Photochemical Synthesis and Identification of Tetracarbonyl-bis(olefin)metal(0) Complexes of Group VI B Elements

I. A. Morkan and A. Uzettik-Morkan

Department of Chemistry, Abant Izzet Baysal University, 14280 Bolu, Turkey
Reprint requests to Dr. Izzet Morkan, Fax: 90-374-2534642. E-mail: morkan@ibu.edu.tr

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Carbonyl, Tetracyanoethylene, Fumaronitrile

The resulting complexes were purified by using 0932-0776/00/1200-1153 $ 06.00 © 2000 Verlag der Zeitschrift für Naturforschung, Tübingen • www.znaturforsch.com K

Photosubstitution of group 6B metal carbonyls is a highly efficient process which provides convenient access to a large variety of mono- and poly-substituted derivatives [1 - 7]. Reactions involving olefin complexes are less documented, despite of their relevance to photocatalytic processes such as isomerization and hydrogenation [8 - 10] of mono- and diolefins. Based on an early report [2], it was accepted that group 6B metal carbonyl complexes with \( \pi^2 \)-coordinated mono- or diolefins are at best moderately stable, which severely hampers any detailed examination of their spectroscopic and photochemical properties. It has been shown that the \( \pi^2 \)-olefin)M(CO)\(_5\) complexes are less stable than \( \pi^2 \)-olefin)\(_2\)M(CO)\(_4\) complexes [4 - 7]. The former examples are known to be most stable if the olefinic ligands are in a trans-orthogonal arrangement [7 - 11]. The presence of a \( \sigma \)-donor ligand forces the olefin ligand to accept \( \pi \)-electron density from the metal atom. Thus a large number of \( \pi^2 \)-olefin-carbonyl-metal complexes containing one or two \( \sigma \)-donor ligands have been synthesized [12]. A similar effect is expected if the olefin has electron withdrawing substituents. This will lower the LUMO level of the olefin and thus increase its \( \pi \)-acceptor ability. The cyano substituted olefins are expected to form stable carbonyl-olefin-metal complexes of group 6B elements.

Our group has previously reported the synthesis of \( \pi^2\)-TCNE)M(CO)\(_5\), and (FN)M(CO)\(_5\) complexes (M:Cr, Mo, W) and their structures have been characterized by UV, IR and NMR spectroscopy [13, 14]. The present work aimed at the photochemical synthesis and isolation of trans-bis(olefin)tetracarbonyl-metal(0), (M = Cr, Mo, W), complexes derived from \( \pi^2\)-1,3-butadiene)M(CO)\(_4\) in the presence of tetracyanoethylene and fumaronitrile to yield trans-bis(\( \pi^2\)-tetracyanoethylene)tetracarbonyl-metal(0) and trans-bis(fumaronitrile)tetracarbonyl-metal(0) complexes of group 6B elements.

\[
\begin{align*}
\text{M(CO)\(_5\) + 1,3-butadiene} & \\
\text{\( h_\nu \), 235 K} & \rightarrow (\pi^4\text{-1,3-butadiene})M(CO)\(_4\) \\
(\pi^2\text{-1,3-butadiene})M(CO)\(_4\) + TCNE & \\
\text{\( h_\nu \), R.T} & \rightarrow \text{trans}(\pi^2\text{-TCNE})M(CO)\(_4\) \\
(1: M = Cr, 2: M = Mo, 3: M = W) & \\
(\pi^2\text{-1,3-butadiene})M(CO)\(_4\) + FN & \\
\text{\( h_\nu \), R.T} & \rightarrow \text{trans}(\text{FN})M(CO)\(_4\) \\
(4: M = Cr, 5: M = W) & \\
\end{align*}
\]

The resulting complexes were purified by using a large amount of solvent and recrystallization and characterized by IR, 'H, C NMR and mass spectroscopies. It is shown that two tetracyanoethylene ligands are symmetrically bonded to the M(CO)\(_4\) moiety through their carbon-carbon double bond in the form of \( \eta^2 \)-TCNE. The two fumaronitrile ligands are bonded to the central atom through their nitrogen atoms. The spectral data are discussed in terms of metal \( \rightarrow \) ligand \( \pi \)-interaction.

