A DFT and structural investigation of the conformations of Fischer carbene complexes

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Abstract. A set of different Fischer carbene complexes of group VI and VII metals, with varied heteroatom and heteroaromatic substituents on the carbene carbon atom, was studied. Density functional theory as well as single crystal diffraction techniques were employed to investigated the most stable conformation of these complexes. The complexes studied, [M(CO)$_4$L{C(X)Z}], with L = PPh$_3$ or CO, X = ethoxy (-OCH$_2$CH$_3$) or amino (-NH$_2$ or NHCy) substituents as the heteroatom carbene substituents, Z = 2-furyl (-C$_4$H$_3$O), 2-thienyl (-C$_4$H$_3$S), 2-(N-methyl)pyrrolyl (-C$_4$H$_3$NCH$_3$) as the second carbene substituent had their substituents varied systematically to give all the possible conformations of these complexes. The conformations of the complexes, in particular the relative orientations of the heteroatoms in the molecule (syn vs. anti), E/Z isomerism in the aminocarbene complexes and cis/trans isomerism in the ligand substituted complexes as well as various combinations of these aspects, were studied. In general, it was found that the most stable conformation theoretically as well as in the solid state for most of the complexes preferred the syn conformation. The Z-isomer is generally preferred over the E isomer while the cis is more predominant than the trans isomer. Using DFT and NBO calculations, explanations for the preferred conformations were explored. It was concluded that both steric and electronic factors influence the conformations of the carbene complexes, with the extent of contribution of these two factors varying for each of the different carbene substituents.

1. Introduction
Since the discovery of the first transition metal carbene complex, (CO)$_5$W=C(Ph)(OMe), in 1964 [1], Fischer carbene complexes have attracted attention as useful compounds in organic syntheses [2] and in catalytic processes [3]. Isomerism in Fischer carbene complexes has been shown to influence the reactivity and final product formation in reactions with different isomers [4].

Studies focusing on the synthesis, electronic (particularly of the M-C$_{carbene}$ bond) and spectroscopic properties of Fischer carbene complexes have been reported in the early 1970’s[5]; however, little has been reported on the structure of these complexes, and more specifically on the conformations of these molecules. Selected mononuclear Fischer-type carbene complexes with heteroaromatic substituents of the form [M(CO)$_4$L{C(X)Z}], with L = PPh$_3$ or CO, X = ethoxy (-OCH$_2$CH$_3$) or amino (-NH$_2$ or NHCy) substituents as the heteroatom carbene substituents, Z = 2-furyl (-C$_4$H$_3$O), 2-thienyl (-C$_4$H$_3$S), 2-(N-methyl)pyrrolyl (-C$_4$H$_3$NCH$_3$) of group VI metals have been synthesized and the different isomers/conformers formed in the reactions were studied using X-ray crystallography. In this study we report the experimental results compared with DFT calculated data for the different possible conformations.
2. Results and discussion

2.1. Pentacarbonyl metal carbene complexes

For the pentacarbonyl metal carbene complexes with general formula \([\text{M(CO)}_5\{\text{C(X)Z}\}]\), with \(\text{X} = \text{OEt or NH}_2\) and \(\text{Z} = \text{2-furyl, 2-thienyl or 2-(N-methyl)pyrrolyl}\), six model chromium complexes were investigated. Similar results were obtained with selected Mo and W complexes and therefore these six complexes can be seen as representative of group VI metal Fischer carbene complexes [6]. The complexes are listed in Table 1.

| Complex | \(\text{X Substituent}\) | \(\text{Z Substituent = C}_4\text{H}_3\text{Y}\) |
|---------|-----------------|-----------------|
| 1       | \(\text{OEt}\)  | 2-Furyl         |
| 2       | \(\text{OEt}\)  | 2-Thienyl       |
| 3       | \(\text{OEt}\)  | 2-(N-Methyl)pyrrolyl |
| 1\*     | \(\text{NH}_2\) | 2-Furyl         |
| 2\*     | \(\text{NH}_2\) | 2-Thienyl       |
| 3\*     | \(\text{NH}_2\) | 2-(N-Methyl)pyrrolyl |

For these pentacarbonyl metal carbene complexes, only one conformational difference is possible. This difference lies in the orientation of the heteroatom (\(\text{Y}\)) of the heteroarene carbene substituent (\(\text{Z} = \text{C}_4\text{H}_3\text{Y}\)) relative to the heteroatom substituent (\(\text{X}\)), leading to \textit{syn} or \textit{anti} conformations (see figure 1).

\[
\text{Syn} \quad \text{Anti}
\]

\[
\begin{align*}
\text{X} & = \text{OEt, NH}_2 \\
\text{Y} & = \text{O, S, NMe} \\
\text{L} & = \text{CO, PPh}_3
\end{align*}
\]

