Synthesis and electrochemical investigation of chromium(0) ferrocenyl-substituted carbene complexes

Daniela I. Bezuidenhout,[a,*] Belinda van der Westhuizen,[a] Ian Strydom,[a] Pieter J. Swarts,[b] Jannie C. Swarts,[b,*] Israel Fernández,[c,*]

[a] *Chemistry Department, University of Pretoria, Private Bag X20, Hatfield, 0028, South Africa.*
[b] *Chemistry Department, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa.*
[c] *Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense, 28040-Madrid,Spain.*

*Corresponding authors. Address: Chemistry Department, University of Pretoria, Private Bag X20, Hatfield, 0028, South Africa. Fax: +27-(0)12-420-4687; Tel: +27-(0)12- 420-2626 (D.I. Bezuidenhout). Address: Chemistry Department, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa. Fax:+27-(0)51-444-6384; Tel: +27-(0)51-401-2781 (J.C. Swarts). Address: Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain (I. Fernández).
E-mail addresses: daniela.bezuidenhout@up.ac.za (D.I. Bezuidenhout), swartsjc@ufs.ac.za (J.C. Swarts), israel@quim.ucm.es (I. Fernández).

ABSTRACT

The series $[(CO)_5Cr{=}C(R)Fc]$, (**1**, R = OEt; **2**, R = NH^nBu) as well as $[(OC)_5Cr{=}C(R)\text{-}Fc'\text{-}(R)C{=}Cr(CO)_5]$, (**3**, R = OEt; **4**, R = NH^nPr) of mono- and biscarbene chromium(0) complexes with Fc = $Fe^{II}(C_5H_5)(C_5H_4)$ and Fc′ = $Fe^{II}(C_5H_4)_2$, were synthesized and characterized spectroscopically, electrochemically and computationally. Electrochemical studies on the new aminocarbene complexes revealed that **2** and **4** are oxidized (and reduced) at lower potential than the EtO derivatives **1** and **3** while the biscarbene complexes **3** and **4** provided evidence for interaction between different redox sites, including the Cr-centers. The $Cr^{0/I}$ couples are electrochemically reversible with the difference in formal potentials $\Delta E^{o\prime}$ for the consecutive oxidations of the chromium carbene entities being 151 and 105 mV in **3** and **4** respectively. Computational and electrochemical results were mutually consistent in showing unambiguously that the Cr(0) centre is oxidized before the ferrocenyl group in the carbene complexes **2**, **3** and **4**. Electrochemical experiments on **1** were also consistent with this redox sequence of events, but differently, our calculations suggest that for **1**, the ferrocenyl group may be oxidised *before* Cr(0) oxidation. The ethoxycarbenes **1** and **3** also showed a carbene double bond reduction to an anion

radical, $^{-}Cr=C^{\bullet}$, while the new aminocarbene **4** was the only derivative to show irreversible Cr(I) oxidation to Cr(II) within the potential window of the solvent.

KEYWORDS

Fischer carbene complex, electrochemistry, ferrocenyl aminocarbene, chromium(0)

1. Introduction

The development of bi- and polymetallic complexes with σ,σ-attachments to transition metal fragments and containing a π-conjugated bridge has attracted considerable attention in recent years. Applied to Fischer carbene complexes, their potential use to obtain bi- or trimetallic polyenes that show metal-metal interactions are especially attractive [1]. Such systems may have interesting optical and electrochemical properties [2]. Fischer carbene complexes have also been extensively studied as catalysts [3], as reactants to facilitate many organic transformations [4], or as electrochemical probes [5]. Thermal [3,6] and photochemical transformations [7] have also been investigated.

Incorporation of the redox-active ferrocenyl group in complexes may be beneficial for a number of reasons. The electron-donating [8] characteristics of the ferrocenyl group, the electron-withdrawing properties of the oxidized ferrocenium species [9], the high thermal stability of both the oxidized and reduced states, and the electrochemical reversible nature of the Fc/Fc^{+} couple [10] are but some of the reasons why ferrocene derivatives have been studied as molecular sensors [11] and in energy transfer processes [12]. Considering reaction rates, as a part of a ligand system it will enhance oxidative addition reactions [13] but retard substitution processes [14]. A particularly interesting application of ferrocene derivatives, which are strongly dependent on fine tuning of the ferrocenyl oxidation potential with suitable substituents, lies in the field of cancer therapy [15]. Differences in drug activity, catalyst specificity and reaction rates in the above cited applications are frequently the result of electronic interactions between the ferrocenyl group and functional groups in the substrate.

Recent reports suggest that any two non-conjugated metal carbene moieties in homo- and heterobimetallic biscarbene complexes behave as two independent monocarbene entities with

separate, localized redox centres [16]. From our recently published results related to an electrochemical and theoretical investigation of 2,5-thiendiyl (Th′) and 2,5-furadiyl (Fu′) bis-heteroaryl carbene chromium(0) complexes [17,18], it is known that no significant electronic interaction exists between the two Cr(0) centers of $[(CO)_5Cr=C(OEt)(Ar')C(OEt)=Cr(CO)_5]$ with Ar′ = Th′ or Fu′. Because of this, the computational study of the recently published Cr(0) oxidation to Cr(I) of 2,5-thiendiyl- [17] and 2,5-furadiyl-biscarbene complexes [18] treated these redox processes as a two-electron transfer process comprised of two simultaneously occurring but independent one-electron transfer steps, one for each Cr(0) center. However, for $[(CO)_5Cr=C(OEt)(Fc')C(OEt)=Cr(CO)_5]$, where the 2,5-thiendiyl or 2,5-furadiyl linking aryl unit between the two Cr carbene functionalities was replaced by a ferrocen-1,1′-diyl functionality, we *did* observe electrochemical evidence that some interaction may exist between the two Cr(0) centers [17], which needs further investigation. We herewith report the synthesis of the two new aminocarbene complexes $[Cr(CO)_5=C(NH^nBu)Fc]$, **2**, and $[(CO)_5Cr=C(NH^nPr)(Fc')C(NH^nPr)=Cr(CO)_5]$, **4**, from the previously reported ethoxy complexes $[Cr(CO)_5\{C(OEt)Fc\}]$, **1** [19], and $[(CO)_5Cr\{C(OEt)(Fc')C(OEt)\}Cr(CO)_5]$, **3** [20]. Results from an electrochemical study on **1 – 4**, and new insights from a computational study to elucidate the species generated in each redox process, are also presented.

2. Experimental

2.1 General Procedures

All manipulations involving organometallic compounds made use of standard Schlenk techniques under inert atmosphere. Solvents were dried over sodium metal (hexane, tetrahydrofuran and diethylether) and phosphorous pentoxide (CH_2Cl_2); and distilled under nitrogen gas prior to use. All chemicals were used as purchased without further purification unless stated otherwise. Triethyloxonium tetrafluoroborate was prepared according to literature procedures [21]. Complexes **1** and **3** were synthesized according to literature procedures [20]. Purification of complexes was done with column chromatography using silica gel 60 (0.0063-0.200 mm) as the stationary phase. NMR spectra were recorded on a Bruker AVANCE 500 spectrometer. ^1H NMR spectra were recorded at 500.139 MHz and ^{13}C NMR at 125.75 MHz.

The signals of the deuterated solvent were used as a reference: ^{1}H $CDCl_3$ at 7.24 ppm and C_6D_6 7.15 ppm; ^{13}C $CDCl_3$ at 77.00 ppm and C_6D_6 128.00 ppm. IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer in hexane. Only the vibration bands in the carbonyl-stretching region (*ca.* 1600-2200 cm^{-1}) were recorded.