Introduction

Photosubstitution of group 6B metal carbonyls is a highly efficient process which provides convenient access to a large variety of mono- and poly-substituted derivatives [1 - 7]. Reactions involving olefin complexes are less documented, despite of their relevance to photocatalytic processes such as isomerization and hydrogenation [8 - 10] of mono- and diolefins. Based on an early report [2], it was accepted that group 6B metal carbonyl complexes with \( \pi^2 \)-coordinated mono- or diolefins are at best moderately stable, which severely hampers any detailed examination of their spectroscopic and photochemical properties. It has been shown that the \( \pi^2 \)-olefin)M(CO)\(_5\) complexes are less stable than \( \pi^2 \)-olefin)\(_2\)M(CO)\(_4\) complexes [4 - 7]. The latter examples are known to be most stable if the olefinic ligands are in a trans-orthogonal arrangement [7 - 11]. The presence of a \( \sigma \)-donor ligand forces the olefin ligand to accept \( \pi \)-electron density from the metal atom. Thus a large number of \( \pi^2 \)-olefin-carbonyl-metal complexes containing one or two \( \sigma \)-donor ligands have been synthesized [12]. A similar effect is expected if the olefin has electron withdrawing substituents. This will lower the LUMO level of the olefin and thus increase its \( \pi \)-acceptor ability. The cyano substituted olefins are expected to form stable carbonyl-olefin-metal complexes of group 6B elements.

Our group has previously reported the synthesis of \( \pi^2\)-TCNE)M(CO)\(_5\), and (FN)M(CO)\(_5\) complexes (M:Cr, Mo, W) and their structures have been characterized by UV, IR and NMR spectroscopy [13, 14]. The present work aimed at the photochemical synthesis and isolation of trans-bis(olefin)tetracarbonyl-metal(0), (M = Cr, Mo, W), complexes derived from \( \pi^2\)-1,3-butadiene)M(CO)\(_4\) in the presence of tetracyanoethylene and fumaronitrile to yield trans-bis(\( \pi^2\)-tetracyanoethylene)tetracarbonyl-metal(0) and trans-bis(fumaronitrile)tetracarbonyl-metal(0) complexes of group 6B elements.

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(\pi^2\text{-1,3-butadiene})M(CO)\(_4\) + TCNE & \\
\text{\( h_\nu \), R.T} & \rightarrow \text{trans}(\pi^2\text{-TCNE})M(CO)\(_4\) \\
(1: M = Cr, 2: M = Mo, 3: M = W) & \\
(\pi^2\text{-1,3-butadiene})M(CO)\(_4\) + FN & \\
\text{\( h_\nu \), R.T} & \rightarrow \text{trans}(\text{FN})M(CO)\(_4\) \\
(4: M = Cr, 5: M = W) & \\
\end{align*}
\]

The resulting complexes were purified by using
column chromatography and recrystallization from dichloromethane. The products have been characterized by means of IR, NMR and mass spectroscopy.

Results and Discussion

The IR spectra of the complexes 1 - 5 from their dichloromethane solutions exhibit two absorption bands for the CO stretchings. The observation of only two (one of them is very weak) CO stretching vibration bands in the IR spectra immediately rules out the cis-(η^2-TCNE)_{2}M(CO)_{4} and cis-(FN)_{2}M(CO)_{4} structures with C_{2v} symmetry (four IR-active CO stretchings) in favour of the trans-(η^2-TCNE)_{2}M(CO)_{4} and trans-(FN)_{2}M(CO)_{4} geometries. Previous studies [4, 7, 11, 15, 16] have shown that transition metal complexes with trans olefinic ligands show a variety of structures, with olefinic ligands either eclipsed (D_{2h}) or staggered (D_{2d}), the D_{2d} structure being favoured, which is also shown to be favoured when the metal d-orbital and the olefin π* orbitals are close in energy. Such a reduction in the d(π*) energy separation is expected when strong electron withdrawing substituents exist in the olefinic ligands as in the case of tetracyanoethylene and fumaronitrile. Based on these previous studies, the symmetry of the synthesized complexes is assigned as D_{2d} with the two olefins in orthogonal orientation [17].

