



## Structural flexibility of 2-hetaryl chromium aminocarbene complexes: Experimental and theoretical evidence



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### ABSTRACT

Chromium aminocarbene complexes  $[(CO)_5Cr=C(N(CH_3)_2)R]$ ,  $R = N$ -methyl-2-pyrrolyl, 2-thienyl and 2-furyl were prepared and structurally characterized. X-ray study indicated two stable rotamers in case of compounds containing 2-thienyl and 2-furyl substituents. DFT calculations well interpreted structural parameters of all studied complexes. Calculations of potential energy surfaces (PES) for neutral species confirmed existence of two energy minima on the potential energy surfaces. Calculated rotation barriers increase in the series 2-furyl, 2-thienyl and  $N$ -methyl-2-pyrrolyl, respectively. The PES scans for compounds in one-electron reduced states essentially reveal opposite behavior to the one observed for neutral complexes. Connection is drawn between the observed structural flexibility and electrochemical properties of the compounds.

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### 1. Introduction

Carbene complexes are characterized by presence of a metal–carbon double bond,  $[L_nM=CR_2]$ . Polarity of the  $M=C$  bond ensues from electronic properties of the central metal and the ligands and this characteristic feature divides carbene complexes into two main groups: Schrock carbenes with nucleophilic character of the carbene carbon,  $M^{\delta+}=C^{\delta-}$ , and Fischer carbenes with the bond polarized the opposite way,  $M^{\delta-}=C^{\delta+}$ . Constant interest is focused on their reactivity and properties, papers dealing with carbene complexes are reviewed annually. The most recent review on carbene and carbyne compounds covers more than 1100 works [1].

Fischer carbenes, possessing electrophilic character of the carbene carbon, are stabilized by an electron rich heteroatom, mostly oxygen or nitrogen, bonded to the carbene carbon atom. The whole structure can be described as  $[L_nM=C(OR)R']$  (alkoxycarbenes) and  $[L_nM=C(NR_2)R']$  (aminocarbenes). Delocalized  $\pi$ -electron system is present along the  $M=C-X$  bonds ( $X = O, N$ ) and electron distribution in the carbene ligand and reactivity of this ligand is modified also by electron donating–withdrawing character of the substituent  $R'$  on the carbene carbon. Nucleophilic character of the metal atom is further stabilized by  $\pi$ -accepting ligands such as carbonyl

groups coordinated to the metal atom in place of the ligands  $L$  in the formulae [2].

Relationship between the carbene complex structure and its reactivity can be evaluated electrochemically by measuring its oxidation and reduction potentials,  $E_{ox}$  and  $E_{red}$ . In accordance with the typical  $M=C$  polarity of Fischer type carbene complexes it was found that  $E_{ox}$  values depend mainly on the central metal nature. On the other hand,  $E_{red}$  values are very sensitive to the carbene ligand structure, i.e., nature of the heteroatom (alkoxycarbenes are reduced more easily than aminocarbenes due to higher electronegativity of O) and electron donating properties of the carbene carbon substituent  $R'$  [3,4].

Large series of complexes may be treated by Linear Free Energy Relationship [5] (LFER) method. Here the Hammett equation  $E_{red} = \rho \cdot \sigma + c$  is introduced, slope  $\rho$  of which being proportional to extent of electronic communication between the substituent  $R'$  and the carbene carbon as the reduced part of the molecule. Electrophilicity/reducibility of series of about 40 chromium, iron and tungsten aminocarbene complexes with variously substituted phenyl group in place of  $R'$ ,  $[(CO)_nM=C(NR_2)(Ph-X)]$ , was described this way. The results [3,6] showed that ease of the reduction process depends at the same time on electron donating properties of the carbene carbon substituents and on presence of a delocalized  $\pi$ -electron system, which encloses both the  $M=C-NR_2$  system and the phenyl ring. In order to achieve such extended conjugation, it is necessary that the

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plane of the three  $\sigma$  bonds of the carbene carbon (M=C–N, “carbene plane”) is capable of achieving coplanar orientation with respect to the plane of the phenyl ring. While in solid state the phenyl substituent is always perpendicular to the carbene plane [7], it rotates in solution and this rotation seems to add an important contribution to the structure – reactivity description. When the free rotation of the phenyl ring in solution is hindered [8] (e.g. by presence of a bulky substituent), electronic communication within the molecule diminishes and the slope of the Hammett equation decreases.

In order to distinguish between inductive and mesomeric effects of the carbene carbon substituent R', a series of chromium aminocarbenes was synthesized where five-membered heterocycles were introduced in place of the substituent R': furan, thiophene and *N*-methylpyrrole bound to the carbene carbon as 2-hetaryl or 3-hetaryl residues [9]. Electrochemical behavior of these compounds confirmed the important role of the delocalized  $\pi$ -electron system in course of reduction, the reduction process being less difficult concerning molecules with the 2-hetaryl substituents, in accordance with their ability to conjugate with the rest of the molecule. However, unexpected behavior was observed when *N*-methyl-2-pyrrolyl residue was used in place of the R', reduction of this compound being the most difficult. The exceptionally low  $E_{\text{red}}$  in this case was explained by lack of conjugation throughout the carbene ligand caused by hindered rotation of the heterocycle due to the bulky methyl group on the pyrrole ring.

