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Carbonyltungsten(0) complexes of acryloylferrocene: Synthesis and characterization

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Abstract

Photolysis of hexacarbonyltungsten(0) in the presence of acryloylferrocene in *n*-hexane solution at 10 °C yields pentacarbonyl(η^2-acryloylferrocene)tungsten(0) (**1**) as the only photo-substitution product, different from the general reaction pattern observed for the Group 6 metal carbonyls with other olefins. $W(CO)_5(\eta^2$-acryloylferrocene) (**1**) decomposes in solution to the parent hexacarbonyltungsten(0) and free acryloylferrocene. Trimethylphosphite was introduced as ligand into the molecule to increase the stability. The photolysis of pentacarbonyl(trimethylphosphite)tungsten(0) in the presence of acryloylferrocene in *n*-hexane solution at 10 °C yields only *cis*-$W(CO)_4[P(OCH_3)_3](\eta^2$-acryloylferrocene) (**2**) as the monosubstitution product. Both η^2-acryloylferrocene complexes (**1** and **2**) could be isolated and characterized by MS, IR and NMR spectroscopy. The trimethylphosphite complex (**2**) is found to be even less stable than $W(CO)_5(\eta^2$-acryloylferrocene) (**1**).

Keywords: Tungstencarbonyl; Acryloylferrocene; Trimethylphosphite; Photolysis; Substitution

1. Introduction

Ferrocene [1] has been used in the synthesis of many new materials having interesting properties [2,3]. For instance, molecules containing ferrocene units have been used as homogeneous catalysts [3], molecular sensors [4], molecular magnets [5], non-linear optic materials [6], and liquid crystals [7]. The presence of ferrocene in a molecule is expected to influence its electron transfer ability [8]. For example, introducing the ferrocenyl group into an olefin ligand is expected to influence the stability and catalytic properties of its complexes with the transition metal. Vinylferrocene has already been employed as an olefin ligand containing a ferrocenyl unit [9]. However, Group 6 metal carbonyl complexes of the type $M(CO)_5(\eta^2$-vinylferrocene) have been found to be unstable [9]. Another potential olefinic ligand containing a ferrocenyl substituent is acryloylferrocene which has been recently isolated [10]. Acryloylferrocene is an olefin bearing a carbonyl group in addition to the ferrocenyl unit. This carbonyl group may additionally interact with the transition metal atom to which the olefin ligand is already coordinated through its C=C bond. Therefore, this potential feature of acryloylferrocene prompted us to investigate its carbonylmetal complexes.

Olefin-substituted metal carbonyls are relevant to the homogeneous photocatalytic processes [11] such as isomerization [12], hydrogenation [13], and hydrosilylation [14] of mono- and diolefins. Olefin-substituted Group 6 metal carbonyls are conveniently accessible from the parent $M(CO)_6$ complexes (M = Cr, Mo, W) by means of photolytic CO displacement in the presence of olefins: ethene and linear alkenes [15–19], cycloalkenes [19–21], α,β-unsaturated esters [22] and tetracyanoethene [23]. A recent kinetic study [24] on the photochemical conversion of $W(CO)_6$ into a *trans*-$W(CO)_4(\eta^2$-olefin$)_2$ complex using *E*-cyclooctene as a model olefin owing to its extraordinary coordination properties [25] showed that the photolysis of $M(CO)_6$ in

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the presence of an olefin is expected to yield the stable final product *trans*-M(CO)$_4$(η^2-olefin)$_2$ through the intermediate M(CO)$_5$(η^2-olefin) and *cis*-M(CO)$_4$(η^2-olefin)$_2$ complexes. Indeed, with a few exceptions, *trans*-M(CO)$_4$(η^2-olefin)$_2$ is always found to be the final product of the photosubstitution of CO in the Group 6 metal carbonyls in the presence of excess olefin. In the case of tetracyanoethene [23] and *Z*-cyclooctene with chromium [20], and vinylferrocene with all three metals [9], the photosubstitution stops at the first step, forming M(CO)$_5$(η^2-olefin). Here, we report the photolysis of hexacarbonyltungsten(0) in the presence of acryloylferrocene (acfc). Photo-substitution yields only pentacarbonyl(η^2-acryloylferrocene)tungsten(0), W(CO)$_5$(η^2-acfc) (**1**), as the final product, which was isolated from the reaction solution and characterized by using IR, MS, and NMR spectroscopy and elemental analysis.