The IR spectra of the complexes 1 - 3 exhibit only one band for the CN stretchings. The most remarkable feature of the IR data is the large bathochromic shift ν_{CN} upon coordination. This shift (Δν_{CN} = ν_{CN} in free TCNE - ν_{CN} in coordinated TCNE [18]) is caused by metal (d_{z}) - olefin (π) back donation leading to a strong metal-olefin bond, and rules out coordination of the ligand through the nitrogen lone pairs for the complexes 1 - 3. By going from chromium to tungsten, one observes a smooth, noticeable decrease in both the CN and CO stretching frequencies. It reflects the effect of increasing metal (d_{z}) - olefin (π*) back donation. On the other hand, the IR spectra of the complexes 4 and 5 exhibit two absorption bands for the CN stretchings in contrast to the free fumaronitrile which has only one IR active ν_{CN} (at 2240 cm^{-1}). This implies an asymmetric coordination of the fumaronitrile ligand through its nitrile group. The small bathochromic coordination shift in the CN stretching frequency can be attributed to the M→N π-donation.

The ^{13}C NMR spectra of the complexes 1 - 5 recorded from d_{8}-toluene solutions show only one signal for the CO groups. This observation confirms the formation of trans-(η^2-TCNE)_{2}M(CO)_{4} and trans-(FN)_{2}M(CO)_{4} complexes with D_{2d} symmetry rather than cis-(η^2-TCNE)_{2}M(CO)_{4} and cis-(FN)_{2}M(CO)_{4} with C_{2v} symmetry for which two carbonyl signals of relative intensities 1:1 should be observed. The fact that the ^{13}C NMR spectra of the complexes 1 - 3 show only two signals for the tetracyanoethylene ligand indicates the coordination of the TCNE ligand to the M(CO)_{4} moiety through its C=C bond. The olefin coordination shift, Δδ = δ (free olefin) - δ (coordinated olefin), is remarkably large, as for η^2-olefin ligands. By contrast, the ^{13}C NMR signal of the CN substituents does not show a significant change upon coordination. On the other hand, the ^{13}C/^1H NMR spectra of the complexes 4 and 5 show four signals for the fumaronitrile ligands. As study of the coupled ^{13}C NMR spectra of these complexes shows that two of the four signals belong to the carbon atoms of the carbon-carbon double bond. The other two signals are assigned to the nitrile carbon atoms. The appearance of two signals for the double bond carbons with different coupling constant values indicates that the fumaronitrile ligand is bonded to the M(CO)_{4} moiety through one nitrile group nitrogen atom lone pair.

The ^1H NMR spectra of the complexes 4 and 5 in d-chloroform solutions show the appearance of two doublets in contrast to the free trans-fumaronitrile which has only one signal for the hydrogen atoms. This observation again confirms the presence of asymmetric coordination of the olefin to the central atom through its nitrile group.

It was not possible to isolate the crystals of the molybdenum complex of the fumaronitrile ligand for analysis even though the IR spectra indicate complex formation.

In all our experiments we see no evidence for the formation of any of the cis-(η^2-TCNE)_{2}M(CO)_{4} and cis-(FN)_{2}M(CO)_{4} complexes, but we have to consider the possibility that such species may be involved as short lived intermediates.

Experimental

All reactions were carried out either in a vacuum or under dry and deoxygenated nitrogen atmosphere. Solvents used were distilled after refluxing over metallic sodium
or anhydrous phosphorus pentoxide under nitrogen atmosphere for a period of four to five days. Hexacar- bonylmetal(0) (metal: Cr, Mo, W), tetracyanoethylene and fumaronitrile were purchased from Merck GmbH, Germany, and used without further purification. The photochemical reactions and other treatments were followed by IR spectra taken at appropriate time intervals.

IR spectra were recorded from dichloromethane solutions on a Jasco 430 FT-IR spectrophotometer. $^{13}$C NMR spectra were recorded from d-toluene solutions on a Bruker AMX 400 FT-NMR spectrometer at 100.62 MHz. $^1$H NMR spectra were recorded from d-chloroform solutions on a Bruker WP 200 at 200 MHz. TMS was used as an internal reference for NMR chemical shifts. Elemental analyses were carried out on a HP 185 CNH analyzer.

