Electrochemical study of Chromium(0) Fischer Carbene complexes: Trends in redox potential

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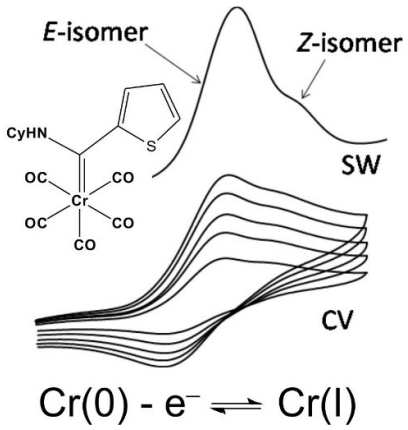


Keywords:

Fischer carbene; electrochemistry; DFT; chromium; isomer

Highlights

- Electrochemical study of Fischer ethoxy- and aminocarbenes
- Distinguish between oxidation potential of *E* and *Z* isomer of Cr-aminocarbene

- Computational chemistry of ethoxy- and aminocarbene isomers and conformations
- Linear relationship between redox potentials and frontier orbital energies

Synopsis

The redox potentials of chromium(0) Fischer carbene complexes containing a heteroaromatic substituent can be determined to a high degree of accuracy utilizing DFT methods and experimental redox potentials values.

Abstract

It is illustrated that the electrochemical redox potentials of chromium(0) Fischer carbene complexes containing a heteroaromatic substituent can be determined to a high degree of accuracy from the gas phase density functional theory (DFT) optimized frontier orbital energies, with a mean average error of the calculated redox potentials of 0.047 V for the chromium-based oxidation potential and 0.057 V for the carbene ligand based reduction potential. For the first time it was possible to distinguish between the $Cr^{0/I}$ oxidation peaks of the *E* and the *Z*-isomer of a cyclohexylamino pentacarbonyl chromium Fischer carbene complex, namely [$(CO)_5$CrC(NHCy)(2-thienyl)]. The linear relationship obtained between the oxidation potential and the DFT calculated highest molecular orbital energies, made it possible to assign the oxidation peak at the lower less positive oxidation potential to the oxidation of the *E* isomer, and the peak at the slightly higher (more positive) oxidation potential to the oxidation of the *Z* isomer of [$(CO)_5$CrC(NHCy)(2-thienyl)].

1. Introduction

Several applications of carbene complexes rely on their electrochemical properties. For instance, to serve as electrochemical probes in PNA-DNA recognition, chromium Fischer carbene complexes were identified as a class of compounds of significant electrochemical activity [1]. The easily detected CO bands in the IR spectra could be used as tool for the analytical detection of a metal-modified biomolecule. It was observed that by changing carbene substituents as well as the ligand environment, the electrochemical properties of the Fischer carbene complex could be modulated. Electrochemistry has also been used to determine the rate of heterogeneous electron transfer for carbene catalysts in cycloaddition reactions [2].

Electrochemical studies on different chromium Fischer-type carbene complexes were done by polarography and cyclic voltammetry methods [1-9]. Generally a chromium metal oxidation and a carbene carbon reduction process were observed. Both the oxidation and reduction of pentacarbonyl chromium(0) Fischer ethoxycarbene complexes of the general formula $[(CO)_5CrC(X)(OEt)]$, where X is the heteroaromatic substituent such as 2-furyl (Fu), 2-thienyl (Th) or 2-(N-methyl)pyrrolyl, are found to be linearly related to DFT calculated energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the complexes respectively [10]. The oxidation process was found to be dependent on the electrophilic character of the heteroarene ring. The same behaviour regarding the heteroarene ring (2-furyl *vs* 2-thienyl) was also detected for tricarbonyl chromium(0) Fischer carbene complexes [11], where two of the carbonyl groups were substituted by phosphine ligands and the heteroatomic substituent was either an ethoxy or an amino group. An NMR study on pentacarbonyl chromium Fischer aminocarbene complexes where the heteroaromatic substituent is either Fu or Th, showed that in solution two isomers, namely the *E* and the *Z*-isomer, were present [12]. Cyclic voltammograms of the chromium Fischer aminocarbene complexes $[(CO)_5CrC(X)(NHBu)]$ (X = Th or Fu), obtained in dichchloromethane, showed splitting of the $Cr^{0/1}$ oxidation peak into two poorly resolved components, consistent with oxidation of the the *E* and the *Z*-isomer separately [13]. However, the cyclic voltammograms of related W and Mo-Fischer aminocarbene complexes $[(CO)_5MC(X)(NHCy)]$ (X = Th or Fu) did not reveal different metal oxidation peaks for *E* and the *Z*-isomers [14,15]. It would thus be of interest to investigate the electrochemical properties of more pentacarbonyl chromium Fischer aminocarbene complexes to see if the oxidation of the *E* and the *Z*-isomers could more clearly be distinguished on a cyclic voltammogram. We thus hereby report an electrochemical study complemented by DFT calculations on cyclohexylamino chromium Fischer carbene pentacarbonyl complexes of general formula $[(CO)_5CrC(NHCy)R]$ with R = Th or Fu and compare the data to published data of related ethoxy chromium Fischer carbene pentacarbonyl complexes [10], as well as tetra- [16] and tricarbonyl [11] chromium Fischer complexes, see Figure 1.