Since W(CO)$_5$(η^2-acfc) (**1**) appears to be unstable, particularly in solution, we attempted to stabilize the tungsten–acryloylferrocene complex by introducing trimethylphosphite into the molecule. For this purpose, *cis*-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acfc) (**2**) was synthesized from the irradiation of W(CO)$_5$[P(OCH$_3$)$_3$] and acryloylferrocene in *n*-hexane at 10 °C and characterized by MS, IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopies.

2. Experimental

2.1. General remarks

All reactions and manipulations were carried out either in a vacuum or under a dry and oxygen-free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used.

Analytical grade and deuterated solvents, ferrocene, acryloyl chloride, trimethylaluminum, ethylaluminumdichloride, trimethylphosphite and hexacarbonyltungsten(0) were purchased from Aldrich Chemical Co. Ltd., Dorset, England, and used as received. The thermal reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra from solutions on a Perkin–Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for ^{1}H; 100.6 MHz for ^{13}C; 161.3 MHz for ^{31}P). TMS was used as internal reference for ^{1}H and ^{13}C NMR chemical shifts. H$_3$PO$_4$ (85%, in a glass capillary) was used as reference for ^{31}P NMR chemical shifts. FAB-MS was done on a Fisons VG Autospec with *m*-nitrobenzylalcohol as matrix. Elemental analyses were performed on a LECO CHNS-932 instrument at METU Central Laboratory.

Photochemical reactions were carried out in an immersion-well apparatus [26] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high pressure mercury lamp, which was cooled by circulating water. Acryloylferrocene [10] and W(CO)$_5$[P(OCH$_3$)$_3$] [27] were prepared according to the literature procedures.