The importance of steric substituent effects besides the electronic effects has been recognized and it was studied by Bezuidenhout et al. [10,11] on structurally related alcoxycarbene complexes and complexes with metal-containing substituents, and by Andrada et al. [12] on alcoxycarbene and thiocarbene complexes.

The present work focuses on the recently reported 2-hetaryl chromium aminocarbene complexes with heteroaromatic substituents on the carbene carbon. The aim of this work is to describe in detail and quantify structural flexibility of these compounds. Trends found in experimentally observed rigidity of crystal structures are compared with calculated values of the rotation barriers. The mutually complementing sets of data are used to stress the importance of the structural effects on electrochemistry of the studied complexes.

## 2. Experimental

### 2.1. Synthesis and crystal preparation

All compounds were synthesized according to the published procedures [9]. Suitable crystals of **1** and **2** were prepared from acetonitrile (AN) solutions: 50 mg of the compound was dissolved in 5 mL of extra dry AN 99.9% (water <10 ppm), Acros Organics, and deaerated by a stream of argon. The solvent was then distilled off the solution using standard Schlenk technique. Single crystals of good quality were readily formed in case of compound **1**. In order to obtain crystals of compound **2**, the solvent had to be slowly distilled for about 5 hours while the apparatus was protected from light. Crystals of compound **3** could not be prepared this way as the solution decomposed prior to appearance of the solid phase. Crystals were prepared from a solution of compound **3** in hexane–dichloromethane 1:1 (hexane 95+% mixture of isomers by Acros Organics, dichloromethane p.a. by Lachner): 130 mg of compound **3** was dissolved in 5 mL of the solvent mixture deaerated by argon and the resulting solution was filtered into a Schlenk tube protected from light. Crystals were obtained after 4 hours of slow vacuum evaporation of the solvent.

### 2.2. Structure determination

The crystallographic data for compounds **1**, **2** and **3** were collected at 170 K using graphite monochromated Cu  $K\alpha$

(1.54180 Å) on Xcalibur Onyx CCD diffractometer. The structures were solved using direct methods [13] and charge flipping methods [14] and refined using full-matrix least-squares refinement against  $F^2$ . CRYSTALS suite of programs [15] and JANA2006 suite of programs [16] were used. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in idealized positions and were allowed to refine riding on parent atom.

Disorder very close to the mirror plane was observed in structure **2**. Both of the disordered parts are related by the mirror plane. The symmetry of the model was not lowered, since the solution in lower symmetry was of significantly low stability and was not followed by decrease of R factors.

The disordered furyl ring in structure **3** was refined using rigid body refinement, keeping the geometry equal for the both positions. Since there are no stereogenic centers in the molecule the unambiguous Flack parameter (0.438(19)) is not an issue.

The crystallographic data for all the compounds are summarized in Table 1.

### 2.3. Quantum chemical calculations

Theoretical calculations of the studied complexes were performed using the GAUSSIAN 09 (G09) [17] program package. Density functional theory (DFT) was employed as suitable computational method. For optimizations of the molecules' geometries, Becke's three-parameter hybrid functional (B3LYP) [18,19] was used together with triple- $\zeta$  polarized 6-311G(d,p) [20] basis sets for C, O, N, Si and H atoms, 6-311G(3df) [21,22] for Cr atom and 6-311+G(3df) [23] basis set for S atom. The geometry optimizations were done on complexes in the ground state (neutral structures) as well as on complexes in one-electron reduced state with negative (–1) charge. To verify character of the stationary states, vibrational analyses were carried out following the geometry optimizations. No symmetry constraints were applied in any of the calculations. All the calculations were carried out *in vacuo*, i.e. without interactions with any other medium or particles. To obtain values of molecular orbital energies for comparison with the electrochemical data, structures of the ground state compounds were recomputed under the same conditions including effect of solvation using the polarizable continuum model (PCM) [24].

In the next step, relaxed potential energy surface (PES) scan was performed for the complexes in both the neutral and reduced states. The previously optimized structures were taken as initial points and same basis sets were used as in the geometry optimization calculations. During the PES scan, the geometry of the molecule was re-optimized while an angle of rotation of the heteroaromatic residue was kept fixed. In each step of the scan, the torsion angle was changed by a defined value until the initial state was reached. This way the dependence of electronic energy of the molecules on rotation of the heteroaromatic residue was surveyed.

## 3. Results and discussion

### 3.1. Description of the crystal structures

The recently published studies on electrochemical behavior of Fischer aminocarbene complexes with aromatic and heteroaromatic substituents on the carbene carbon have indicated that structural flexibility of these molecules may influence their redox properties, particularly the reduction potential [3,9]. In order to better describe and quantify this effect, a combined experimental and theoretical study was carried out on a series of mutually analogous complexes. An attempt was done to prepare monocrystals of three 2-hetaryl chromium aminocarbenes, structures of which differ only in the heteroatom in the cyclic substituent. General

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