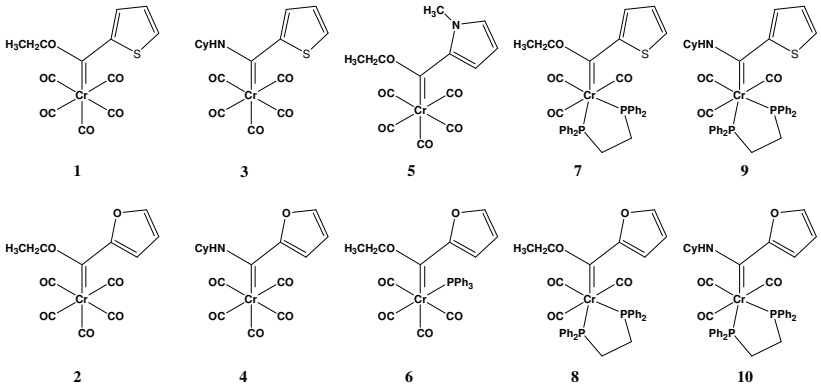


Figure 1. Cr-carbene complexes **1**-**10**

2. Experimental

2.1. Synthesis

The carbene complexes were synthesized according to known literature methods: $[Cr(CO)_5C(OEt)(Th)]$ (**1**), $[Cr(CO)_5C(OEt)(Fu)]$ (**2**), $[Cr(CO)_5C(NHCy)(Th)]$ (**3**), and $[Cr(CO)_5C(NHCy)(Fu)]$ (**4**) [15,17]. Characterization data of **1-4** were in agreement with literature reports [10,12].

2.2. DFT

Density functional theory (DFT) calculations of this study were performed with the hybrid functional B3LYP [18,19], (20% Hartree-Fock exchange) [20] as implemented in the Gaussian 09 program package [21]. Geometries of the neutral complexes were optimized in gas phase with the triple-ζ basis set 6-311G(d,p) on all atoms except Cr, where def2-TZVPP [22] was used. Energies reported are gas phase electronic energies.

2.3. Electrochemistry

Electrochemical studies by means of cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (SW) were performed on 0.001mol dm^{-3} compound solutions in dry acetonitrile containing 0.1 mol.dm^{-3} tetra-*n*-butyl ammonium hexafluorophosphate, $[^n(Bu_4)N][PF_6]$, as supporting electrolyte, under a blanket of purified argon at 25 °C utilizing a BAS 100B/W electrochemical analyser. A three-electrode cell, with a glassy carbon (surface area 7.07 x 10^{-6} m^2) working electrode, Pt auxiliary electrode and an Ag/Ag^+ (10 mmol dm^{-3} $AgNO_3$ in CH_3CN) reference electrode [23], mounted on a Luggin capillary were used [24]. Scan rates for CVs were 0.05-5.0 $V.s^{-1}$. Successive experiments under the same experimental conditions showed that all oxidation and formal reduction potentials were

reproducible within 0.01 V. All cited potentials were referenced against the FcH/FcH^+ couple as suggested by IUPAC [25]. Decamethylferrocene (Fc*, -0.508 V *vs.* FcH/FcH^+ under our experimental conditions) were used as internal standard.

3. Results and Discussion

3.1 DFT

Four different stereoisomers and conformers are possible for the chromium Fischer aminocarbene complexes **3** and **4**, see Figure 2. The *syn* and *anti* conformations refer to the orientation of the aryl group relative to the heteroatom (N). The two isomers, *Z* and *E,* arise from restricted rotation around the $N\text{-}C_{carbene}$ bond, which exhibits double bond character due to π-donation from the nitrogen atom to the carbene carbon. Both **3** and **4** could thus have any of the following four conformations: *syn*,Z, *anti*,Z, *syn*,E or *anti*,E. Both experimental results as well as DFT calculations for **3** and **4**, have shown that the two different conformers of the *Z* isomer (*syn*,Z and *anti*,Z) are in fast equilibrium with each other, and the same for conformers *syn*,E and *anti*,E of the *E* isomer [12]. However, no dynamic equilibrium could experimentally be detected between the *Z* and *E* isomers, thus the *E*:*Z* ratio of each sample had to be determined by NMR. For complexes **3** and **4**, the experimental *Z*: *E* ratios are 64.4:35.6 (R = Th (**3**)) and 55.7: 44.3 (R = Fu (**4**)) respectively [12].

From an application perspective, identifying the isomer ratio of a complex becomes important. Different isomers may behave differently in binding key intermediates in catalytic reactions or have different reactivities [26]. This may result in the formation of different reaction products, where, in most cases, both products are not equally desirable. Much research has been dedicated to the quest for catalysts that are selective in producing only the desired product [27]. Knowledge of the isomer ratio of the catalyst may guide in prediction of specific products.