2.2. W(CO)$_5$(η^2-acryloylferrocene) (**1**)

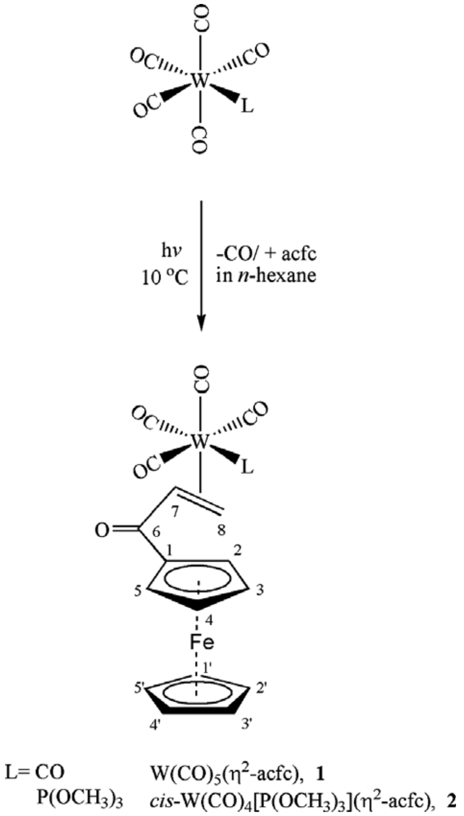
A solution of 0.48 g (1.4 mmol) W(CO)$_6$ and 0.33 g (1.4 mmol) acryloylferrocene in *n*-hexane (150 mL) was irradiated at 10 °C until the starting material was no longer observed in the IR spectrum (ca. 4 h). When the reaction was complete, volatiles were evaporated under vacuum and the dark red residue dissolved in *n*-hexane, and the solution was left overnight at −35 °C. The red precipitate was separated from the supernatant solution and dried under vacuum (0.2 g, 26% yield). Anal. Calc. for C$_{18}$H$_{12}$O$_6$WFe (M = 563.9): C, 38.30; H, 2.13. Found: C, 38.85; H, 2.26%. MS: *m*/*z* 563.9 (M$^+$). IR (ν(CO), *n*-hexane): 2091, 2013, 1975, 1956, 1655 cm^{-1} (CO of the acfc ligand); (ν(CO), KBr pellet): 2084, 1970 (sh), 1960, 1943, 1921, 1640 cm^{-1} (CO of the acfc ligand). Raman (ν(CO), solid): 2084, 2008, 1964, 1945 and 1918 cm^{-1}. ^{1}H NMR (δ ppm, rel. to TMS, in CD$_2$Cl$_2$): 4.99 (m, H2), 4.95 (m, H7), 4.94 (m, H5), 4.71 (m, H3), 4.66 (m, H4), 4.30 (s, H1′-H5′), 4.14 (d, H8, $J_{\text{H7–H8}} = 17.9$ Hz) and 3.80 (d, H8′, $J_{\text{H7–H8}'} = 12.6$ Hz). ^{13}C NMR (δ ppm, rel. to TMS, in CD$_2$Cl$_2$): 202.4 (CO *trans* to acfc), 195.2 (CO *cis* to acfc), 194.4 (C6, CO of acfc ligand), 78.94 (C1), 73.50 (C3), 73.13 (C4), 70.56 (C1′-C5′), 70.28 (C7), 69.86 (C2), 69.33 (C8), 68.63 (C5).

2.3. *cis*-W(CO)$_4$[P(OCH$_3$)$_3$](η^2-acryloylferrocene) (**2**)

A solution of 0.63 g (1.4 mmol) W(CO)$_5$[P(OCH$_3$)$_3$] and 0.33 g (1.4 mmol) acryloylferrocene in *n*-hexane (150 mL) was irradiated at 10 °C until the starting material was no longer observed in the IR spectrum (ca. 4 h). After the reaction was completed the solvent was evaporated in vacuum. The solid residue was dissolved in *n*-hexane and the solution was left overnight at −35 °C. A red precipitate was separated from the supernatant solution and dried under vacuum. (0.14 g, 15% yield). MS: *m*/*z* 660.0 (M$^+$). IR(*n*-hexane) ν(CO) = 2051, 1966, 1944, 1926, 1652 cm^{-1} (CO of the acfc ligand). ^{1}H NMR (δ ppm, rel. to TMS, in CD$_2$Cl$_2$): 4.92 (H2), 4.78 (H7), 4.59 (H3), 4.55 (H4), 4.51 (H8), 4.24 (s, H1′–H5′), 4.18 (H5), 3.68 (d, P(OCH$_3$)$_3$, $J(^{31}\text{P}–^{13}\text{C}) = 14$ Hz), 3.56 (H8′). ^{13}C NMR (δ ppm, rel. to TMS, in CD$_2$Cl$_2$): 198.1 (s, C6, CO of acfc ligand), 207.3 (d, CO *trans* to acfc, $J(^{31}\text{P}–^{13}\text{C}) = 16.4$ Hz), 204.5 (d, CO *trans* to trimethylphosphite, $J(^{31}\text{P}–^{13}\text{C}) = 27.3$ Hz), 197.4 (d, CO *cis* to acfc and P(OCH$_3$)$_3$, $J(^{31}\text{P}–^{13}\text{C}) = 11.0$), 197.0 (d, CO *cis* to acfc and P(OCH$_3$)$_3$, $J(^{31}\text{P}–^{13}\text{C}) = 10.9$ Hz), 80.0 (C1), 72.64 (C2), 72.42 (C5), 70.31 (C1′–C5′), 69.87 (C3), 69.34 (C4), 69.03 (C7), 62.49 (C8), 52.85 (d, P(OCH$_3$)$_3$, $J(^{31}\text{P}–^{13}\text{C}) = 5.4$ Hz). ^{31}P NMR (δ ppm, rel. to H$_3$PO$_4$, in CD$_2$Cl$_2$): 146.1.

