

NOTIZEN

Synthesis and Spectroscopic Study of Pentacarbonyl(η^2 -tetracyanoethylene) Metal(0) Complexes of the Group 6B Elements

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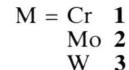
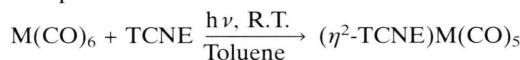
Chromium, Molybdenum, Tungsten, Carbonyl,
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Pentacarbonyl(η^2 -tetracyanoethylene) metal(0) complexes of chromium, molybdenum and tungsten have been synthesized by the photochemical reaction of hexacarbonyl metal(0) with tetracyanoethylene in toluene at room temperature. The complexes were purified by chromatography and recrystallization, and characterized by UV-visible, IR and ^{13}C NMR spectroscopy. Tetracyanoethylene is symmetrically bonded to the $\text{M}(\text{CO})_5$ unit through its carbon–carbon double bond as an η^2 -ligand. The spectral data are discussed in terms of the metal–ligand π interaction.

Introduction

Group 6B metal hexacarbonyls undergo sequential photosubstitution of one or two carbonyl groups by olefin ligands to yield $(\eta^2\text{-olefin})_n\text{M}(\text{CO})_{6-n}$ complexes where $n = 1, 2$ [1–7]. It has been shown that the $(\eta^2\text{-olefin})\text{M}(\text{CO})_5$ complexes are less stable than the $(\eta^2\text{-olefin})_2\text{M}(\text{CO})_4$ complexes [4, 7]. The latter complexes 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-olefin metal(0) complexes. Thus a large number of carbonyl-olefin metal(0) complexes containing one or two σ -donor ligands have been synthesized [9]. The stabilization of olefin-carbonyl 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 donated the excess electron density to the olefin ligand through the metal-olefin π -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 olefin-carbonyl-metal complexes of group 6B elements were those of methyl acrylate or dimethyl fumarate [2]. The cyano substituted olefins are also expected to form stable carbonyl-olefin-metal complexes of group 6B elements. Indeed, the first example, $(\eta^2\text{-tetracyanoethylene})\text{Cr}(\text{CO})_5$ was synthesized by M. Herberhold in 1968 and characterized by MS and IR spectroscopy [10]. Quite recently, W. Kaim reported the isolation of the tungsten analogous, $(\eta^2\text{-TCNE})\text{W}(\text{CO})_5$, from TCNE and $(\text{THF})\text{W}(\text{CO})_5$ photogenerated in tetrahydrofuran [11]. The solvatochromism, 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, but no NMR spectroscopic study has been reported. Here we would like to report the photochemical synthesis and further study of $(\eta^2\text{-tetracyanoethylene})\text{M}(\text{CO})_5$ complexes, where M: Cr, Mo, W. The photolysis of hexacarbonylmetal(0) in the presence of tetracyanoethylene yields the pentacarbonyl(η^2 -tetracyanoethylene)metal(0) complexes.



The complexes were purified by column chromatography and recrystallization, and characterized by means of UV-visible, IR and ^{13}C NMR spectroscopies.

Experimental

All reactions and manipulations were carried out either in a vacuum or under a dry and deoxy-

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Complex No.	Formula	Yield (%)	C (%) Calcd	Found	N (%) Calcd	Found
1	$C_{11}O_5N_4Cr$	82	41.25	41.96	17.50	18.01
2	$C_{11}O_5N_4Mo$	68	36.26	37.16	15.38	16.09
3	$C_{11}O_5N_4W$	64	29.20	29.60	12.40	13.20

Table I. Analytical data of the $(\eta^2\text{-tetracyanoethylene})M(CO)_5$ complexes.

generated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or di-phosphorus pentoxide under nitrogen for three to four days and stored until use.

Hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0) and tetracyanoethylene were purchased from Ventron GmbH, Germany, and used without any further purification. The photochemical reactions and other treatment of organometallic compounds such as purification and crystallization were followed by IR spectra taken at appropriate time intervals.

NMR spectra were recorded on a Bruker AC-80 spectrometer (20.149 MHz for ^{13}C). TMS was used as the internal reference for ^{13}C NMR chemical shifts. Infrared spectra were recorded from toluene solution on a Perkin-Elmer 1430 instrument. UV-visible absorption spectra were recorded on a HP 8452 A Diod Array Spectrophotometer. Elemental analyses were carried out on a HP 185 CHN analyzer.

A solution of 1.0 g $M(CO)_6$ ($M: \text{Cr, Mo, W}$) and one equivalent amount of tetracyanoethylene in 100 ml toluene is irradiated for 5 h using a high-pressure mercury lamp (Hg-Tauchlampe TQ 150, Quarzlampen GmbH, Hanau, Germany) which is

housed in a water-cooled glass jacket. Following the evaporation of solvent in vacuum, the dark colored oily residue is chromatographed on silica gel using a *n*-hexane-dichloromethane (4:1) mixture. The blue eluate is then evaporated to remove the solvents. The residue is dissolved in about 5 ml dichloromethane. Dark blue crystals are obtained upon leaving the solution at -78°C for one day. Analytical data are given in Table I.