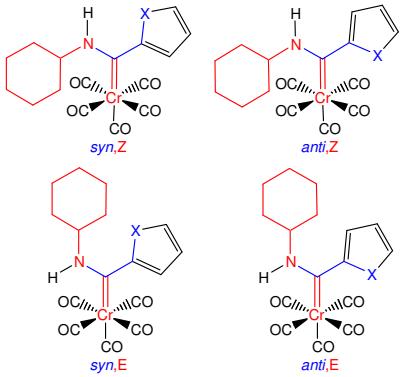


Figure 2. The possible isomers (E and Z) and conformers (*syn* and *anti*) of the amino Fischer carbene complexes **3** (X = S) and **4** (X = O).

We have previously analyzed the geometries and energies of complexes **1-4** [10,12] utilizing DFT calculations at the B3LYP/6-311G(d,p) level, using a double-ζ basis set for Cr (Lanl2dz or def2svp) [28]. Here we present DFT calculations at the B3LYP/6-311G(d,p), def2-TZVPP level, using a triple-ζ plus polarisation basis set for Cr. Results from the DFT calculations on the different conformations for **1-4** are presented in Table 1 and Table 2. Selected DFT results obtained on the same level of theory, of complexes **5-10**, is provided in Table 2.

The small energy differences found between the *E* and *Z* isomers for complexes **3** and **4**, suggest that both isomers should be observed experimentally. For both **3** and **4** the lowest energy configuration was found to be the *syn,Z* isomer (see Table 1). The reported X-ray structure for **3** and **4** was the *Z* isomer, and NMR studies also showed that the Z isomer was the major configuration [12], which is in agreement with the calculated electronic energies of the optimized geometries reported in this study.

To gain insight into the electronic structure of d^6 Cr(0)-Fischer carbene complexes, the energies and character of the frontier orbitals of **1-10** were evaluated, see Figure 3 for **4** as example. The ordering of mainly d-based molecular orbitals, namely $d_{xy} < d_{xz} < d_{yz} << d_{z^2} < d_{x^2-y^2}$, is as expected for an octahedral ligand field [29]. The energy difference Δ_{oct} (the crystal-field splitting parameter) between the occupied t_{2g} set (d_{xy}, d_{xz}, and d_{xz}) and the unoccupied e_g set ($d_{x^2-y^2}$ and d_{z^2}) is more than 6.8 eV for complex **4**. Since the top three HOMOs all have chromium d-character, the electron(s) to be removed during oxidation from

the HOMO of the neutral Cr(0) Fischer carbene complex will thus be metal d electrons. The LUMO, however, is mainly located on the carbene carbon, with further distribution over the heteroatom and the aryl group. LUMO +1 to LUMO + 4 are all located on the CO groups. The character of the LUMO reveals that the electron that is added during electrochemical reduction of the Cr(0) Fischer carbene complexes, will be distributed over the carbene carbon and carbene ligand. The nature of the frontier orbitals thus indicate that oxidation is metal-based and reduction carbene carbon and carbene ligand-based.

Table 1. Summary of the energies of the optimized geometries (Gaussian, B3LYP, 6-311G(d,p), def2tzvpp) of the isomers and conformers of the indicated Fischer carbene complexes.

Complex	**Conformation**	**$E_{complex}$ (eV)**	**E_{HOMO}**	**E_{LUMO}**	**Crystal structure**	**NMR**
$[Cr(CO)_5=C(OEt)(Th)]$	*syn*	0.00	-6.074	-2.754	*syn* [30]	
1	*anti*	0.12	-6.034	-2.700		
$[Cr(CO)_5=C(OEt)(Fu)]$	*syn*	0.08	-6.050	-2.571		
2	*anti*	0.00	-5.962	-2.583	*anti* [30]	
$[Cr(CO)_5=C(NHCy)(Th)]$	*syn,Z*	0.00	-5.820	-2.181	45% *syn,Z* 55% *anti,Z* [12]	64.4% [12]
3-Z	*anti,Z*	0.04	-5.796	-2.032		
3-E	*syn,E*	0.06	-5.780	-1.934		35.6% [12]
	anti,E	0.08	-5.767	-1.928		
$[Cr(CO)_5=C(NHCy)(Fu)]$	*syn,Z*	0.00	-5.784	-2.141	*syn,Z* [12]	55.7% [12]
4-Z	*anti,Z*	0.12	-5.709	-2.087		
4-E	*syn,E*	0.11	-5.759	-2.211		44.3% [12]
	anti,E	0.17	-5.658	-2.120		