3. Results and discussion

Irradiation of W(CO)$_6$ in the presence of acryloylferrocene (acfc) in *n*-hexane at 10 °C results in nearly complete conversion into $W(CO)_5(\eta^2\text{-acfc})$ (**1**), Scheme 1, which was isolated and characterized by elemental analysis, MS, IR, Raman, ^1H and ^{13}C NMR spectroscopy.



Scheme 1. Photolysis of $W(CO)_6$ or $W(CO)_5[P(OCH_3)_3]$ at 10 °C in *n*-hexane solution in the presence of acryloylferrocene (acfc).

Fig. 1 shows the IR spectrum of **1** in the CO stretching region. The observation of four prominent bands and one weak absorption indicates that the $W(CO)_5$ skeleton in **1** with the single-face π-alkene ligand (by disregarding the substituent effect on its symmetry) has a C_{2v} symmetry with five IR-active CO stretching modes: $3A_1$, B_1, B_2 [28]. The two very strong bands in the spectrum are readily assigned to the B_1 and B_2 modes. All five CO stretching bands of the $W(CO)_5$ unit are also observable in the Raman spectrum. The IR spectrum also shows an absorption band at 1655 cm^{-1} (in *n*-hexane) or 1640 cm^{-1} (in KBr) due the carbonyl group of the acryloylferrocene ligand in **1**. The same absorption is observed at 1665 cm^{-1} for the free acryloylferrocene in *n*-hexane. This relatively small shift in the CO stretching frequency is indicative for the coordination of acryloylferrocene to tungsten through the C=C bond, not through the carbonyl group.

The ^1H NMR spectrum of **1** in CD_2Cl_2shows three multiplets at 4.95, 4.14 and 3.80 ppm due to the olefinic protons of the acryloylferrocene ligand. Compared to the free acryloylferrocene molecule (6.85, 6.40 and 5.73 ppm, respectively), the relatively large shift of the olefinic proton signals toward higher magnetic field ($\Delta\delta = 1.90$, 2.26 and 1.93 ppm, respectively) indicates the coordination of acryloylferrocene to the metal through its C=C double bond. The ^1H NMR spectrum of **1** also exhibits four multiplets and a singlet due to the hydrogen atoms of the substituted and unsubstituted cyclopentadienyl ring, respectively. Although the cyclopentadienyl ring protons experience only slight changes in their chemical shifts upon coordination, the substituted cyclopentadienyl ring looses its symmetry plane upon coordination, so that the four hydrogen atoms are different in the acfc ligand of **1**.