2.2 Synthesis of complexes

[(CO)$_5$Cr=C(NH^{n}Bu)Fc] (**2**)

A diethylether solution of **1** (2 mmol, 0.87g) was stirred at room temperature (rt) and *n*-butylamine (2 mmol, 0.20 mL) was added. The colour changed rapidly from dark red to deep yellow. Purification was performed using column chromatography and a 1:1 mixture of hexane/CH_2Cl_2 as eluent. Yield: 0.72g (78%), yellow solid. Anal. Calcd for $CrFeC_{20}H_{19}NO_5$: C, 52.08; H, 4.16, % Found: C, 52.05; H, 4.10, %. ^{1}HNMR (500 MHz, $CDCl_3$, δ, ppm): 9.48 (s, 1H, N**H**), 4.42 (br, 4H, $H_{\alpha,}H_{\beta}$ overlapping resonances), 4.17 (s, 5H, Cp), 4.10-3.96 (m, 2H, NC**H**$_2$), 1.85 (p, *J* = 7.5 Hz, 2H, C**H**$_2$CH$_2$), 1.57 (s, 2H, CH$_2$C**H**$_2$), 1.06 (t, *J* = 7.4 Hz, 3H, C**H$_3$**). ^{13}CNMR (125 MHz, $CDCl_3$, δ, ppm): 270.6 ($C_{carbene}$), 223.6 (*trans*-**C**O), 217.8 (*cis*-**C**O) , 99.6 (**C**$_{ipso}$), 70.0 (C_{α}), 68.3 (C_{β}), 69.4 (Cp), 52.6 (N**C**H$_2$), 31.9 (**C**H$_2$CH$_2$), 20.1 (CH$_2$**C**H$_2$), 13.8 (**C**H$_3$). FTIR (hexane, νCO, cm^{-1}): 2053 s (A″$_1$), 1971 w (B), 1931 s (A′$_1$ overlap E).

[(CO)$_5$Cr=C(NH^{n}Pr)(Fc′)C(NH^{n}Pr)=Cr(CO)$_5$] (**4**)

Complex **3** (2 mmol, 1.27g) was dissolved in diethylether and *n*-propylamine (2 mmol, 0.16 mL) was added at rt. The colour of the solution turned from dark red to deep yellow and volatiles were removed by reduced pressure. Purification was performed by employing column chromatography with a 1:1 hexane/CH_2Cl_2 solvent mixture. Yield: 0.96g (68%), deep yellow crystals. Anal. Calcd for $Cr_2FeC_{28}H_{24}N_2O_{10}$: C, 56.82; H, 5.08, %. Found: C, 55.72; H, 4.90, %. ^{1}HNMR (500 MHz, $CDCl_3$, δ,ppm): 9.38 (s, 2H, **H**N), 4.42 (m, 8H, $H_{\alpha,}$ $H_{ß}$ overlapping resonances), 4.01 (m, 4H, NC**H**$_2$), 1.89 (m, 4H, C**H**$_2$CH$_3$), 1.15 (t, *J* = 7.4 Hz, 6H, C**H**$_3$). ^{13}CNMR (125 MHz, $CDCl_3$, δ, ppm): 270.6($C_{carbene}$), 223.2 (CO_{trans}), 217.5 (CO_{cis}), 101.4 (C_{ipso}), 70.9 (C_{α}), 68.7 ($C_{ß}$), 54.7 (HN**C**H$_2$), 23.2 (**C**H$_2$CH$_3$), 11.2 (**C**H$_3$). FTIR (hexane, νCO, cm^{-1}): 2051 m (A″$_1$), 1972 w (B), 1925 vs (A′$_1$ overlap E).

2.3 Electrochemistry

Cyclic voltammograms (CVs), square wave voltammograms (SWVs) and linear sweep voltammograms (LSVs) were recorded on a Princeton Applied Research PARSTAT 2273 voltammograph running PowerSuite (Version 2.58) utilizing a standard three-electrode cell in a M Braun Lab Master SP glovebox filled with high purity argon (H_2O and O_2 < 5 ppm) as described before [17,18]. CVs were recorded from 0.5 mmol.dm^{-3} solutions of analyte in CH_2Cl_2 containing 0.1 mol.dm^{-3} $[N(^nBu)_4][PF_6]$ as supporting electrolyte. A platinum wire was used as auxiliary electrode while a glassy carbon working electrode (surface area 3.14 mm^2) was utilized after polishing on a Buhler polishing mat first with 1 micron and then with 1/4 micron diamond paste. A silver wire was used as pseudo internal reference. All electrode potentials are reported *versus* the ferrocene/ferrocenium redox couple (FcH/FcH^+, $FcH = Fe(\eta^5\text{-}C_5H_5)_2$, $E^{o\prime}$ = 0.00 V) [22]. However, decamethylferrocene, Fc*, was used as internal standard to prevent signal overlap with the ferrocenyl of **1** and **2**. Decamethylferrocene has a potential of -550 mV versus free ferrocene with ΔE = 72 mV and i_{pc}/i_{pa} = 1 under the conditions employed [23]. Experiments were performed first in the absence of the internal standard and then repeated in the presence of decamethylferrocene to identify and eliminate any interactions between the reference couple and the complexes under study. No corrections were made for ohmic drop.

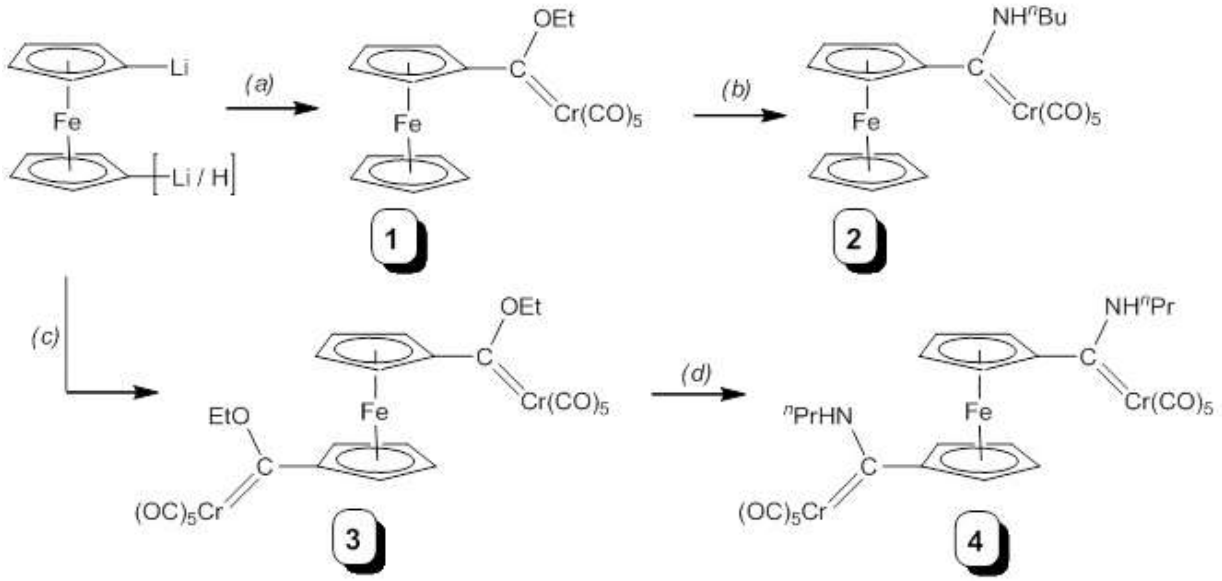
2.4 Computational details

Geometry optimizations without symmetry constraints were carried out using the Gaussian09 suite of programs [24] at the B3LYP level (uB3LYP for open-shell species) [25] using the double-ζ plus polarization def2-SVP [26] basis set for all atoms. This protocol is denoted B3LYP/def2-SVP. All species were characterized by frequency calculations, and have a positive defined Hessian matrix indicating that they are minima on the potential energy surface. In order to check the reliability of the B3LYP results, different functionals (BP86 [27] and OLYP [25b,28]) were used as well.