Results and Discussion

The ^{13}C NMR spectra of the complexes show two signals for the CO groups and two signals for the olefin ligand (Table II). The observation of two carbonyl signals with relative intensities of 1:4 indicates the presence of a $M(CO)_5$ moiety with C_{4v} symmetry. The remarkable deshielding of the carbonyl carbon trans to the olefin ligand denotes the lower π -accepting and higher σ -donating abilities of the olefin compared to carbon monoxide [15]. The fact that the ^{13}C NMR spectra of the complexes show only two signals for the olefin ligand, one for the olefinic carbons and one for the CN substituents, indicates the symmetric coordination of the olefin ligand to the $M(CO)_5$ moiety. Any coordination of the TCNE ligand through the

		TCNE	1	2	3
IR	νCN (cm $^{-1}$)	2250 2220	2182	2178	2172
	νCO (cm $^{-1}$)		1937 2045 1979	1935 2041 1973	1932 2039 1970
CO force constants (Nm $^{-1}$)	k_i k_1 k_2		17 1522 1615	17 1519 1606	17 1515 1602
^{13}C NMR (δ ppm)	CO _{eq} (4) CC _{ax} (1) C=C CN		213.57 222.09 138.37 108.58	201.04 215.41 111.92 107.85	192.74 199.91 111.99 107.80
Electronic Spectrum	λ_{max} (nm) ϵ (M $^{-1}\cdot\text{cm}^{-1}$)	405 3200	816	778 3944	748 6214

Table II. CN and CO stretching frequencies (cm $^{-1}$, in dichloromethane), CO force constants (Nm $^{-1}$), ^{13}C NMR chemical shifts (δ ppm, rel. to TMS, chloroform-d), and electronic spectral data (λ_{max} nm, ϵ M $^{-1}\cdot\text{cm}^{-1}$, toluene) of the free tetracyanoethylene molecule and its complexes $M(CO)_5(\text{TCNE})$. k_1 is for the axial, k_2 for the equatorial CO ligands, k_i is the interaction constant.

nitrogen lone pair can therefore be ruled out. The olefin coordination shift, $\Delta\delta = \delta(\text{free olefin}) - \delta(\text{coordinated olefin})$, is remarkably large and demonstrates the coordination of olefin through its C=C double bond as an η^2 -olefin ligand. By contrast, the signal of the CN substituents does not show any significant changes upon coordination. The large olefin coordination shift correlates with the degree of metal (d_{π}) \rightarrow olefin (π^*) back-donation compared to that of metal (d_{π}) \rightarrow carbonyl (π^*) back-donation [8, 16].

The IR spectra of the complexes exhibit only one absorption band for CN stretching and three absorption bands for CO stretching indicating a local C_{4v} symmetry for the $M(CO)_5$ moiety with the IR active $2 A_1 + E$ CO-stretching modes [17]. The CO force constants were calculated from the observed CO stretching frequencies by using the Cotton-Kraihanzel approximation [18]. The CN and CO stretching frequencies as well as the CO force constants of the complexes **1–3** are listed in Table II. The most remarkable feature of the IR data is the large bathochromic shift in the C≡N stretching frequencies upon coordination. This coordination shift, $\Delta\nu(\text{CN}) = \nu(\text{CN in free TCNE}) - \nu(\text{CN in coordinated TCNE})$ [19], originates from the metal (d_{π}) \rightarrow olefin (π^*) back-donation whereby some electron density flows into an anti-bonding molecular orbital of the olefin which has also a contribution from the CN substituents. Fill-

ing the antibonding orbital of the olefin will weaken both the C=C and C≡N bonds, and causes the corresponding stretching frequencies to decrease. The correlation between the CN stretching frequency of TCNE and the CO force constant of the carbonyl trans to the olefin ligand deserves a particular consideration. By going from chromium to tungsten one observes a smooth, noticeable decrease in both the CN and CO stretching frequencies. This decrease reflects the effect of the increasing metal (d_{π}) \rightarrow ligand (π^*) back-donation.

A similar effect is observed in the electronic spectra of the complexes which exhibit an intensive charge-transfer band at the lower energy side of the visible region (Table II). The charge transfer band shows a noticeable blue shift on passing from chromium to molybdenum and tungsten. Since the TCNE ligand is a weaker π -acceptor than a CO group, the HOMO and LUMO of $M(CO)_5(\text{TCNE})$ must be the bonding and anti-bonding molecular orbitals formed from the π interaction between the metal e (d_{xz} and d_{yz}) orbitals and the π^* -orbital of the TCNE molecule [16]. As the π interaction increases by going down within the group 6B the energy of the charge transfer transition will increase, too.

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