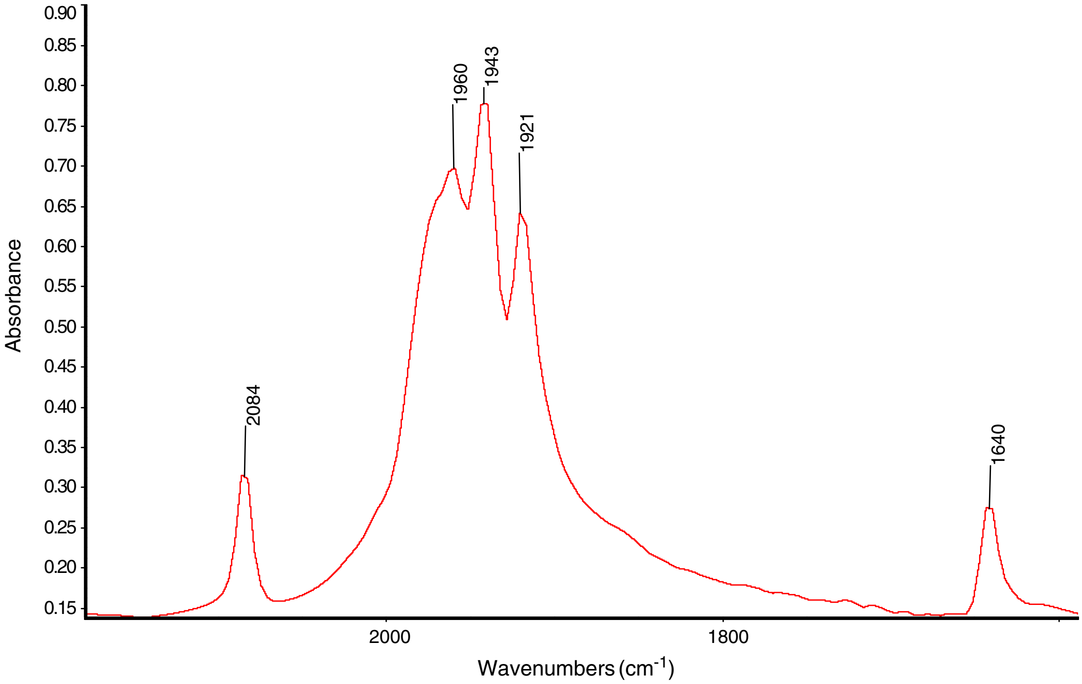


Fig. 1. Part of the IR spectrum of $W(CO)_5(\eta^2\text{-acfc})$ (**1**), recorded from KBr pellet, showing *ν*(CO) bands (2084 cm^{-1}, A_1; a shoulder at about 1970 cm^{-1}, A_1; 1960 cm^{-1}, B_1; 1943 cm^{-1}, B_2; 1921 cm^{-1}, A_1 and 1640 cm^{-1}, CO group of the acfc ligand).

The ^{13}C NMR spectrum of **1** in CD_2Cl_2 gives two signals for the CO ligands, one signal due to the carbonyl carbon of the acfc ligand, two signals for the olefinic carbon atoms, and six signals for the ferrocenyl unit. The appearance of only one signal for the four equatorial CO groups suggests that the molecule is fluxional with respect to rotation about the metal–alkene bond axis. Compared to the ^{13}C NMR spectrum of the free acryloylferrocene molecule, the coordination shifts of the olefinic carbons are $\Delta\delta = 63.1$ and 57.4 ppm, respectively, while the shift of the carbonyl carbon of the ligand in **1** is $\Delta\delta = 2.6$ ppm. The large coordination shift of the olefinic carbon signals supports the coordination of acryloyferrocene to the metal through its C=C double bond. The signals of the cyclopentadienyl carbons show only slight changes upon coordination. However, all five carbon atoms of the substituted cyclopentadienyl ring become different upon coordination of acryloylferrocene.

Photolysis of an *n*-hexane solution of hexacarbonyltungsten(0) in the presence of acryloylferrocene gives only the monosubstitution product. The photosubstitution of one CO group in $W(CO)_6$ by acryloylferrocene is the only reaction in this photolysis and continues practically until the complete conversion of $W(CO)_6$ to the mono-substitution product. Prolonged irradiation of the solution does not give any further CO substitution; it causes rather **1** to decompose slowly. ^{13}C NMR and IR spectra show the slow formation of $W(CO)_6$ and free acryloylferrocene when the complex **1** left in solution. This observation indicates that **1** is labile in solution and decomposes into hexacarbonyltungsten(0) and acryloylferrocene.

