Russian Journal of General Chemistry, Vol. 71, No. 2, 2001, pp. 191–195. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 2, 2001, pp. 215–220.
Original Russian Text Copyright © 2001 by Kuramshin, Karpenko, Cherkasov.

Hydrophosphorylation of 1,3-Diphenyl-2-propen-1-one and 4-Phenyl-3-buten-2-one in the Coordinational Sphere of Carbonyl Complexes of Group VIB Metals

A. I. Kuramshin, E. A. Karpenko, and R. A. Cherkasov

Kazan State University, Kazan, Tatarstan, Russia

Received November 22, 1999

Abstract—Synthetic procedures for preparing η^2 and η^4 complexes of chalcone and benzalacetone with hexacarbonyl mononuclear complexes of Group VIB metals were developed and conditions for selective η^2- and η^4-coordination of the heterodiene ligand were established. Hydrophosphorylation of the obtained complexes proceeds in the coordination sphere of the metal by the Abramov reaction scheme and yields the corresponding η^2-coordinated α-hydroxyphosphonates. As follows from quantum-chemical calculations, π-coordination with metals makes the heterodienes no longer planar, which explains their regioselective phosphorylation by the more electrophilic carbonyl group.

Inspite of the high stability of π-complexes of Group VIB metals with alkenes and arenes, as well as the fair availability of mononuclear hexacarbonyl complexes of these metals, usually applied for preparing π complexes, there is only scarce information in the literature concerning coordination of molecules containing heterodiene systems like –C=C–C=O and changes in the reactivity of the coordinated molecules toward organophosphorus compounds. In detail, it has been shown [1, 2] that enones η^2-coordinated with iron carbonyls are selectively phosphorylated by the carbonyl group of the α-enone, allowing synthesis of α-hydroxyphosphonates under conditions of kinetic control. Group VIB metals have never been involved in such processes.

Previously we reported the synthesis of adducts of 1,3-diphenyl-2-propen-1-one (chalcone) and 4-phenyl-3-buten-2-one (benzalacetone) with hexacarbonyl complexes of chromium subgroup metals and the reaction of the resulting organometallic compounds with dialkyl hydrogen phosphites by the Abramov scheme [3]. Here we describe in more detail the results of investigations on formation and chemical transformation of complexes of the above-mentioned unsaturated systems with chromium, molybdenum, and tungsten carbonyls.

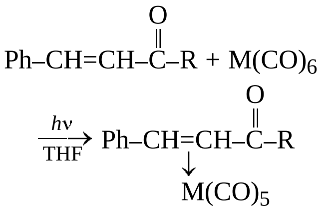
Previously unknown adducts of 1,3-diphenyl-2-propen-1-one (chalcone) and 4-phenyl-3-buten-2-one (benzalacetone) with the homoligand Group VIB metal carbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were synthesized by our original procedure of two-stage photochemical substitution of carbonyl ligands with π-functional groups of heterodienes.

In the first stage, a THF solution of hexacarbonylmetal(0) was subjected to short (30–40 min) UV irradiation in the absence of unsaturated ketone with the purpose of generation of coordinately unsaturated metal intermediates $M(CO)_5$ and labile pentacarbonyl complexes $M(CO)_5(THF)$. In the second stage, they easily reacted with α-enones to form π complexes of α,β-unsaturated ketones. Note that a more continuous (1 h) irradiation of the hexacarbonylmetal solution results in substitution of a greater amount of carbonyl ligands by THF to give mixed-ligand complexes of the composition $(\alpha\text{-enone})M(CO)_x(THF)_y$. This procedure allowed to shorten considerably the time of synthesis of π complexes **I**–**IV**: The total irradiation time in both stages of the reactions in THF solutions was no more than 3 h against 40 h in hexane solutions [2, 4].

Two types of π complexes were obtained: η^2-coordinated (**Ia**–**Ic** and **IIa**–**IIc**) and η^4-coordinated (**IIIa**–**IIIc** and **IVa**–**IVc**).

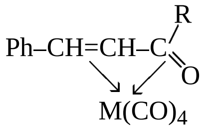
Coordination induces upfield shifts of signals of protons bound with sp^2-carbon atoms (5.3 and 6.4 ppm).