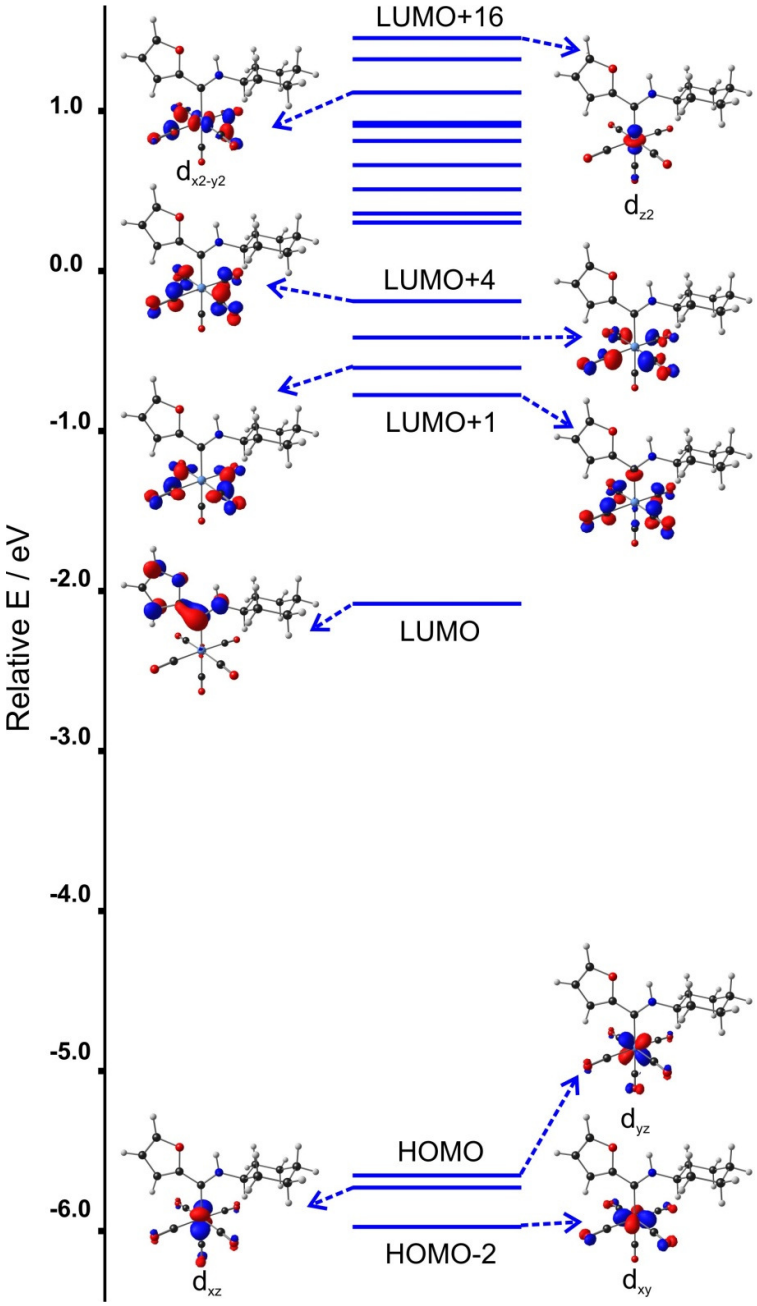


Figure 3. Visualization of the relative energies and character of selected frontier orbitals of the *syn,*Z isomer of [Cr(CO_5)=C(NHCy)(Fu)] **4**.

3.2 Electrochemistry

Cyclic voltammograms of **1-4** obtained at a scan rate of 0.100 V s^{-1}, are shown in Figure 4, while graphs and data for scan rates 0.05-5 V s^{-1} is provided in the Supplementary information. The electrochemical behaviour of the ethoxy-functionalised chromium Fischer carbene complexes **1-2** was previously reported [10] to exhibit two one-electron processes

marked **O1** and **O3** in Figure 4. The first peak marked as **O1** is assigned to the electrochemically and chemically reversible Cr^{0}/Cr^{1+} couple, while **O3** is assigned to the electrochemically and chemically irreversible Cr^{1+}/Cr^{2+} couple, in agreement with the DFT study presented above. In contrast to the first oxidation of **1-2**, with $\Delta E < 0.08$ V and i_{pc}/i_{pa} = 1.00 for **O1**, the first oxidation process of the cyclohexylamino-functionalised chromium Fischer carbene complexes, **3-4**, exhibited peak voltage separations and peak current ratios consistent with an electrochemically and chemically quasi-reversible process. Both complexes **3** and **4** also showed the additional oxidation peak **O3**, at *ca.* 0.99 and 1.31 V respectively, with no reduction peak coupled to it, which in correlation with the second Cr^{1+}/Cr^{2+} couple of **1-2**, published data [7,9,10,13], and the DFT results presented above, is assigned to the oxidation of the Cr^{1+} species generated during the electrochemical oxidation process at **O1/O2** for **3** and **4**.