With the anticipation that introducing a different ligand into the carbonyl-olefin–metal complex may strengthen the metal–olefin bond, *cis*-$W(CO)_4[P(OCH_3)_3](\eta^2\text{-acfc})$ (**2**) was synthesized. Irradiation of $W(CO)_5[P(OCH_3)_3]$ [27] in the presence of acryloylferrocene in *n*-hexane at 10 °C yields the complex **2** (Scheme 1), which was isolated and characterized by using IR, MS, ^{1}H, ^{13}C and ^{31}P NMR spectroscopies.

The IR spectrum of **2** taken in *n*-hexane exhibits four strong absorption bands for CO stretching. The observation of four bands indicates a *cis* arrangement for the $W(CO)_4$ moiety, which has then a C_s local symmetry with $3A' + A''$ CO stretching modes [28]. The IR spectrum also shows an absorption band at 1652 cm^{-1} due the carbonyl group of the acfc ligand in complex **2**. This relatively small shift in the CO stretching frequency compared to the free acryloylferrocene (1665 cm^{-1}) is also indicative for the coordination of acryloylferrocene to the tungsten through C=C bond.

The ^{1}H NMR spectrum of **2** in CD_2Cl_2 shows a doublet for the $P(OCH_3)_3$ ligand, three multiplets for the olefinic protons, four signals for the hydrogen atoms of the substituted cyclopentadienyl and a singlet for the hydrogen atoms of the unsubstituted cyclopentadienyl ring. Compared to the free acryloylferrocene, the signals of olefinic protons show a remarkable coordination shift ($\Delta\delta = 1.91$, 1.88 and 2.1 ppm, respectively), indicating the coordination of acryloylferrocene through the C=C bond.

The ^{13}C NMR spectrum of **2** in CD_2Cl_2 exhibits four doublets and one singlet in carbonyl region. The singlet at 198.1 ppm can readily be assigned to the carbonyl carbon of the acryloylferrocene ligand. The four doublets (because of ^{31}P–^{13}C coupling) are due to the four different CO ligands in **2**. The doublet at the highest chemical shift of 207.3 ppm with $J(^{31}P–^{13}C) = 16.4$ Hz is assigned to the CO *trans* to the acfc ligand. The doublet at 204.5 ppm with the largest ^{31}P–^{13}C coupling constant of 27.3 Hz is assigned to the CO ligand *trans* to the trimethylphosphite. The other two doublets at 197.4 and 197.0 ppm with ^{31}P–^{13}C coupling constants of 11.0 and 10.9 Hz, respectively, are assigned to the CO ligands *trans* to each other (*cis* to both acfc and $P(OCH_3)_3$). The doublet at 52.85 ppm with the ^{31}P–^{13}C coupling constant of 6 Hz is due to the $P(OCH_3)_3$ ligand. The olefinic carbon atoms give two signals at 69.03 and 62.49 ppm which have been shifted by $\Delta\delta = 64.4$ and 64.2 ppm, respectively, compared to the free acryloylferrocene. The large coordination shift of the olefinic carbon signals supports the coordination of acryloyferrocene to the metal through its C=C double bond. The ferrocenyl part gives five signals for the five different carbon atoms of the substituted cyclopentadienyl ring and one signal for the five equal carbon atoms of the unsubstituted cyclopentadienyl ring. The signals of the cyclopentadienyl ring carbons show only slight changes upon coordination to tungsten through the C=C bond.

The higher kinetic lability of **2** as compared to **1** can be ascribed to steric crowding. Thus, introducing a donor/acceptor ligand into the molecule does not provide additional stability for the tungsten–olefin bond in the case of acryloylferrocene.

In both complexes **1** and **2**, the acfc ligand is bonded to the metal only through the C=C bond. There is no indication that acryloylferrocene interacts with the metal through its CO group.

In general, the carbonylmetal complexes of acryloylferrocene are labile in solution. Attempts to prepare the chromium and molybdenum analogs failed. Together with the large coordination shifts of the olefinic carbon and proton signals in **1** and **2**, this lability may be considered as an indication for the activation of the acryloylferrocene C=C bond upon coordination to a transition metal.

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