3. Results and Discussion

*3.1 Synthesis and spectroscopic characterization of complexes **1** - **4***

The Fischer reaction between ferrocenyllithium [29] and $[Cr(CO)_6]$ and subsequent alkylation with Et_3OBF_4 [21] yielded the known complex **1** $[(CO)_5Cr=C(OEt)Fc]$, for which the crystal structure has been previously reported [16,30]. 1,1'-Dilithiated ferrocene [31] was reacted according to literature procedures with two equivalents of metal carbonyl. The resulting metal bisacylate is then quenched with oxonium salt, to yield the known bridging ferrocenyl biscarbene complex **3**, $[(CO)_5Cr=C(OEt)(Fc')C(OEt)=Cr(CO)_5]$ [20]. Considering the ease of dilithiation of ferrocene, it is surprising that so few Fischer biscarbene complexes containing a bridging ferrocen-1,1'-diyl (Fc') spacer have been reported, and the first crystal structure of this complex was only reported in 2008 [20a].



Scheme 1. Synthesis of ferrocenyl mono- and biscarbene complexes. Reagents and conditions: (a) (i) 1eq $[Cr(CO)_6]$, thf, -50°C; (ii) 1.3eq Et_3OBF_4, CH_2Cl_2, -30°C; (b) 1eq $NH_2{}^nBu$, Et_2O, rt; (c) (i) 2eq $[Cr(CO)_6]$, thf, -50°C; (ii) 2.5eq Et_3OBF_4, CH_2Cl_2, -30°C; (d) 2eq $NH_2{}^nPr$, Et_2O, rt.

Aminolysis [32] of the ethoxycarbene complexes **1** and **3** was achieved by reaction with either *n*-butylamine or *n*-propylamine to yield the new complexes $[Cr(CO)_5=C(NH^nBu)Fc]$ (**2**) and $[(CO)_5Cr=C(NH^nPr)(Fc')C(NH^nPr)=Cr(CO)_5]$ (**4**), see Scheme 1. The shorter-chain *n*-

propylamino substituent, rather than *n*-butylamino, was employed for the biscarbene complex in an attempt to improve the crystallinity of the complex.

Notably, only the *syn* isomer was observed for both the mono- and bisaminocarbene complexes **2** and **4**, and contrasts the mixture of *syn*- and *anti*-isomers around the $C_{carbene}$-N bond that was found for 2,5-thiendiyl and 2,5-furadiyl aminocarbene complexes [17,18]. The lack of formation of *anti*-configurational isomers for **3** and **4** can presumably be ascribed to the steric bulk of the ferrocenyl carbene substituent. Stabilization of ferrocene-containing carbenes is achieved in both the σ (through inductive effects) and the π (through π-resonance effects) modes of the bridging ligand [33]. Additionally, aminocarbenes are further stabilized by imine formation. Fig.1 demonstrates both stabilization modes.

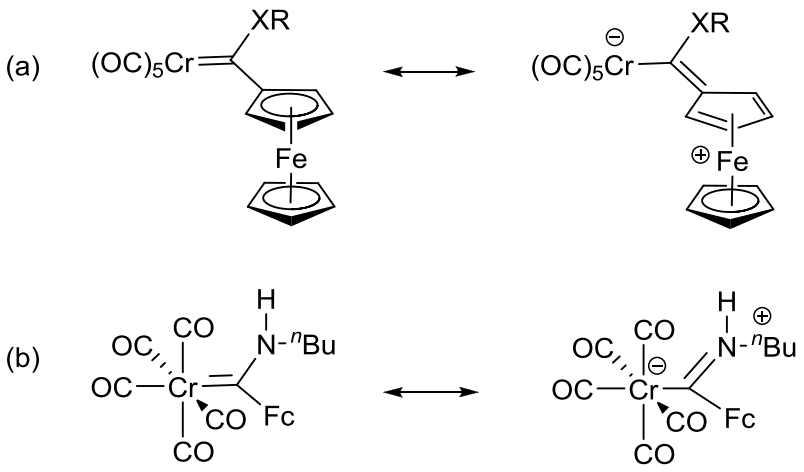


Fig. 1. Stabilization modes of the Fischer chromium(0) carbene complexes **1** and/or **2** (XR = OEt or NH^nBu) due to the (a) ferrocenyl and (b) amino substituents. For **2**, only the *syn* isomer is observed.

In all cases, spectroscopic characterization gave the expected upfield shift of the carbene carbon atom in the ^{13}C NMR spectra for the aminocarbene ligand compared to the corresponding ethoxycarbene ligand, see Table 1. This is in accordance with increased heteroatom stabilization from the nitrogen carbene substituent (Fig. 1(b)). The IR spectra of the carbonyl frequencies also demonstrate decreased π-backbonding required from the central metal atom for the aminocarbene complexes, as seen by the lower frequencies of the A'_1 mode carbonyl vibration

(Table 1) [33,34]. The most significant observable, however, was the diminished electronic ring substituent involvement of the Fc-Cp bound to the $C_{carbene}$ atom. Usually, a marked downfield shift of H_α of the ring is observed, consistent with the electron-withdrawing effect of the metal carbonyl fragment and the π-delocalization of the aryl carbene substituent towards stabilizing the electrophilic carbene carbon atom [20,35]. In the case of the aminocarbene complexes **2** and **4**, the observed H_α ^{1}H NMR resonance was consistently shifted upfield from the corresponding ethoxycarbene **1** and **3** H_α shifts (Table 1), but also found to be much closer in value to the H_β chemical resonances; even overlapping in the case of **4** ($\delta(H_{\alpha,\beta})$ = 4.42 ppm). This evidences considerably less ring-involvement required for the aminocarbene complexes.

Table 1 Selected ^{1}H and ^{13}C NMR data and IR ν(CO) stretching frequencies for **1** – **4**.

Complex	H_α δ ^{1}H / ppm	H_β δ ^{1}H / ppm	$C_{carbene}$ δ ^{13}C / ppm	A'_1 ν(CO) / cm^{-1}
1 [21]	4.93	4.71	329.7	1949
2	4.42	4.17	270.6	1931 (overlap E)
3 [22]	5.00	4.73	306.7	1938 (overlap E)
4	4.42	4.42	270.6	1925 (overlap E)

3.2 Electrochemistry and computational analyses

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and Osteryoung square-wave voltammetry (SWV) were conducted on 0.5 mmol.dm^{-3} solutions of **1** – **4** in dry, oxygen-free CH_2Cl_2 utilizing 0.1 mol dm^{-3} $[N(^nBu)_4][PF_6]$ as supporting electrolyte. Electrochemical data are summarized in Table 2, CVs are shown in Figs. 4 and 5. Up to four redox processes were observed. The first of these is associated with wave I in Fig. 4 and Table 2 and is ascribed to the one-electron reduction of the carbene double bond to $^-$Cr-C• [36], as the LUMO (i.e. the orbital accepting the additional electron) is mainly located on the p_z atomic orbital of the carbene carbon atom (see Fig. 2) [37]. Only the ethoxy derivatives **1** and **3** showed this redox process at formal reduction potentials $E^{o'} = (E_{pa} + E_{pc})/2 < -1.8$ V (Fig. 4). The electrochemistry of **1** and **3** were described in an earlier communication [17] and we refrain from further commenting here

on Cr=C reduction. That the new aminocarbene analogues **2** and **4** do not exhibit this redox process within the solvent potential window of CH_2Cl_2, but furyl (Fu) and thienyl (Th) monocarbene derivatives do [18], bears testimony to the stronger electron-donating power of the ferrocenyl group compared to Fu and Th. Also, the amino-groups of **2** and **4** are much more electron-donating than OEt, which results in the stabilizing zwitterionic iminium chromate resonance form shown in Fig. 1(b). As a consequence of such donation, the electronic occupation of the "empty" p_z atomic orbital of the carbene carbon atom is significantly higher in complexes **2** and **4** compared to **1** and **3**. This makes the reduction process far more difficult and therefore, the Cr=C reduction potentials appear at more negative potentials than the supporting electrolyte, $CH_2Cl_2/[N(^nBu)_4][PF_6]$ can accommodate.