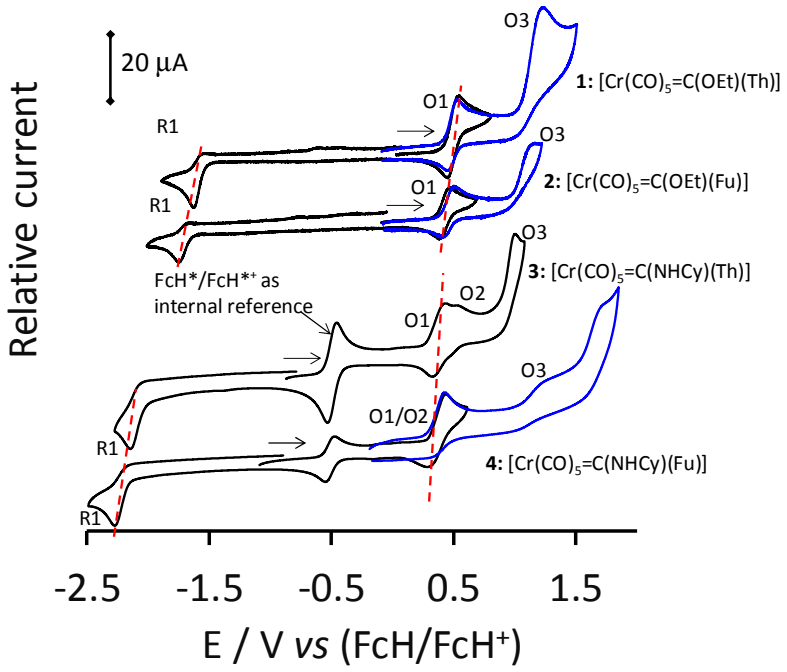


Figure 4. The comparative cyclic voltammograms of various 1.0 mM solutions of the chromium Fischer carbene complexes **1-4** (supporting electrolyte is 0.1 M tetrabutylammonium hexafluorophosphate) in acetonitrile on a glassy carbon working electrode at 25˚C and a scan rate of 0.10 $V.s^{-1}$. Data are reported against FcH/FcH^{+} with decamethylferrocene as an internal standard; the CV initiated in the direction of the arrows. The red dotted line indicates the shift in potential, while the blue line shows the extended CV to include **O3**.

Closer inspection of the cyclic voltammogram of [$Cr(CO)_5$=C(NHCy)(Th)], **3**, in Figure 5, showed that the first oxidation peak consists of two closely overlapping peaks *ca.* 0.1 V apart, also highlighted by the Osteryoung square-wave voltammetry (SW) scan of the peak. This splitting of the peak is attributed to the *E* and *Z* isomers of the complex, since both isomers were experimentally observed on NMR [12]. From the DFT calculations of the different isomers and conformers of **3**, as summarized in Table 1, it was found that the energies of the HOMO of the two conformers of the *E* isomer are higher (less negative) than the energies of the HOMO of the two conformers of the *Z* isomer of **3**. A higher energy HOMO implies that less energy is needed to remove an electron from the specific HOMO in order to oxidize it (also see Figure 7 below). Less energy thus implies that a complex with a higher HOMO energy has a lower (less positive) oxidation potential. Therefore the peak at the lower (less positive) oxidation potential (E_{pa}) is attributed to the oxidation of the *E* isomer of **3** and the peak at the slightly higher (more positive) oxidation potential to the oxidation of the *Z* isomer of **3**. Similarly, it is expected that complex **4** for which also two isomers have experimentally been observed, should also have two peaks. However, this was not electrochemically observed, although the large peak voltage separation (ΔE_p > 0.13 V) is consistent with two closely overlapping peaks. Also, from the DFT calculations in Table 1 it was found that the HOMO energies of the two *E* isomers of **4** are not consistently higher than the HOMO energies of the two conformers of the *Z* isomers. This result is an indication that the oxidation potential of the *Z* and *E* isomers are too closely overlapping to observe separately (see Figure 4).

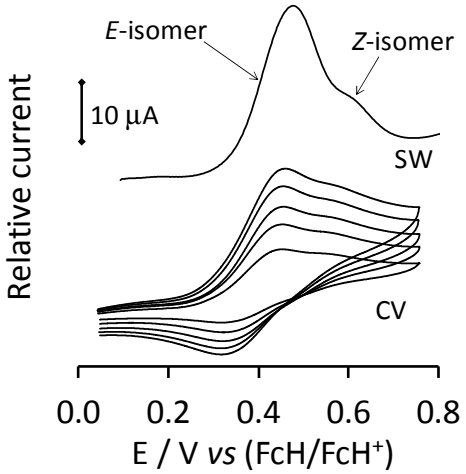
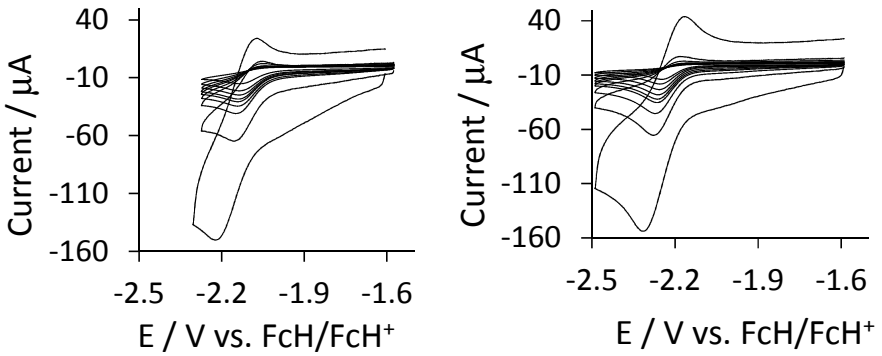


Figure 5. Cyclic voltammogram showing the two peaks observed for the *Z* and *E* isomers of [$Cr(CO)_5$=C(NHCy)(Th)], **3**, at scan rates of 0.05, 0.10, 0.15, 0.20 and 0.25 V s^{-1}. Measurements were performed in 0.1 M [$^n(Bu_4)N$][PF_6]/CH_3CN on a glassy carbon working electrode and are reported *vs.* ferrocene; the CV initiated in a positive direction from 0. Top: The split of the Cr^0/Cr^{1+} couple into two components, as highlighted by the SW at 100 Hz.