In the IR spectra of compounds **I**–**IV**, the C=C stretching vibration frequencies decrease from 1637 to 1530–1520 cm^{-1} in chalcone and from 1645 to 1540–1530 cm^{-1} in benzalacetone. The C=O group of coordinated heterodienes gives two bands: a high-frequency band at 1660 cm^{-1} for η^2 products and a



$$\mathrm{Ph{-}CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + M(CO)_6 \xrightarrow[THF]{h\nu} Ph{-}CH{=}\underset{\underset{\displaystyle M(CO)_5}{\downarrow}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R}$$

Ia–Ic, IIa–IIc



IIIa–IIIc, IVa–IVc

R = Ph (**I, III**); CH_3 (**II, IV**); M = W (**a**), Cr (**b**), Mo (**c**).

low-frequency band at 1620 cm^{-} for η^4 complexes, belonging respectively to the free carbonyl group of chalkone and to the carbonyl group coordinated with tungsten. As the reaction time increases, the band at 1620 cm^{-1} inreases and the band at 1660 cm^{-1} decreases until it disappears completely. Hence, our procedure allows controlling the $\eta^2:\eta^4$ ratio by varying the time of irradiation of the reaction mixture.

Analysis of the intensity ratio of the above two bands led us to conclude that, at the same conditions (reaction time and reactant concentrations), the fraction of the η^4-product with benzalacetone is higher than with chalcone.

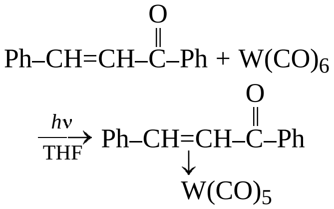
The intensity ratio of the bands at 1620 and 1660 cm^{-1} in the spectra of the products of coordination of chalcone with hexacarbonylmetals decreases in the order Mo > Cr > W. In the spectrum of the product of the reaction of chalcone with hexacarbonylmolybdenum(0), a 1 : 1 ratio is observed, while in the spectrum of the product of the reaction of hexacarbonyltungsten(0) with chalcone, the band at 1620 cm^{-1} is practically absent.

These results suggest that the initially formed η^2-(enone)pentacarbonylmetal(0) undergo a haptotropic rearrangement to η^4-(enone)tetracarbonylmetal(0) during the synthesis. The enhanced ability of coordinated α-enone to rearrangement in going from chalcone to benzalacetone can be explained by increase in the π-electron density on the carbonyl group in going from the methyl to phenyl derivative. Analogous dependence for oxygen-containing heterodiene systems was observed previously for iron enone complexes [5]. The referees established the following order of ability of the heterodienes to η-coordination: –C(O)–Ar < –C(O)–H < –C(O)–Alk. Since the first stage of haptotropic rearrangement is a dissociative process [6], the fact that the facility of the present haptotropic rearrangement depends on the nature of the complex-forming metal is explained by the strength of the metal–C=C and metal–C=O bonds. Both these bonds strengthen in the series Mo–Cr–W [7], and, therefore, the ability of the corresponding complex to the $\eta^2 \to \eta^4$ transformation decreases.

In terms of the aforesaid, the η^2 complexes can be considered as kinetically controlled products and the η^4-complexes, as thermodynamically controlled products of the π-complex formation reaction.

The reaction of excess α-enone with hexacarbonylmetal(0) under short photochemical activation must give η^2-(α-enone)pentacarbonylmetal(0) (excess α-enone inhibits haptotropic rearrangement [6]). The reaction of α-enone with hexacarbonylmetal(0) at a stoichiometric complex:ligand ratio and under continuous irradiation of the reaction mixture (or under thermochemical activation [8]) must result in formation of η^4-(α-enone)tetracarbonylmetal(0).

We performed the target synthesis of pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) (**Ia**) and tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten(0) (**III**) under various experimental conditions and isolated each of the compounds pure. Pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) (**I**) was obtained by a photochemically initiated reaction between hexacarbonyltungsten(0) and a considerable excess of 1,3-diphenyl-2-propen-1-one in THF.

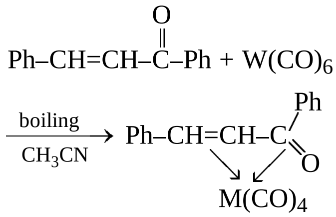


$$\mathrm{Ph{-}CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph + W(CO)_6 \xrightarrow[THF]{h\nu} Ph{-}CH{=}\underset{\underset{\displaystyle W(CO)_5}{\downarrow}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph}$$

Ia

The IR spectrum of **Ia** displays bands at 1530 cm^{-1} due to the C=C bond of chalcone, coordinated with tungsten, and at 1660 cm^{-1} due to the carbonyl group of 1,3-diphenyl-2-propen-1-one, not involved in coordination. In the range of stretching vibrations of carbon monoxide coordinated with transition metal (2000–1800 cm^{-1}), there are five well-resolved absorption bands at 1990, 1970, 1940, 1920, and 1900. The upfield shift of signals of double-bond protons (5.42 and 6.39 ppm) also confirms the fact of coordination of the C=C bond of 1,3-diphenyl-2-propen-1-one with tungsten.

Tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten(0) (**IIIa**) was obtained by a thermochemically initiated reaction of hexacarbonyltungsten(0) with 1,3-diphenyl-2-propen-1-one in acetonitrile at a stoichiometric reactant ratio.

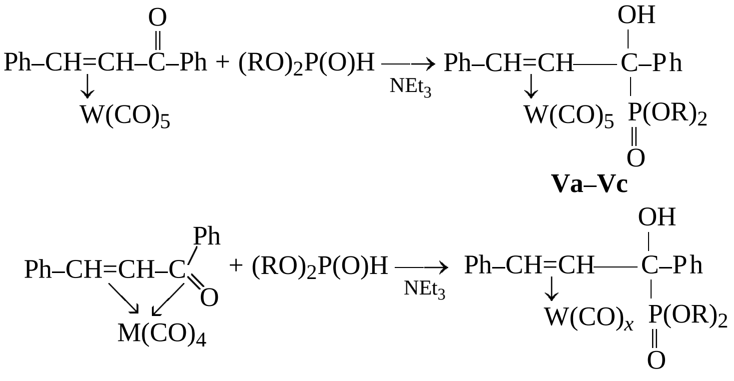


IIIa

The IR spectrum of complex **IIIa** shows bands at 1530 cm^{-1} due to the C=C bond of chalcone, coordinated with tungsten, and 1620 cm^{-1} due to the carbonyl group of 1,3-diphenyl-2-propen-1-one, involved in coordination. In the range of stretching vibrations of carbon monoxide coordinated with transition metal, there are four well-resolved absorption bands at 1970, 1940, 1920, and 1900 cm^{-1}. The upfield shift of signals of double-bond protons (5.37 and 6.41 ppm) is associated with the coordination of the C=C bond of 1,3-diphenyl-2-propen-1-one with tungsten. The IR and ^{1}H NMR spectra show that no acetonitrile ligand is present in the coordination sphere of **IIIa**. The individuality of complexes **Ia** and **IIIa** is confirmed by TLC.

Pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) and tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten(0) were reacted with dialkyl hydrogen phosphites. The reactions were carried out either in a dialkyl hydrogen phosphite solution (an almost 30-fold excess of hydrophosphoryl compound with respect to π-complex) or in benzene at a stoichiometric dialkyl hydrogen phosphite : π complex ratio in the presence of a base catalyst.

Some time after the reaction onset, in the ^{31}P NMR spectra of the reaction mixtures we observed singlets downfield from the signals of dialkyl hydrogen phosphites (δ_P 20.93, 16.72, 13.61, 21, and 17 ppm for **Va, Vb, Vc, VIa**, and **VIc**, respectively). The new signals were assigned to hydroxyphosphonates [1, 2, 8].



R = CH_3 (**a**), C_2H_5 (**b**), *i*-C_3H_7 (**c**).

The intensity ratio of the phosphorus signals of phosphonates **V, VI** and dialkyl hydrogen phosphites, established with time in benzene solutions, varies from 7 : 1 for $(i\text{-}C_3H_7O)_2P(O)H$ to 10 : 1 for $(CH_3O)_2 \cdot P(O)H$, which implies a 80–90% yield of phosphonate. The IR spectrum of the mixture of the reaction product (phosphonate) and dialkyl hydrogen phosphite no longer shows signals of the carbonyl group of chalcone (1660 cm^{-1} for **Ia** and 1620 cm^{-1} for **IIIa**). At the same time, a broad band at 3550 cm^{-1} appears, assignable to OH stretching vibrations. The IR spectrum preserves bands due to stretching vibrations of the C=C bonds coordinated with tungsten (1525 cm^{-1} for **Ia** and 1510 cm^{-1} for **IIIa**).

These data permit to state that π complexes **Ia** and **IIIa** enter with dialkyl hydrogen phosphites an Abramov reaction; therewith, and the resulting α-hydroxyphosphonates do not leave the coordination sphere of the metal in structures **Va**–**Vc** and **VIa, VIc**.