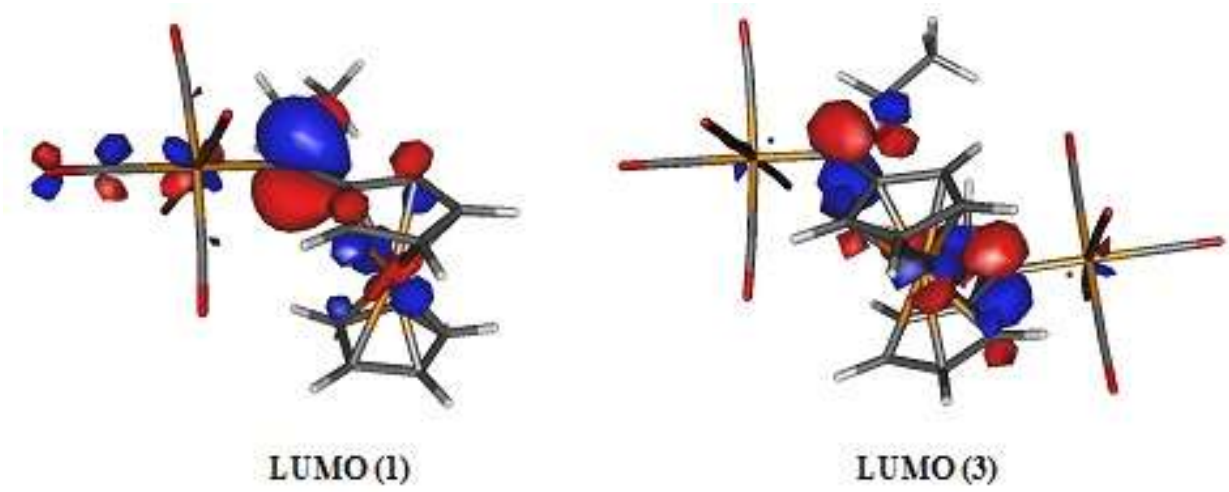


Fig. 2. Computed LUMO of complexes **1** and **3** (isosurface value of 0.045 au).

In our recent report on the second redox process (wave 1) for **3** we described electrochemical evidence that is consistent with both Cr(0) centers being oxidized *before* the ferrocenyl group [17,18]. This finding is analogous to what is observed for cymantrene Fischer carbene complexes where the Mn(I) centre is first oxidized to Mn(II) before the ferrocenyl carbene substituent [38], but is in contrast to the finding that when tungsten(0) Fischer ferrocenyl carbenes are oxidized, the ferrocenyl group is oxidized first and the monooxidized tungsten(0) ferrocenium radical cation could be isolated [39]. By way of analogy, and consistent with peak

separations, we interpreted the electrochemical results of the monoethoxycarbene derivative **1** to indicate that in **1**, Cr(0) is also oxidized before the ferrocenyl centre. However, results from the computational study, DFT calculations at the B3LYP/def2-SVP level, indicated that complex **1** may electrochemically be oxidized to the radical cation $\mathbf{1}^{\bullet+}$ because of ferrocenyl oxidation, not Cr(0) oxidation (see Fig. 3, top). The computed spin density of this species indicates that the unpaired electron is located at the iron atom (1.27e). Differently, for biscarbene complex **3**, the spin density of the corresponding radical cation $\mathbf{3}^{\bullet+}$ is not located at the iron atom but at one of the chromium centers (1.17e, Fig. 3, bottom). Thus, for **3**, results from our electrochemical and DFT studies are mutually consistent in indicating that the oxidation process associated with wave 1 in the biscarbene complex **3** involves Cr(0) oxidation to Cr(I) rather than ferrocenyl oxidation. It is clear that for **1**, DFT calculations cast a different perspective than the results obtained from the experimental electrochemistry. In an attempt to validate the B3LYP calculations on carbene complex **1** by using different functionals (at the BP86/def2-SVP and OLYP/def2-SVP levels), the computed spin density was found to be located *ca.* 70 % on the Fe(III) center.

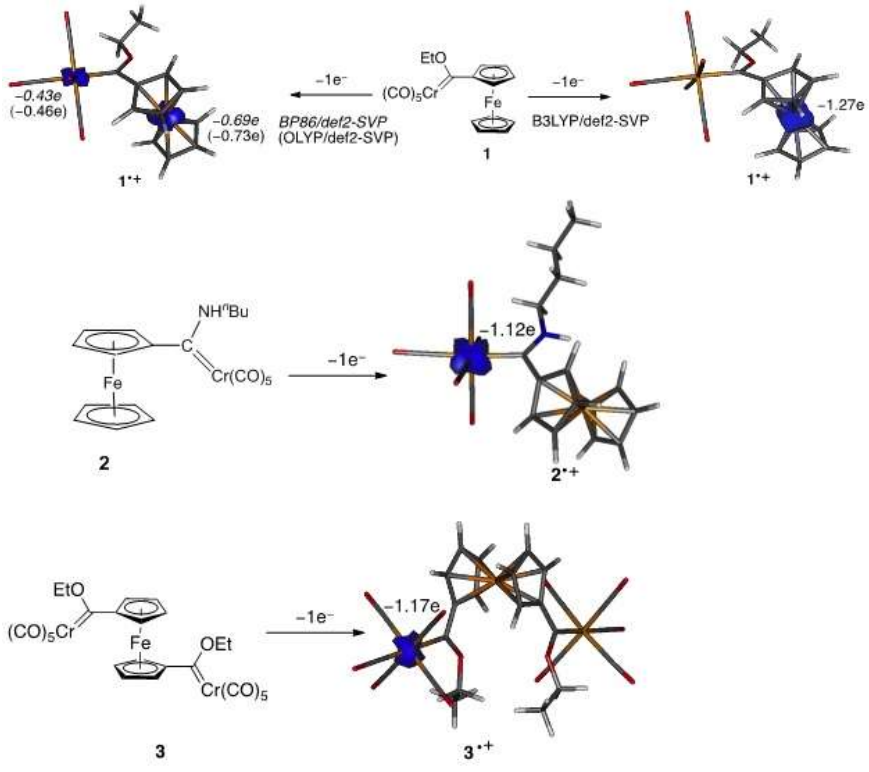


Fig. 3. First one-electron oxidation processes of complexes **1**, **2** and **3**.