This first reduction process observed for **1**-**4**, labelled **R1** in Figure 4, is assigned to the reduction of the carbene ligand, as indicated by the character of the DFT calculated LUMO of the neutral complex that is located over the carbene ligand (see Figure 3 for **4**). This finding is in agreement with published data [7,9,10,13]. The reduction process of the chromium Fischer carbene complexes, **3** and **4**, are chemically and electrochemically irreversible at low scan rates, while a small re-oxidation peak coupled to the reduction peak is observed at higher scan rates (Figure 6). The reduced species are thus stable enough on the timescale of the CV at higher scan rates to be re-oxidized with $\Delta E_p < 0.10$ V.



(a) Complex **3** (b) Complex **4**

Figure 6. The cyclic voltammograms of the reduction of 0.001 M solutions of the chromium Fischer carbene complexes (a) complex **3** and (b) complex **4**. The supporting electrolyte is 0.1 M tetrabutylammonium hexafluorophosphate) in acetonitrile on a glassy carbon working electrode at 25˚C and a scan rate of 0.05, 0.100, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50, 1.00 and 5.00 V.s^{-1}.

Comparison of the E_{pa} of the oxidation wave of **1-4**, revealed that the aminocarbene complexes **3-4**, are more easily oxidized at a lower, less positive, potential than the ethoxycarbene complexes **1-2** (see Figure 4 and the data in Table 2). Changing the heteroatom from O-containing to N-containing (by substitution of OEt with NHCy), leads to

a lower (less positive) oxidation potential, in agreement with the electron withdrawing properties of N (χ = 3.04) and O (χ = 3.44), according the Pauling scale of electronegativity. Since oxygen is more electron withdrawing, it implies that the chromium atom of the ethoxycarbene complexes, **1** and **2**, has relatively less electron density on it, making it more difficult to remove an electron from it than from the chromium atom of complexes **3-4**. This leads to the higher (more positive) oxidation potentials for **1** and **2** in comparison to the amino-containing complexes, **3** and **4**. The same trend is observed for the reduction of **1** and **2** relative to **3** and **4**, although more enhanced. Since the heteroatom (O or N) is attached to the carbene carbon, the influence on carbene reduction is larger (*ca.* 0.5 V) than on the chromium oxidation potential (*ca.* 0.1 V).

The 2-thienyl-containing complexes, **1** and **3**, are oxidized at a potential *ca.* 0.03 V higher (more positive) than the 2-furyl-containing complexes, **2** and **4** respectively. The same but enhanced trend is observed for the reduction, **1** and **3** are reduced at a potential *ca.* 0.08 V higher (less negative) than **2** and **4**. Similar 2-thienyl and 2-furyl carbene complexes of W [15,31] and Mo [32] showed the same trend, namely a 2-thienyl complex is oxidized and reduced at higher more positive (less negative) potentials than the same 2-furyl complex.

The order of oxidation and reduction (from low to high potential) of the Fischer carbenes **1-4** is: $[Cr(CO)_5=C(NHCy)(Fu)]$, **4** < $[Cr(CO)_5=C(NHCy)(Th)]$, **3** < $[Cr(CO)_5=C(OEt)(Fu)]$, **2** < $[Cr(CO)_5=C(OEt)(Th)]$, **1**.

Table 2. Selected electrochemical data of the Fischer carbene complexes **1-4**, as well as the indicated complexes **5-10** from references [10], [11] and [16]. HOMO and LUMO energies of the most stable isomer of each complex are included. All cited potentials are in V and referenced against the FcH/FcH^+ couple.

No	Formula	Oxidation				Reduction	E_{HOMO}	E_{LUMO}
		E_{pa} (V)	E_{pc} (V)	ΔE (V)	$E^{0'}$ (V)	E_{pc} (V)	(eV)	(eV)
1	$[Cr(CO)_5=C(OEt)(Th)]$	0.538	0.453	0.085	0.496	-1.625	-6.074	-2.754
2	$[Cr(CO)_5=C(OEt)(Fu)]$	0.494	0.414	0.080	0.454	-1.719	-5.962	-2.583
3 ***E***	$[Cr(CO)_5=C(NHCy)(Th)]$	0.456	0.323	0.133	0.389	-2.145	-5.780	-1.934
4	$[Cr(CO)_5=C(NHCy)(Fu)]$	0.432	0.287	0.145	0.359	-2.278[a]	-5.759	-2.211
5	$[Cr(CO)_5=C(OEt)(NMepy)]$	0.463	0.396	0.067	0.430	-2.019	-5.833	-2.204
6	$[Cr(CO)_4(PPh_3)=C(OEt)(Fu)]$	-0.029	-0.086	0.057	-0.057	-1.900	-5.339	-2.184
7 ***mer***	$[(CO)_3(dppe)Cr=C(OEt)(Th)]$[b]	-0.275	-0.353	0.078	-0.314	-	-4.811	-1.812
7 ***fac***		-	-	-	-	-2.162	-4.916	-1.792
8 ***mer***	$[(CO)_3(dppe)Cr=C(OEt)(Fu)]$[b]	-0.356	-0.410	0.054	-0.383	-2.269	-4.743	-1.632
8 ***fac***		-0.235	-	-	-	-2.124	-4.900	-1.958