Mass spectra were taken on a Varian MAT 311 instrument.

trans-Bis($\eta^2$-tetracyanoethylene)tetracarbonyl-metal(0) (1), blue crystals.

A solution of 0.5 g M(CO)$_6$ [M: Cr(2.27 mmol), Mo(1.89 mmol), W(1.42 mmol)] and 1.0 g (9.26 mmol) of 1,3-butadiene in n-hexane is irradiated at 253 K for 250 min. The resulting solution is filtered and then evaporated under high vacuum, to yield ($\eta^2$-1,3-butadiene)Cr(CO)$_4$. Yield: 0.85 g (48 % rel. ($\eta^2$-1,3-butadiene)Cr(CO)$_4$).

trans-Bis($\eta^2$-tetracyanoethylene)tetracarbonyl-tungsten(0) (2), blue crystals.

Yield: 1.20 g (56 % rel. ($\eta^2$-1,3-butadiene)Cr(CO)$_4$, C$_{16}$CrO$_4$N$_8$ (464.15) molar mass by mass spectroscopy 465 g mol$^{-1}$. IR($\nu_{\max}$/ cm$^{-1}$, CH$_2$Cl$_2$): 2175 (CN), 1993(w), 1964(vs) (CO). $^{13}$C NMR (100.62 MHz, C$_2$D$_2$): $\delta$ = 111.62 (C=C), 106.90 (CN), 205.60 (CO) ppm. C$_{16}$CrO$_4$N$_8$ (464.15): calcd. C 41.38, N 24.14; found C 40.65, N 24.78.

trans-Bis($\eta^2$-tetracyanoethylene)tetracarbonyl-chromium(0) (3), blue crystals.

Yield: 0.85 g (48 % rel. ($\eta^2$-1,3-butadiene)Cr(CO)$_4$).

trans-Bis(fumaronitrile)tetracarbonyl-tungsten(0) (4), red crystals.

Yield: 0.85 g (72% rel. ($\eta^4$-1,3-butadiene)Cr(CO)$_4$).

trans-Bis($\eta^2$-tetracyanoethylene)tetracarbonyl-chromium(0) (5), red crystals.

Yield: 0.55 g (50 % rel. ($\eta^4$-1,3-butadiene)Cr(CO)$_4$).

trans-Bis($\eta^2$-tetracyanoethylene)tetracarbonyl-molybdenum(0) (1), blue crystals. Yield: 1.60 g (64% rel. ($\eta^2$-1,3-butadiene)Cr(CO)$_4$. C$_{16}$CrO$_4$N$_8$ (420.21) molar mass by mass spectroscopy 420 g mol$^{-1}$. IR($\nu_{\max}$/ cm$^{-1}$, CH$_2$Cl$_2$): 2180 (CN), 1994(w), 1965(vs) (CO). $^{13}$C NMR (100.62 MHz, C$_2$D$_2$): $\delta$ = 112.92 (C=C), 106.92 (CN), 208.82 (CO) ppm. C$_{16}$CrO$_4$N$_8$ (420.21): calcd. C 45.71, N 26.67; found C 45.25, N 27.14.

trans-Bis($\eta^2$-tetracyanoethylene)tetracarbonyl-molybdenum(0) (2), blue crystals.

Yield: 1.20 g (56 % rel. ($\eta^2$-1,3-butadiene)Cr(CO)$_4$. C$_{16}$MoO$_4$N$_8$ (464.15) molar mass by mass spectroscopy 465 g mol$^{-1}$. IR($\nu_{\max}$/ cm$^{-1}$, CH$_2$Cl$_2$): 2175 (CN), 1993(w), 1964(vs) (CO). $^{13}$C NMR (100.62 MHz, C$_2$D$_2$): $\delta$ = 111.62 (C=C), 106.90 (CN), 205.60 (CO) ppm. C$_{16}$CrO$_4$N$_8$ (464.15): calcd. C 41.38, N 24.14; found C 40.65, N 24.78.
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