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Computational and experimental structural studies of selected chromium(0) monocarbene complexes

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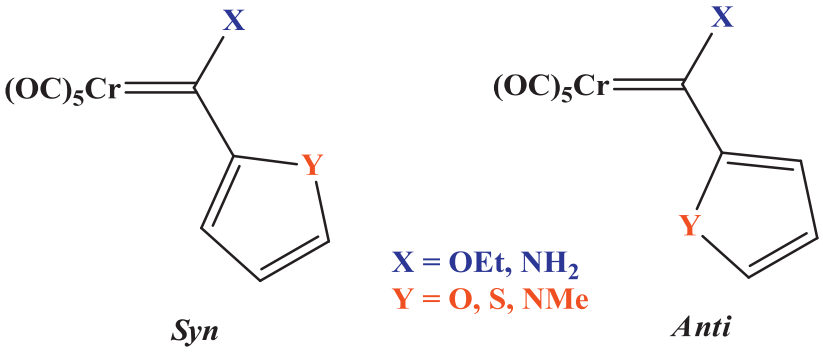
HIGHLIGHTS

- Synthesis of chromium Fischer carbene complexes, with different heteroatom and heteroaromatic substituents.
- Density functional theory calculations on different conformations of the carbene substituents.
- Comparison with X-ray crystal structures.
- NBO calculations of carbonyl-heteroarene interactions.

GRAPHICAL ABSTRACT

A DFT and X-ray structural study was undertaken to explain the preference for the *anti* conformation of the carbene complex $[Cr(CO)_5C(OEt)(F)]$, (F = 2-furyl) **1**, while the trend for analogous heteroarene-containing carbene complexes with general formula $[Cr(CO)_5C(X)(Z)]$, (X = OEt, NH_2; Z = 2-furyl, 2-thienyl) is to exhibit the *syn* conformation.



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Dedicated to the memory of Professor Casper J.H. Schutte (1934–2013)

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ABSTRACT

A set of chromium Fischer carbene complexes, with different heteroatom and heteroaromatic substituents on the carbene carbon atom, were studied. Density functional theory as well as single crystal diffraction techniques were employed. The complexes studied, $[Cr(CO)_5\{C(X)Z\}]$, had their substituents varied systematically to give six complexes, with X = ethoxy ($-OCH_2CH_3$) or amino ($-NH_2$,) substituents as the heteroatom substituents and Z = 2-furyl ($-C_4H_3O$), 2-thienyl ($-C_4H_3S$), or 2-(N-methyl)pyrrolyl ($-C_4H_3NCH_3$) as the heteroaromatic substituents. These complexes were studied in terms of the conformation of the complexes, in particular the dihedral angle between the heteroatom of the heteroatom substituent and the heteroatom of the heteroaromatic substituents. Five of the six complexes preferred the *syn* conformation, which seems to be the trend for this type of complex. Only one complex, $[Cr(CO)_5\{C(OEt)2\text{-furyl}\}]$, (**1**), has a distinct preference for the *anti* conformation according to DFT calculations. Calculated and experimentally measured infrared vibrational spectra of the complexes were compared. X-ray structural studies in the solid state were performed for all six of the complexes. It was found that these structures corresponded to the calculated structures. Using NBO calculations, an explanation for the unexpected *anti* conformation of $[Cr(CO)_5\{C(OEt)2\text{-furyl}\}]$, (**1**) was investigated. 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.

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1. Introduction

Selected mononuclear Fischer-type carbene complexes with heteroaromatic substituents of the form $[(CO)_5CrC(X)Z]$, where X is a heteroatomic substituent (ethoxy, amino), and Z is the heteroaromatic substituent (2-furyl, 2-thienyl and 2-(N-methyl)pyrrolyl) have been studied since the 1970s. These studies focused on the complexes' synthesis, electronic (particularly of the $M—C_{carbene}$ bond) and spectroscopic properties [1–3], however, there was little study of the structure, and more specifically the conformations of these molecules. Synthetically, these carbene complexes were produced from hexacarbonylchromium(0) and the specific lithiated reagents [1] or from the [acetoxy(2-furyl)carbene] pentacarbonylchromium complex, with reactions from the starting complex being similar to that of an acid anhydride. The spectroscopic studies [1,2] included IR, UV, Visible and NMR spectral studies, and were directed at the investigation of the electronic properties of these complexes, specifically the donation of electron density from X and Z into the empty *p* orbital on the carbene carbon. By examination of the changes in the chemical shift values of particular protons in the complexes, it was concluded that stabilization occurs by conjugative release of electrons from the heteroaromatic substituent [1]. The NMR studies provided further insight into the electronic character of the complex, specifically at the carbene carbon [2]. This includes the fact that electronic character of the carbene carbon is more strongly influenced by the X group than either the metal or Z group. Further evidence was also provided to support that Z releases electron density through conjugative release, rather than specific $\pi \rightarrow p$ donation.