9 ***mer***	$[(CO)_3(dppe)Cr{=}C(NHCy)(Th)]$[b]	-0.500	-0.569	0.069	-0.534	-2.8	-4.658	-1.181
9 ***fac***		-0.306	-	-	-	-2.545	-4.730	-1.248
10 ***mer***	$[(CO)_3(dppe)Cr{=}C(NHCy)(Fu)]$[b]	-0.545	-0.600	0.055	-0.573	-2.615	-4.523	-1.328
10 ***fac***		-0.368	-	-	-	-	-4.671	-1.596

[a] This value did not fit into the trend shown in Figure 7
[b] dppe = bis(diphenylphosphino)ethane

3.3 Relationships

Since removing an electron from the HOMO is associated with the oxidation process while adding an electron to the LUMO is associated with the reduction process, relationships exist between the HOMO energy and oxidation potential, as well as between the LUMO energy and reduction potential for the chromium Fischer carbenes **1**, **2**, **5-10,** containing an aryl group [10,11,16]. To ensure that the complexes of this study also fit into the trends, electrochemical data were obtained under the same experimental conditions as that of the series of complexes **5-10**. All complexes were therefore re-optimized with the B3LYP/6-311G(d,p), def2-TZVPP method, and included in the relationship data between the redox potentials and frontier orbital energies shown in Figure 7; the data is summarized in Table 2. The correlation of the oxidation potential (E_{pa}) and reduction potential (E_{pc}) with the DFT calculated HOMO energy (E_{HOMO}) and LUMO energy (E_{LUMO}) respectively, showed that with decreasing molecular orbital energy an increase to more positive redox potentials are obtained. It is easier to remove an electron from complexes with higher, more positive HOMO energy (E_{HOMO}), which gives rise to lower less positive oxidation potentials (E_{pa}). When the LUMO energy (E_{LUMO}) of a complex is more positive, the more difficult it is for the complex to accept an electron, therefore more negative reduction potential (E_{pc}) is observed. The linear relationships obtained in Figure 7 fit the following equations:

$$E_{pa} = -0.72\, E_{HOMO} - 3.77; \qquad R^2 = 0.98 \qquad (1)$$

$$E_{pc} = -0.69\, E_{LUMO} - 3.48; \qquad R^2 = 0.98 \qquad (2)$$

These slopes of the lines are near parallel, emphasizing the similar influence of the various heteroatoms (O or N) and substituents (Th, Fu or 2-(N-methyl)pyrrolyl) and ligands (CO or 1,2-bis(diphenylphosphino)ethane)) on the redox processes of chromium Fischer carbenes relative to the DFT calculated electronic structure of the carbene.

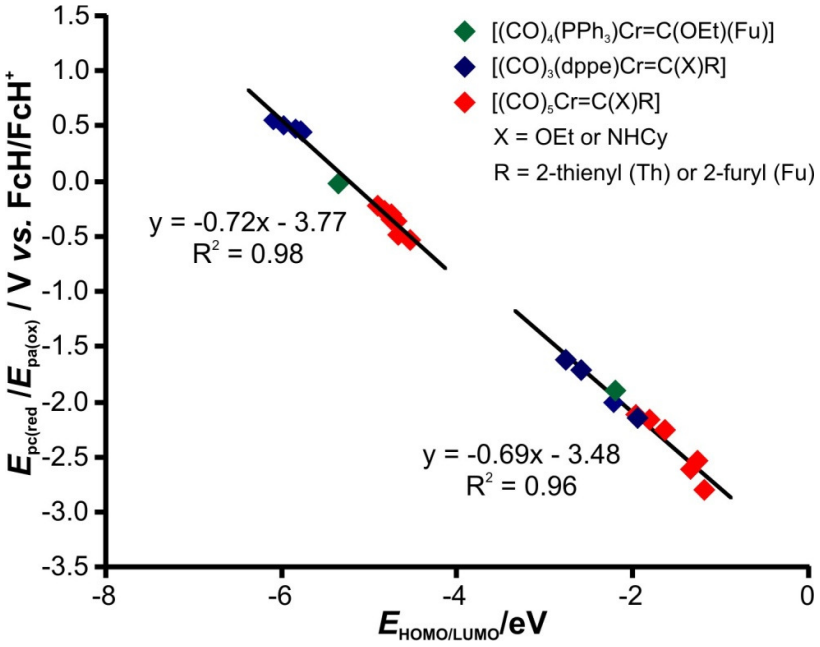


Figure 7. Linear relationships between the E_{pa} of the oxidation process and the DFT calculated E_{HOMO} (markers top left) and the E_{pc} of the reduction process and the DFT calculated E_{LUMO} (markers bottom right) of tri-([(CO)$_3$(dppe)Cr=C(X)R] (red markers), tetra-([(CO)$_4$(PPh$_3$)Cr=C(OEt)(Fu)] (green marker) and penta-carbonyl ([(CO)$_5$Cr=C(X)R] (blue markers) chromium carbenes with R = 2-thienyl, 2-furyl or 2-(N-methyl)pyrrolyl and X = OEt or NHCy. The data are from Table 2.