\textbf{Figure 1. Syn versus Anti conformations}

To determine the lowest energy conformation of the heteroaromatic substituent using DFT calculations, an energy scan around the dihedral angle of interest (\(\text{X-Carbene-C-Y}\)) was performed to ascertain at which dihedral angle a minimum conformation of the complex can be expected. In this way the minimum energy \textit{syn} and a \textit{anti} conformations were obtained, as well as the transition between the two conformations. Default convergence criteria were used during the geometric optimizations. Vibrational frequencies were calculated at the optimized \textit{syn} and \textit{anti} geometries and no imaginary frequencies were observed for the \(E_{\text{min}}\) conformers. DFT calculated data is summarized in Table 2. From the data in the table it is clear that the predominantly favoured conformation for pentacarbonyl metal carbenes, is the \textit{syn} conformation. The only complex for which the \textit{anti} form (with the \(\text{X-C-C-Y}\) angle 180\(^\circ\)) is most favoured is 1, a 2-furyl complex. The DFT theoretical model predicts the geometries of the carbene complexes studies particularly well when compared to experimentally determined X-ray crystal structures.
Table 2. Results of syn- and anti conformation optimization of 1-3*

| Complex | Dihedral Angle X-C-C-Y (°) | Conformation | Energy (kJ/mol) | Boltzmann Distribution |
|---------|---------------------------|--------------|----------------|------------------------|
| 1       | 0.0                       | Syn          | 7.6            | 4.5%                   |
|         | 180.0                     | Anti         | 0.0            | 95.5%                  |
|         | 90.0                      | TS¹          | 51.2           |                        |
| 2       | 0.0                       | Syn          | 0.0            | 99.4%                  |
|         | 177.3                     | Anti         | 12.8           | 0.6%                   |
|         | 90.0                      | TS           | 42.7           |                        |
| 3       | 4.2                       | Syn          | 0.0            | 100%                   |
|         | 153.1                     | Anti         | 23.9           | 0%                     |
|         | 90.0                      | TS           | 43.7           |                        |
| 1*      | 0.0                       | Syn          | 0.0            | 99.6%                  |
|         | 170.7                     | Anti         | 13.8           | 0.4%                   |
|         | 90.0                      | TS           | 48.6           |                        |
| 2*      | 23.5                      | Syn          | 0.0            | 93.9%                  |
|         | 148.9                     | Anti         | 6.7            | 6.1%                   |
|         | 90.0                      | TS           | 22.5           |                        |
| 3*      | 26.9                      | Syn          | 0.8            | 42.0%                  |
|         | 144.0                     | Anti         | 0.0            | 58.0%                  |
|         | 90.0                      | TS           | 19.1           |                        |

Data from ref [6]

To understand the preferred anti form of 1, and NBO analysis was performed. The NBO calculations indicate a stabilising interaction in [Cr(CO)₅(C(OEt)₂-furyl)], 1, between the lone pair of electrons on the furyl oxygen atom and an empty antibonding orbital of the neighbouring carbonyl groups when the molecule adopts an anti conformation (figure 2). This interaction is absent or < 0.2 kJmol⁻¹ in the anti-conformation of each of the other cases.

Figure 2. NBO-calculated donor-acceptor interaction in 1

For the pentacarbonyl metal carbene complexes with general formula [M(CO)₅(C(X)Z)], with X = NHCy and Z = 2-furyl or 2-thienyl, two model tungsten complexes were investigated. Due to the amino group containing two different substituents (H and Cy), one can distinguish between E- and Z-conformation of the Cy group relative to the metal M (figure 3).
This isomerism in combination with the possible \textit{syn} or \textit{anti} conformations of the heteroaryl substituent, lead to four different possible conformations for each complex. These four conformations were optimized with DFT to determine the lowest energy conformation.

**Table 2. DFT results of optimization of 4 and 5**

| Complex | Conformation | PW91  | B3LYP | % NMR | X-ray structure | PW91  |
|---------|--------------|-------|-------|-------|-----------------|-------|
| 4       | \(\text{syn,Z}\)  | 0.00  | 0.00  | 96.7  | Crystal structure | 0.38  |
|         | \(\text{anti,Z}\) | 0.13  | 0.14  |       |                 |       |
|         | \(\text{syn,E}\)  | 0.16  | 0.15  | 3.3   |                 | 0.25  |
|         | \(\text{anti,E}\) | 0.21  | 0.22  |       |                 |       |
| 5       | \(\text{syn,Z}\)  | 0.00  | 0.00  | 87.7  | 56 \% disorder  | 0.18  |
|         | \(\text{anti,Z}\) | 0.03  | 0.03  |       | 44 \% disorder  |       |
|         | \(\text{syn,E}\)  | 0.11  | 0.10  | 12.3  |                 | 0.09  |
|         | \(\text{anti,E}\) | 0.12  | 0.11  |       |                 |       |

Data from ref [6]

The lowest energy conformer in each case was the \(\text{syn,Z}\) conformer, the same conformer as was characterized by X-ray crystallography. The barrier of rotation of a furyl ring is on average 0.2 eV larger than that of the thienyl ring for related complexes. The rotation barrier of the \(\text{Z}\) isomers is generally higher than that of the \(\text{E}\) isomers.