There have also been a number of studies on the use of these specific classes of carbene complexes in certain reactions, primarily for $[Cr(CO)_5\{C(OEt)2\text{-thienyl}\}]$, (**2**), and its involvement in phosphaannulation reactions [4], ketenimine complex formation [5] and aldehyde production [6]. This highlights the potential use of these complexes in organic synthesis, though there has been little investigation into the reactions of the other complexes.

Electrochemical studies of some of these carbene complexes were undertaken in order to study the electronic influences of the ligands [7]. It was found in these studies that the half wave potential ($E_{½}$) of the oxidation of these complexes followed the σ-donor/π-acceptor ratios of the ligands.

Investigations into the conformation of the ethoxy substituent of Fischer carbene complexes found, both computationally and experimentally, that two possible conformations exist, designated *syn* and *anti*, as shown in Fig. 1 [8]. It was found computationally that the *anti* conformation was more stable, and this was corroborated by available X-ray crystallographic data. The conformation was explained as being due to an electronic interaction between the R_1 group and two of the carbonyl ligands on the metal atom. This interaction was then concluded to stabilize the predicted lowest energy form of the complex, i.e. the *anti* form.

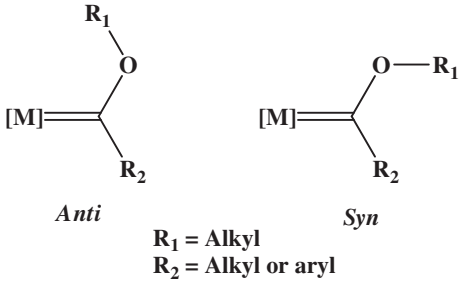


Fig. 1. *Syn* and *anti* conformations of alkoxy substituents of carbene complexes [8].

The study described in this paper focused on the conformation of the heteroaromatic substituent (R_2) of the above-mentioned complexes. The complexes which were studied are listed in Table 1. In all calculations the complexes exhibited the *anti* conformation of the R_1 group relative to the R_2 group and the *syn* conformation was not investigated.

The complexes listed in Table 1 were chosen to provide a representative set of the possible carbene complexes, with the systematic variation of the X and Z substituents being done to allow the study of the various potential interactions, and to allow the development of a model whereby the effect of each substituent can be compared in a systematic fashion. The conformations investigated are shown in Fig. 2, and were labelled *syn* and *anti* with respect to the positions of the two heteroatoms in the molecule.

The conformations were assigned based on the dihedral angle X—C—C—Y, where a dihedral angle equal or close to 0° was assigned the *syn* conformation, while a dihedral angle of approximately 180° indicated an *anti* conformation. These two conformations are the most favourable, as they allow for a complete alignment of the p-orbitals in the molecule, favouring the formation of a conjugated, delocalised electronic system, which would contribute to the overall stability of this class of complexes.

2. Experimental

2.1. General

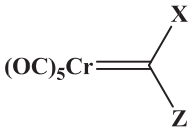
All syntheses were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen or argon gas. Solvents were dried prior to use. Triethyloxonium tetrafluoroborate was synthesised according to the literature method [9]. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 spectrometer in $CDCl_3$ (**1**–**5**) or $(CD_3)_2CO$ (**6**) as solvent. ^1H NMR spectra were recorded at 300.135 MHz and ^{13}C NMR spectra at 75.469 MHz with the solvent signal as reference. Infrared spectra were recorded as KBr pellets on a PerkinElmer Spectrum RX FT-IR instrument and the vibrational bands of the carbonyl ligands in the region 1700–2200 cm^{-1} reported.

2.2. Synthesis

Complexes **1**–**6** were synthesised similar to known literature methods [10]. Although the complexes **1**–**5** have been synthesised previously [1,11], the NMR data supplied in literature were limited and therefore the data are reported here. IR data of **1**–**6** are reported in Table 4.

$[Cr(CO)_5\{C(OEt)2\text{-Furyl}\}]$, **1**: ^1H NMR(δ(ppm), J(Hz)): H10 7.82 (d), 3.7; H8 6.56 (dd), 3.7; H9 6.96 (d), 3.7; $O\mathbf{CH_2}CH_3$ 5.15 (q), 6.9; $OCH_2\mathbf{CH_3}$ 1.67 (t), 6.9. ^{13}C NMR (δ_{ppm}): C(carbene) 310.8;

Table 1
List of complexes.



Complex	X Substituent	Z Substituent
1	OEt	2-Furyl
2	OEt	2-Thienyl
3	OEt	2-(N-Methyl)pyrrolyl
4	NH_2	2-Furyl
5	NH_2	2-Thienyl
6	NH_2	2-(N-Methyl)pyrrolyl