In Table 3 the experimental and the calculated redox potentials, obtained from the relationships (1) and (2) above are presented. The mean average error of the calculated redox potentials is 0.047 V for the chromium-based oxidation potential and 0.057 V for the carbene ligand based reduction potential. This result indicates that electrochemical redox potentials for the indicated and related chromium(0) Fischer carbene complexes can be determined to a high degree of accuracy from the gas phase DFT optimized frontier orbital energies. However, more sophisticated and computer resource intensive DFT methods do exist to directly calculate redox potentials of complexes by application of the Born–Haber cycle for redox half-reactions using DFT calculated free energy changes and the Nernst equation [33,34]. For example, the redox potentials of a series of chromium aminocarbene complexes were calculated in the gas phase with a total mean average absolute error of 1.394 V [8]. When the polarizable continuum model was used, the mean average error of the calculated redox potentials is reduced to 0.111 V and when counter ions of the supporting electrolyte were included in the calculations, results that are in good agreement with the experimental

data were obtained, with a mean average error of the calculated redox potentials of 0.088 V [8].

Table 3. Experimental and calculated redox potentials (in V *vs* FcH/FcH^+) of the indicated Fischer carbene complexes **1-10**. The differences between the calculated and experimental value are also tabulated.

No	Formula	$E_{pa,\ oxidation}$ (V)			$E_{pc,\ reduction}$ (V)		
		Exp	Calc	Diff	Exp	Calc	Diff
1	$[Cr(CO)_5{=}C(OEt)(Th)]$	0.538	0.601	-0.063	-1.625	-1.581	-0.044
2	$[Cr(CO)_5{=}C(OEt)(Fu)]$	0.494	0.521	-0.027	-1.719	-1.699	-0.020
3	$[Cr(CO)_5{=}C(NHCy)(Th)]$	0.456	0.390	0.066	-2.145	-2.145	-0.003
4	$[Cr(CO)_5{=}C(NHCy)(Fu)]$	0.432	0.375	0.057	-2.278[a]	-	-
5	$[Cr(CO)_5{=}C(OEt)(NMepy)]$	0.463	0.428	0.035	-2.019	-1.959	-0.060
6	$[Cr(CO)_4(PPh_3){=}C(OEt)(Fu)]$	-0.029	0.073	-0.101	-1.900	-1.974	0.074
7 ***mer***	$[(CO)_3(dppe)Cr{=}C(OEt)(Th)]$[b]	-0.275	-0.308	0.033	-	-	-
7 ***fac***		-	-	-	-2.162	-2.243	0.081
8 ***mer***	$[(CO)_3(dppe)Cr{=}C(OEt)(Fu)]$[b]	-0.356	-0.357	0.001	-2.269	-2.353	0.084
8 ***fac***		-0.235	-0.244	0.009	-2.124	-2.129	0.005
9 ***mer***	$[(CO)_3(dppe)Cr{=}C(NHCy)(Th)]$[b]	-0.500	-0.419	-0.081	-2.800	-2.664	-0.136
9 ***fac***		-0.306	-0.367	0.060	-2.545	-2.618	0.073
10 ***mer***	$[(CO)_3(dppe)Cr{=}C(NHCy)(Fu)]$[b]	-0.545	-0.516	-0.029	-2.615	-2.563	-0.052
10 ***fac***		-0.368	-0.409	0.041	-	-	-
	mean average error		**0.047**			**0.057**	

[a] This value not used in the fit of the trend shown in Figure 7
[b] dppe = bis(diphenylphosphino)ethane

4. Conclusion

DFT calculation showed very small energy differences between the *E* and *Z* isomers of the chromium Fischer aminocarbene complexes $[(CO)_5CrC(NHCy)R]$ with R = 2-thienyl (**3**) or 2-furyl (**4**). Both the *Z* and *E* stereo isomers are experimentally detected on NMR and by cyclic voltammetry scans for **3**. From the DFT calculations it was found that the energies of the HOMO of the two conformers of the *E* isomer are higher than the energies of the HOMO of the two conformers of the *Z* isomer of **3**, implying that the peak at the lower oxidation potential (E_{pa}) is attributed to the oxidation of the *E* isomer of **3** and the peak at the slightly higher oxidation potential to the oxidation of the *Z* isomer. The linear correlation of the oxidation potential (E_{pa}) and reduction potential (E_{pc}) of a series of penta-, tetra- [16] and tricarbonyl [11] chromium Fischer complexes containing a heteroarene ring with DFT calculated HOMO energy (E_{HOMO}) and LUMO energy (E_{LUMO}) respectively, provides a relative easy theoretical method to predict redox potentials of related chromium Fischer carbene complexes to a high level of confidence.

Supporting Information

Optimised coordinates of the DFT calculations and electrochemical graphs and data are given in the Supporting Information.

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