2.2. \textit{Tetracarbonyl metal carbene complexes}

For the tetracarbonyl carbene complexes, such as 6-8 in figure 4, one can distinguish between \textit{cis} and \textit{trans} isomers, with respect to substitution by \text{PPh}$_3$ relative to the carbene ligand. Three model molybdenum complexes of general formula [\(\text{M(CO)}$_5$L\{C(X)Z\}\)], with \(L = \text{PPh}_3, X = \text{OEt}, \text{NH}_2\) or \text{NHCy} and \(Z = 2\)-furyl will be discussed. It is suggested on grounds of pi acceptor/donor arguments that the \textit{cis} complex is formed by preference because the phosphine reduces the electrophilicity of the \textit{trans}-carbonyl carbon due to the increased backbonding from the metal. The CO group trans to the M=carbene bond is therefore less available to react with the organolithium reagent, hence reducing the chance of the \textit{trans} isomer forming. However, in a recent paper both \textit{cis}- and \textit{trans} isomers of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Z-isomer versus \(\text{E}\)-isomer}
\end{figure}
[
\begin{align}
\text{[(CO)}_4\text{(PPh)}_3\text{W=C(OEt)(2-furyl)]}
\end{align}
were reported and a crystal structure for the trans isomer was obtained [7].

For each of the Mo-carbene complexes shown in figure 4, a number of conformers of the different isomers are possible. Complexes 6-8 have PPh\textsubscript{3} ligands in the cis position relative to the carbene ligand, either nearest to the furyl ring or nearest to the heteroatom substituent X (OEt, NH\textsubscript{Cy} or NH\textsubscript{2}), leading to four, eight and four possible cis-PPh\textsubscript{3} conformers, respectively. If the PPh\textsubscript{3} is in the trans position, two, four and four trans-PPh\textsubscript{3} conformers are possible, respectively, in combination with syn or anti and E or Z configurations, where applicable (Table 4).

![Figure 4. Phosphine-substituted carbene complexes 6-8](image)

**Table 4.** DFT results of optimization of 6-8

| Complex | Conformation         | Relative energy/ kJmol\textsuperscript{1} |
|---------|----------------------|--------------------------------------------|
| 6       | cis-anti (1)         | 0.0                                        |
|         | cis-syn (1)          | 7.5                                        |
|         | cis-anti (2)         | 1.1                                        |
|         | cis-syn (2)          | 8.1                                        |
|         | trans-anti           | 7.6                                        |
|         | trans-syn            | 17.1                                       |
| 7       | trans-anti, Z        | 18.3                                       |
|         | trans-anti, E        | 24.8                                       |
|         | trans-syn, Z         | 7.4                                        |
|         | trans-syn, E         | 19.0                                       |
|         | cis-anti, Z (1)      | 8.2                                        |
|         | cis-anti, E (1)      | 14.1                                       |
|         | cis-syn, Z (1)       | 0.04                                       |
|         | cis-syn, E (1)       | 10.6                                       |
|         | cis-anti, Z (2)      | 13.7                                       |
|         | cis-anti, E (2)      | 11.2                                       |
|         | cis-syn, Z (2)       | 0.0                                        |
|         | cis-syn, E (2)       | 0.2                                        |
| 8       | cis-syn (2)          | 0.0                                        |
|         | cis-anti (2)         | 15.3                                       |
|         | cis-anti (1)         | 20.5                                       |
|         | cis-syn (1)          | 6.4                                        |
|         | trans-anti           | 30.0                                       |
|         | trans-syn            | 16.9                                       |
The experimental solid state crystal structures of the complexes corresponded to the lowest DFT calculated gas phase electronic energy conformation determined by DFT calculations for 6-8. However, it was possible to obtain also the E-isomer of 7 in the solid state. The corresponding E-isomer is only 0.2 kJ/mol higher in energy as the lowest energy Z-isomer. Therefore it is concluded that both are experimentally feasible. Further DFT calculations showed that the shorter experimental and DFT calculated intramolecular distance N–H · · · O_{Fu} in cis-syn,Z (2) and the stronger conjugative LP_{1}(O) → BD^{*}(N–H) NBO calculated interaction associated with cis-syn,Z (2) compared to the related properties of the C–H · · · O_{Fu} hydrogen bond in cis-syn,E (2), confirm the higher stabilization of the Z configuration of 7 compared to that of 7-E (figure 5).

![cis-syn,Z (2) and cis-syn,E (2)](image)

**Figure 5.** Two isomers of 7

3. Conclusion
The experimental and DFT calculated results correlated very well. It was possible to explain the conformational preference of the metal carbonyl carbene systems, obtained experimentally, with DFT calculations.

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