When the first oxidation process for the aminocarbene derivative **2** was computed for comparison's sake, the calculations indicated that the corresponding one-electron oxidized radical cation $\mathbf{2}^{\bullet+}$ exhibits a spin density mainly located on the chromium atom (see Fig. 3). This result shows that, unlike what was found for **1**, the presence of an amino-group directly attached to the carbene carbon atom does not change the *computed* or electrochemically determined order of oxidation events of **2** compared to **3**. The oxidation order was still such that the ferrocenyl center is oxidized *after* the Cr(0) moiety. An additional computational study on **4** (see further below, Fig. 7) confirmed that for this complex, Cr(0) oxidation is also preceding Fe(II) oxidation. Attempts at chemical oxidation of **1** with $AgPF_6$, similar to what was reported for ferrocenyl carbene complexes of W(0) [39] and Mn(I) [38], was unsuccessful as the formed species proved too unstable, even at low temperature, to characterize or isolate. In the absence of any experimentally determined evidence as well as an explanation of why **1** should exhibit a different sequence of redox events than **2** – **4**, we conclude that, while note should be taken of the suggested computational order of oxidation for this complex, compound **1** probably also undergoes first a Cr(0) oxidation to Cr(1) followed by ferrocenyl oxidation.

To quantify the influence of the NH^{n}Bu group on the oxidative redox processes of the monocarbene **2**, it is noted that **2** exhibits the Cr(0) electrochemical reversible oxidation process at 0.196 V vs. FcH/FcH^+ (Table 2). This potential is 93 mV lower than for **1**, and again reflects the stronger electron-donating power of NH^{n}Bu compared to the OEt group. The Cr(0) centre of the NH^{n}Bu-ferrocenyl complex **2** is oxidized at potentials 144 and 239 mV smaller than those observed for the recently reported furyl and thienyl NH^{n}Bu monocarbene complexes. These different potentials as well as those observed for wave I above are indicative of interactions between redox-active fragments within the molecules.

A further key observation in favor of such interactions is associated with the splitting of the $Cr^{0/I}$ couple into two definite "a" and "b" components, one for each of the two Cr(0) centers of the biscarbene complexes **3** and **4** (Fig. 4, middle two CVs and Fig. 5). The separation between Cr(0) formal oxidation potentials for waves 1a and 1b of **3** and **4** are $\Delta E^{o'} = E^{o'}_{Cr(0)\ Ox1b} - E^{o'}_{Cr(0)\ Ox1a} = 151$ and 105 mV, respectively. In contrast, when the Fc′-linking functionality is changed to a 2,5-thiendiyl or 2,5-furadiyl functionality, no similar peak splitting for wave 1 was observed [17,18]. Different formal reduction potentials, $E^{o'}$, for symmetrical substituted

dinuclear complexes in which mixed-valent intermediates are generated (for **3** and **4** this refers to complexes where the Cr(0) center of one of the two carbene functionalities was oxidized to a Cr(I) center but not the other) are well known [40,41] in systems that allow electron delocalization or where electrostatic interactions are possible. It is important to recognize, though, that the electrode potentials of closely-spaced redox events are notoriously difficult to assess using CV methods. Richardson and Taube discussed this in detail [42].

Table 2 Cyclic voltammetry data of 0.5 mmol.dm^{-3} solution of [$(OC)_5Cr=C(Fc)X$] and [$(OC)_5Cr=C(X)$-Fc′-$(X)C=Cr(CO)_5$] complexes in CH_2Cl_2 containing 0.1 mol.dm^{-3} [$N(^nBu)_4$][PF_6] as supporting electrolyte at a scan rate of 100 mV s^{-1} and 20 ^oC. Potentials are relative to the FcH/FcH^+ couple.

Complex	Peak label	$E^{o'}$/V, ΔE/mV	$i_{pa}/\mu A$, i_{pc}/i_{pa}
1	I(=)	-2.148, 111	3.20 [b], 0.41
X = OEt	1($Cr^{0/I}$)	0.289, 102	3.48, 0.89
	Fc	0.700, 89	3.29, 0.85
	2($Cr^{I/II}$)	- [a] , - [a]	- [a] , - [a]
2	I(=)	- [a] , - [a]	- [a] , - [a]
X = NH^nBu	1($Cr^{0/I}$)	0.196, 78	3.04, 1.00
	Fc	0.539, 78	2.78, 0.98
	2($Cr^{I/II}$)	- [a] , - [a]	- [a] , - [a]
3	I(=)	-1.845, 104	3.81 [b], 0.39
X = OEt	1a($Cr^{0/I}$)	0.499, 83	3.71, 0.73
	1b($Cr^{0/I}$)	0.650, 80	3.51, 0.23
	Fc	0.730, 97	3.78, < 0.1
	2($Cr^{I/II}$)	- [a] , - [a]	- [a] , - [a]
4	I(=)	- [a] , - [a]	- [a] , - [a]
X = NH^nPr	1a($Cr^{0/I}$)	0.341 [c], 76	3.79, 0.83 [c]
	1b($Cr^{0/I}$)	0.446 [c], 78	3.71, 0.63 [c]
	Fc	0.700, 88	3.52, 0.67 [c]
	2($Cr^{I/II}$)	0.977 [d], -	6.66, -

(a) No peak detected within the solvent potential window; (b) i_{pc} and i_{pa}/i_{pc} values to maintain the current ratio convention of $i_{forward\ scan}/i_{reverse\ scan}$ applied in this manuscript. (c) inaccurate values due to poor resolution, especially in the cathodic sweep; (d) E_{pa} value, no E_{pc} or i_{pc} detected.

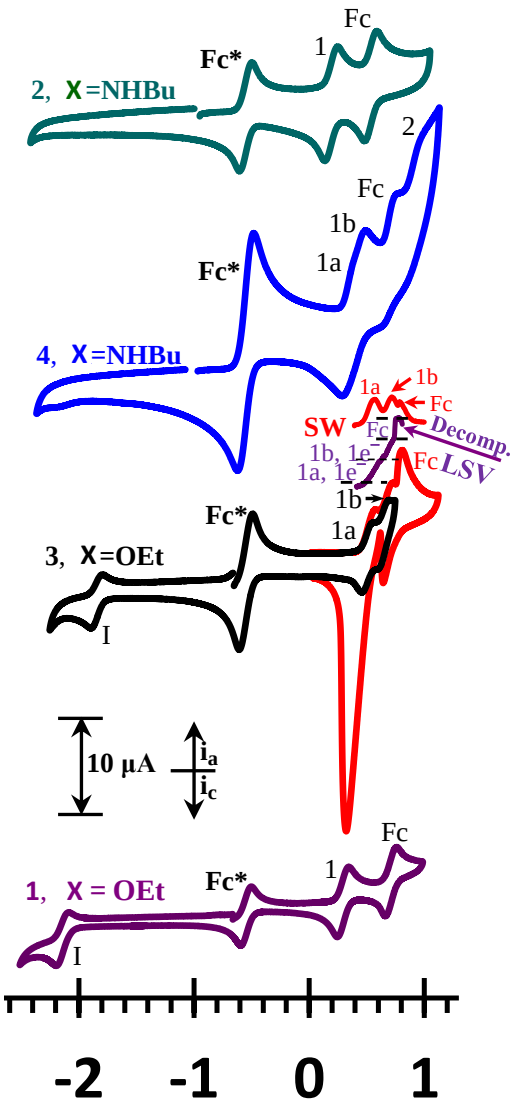


Fig. 4. Cyclic voltammograms of 0.5 mmol.dm^{-3} solutions of monocarbene $[(OC)_5Cr=C(Fc)X]$ **1** and **2** and biscarbene complexes $[(OC)_5Cr=C(X)\text{-}Fc'\text{-}(X)C=Cr(CO)_5]$ **3** and **4** in CH_2Cl_2/0.1 mol.dm^{-3} $[N(^nBu)_4][PF_6]$ on a glassy carbon-working electrode at a scan rate of 200 mV/s. Decamethylferrocene, Fc*, was used as internal standard. For **3**, the black scan was reversed at 880 mV. This excluded oxidation of the ferrocenyl group and no electrode deposition of the substrate on the electrode surface area which led to large cathodic currents at wave 1 as indicated by the red CV was observed.