The IR spectrum of compound **Va** still contain the five well-resolved absorption bands at 2000–1850 cm^{-1}, implying that the tungsten in **Va** have preserved its carbonyl ligands and thus the π complex in question is mononuclear. For compound **VIa**, a poorly resolved band consisting of at least of three bands is observed in the range of stretching vibrations of carbon monoxide coordinated with metal. This picture is characteristic of some bi- and polynuclear carbonyl complexes [9]. It is evident that in compound **VIa** one or several molecules of carbon monoxide begin to play the role of bridges. Due to that the complex can increase its nuclearity, but up to now we failed to obtain a more straightforward evidence for rigorous structural assignment of compound **VIa**.

It is known that the free α-enones, benzalacetone and chalcone, react with hydrophosphoryl compounds under conditions of the Pudovik reaction with thermodynamic control strictly by the carbon–carbon bond to form γ-ketophosphonates.

The reason for change in the regiochemistry of addition of dialkyl hydrogen phosphites to α-enones coordinated with metal in different ways may be associated with change in the geometry of the coordinated unsaturated ketone, capable of breaking conjugation between neighboring fragments of the coordinated molecule [10].

We performed ZINDO/1 quantum-chemical calculations of the steric structure of pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) and tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten(0) to show that the –C=C–C=O fragment of chalcone in the coordination sphere both of the η^2 and η^4 complex is no longer planar. The angle between the C=C and C=O bond planes is 27° for pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) and 22° for tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten(0). It shows that strong decrease in conjugation between This result points to a strongly weakened conjugation between the C=C and C=O bonds in the coordinated chalcone. i.e. one deals here with isolated multiple bonds. As a result, the C=C bond in chalcone no longer exerts the electron-acceptor effect of the C=O group; as a result, it becomes less electrophilic and thus inert to nucleophilic attack of hydrophosphoryl compound, characteristic of noncoordinated chalcone. This factor may be the reason for the selective hydrophosphorylation of heterodienes by the carbonyl group which is more electrophilic than the coordinated C=C bond.

Together with the above-presented methods for preparing α-hydroxyphosphonates [1, 2, 8], their synthesis in the coordination sphere of Croup VIB metals, developed by us, extends the synthetic potential of the Pudovik and Abramov reactions.

EXPERIMENTAL

The IR spectra were recorded on a Specord-M80 spectrometer in Vaseline oil. The ^{1}H NMR spectra were recorded on Varian UNITY 300 (298.4 MHz, ^{1}H), Brucker 100 (100 MHz, ^{1}H), and Brucker Gemini 200 (199.827 MHz, ^{1}H) spectrometers at 25°C. The chemical shifts were measured against residual proton signals of deuterated solvents (benzene-d_6, chloroform-d_1, methanol-d_4). The solution concentrations were 0.7–1.5%. The ^{31}P NMR spectra were recorded on Varian UNITY 300 (121.4 MHz, ^{31}P) and RYa 2303 (8 MHz, ^{31}P) spectrometers against external 85% H_3PO_4.

Thin-layer chromatography was carried out on Silufol plates, eluent isopropanol–benzene (3:1), development in iodine vapor.

Pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0). Hexacarbonyltungsten, 0.400 g, in 20 ml of absolute degassed THF was irradiated in a quartz or glass flask with the UV light of a high-pressure mercury lamp for 40 min (for 2 h in a glass vessel) under argon and with continuous stirring. Then a solution of 0.516 g of 1,3-diphenyl-2-propen-1-one in 2.0 ml of THF was added, and the irradiation and stirring were continued for an additional 2.5 h. The reaction mixture was treated with hexane, and the precipitate that formed was filtered off on a Schott filter to obtain a grayish-green finely crystalline powder, yield 22%, decomp. point 148–152°C. IR spectrum, ν, cm^{-1}: 1530 (coordinated C=C); 1660 (noncoordinated C=O from 1,3-diphenyl-2-propen-1-one); 1990, 1970, 1940, 1920, 1900 (carbonyl ligands bound with tungsten). ^{1}H NMR spectrum: 5.3 and 6.4 ppm (CH=CH coordinated with tungsten).

Pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]-chromium(0), pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)molybdenum(0), pentacarbonyl[η^2-(4-phenyl-3-buten-2-one)]tungsten(0), pentacarbonyl[η^2-(4-phenyl-3-buten-2-one)]chromium(0), and pentacarbonyl[η^2-(4-phenyl-3-buten-2-one)]molybdenum(0) were obtained analogously. The products all contained admixture of the η^4-coordination products of α-enone to metal.

Tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)tungsten(0). A solution of 0.5 g of hexacarbonyltungsten(0) in 20 ml of acetonitrile was refluxed in a flask, equipped with a reflux condenser, a glycerole seal and a gas-inlet tube, for 40 min under argon. 1,3-Diphenyl-2-propen-1-one, 0.26 g, was then added to the reaction mixture, and the resulting solution was refluxed for an additional 14 h, and concentrated 4–5 times in a water-jet pump vacuum without heating. Pale green crystals precipitated and were filtered off in an argon box to isolate a light green finely crystalline powder, yield 45%, decomp. point 171–175°C. IR spectrum, ν, cm^{-1}: 1520 (coordinated C=C); 1620

(C=O of 1,3-diphenyl-2-propen-1-one coordinated with metal); 1970, 1940, 1920, 1900 (carbonyl ligands bound with tungsten). Tetracarbonyl[η^4-(4-phenyl-3-buten-2-one)]tungsten(0) was obtained analogously.

Reaction of pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) with diethyl hydrogen phosphite. Diethyl hydrogen phosphite, 0.2 ml, and 1–2 drops of triethylamine were added to a solution of 0.20 g of pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) in 5 ml of absolute benzene. The resulting mixture was kept for 48 h at room temperature under argon. The benzene was removed in a water-jet-pump vacuum until a viscous amorphous material formed. The yield of α-hydroxyphosphonate was 75% (from the ^{31}P NMR spectrum of the reaction mixture). IR spectrum, ν, cm^{-1}: 1520 (coordinated C=C); 3500 material remained (OH); 1900–2000 (complex system of bands from carbonyl ligands bound with tungsten). ^{31}P NMR spectrum of the reaction mixture: δ_P 16.7 ppm.

The reactions of pentacarbonyl[η^2-(1,3-diphenyl-2-propen-1-one)]tungsten(0) with dimethyl and diisopropyl hydrogen phosphites were performed analogously.

Reaction of tetracarbonyl[η^4-(1,3-diphenyl-2-propen-2-one)]tungsten(0) with diethyl hydrogen phosphite. To a solution of 0.20 g of tetracarbonyl-[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten in 5 ml of absolute benzene, 0.2 ml of diethyl hydrogen phosphite and 2-3 drops of triethylamine were added. The resulting mixture was kept for 48°C at room temperature under argon. The benzene was removed in a water-jet-pump vacuum until a viscous amorphous mass. The yield of α-hydroxyphosphonate was 62% (from the ^{31}P NMR spectrum of the reaction mixture). IR spectrum, ν, cm^{-1}: 1510 (coordinated C=C); 3450 br (OH); 1900–2000 (complex system of bands from carbonyl ligands bound with tungsten). ^{31}P NMR spectrum of the reaction mixture: δ_P 17 ppm.

The reactions of tetracarbonyl[η^4-(1,3-diphenyl-2-propen-1-one)]tungsten(0) with dimethyl and diisopropyl hydrogen phosphites were carried out analogously.

REFERENCES

1. Galkin, V.I., Galkina, I.V., Al Kurdy, Kh., Denisov, B.V., and Cherkasov, R.A., *Metaloorg. Khim.*, 1990, vol. 3, no. 6, pp. 1429–1431.
2. Galkina, I.V., Saakyan, G.M., Galkin, V.I., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 7, pp. 2221–2223.
3. Kuramshin, A.I., Karpenko, E.A., and Cherkasov, R.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 7, pp. 1221–1222.
4. Spirina, I.V. and Maslennikova, V.P., *Usp. Khim.*, 1994, vol. 63, no. 1, pp. 43–55.
5. Howell, J.A.S. and Burkinshaw, P.M., *J. Organomet. Chem.*, 1978, vol. 152, p. C5.
6. Cardaci, G., *J. Am. Chem. Soc.*, 1975, vol. 97, no. 6, pp. 1412–1415.
7. Basolo, F., *Inorg. Chim. Acta*, 1981, vol. 50, pp. 65–70.
8. Galkina, I.V., Saakyan, G.M., Cherkasov, M.A., Galkin, V.I., Cherkasov, R.A., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 3, pp. 355–359.
9. Rybinskaya, M.I. and Rybin, L.V., *Izv. Akad. Nauk, Ser. Khim.*, 1995, no. 1, pp. 159–166.
10. Ittel, S.D. and Ibers, J.A., *Adv. Organomet. Chem.*, 1976, vol. 14, pp. 33–61.