducts **III**–**V**, the solvent was partially removed from the mixture by evacuation, and the resulting concentrated solutions of the products were examined by IR spectroscopy. The IR spectra lacked absorption bands typical of stretching vibrations of the cyclopropenone carbonyl group in compounds **I** and **II** (1730 and 1720 cm^{-1}, respectively). A strong broad band at 3550 cm^{-1} was assigned to stretching vibrations of the hydroxy group. Absorption bands corresponding to stretching vibrations of the C=C bonds coordinated to the metal were observed at 1535 (**III**) and 1550 cm^{-1} (**IV**). In the IR spectrum of addition product **V** we observed no absorption in the regions 3000–3500 and 1550–1600 cm^{-1}, but a band at 1720 cm^{-1} was present, indicating that the phosphorylation occurred at the C=C bond.

A poorly resolved system consisting of at least three bands was observed in the IR region corresponding to stretching vibrations of metal-coordinated carbon(II) oxide. Such a pattern is typical of some di- and polynuclear carbonyl complexes [12]. Therefore, we presumed that one or more carbon(II) oxide molecules in complexes **III** and **IV** are bridging groups and that these complexes contain more than one metal atoms. However, relatively low stability of these compounds did not allow us to obtain more rigorous proofs for their structure.

EXPERIMENTAL

Quantum-chemical calculations were performed with the use of Gamess 98 software [12]. All experiments were carried out in standard Schlenk glassware in a stream of dry argon. The IR spectra were recorded on a Specord M-80 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were obtained on Varian Unity-300 (299.94 MHz), Bruker 100 (100 MHz), and Varian Gemini-200 (199.827 MHz) instruments at 25°C using C_6D_6, $CDCl_3$, and CD_3OD as solvents (c = 0.7–1.5 wt %); the chemical shifts were measured relative to signals from residual protons in the deuterated solvents. The ^{13}C NMR spectra were recorded on a Varian Unity-300 spectrometer operating at 75.4 MHz; the chemical shifts were measured relative to $CDCl_3$.

Bis[η^2-(cyclopropenone)]tricarbonyliron(0) (I). Pentacarbonyliron(0), 0.5 ml, was added to 2 ml of cyclopropenone, a vigorous gas evolution being observed. The mixture was kept for 40 min at room temperature, and the dark violet amorphous material was separated. Yield 37%, mp 67°C (decomp.). IR spectrum, ν, cm^{-1}: 1535 (coord. C=C); 1730 (noncoord. C=O); 2100, 2000, 1950 [C=O in $Fe(CO)_3$]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.45–535 m (CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 155 m (CH=CH); 200 s (C=O, cyclopropenone); 185 s, 190 s, 195 s [$Fe(CO)_3$].

η^2-(Cyclopropenone)pentacarbonyltungsten(0) (II). A solution of 0.5 g of hexacarbonyltungsten(0) in 20 ml of acetonitrile was heated for 40 min under reflux in a stream of argon until (acetonitrile)pentacarbonyltungsten(0) was formed [5], 2 g of cyclopropenone was added, and the mixture was heated for 14 h under reflux. The solvent was distilled off under reduced pressure (without heating) to 1/4–1/5 of the initial volume. The pale green crystals were filtered off under argon and recrystallized from pentane. Yield 35%, mp 123–125°C (decomp.). IR spectrum, ν, cm^{-1}: 1550 (coord. C=C); 1720 (C=O in cyclopropenone); 1820, 1850, 1900, 2000, 2110 [C=O in $W(CO)_5$]. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 5.6–5.8 m (CH=CH).

Reaction of bis[η^2-(cyclopropenone)]tricarbonyliron(0) (I) with diethyl hydrogen phosphite. To a solution of 0.20 g of complex **I** in 5 ml of dry benzene we added 0.2 ml of diethyl hydrogen phosphate and 1–2 drops of triethylamine, and the mixture was kept for 48 h at room temperature under argon. The mixture was concentrated under reduced pressure to obtain a viscous amorphous material. According to the ^{31}P NMR data, the conversion of diethyl hydrogen phosphite was 75%. IR spectrum (film), ν, cm^{-1}: 1535 (coord. C=C); 3500 br (OH); 2100, 2000, 1970 [C=O in $Fe(CO)_3$]. ^{31}P NMR spectrum of the reaction mixture: δ_P 15.3 ppm. The reaction of complex **II** with diethyl hydrogen phosphite was performed in a similar way. ^{31}P NMR spectrum of the reaction mixture: δ_P 16.3 ppm.

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