For **3**, oxidation of both Cr(0) centers (waves 1a and 1b) and the ferrocen-1,1'-diyl group at wave Fc leads to electrode deposition of the substrate as indicated by the large cathodic electrode currents at wave 1 while recording the CV of **3** (printed in red colour) in Fig. 4. However, when switching the potential to exclude wave Fc in the CV of **3**, the resolved oxidations of the two chromium centers at waves 1a and 1b (black CV of **3** in Fig. 4) exhibited electrochemically reversible behavior with i_{pc}/i_{pa} ratios approaching 1 and ΔE_p about 80 mV at slow scan rates (Table 2). Ideally, electrochemically reversible one-electron transfer processes are characterized by $\Delta E_p = E_{pa} - E_{pc} = 59$ mV and peak current ratios approaching unity [43]. For **4**, the resolution between the two Cr(0) oxidations were not as good as for **3**, probably as a result of the NH^nPr conjugation as shown in Fig. 1(b) dominating over ferrocenyl conjugation with the carbene double bond as shown in Fig. 1(a). This at the same time must also contribute to the absence of noticeable amounts of electrode deposition when the potential was allowed to increase enough to oxidize the ferrocenyl group of **4** compared to what was observed for **3**, (Fig. 4).

The third redox process that was observed in **1**– **4** is the one-electron oxidation of the ferrocenyl group (wave Fc in Figs. 4 and 5). This redox process is also electrochemically reversible by virtue of good ΔE_p values at slow scan rates (Table 2). Similarly to the electrochemistry of **3** (Fig. 3) that has been discussed above, we observed by LSV measurements on **4** that poorly resolved waves 1a and 1b both involve the same numbers of electrons, and also involve the same number of electrons as the Fc wave (Fig. 5). Upon recognizing that the ferrocenyl group represents a one electron transfer process, it follows that the current ratio of (wave 1a + wave 1b):wave Fc should be 2:1.

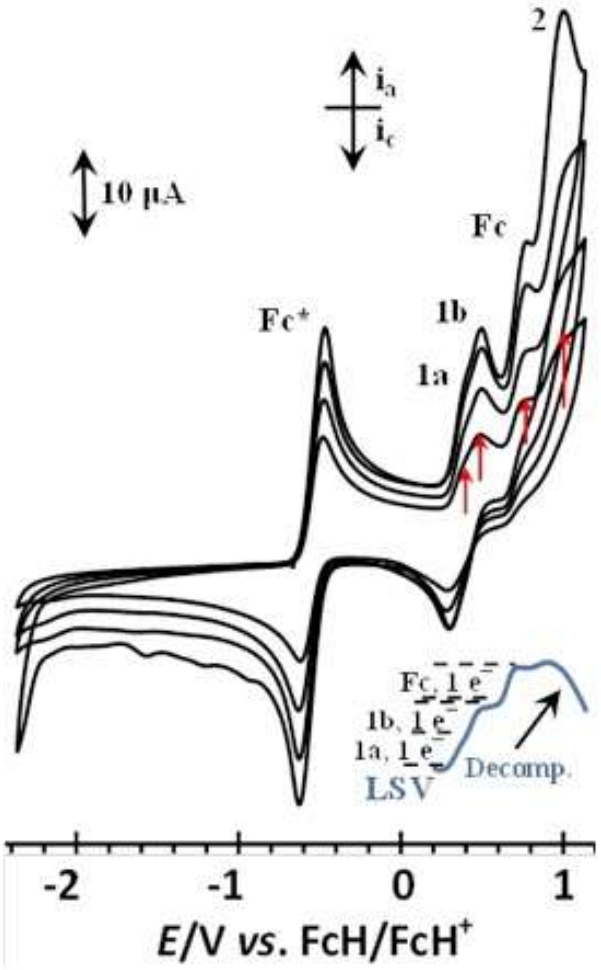
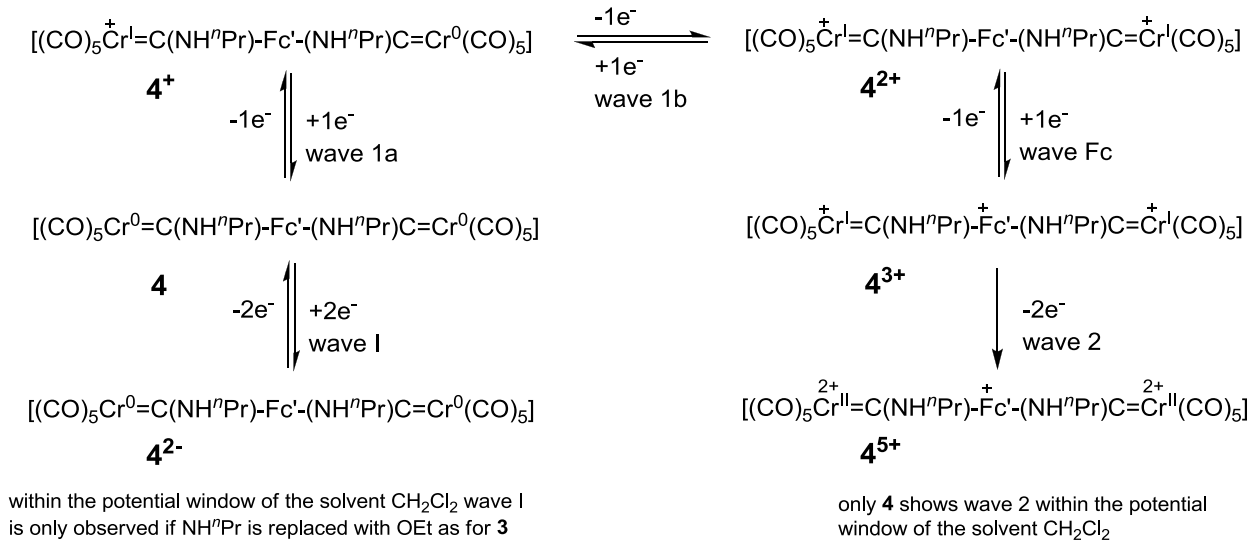


Fig. 5. An LSV at 2 mV/s as well as CVs of 1.0 mmol.dm^{-3} solutions of the biscarbene [(OC)$_5$Cr=C(NH^{n}Pr)-Fc′-(^{n}PrHN)C=Cr(CO)$_5$] **4** in CH_2Cl_2/0.1 mol.dm^{-3} [N(^{n}Bu)$_4$][PF_6] on a glassy carbon-working electrode at scan rates of 100 (smallest currents), 200, 300 and 400 mV/s. Decamethylferrocene, Fc*, was used as internal standard.

Once the ferrocenyl group has been oxidized to ferrocenium, the group electronegativity of this functionality increases from 1.83 to 2.82 on the Gordy scale [8]. This implies that complexes **1** – **4** are after ferrocenyl oxidation under the influence of an electron-withdrawing substituent almost as strong as a CF_3 group which has a Gordy scale group electronegativity of 3.01 [44]. It is therefore expected that any remaining redox processes will be shifted to much more positive potentials. In our previous studies regarding furyl and thienyl complexes, a one-electron Cr(I) oxidation to Cr(II) was observed at *ca.* 1.0 Volt vs FcH/FcH$^+$. In the present compound series only the biscarbene complex [(OC)$_5$Cr=C(NH^{n}Pr)-Fc′-(^{n}PrHN)C=Cr(CO)$_5$], **4**,

exhibited this redox process at E_{pa} = 0.977 V (wave 2 Fig.'s 4 and 5 and Table 2). For compounds **1 - 3**, this fourth redox process fell outside the potential window of the solvent. That wave 2 was observed for **4** is related to this complex having two amino groups that are involved with stabilization via iminium formation, Cr^{-}–C=$N^{+}H^{n}$Pr, compare Fig. 1 for **2**. As with wave I that moved to lower potentials because of this, it is also the case with wave 2. For complex **4** with two amino groups, this negative shift was enough to observe wave 2 in its CV. The number of electrons that are transferred at the redox process associated with wave 2 should be one for each Cr(I) oxidations, but LSV measurements could not confirm this. The complex decomposed on LSV timescale (Fig. 5). Electrode filming, because of immobilization of the oxidized form at the electrode surface, may also contribute to the observed small LSV currents. However, upon comparing the i_{pa} current of wave 2 with that of the one-electron transfer Fc wave and the two one-electron Cr(0) oxidations (Fig. 5, Table 1), we conclude that the observed current of wave 2 is consistent with two one-electron oxidations occurring simultaneously.

Scheme 2 highlights the electrochemical processes associated with **4**. Complexes **2** and **4** undergo essentially the same redox processes, although, of course the monocarbene **2** only shows one electron transferred at each wave, rather than two, and wave 1 does not have an "a" and "b" component. Furthermore, wave I was only detected for ethoxy complexes **1** and **3**; for **2** and **4** this electron transfer process fell outside the potential window of the solvent. With respect to wave 2, only compound **4** exhibited Cr(I) oxidation within the potential window of the solvent. For **1**, **2** and **3**, this process occurred at potentials too large to be measurable in CH_2Cl_2.



Scheme 2. Electrochemical processes associated with **4**. Both the final reduction product possessing the $^{-}$Cr-C$^{\bullet}$ radical anions and the final oxidation product possessing the Cr(II) centers are highly reactive and may undergo further chemical decomposition reactions. The formulas do not show the iminium isomers (Fig. 1); only the carbene mesomeric structures are depicted. The dominance of the imine isomers in carbene structures may well be an important contributing reason why wave I is not observed in the potential window of the solvent, CH_2Cl_2.

To verify the electrochemical assignment of the sequence of redox events, the above described oxidation processes were further studied by computational means utilizing **3** and **4** as substrates. As discussed above (Fig. 3), the first oxidation reaction of biscarbene complex **3** leads to the radical cation $\mathbf{3}^{\cdot+}$ where the computed spin density indicates that the unpaired electron is mainly located at one of the two chromium centers. Further calculations suggest the subsequent second oxidation reaction does not occur at this Cr(I) center leading to the closed-shell singlet dication $\mathbf{3}^{+2}$**(b)** (Fig. 6). Instead, the open-shell singlet species $\mathbf{3}^{+2}$**(a)** is formed in view of the higher stability computed for this complex (ΔE(b-a) = 39.5 kcal/mol). Moreover, the computed spin density for the latter dication indicates that the second oxidation process involves oxidation of the second Cr(0) centre also to Cr(I) rather than oxidation at the ferrocenyl moiety. From the dicationic $\mathbf{3}^{+2}$**(a)** complex, ferrocenyl oxidation leads to the formation of the tricationic species $\mathbf{3}^{\cdot+3}$ where the spin densities are located at the two chromium(I) centers and at the newly generated Fe(III) centre (Fig. 6).

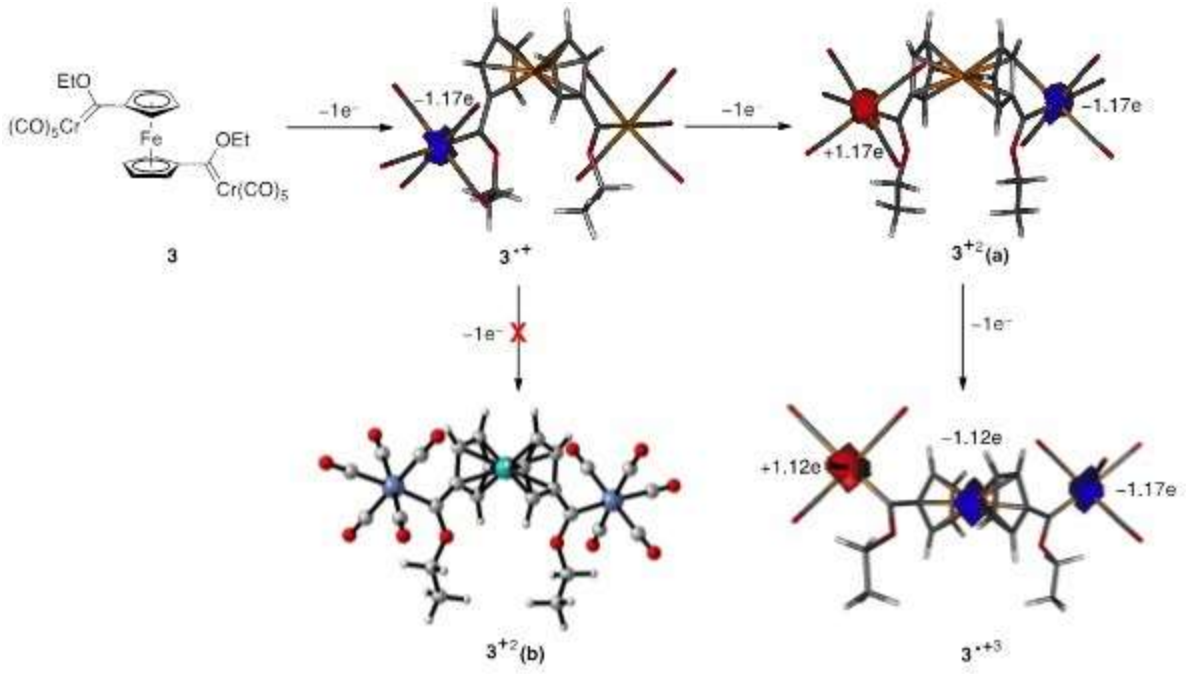


Fig. 6. Oxidation process for complex **3**.

As expected, the bis(aminocarbene) complex **4** follows the same sequence of redox events. As shown in Fig. 7, the first oxidation process involves the formation of the radical cation $\mathbf{4}^{\bullet+}$ where the computed spin density indicates that the unpaired electron is mainly located at one of the chromium centers (1.17e) thus confirming the Cr(0) to Cr(I) reaction. This species is further oxidized to the dication $\mathbf{4}^{+2}$, an open-shell singlet species whose the spin density is located at both Cr(I) centers (-1.18 and 1.18e, respectively). Further oxidation of the ferrocenyl group of **4** produced the corresponding trication $\mathbf{4}^{\bullet+3}$ analogous to $\mathbf{3}^{\bullet+3}$ (see above). We conclude that results from our computational study involving **3** and **4** nicely replicate the redox sequence assignment from the electrochemical analysis described above.

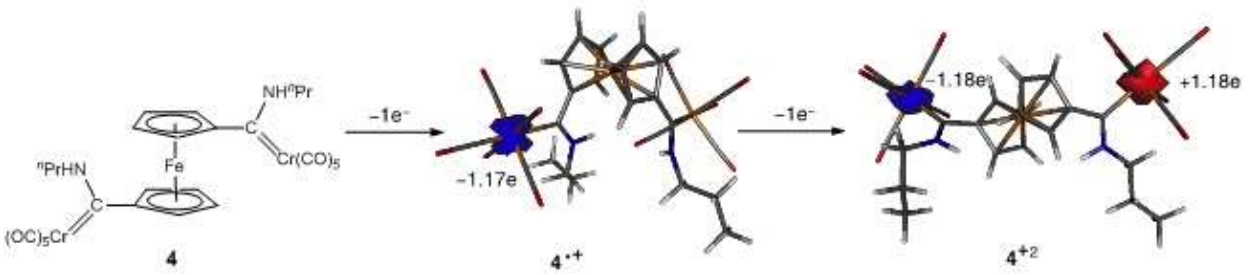


Fig. 7. Oxidation process for complex **4**.

4. Conclusions

New ferrocenyl mono- and bisaminocarbene chromium complexes [(CO)$_5$Cr=C(NH^{n}Bu)Fc], **2**, and [(CO)$_5$Cr=C(NH^{n}Pr)-Fc'-(NH^{n}Pr)C=Cr(CO)$_5$], **4**, were prepared from their ethoxy precursors. From ^{1}H NMR evidence, only the *syn*-rotamer across the restricted $C_{carbene}$–N bond was formed. An electrochemical study revealed up to four redox processes. Electrochemical reversible to quasi-reversible reduction of Cr=C to $^-$Cr-C• was only observed for the ethoxy analogues at far negative potentials; -2.148 or -1.845 V vs FcH/FcH$^+$ for **1** and **3** respectively. This redox process for the amino derivatives **2** and **4** fell outside the negative potential limit of the solvent. Oxidation of Cr(0) to Cr(I) was observed in the 0.196-0.650 V potential range. A striking result of this study is the observation of two resolved Cr$^{0/I}$ couples for the ferrocen-1,1'-diyl biscarbene complexes **2** and **4**. The formal oxidation potentials of these two consecutive Cr(0) oxidations were 105 and 151 mV apart, which hints at the presence of electronic interaction between the Cr(0) centers. The ferrocenyl group of **1** – **4** is oxidized at larger potentials (0.539-0.730 V) than that of the Cr$^{0/I}$ couple. Irreversible oxidation of Cr(I) to Cr(II) at the positive edge of the solvent potential window was only observed for **4** at 0.977 V. This redox process fell outside the positive solvent potential limit for the other complexes. These redox assignments were mutually consistent with the computational results obtained for **2** – **4** at the DFT level.

Acknowledgements

This work is supported by the National Research Foundation, South Africa, (DIB, Grant number 76226; JCS, Grant number 81829), and by the Spanish MICINN and CAM (IF, Grants CTQ2010-20714-CO2-01/BQU, Consolider-Ingenio 2010, CSD2007-00006, S2009/PPQ-1634).

Appendix A. Supplementary data

The LSV and CV of complex **2** and Cartesian coordinates and energies of all the stationary species discussed in the text are included.

References

[1] (a) T.L. Stott, M.O. Wolf, Coord. Chem. Rev. 246 (2003) 89-101;
(b) B.J. Holiday, T.M. Swager, Chem. Commun. 1 (2005) 23-36;
(c) M.O. Wolf, J. Inorg. Organomet. Polym. Mater. 16 (2006) 189-199.

[2] (a) A. Caballero, A. Espinosa, A. Tarraga, P. Molina, J. Org. Chem. 72 (2007) 6924-6937;
(b) M.L. Lage, D. Curiel, I. Fernández, M.J. Mancheño, M. Gómez-Gallego, P. Molina, M.A. Sierra, Organometallics 30 (2011) 1794–1803;
(c) G.M. Chu, I. Fernández, M.A. Sierra, Chem. Eur. J. 19 (2013) 5899-5908.

[3] (a) M.A. Sierra, J.C. del Amo, M.J. Mancheño, M. Gómez-Gallego, J. Am. Chem. Soc. 123 (2001) 851-861;
(b) J.C. del Amo, M.J. Mancheño, M. Gómez-Gallego, M.A. Sierra, Organometallics 23 (2004) 5021-5029;
(c) B. Koo, F.E. McDonald, Org. Lett. 9 (2007) 1737-1740;
(d) I. Fernández, M.J. Mancheño, R. Vicente, L.A. López, M.A. Sierra, Chem. Eur. J. 14 (2008) 11222-11230;
(e) W.I. Dijk, X.P. Zhang, B. de Bruin, Inorg. Chem. 50 (2011) 9896-9903;
(f) M.P. López-Alberca, I. Fernández, M.J. Mancheño, M. Gómez-Gallego, L. Casarrubios, M.A. Sierra, Eur. J. Org. Chem. (2011) 3293-3300;

(g) G. Occhipinti, V.R. Jensen, Organometallics 30 (2011) 3522-3529;

(h) For a revision of the catalytic transmetallation to late transition metals, see M. Gómez-Gallego, M.J. Mancheño, M.A. Sierra, Acc. Chem. Res. 38 (2005) 44-53.

[4] For selected reviews, see: (a) J. Barluenga, J. Santamaría, M. Tomás, Chem. Rev. 104 (2004) 2259-2283;

(b) M.A. Sierra, I. Fernández, F.P. Cossío, Chem. Commun. (2008) 4671-4682;

(c) K.H. Dötz, J. Stendel, Jr., Chem. Rev. 109 (2009) 3227-3274;

(d) M.A. Fernández-Rodríguez, P. García-García, E. Aquilar, Chem. Commun. 46 (2010) 7670-7687.

[5] C. Baldoli, P. Cerea, L. Falciola, C. Giannini, F. Licandro, S. Maiorana, P. Mussini, D.J. Perdiccia, J. Organomet. Chem. 690 (2005) 5777 - 5787.

[6] (a) M.E. Bos, W.D. Wulff, R.A. Miller, S. Chamberlin, T.A. Brandvold, J. Am. Chem. Soc. 113 (1991) 9293 -9319;

(b) B.A. Anderson, J. Bao, T.A. Brandvold, C.A. Challener, W.D. Wulff, Y.C. Xu, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 10671 - 10687.

[7] (a) L.S. Hegedus, Tetrahedron 53 (1997) 4105-4128;

(b) A. Arrieta, F.P. Cossío, I. Fernández, M. Gómez-Gallego, B. Lecea, M.J. Mancheño, M.A. Sierra, J. Am. Chem. Soc. 122 (2000) 11509-11510;

(c) I. Fernández, M.A. Sierra, M. Gómez-Gallego, M.J. Mancheño, F.P. Cossío, Chem. Eur. J. 11 (2005) 5988-5996;

(d) I. Fernández, M.A. Sierra, M.J. Mancheño, M. Gómez- Gallego, F.P. Cossío, J. Am. Chem. Soc. 130 (2008) 13892-13899;

(e) I. Fernández, F.P. Cossío, M.A. Sierra, Acc. Chem. Res. 44 (2011), 479-490;

(f) I. Fernández, M.A. Sierra, Top. Heterocycl. Chem. 30 (2013) 65-84.

[8] (a) S. Otto, A. Roodt, J.J.C. Erasmus, J.C. Swarts, Polyhedron 17 (1998) 2447-2453;

(b) W.C. Du Plessis, W.L. Davis, S.J. Cronje, J.C. Swarts, Inorg. Chim. Acta 314 (2001) 97-104.

[9] A. Hildebrandt, T. Rüffer, E. Erasmus, J.C. Swarts, H. Lang, Organometallics 29 (2010) 4900-4905.

[10] (a) N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877-910;

(b) J.M. Speck, R. Claus, A. Hildebrandt, T. Rüffer, E. Erasmus, L. van As, J.C. Swarts, H. Lang, Organometallics 31 (2012) 6373-6380;

(c) U. Pfaff, A. Hildebrandt, D. Schaarschmidt, T. Hahn, S. Liebing, J. