

Synthesis and Spectroscopic Studies of Pentacarbonylfumaronitrile-chromium(0), -molybdenum(0), and -tungsten(0)

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Z. Naturforsch. **49b**, 1059–1062 (1994); eingegangen am 13. April 1994

Chromium, Molybdenum, Tungsten, Carbonyl, Fumaronitrile Complexes

Photolysis of hexacarbonyl-chromium(0), -molybdenum(0), and -tungsten(0) in presence of fumaronitrile yields at room temperature pentacarbonyl-fumaronitrile-chromium(0) (**1**), -molybdenum(0) (**2**), and -tungsten(0) (**3**). The complexes were purified by crystallization and characterized by IR and ^{13}C -NMR spectroscopy. The fumaronitrile ligand is bonded to the $\text{M}(\text{CO})_5$ moiety by one nitrile nitrogen atom rather than by the carbon-carbon double bond. In toluene **2** dissociates into fumaronitrile and pentacarbonyl-molybdenum(0), which is stabilized by the solvent. Fumaronitrile and solvated pentacarbonyl-molybdenum(0) exist in solution together with **2** in an equilibrium which lies in favour of the former species.

Introduction

Photosubstitution of group 6 metal carbonyls provides a convenient access to a large variety of mono and multi substituted derivatives, including olefin complexes [1–7]. Based on early reports [2], for a long time it was believed that the olefin substituted derivatives of these metal carbonyls are only moderately stable. Quite recently, some stable $\text{M}(\text{CO})_{6-n}(\eta^2\text{-olefin})_n$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; n = 1, 2$) have been synthesized from the sequential photosubstitution of one or two carbonyl groups by olefin ligands [3–7]. It has been shown that the $\text{M}(\text{CO})_5(\eta^2\text{-olefin})$ complexes are less stable than the $\text{M}(\text{CO})_5(\eta^2\text{-olefin})_2$ complexes [4, 5]. The latter are known to be most stable if the olefin ligands are in a *trans-orthogonal* arrangement [7, 8]. The presence of a donor ligand, such as trialkylphosphine, has a stabilizing effect on the carbonyl- η^2 -olefin-metal(0) complexes. Thus a large number of carbonyl- η^2 -olefin-metal(0) complexes containing one or two σ -donor ligands have been synthesized [9]. The stabilization of carbonyl- η^2 -olefin-metal complexes by the σ -donor ligands is attributed to the strengthening of metal-olefin bond. As the electron density flows

from the σ -donor ligand to the transition metal atom, the latter donates the excess electron density to the olefin ligand through the metal-olefin π -back-bonding. Thus the presence of a σ -donor ligand forces the olefin ligand to accept π -electron density from the transition metal atom. A similar effect is expected if the olefin ligand has electron withdrawing substituents. An electron withdrawing substituent will lower the LUMO level of the olefin and increase its π -acceptor ability. Indeed, the first examples of stable carbonyl- η^2 -olefin-metal complexes of group 6 elements were those of methyl acrylate or dimethyl fumarate [3]. The cyano substituted olefins are also expected to form stable carbonyl- η^2 -olefin-metal complexes of group 6 elements. This was manifested in 1968 by the synthesis of $\text{Cr}(\text{CO})_5(\eta^2\text{-tetracyanoethylene})$ which was characterized by MS and IR spectroscopy [10]. Quite recently, W. Kaim reported the isolation of the tungsten analogue, $\text{W}(\text{CO})_5(\eta^2\text{-TCNE})$, from TCNE and $\text{W}(\text{CO})_5\text{-}(\text{THF})$, photogenerated in tetrahydrofuran [11]. The solvatochromism and the electronic and electrochemical behaviour of both complexes have been studied extensively [12–14]. A π -coordination of TCNE to the pentacarbonylmetal fragment was proposed based on the IR and electronic spectra. We have recently reported an extensive study on the photochemical synthesis and spec-

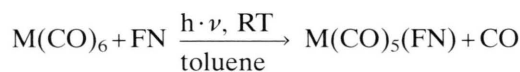
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troscopy, including ^{13}C -NMR, of $\text{M}(\text{CO})_5(\eta^2\text{-tetracyanoethylene})$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [15].

The presence of cyano groups on the olefin affords capabilities for multiple bonding to a central atom. Tetracyanoethylene has been shown to coordinate to metals through its carbon-carbon double bond [10–15]. In the case of acrylonitrile, examples of both types of coordination modes, by the lone pair of nitrogen and by the carbon-carbon double bond have been proved [16, 17]. Complexes in which acrylonitrile is acting as a four-electron donor were also isolated [18]. The coordination of fumaronitrile to a carbonyl metal moiety of group IV, however, has not been studied. Here we would like to report upon the photochemical synthesis and some spectroscopic studies of the pentacarbonyl-fumaronitrile-metal(0) complexes of chromium, molybdenum and tungsten.

Result and Discussion

The photolysis of hexacarbonyl-chromium(0), -molybdenum(0), and -tungsten(0) in the presence of fumaronitrile (FN) yields the corresponding pentacarbonyl-fumaronitrile-metal(0) complexes **1–3**.



The complexes were purified by crystallization, and characterized by IR and ^{13}C NMR spectroscopy.

The IR spectra of the complexes **1–3** exhibit two absorption bands for CN stretching and three absorption bands for CO stretching, indicating a local C_{4v} symmetry for the $\text{M}(\text{CO})_5$ moiety with the IR active CO stretching modes $2\text{A}_1, \text{E}$ [19]. The CO force constants were calculated from the observed CO stretching frequencies using the Cotton-Kraihanzel approximation [20]. The CN and CO stretching frequencies as well as the CO force constants of the complexes **1–3** are listed in Table I. The most remarkable feature of the IR spectrum is the appearance of two absorption bands for the CN stretching upon coordination, in contrast to free FN which has just one IR active

Table I. CN and CO stretching frequencies (cm^{-1}) in dichloromethane of fumaronitrile and the complexes **1–3**. CO force constants k_1 for the axial, k_2 for the equatorial CO ligands, k_i are the interaction constants ($\text{N}\cdot\text{m}^{-1}$).

	νCN	νCO		k_1	k_2	k_i
FN	2248					
1	2240	2220	1922	2080	1955	1508
2	2230	2213	1920	2076	1952	1505
3	2210	2192	1917	2070	1945	1501

Table II. ^{13}C NMR chemical shifts in δ ppm, rel. to TMS, in toluene- d_8 of fumaronitrile and the complexes **1–3**. ^{13}C - ^1H Coupling constants in Hz are given in parentheses.

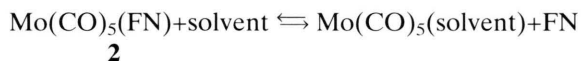
	C=C	CN	CO_{eq}	CO_{ax}
FN	117.39 (181.7)	113.82 (4.3)		
1	117.97 (170.7)	114.16 (6)	218.19	213.75
	113.71 (184.7)	113.34 (6)		
2	117.09 (183.8)	113.67 (4.3)	218.45	213.65
3	118.07 (185)	112.90	199.00	195.66
	112.94 (186)	112.71		

CN stretching because of the *trans* arrangement of two cyano substituents. This implies an asymmetric coordination of FN to the $\text{M}(\text{CO})_5$ moiety. The small bathochromic coordination shift in the CN stretching frequency can be attributed to $\text{M}\rightarrow\text{N}$ π -donation. By going from chromium to tungsten, one observes a smooth, noticeable decrease in both CN and CO stretching frequencies. This decrease reflects the effect of the increasing metal $d_{\pi}\rightarrow$ ligand π^* backbonding by going down within group VI.

The ^{13}C NMR spectra of the complexes show two signals with relative intensities of 1:4 for the CO groups (Table II). This observation confirms the C_{4v} symmetry of the $\text{M}(\text{CO})_5$ moiety. The less intense carbonyl signal at a lower magnetic field is readily assigned to the carbonyl group *trans* to FN. The remarkable deshielding of the carbonyl carbon *trans* to the FN ligand denotes the lower π -accepting and higher σ -donating abilities of the FN ligand compared to the carbonyl group [21].

The molybdenum complex differs from the chromium and tungsten analogues with respect to the number of the ^{13}C NMR signals for the FN ligands. The latter complexes give four ^{13}C NMR signals for the FN ligands. The coupled ^{13}C NMR spectrum shows that two of the four signals belong to the olefinic carbon atoms and the other two are due to the nitrile carbon atoms. This unequivocally indicates that the FN ligand is coordinated to the $\text{M}(\text{CO})_5$ moiety through one nitrile nitrogen atom. A symmetric coordination of FN would give only two ^{13}C NMR signals, one for the olefinic and one for the nitrile carbon atoms. It is to be noted that only one olefinic and one nitrile signal show a significant coordination shift which also confirms the N-bonding of FN to the transition metal atom.

The ^{13}C NMR spectrum of the molybdenum complex **2** in toluene- d_8 shows two carbonyl signals as anticipated. However, for the FN ligand there are only two signals with chemical shifts almost equal to those of the free FN molecule. Indeed, addition of FN to the solution of the complex **2** does not cause any change in the ^{13}C NMR spectrum except for an increase in the intensities of the two signals of FN. This demonstrates that **2** undergoes a dissociation into the solvated pentacarbonyl-molybdenum(0) and free fumaronitrile molecule in solution.



There might be an equilibrium between **2** and the solvated pentacarbonyl-molybdenum(0). Since the addition of fumaronitrile into the solution does not show any noticeable changes in the chemical shifts, the equilibrium must lie in the direction of FN dissociation. The rate at which the equilibrium is established must be fast compared to the NMR time scale, so that an average value for the solvated pentacarbonyl-molybdenum(0) and free fumaronitrile can be observed by NMR spectroscopy.

The observation of two carbonyl signals with relative intensities of 1:4 indicates the existence of the $\text{Mo}(\text{CO})_5$ moiety in the solution of **2**. The ^{13}C NMR chemical shifts of the carbonyl ligands are about 4–5 ppm greater than one would anticipate for a molybdenum complex from the trends observed in the similar compounds of group VI

[15]. This additional deshielding of the carbonyl carbon atoms in **2** implies that the molybdenum-carbonyl bonding is strengthened by a process like the dissociation of the FN ligand in solution.

The IR spectra of all three complexes are alike as the rate at which the equilibrium is established is slow the IR time scale.

Experimental

All reactions and manipulations were carried out either in vacuum or under a dry and deoxygenated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide for three to four days and stored under nitrogen until use.

Hexacarbonyl-chromium(0), hexacarbonyl-molybdenum(0), hexacarbonyl-tungsten(0) and fumaronitrile were purchased from Ventron GmbH, Germany, and used without any further purification. The photochemical reactions and other treatments of the reaction products such as purification and crystallization were followed by IR spectra taken at appropriate time intervals.

^{13}C NMR spectra were recorded on a Bruker AMX 400 FT-NMR spectrometer at 100.62 MHz. TMS was used as internal reference for ^{13}C NMR chemical shifts. Infrared spectra were recorded from toluene solutions on a Perkin-Elmer IR-spectrometer model 1430. Mass spectra were taken on a Varian MAT 311 instrument. Elemental analyses were carried out on a HP 185 CHN analyzer.

Photoreaction of hexacarbonyl-chromium(0), -molybdenum(0), and -tungsten(0) with fumaronitrile

A solution of 1.00 g $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}$ (4.54 mmol), Mo (3.79 mmol), W (2.84 mmol)) and an equivalent amount of fumaronitrile in 100 ml toluene is irradiated for 7 h using a high-pressure mercury lamp (TQ 150, Quarzlampen GmbH, Hanau, Germany) which is housed in a water-cooled glass jacket. Following the evaporation of solvent in vacuum, the dark coloured residue is dissolved in about 5 ml dichloromethane. By cooling the solution down to -78°C crystalline fumaronitrile complexes are obtained.

Pentacarbonyl-fumaronitrile-chromium(0) (**1**), red crystals.

Yield: 1.00 g (82% rel. $\text{Cr}(\text{CO})_6$)

$C_9H_2CrO_5N_2$ (270.12) molar mass by mass spectroscopy $270 \text{ g} \cdot \text{mol}^{-1}$

Calc. C 40.02 H 0.75 N 10.37%,
Found C 40.75 H 0.78 N 11.10%.

Pentacarbonyl-fumaronitrile-molybdenum(0) (**2**), red crystals.

Yield: 0.81 g (68% rel. $Mo(CO)_6$)

$C_9H_2MoO_5N_2$ (314.07) molar mass by mass spectroscopy $314 \text{ g} \cdot \text{mol}^{-1}$

Calc. C 34.42 H 0.64 N 8.92%,
Found C 34.80 H 0.66 N 9.12%.

Pentacarbonyl-fumaronitrile-tungsten(0) (**3**), red crystals.

Yield: 0.73 g (64% rel. $W(CO)_6$)

$C_9H_2O_5N_2W$ (401.98) molar mass by mass spectroscopy $402 \text{ g} \cdot \text{mol}^{-1}$

Calc. C 26.89 H 0.50 N 6.97%,
Found C 27.10 H 0.54 N 6.87%.

Acknowledgement

This work was supported by the Scientific and Technical Research Council of Turkey (TÜBİTAK, TBAG-957) and the Volkswagen-Stiftung.

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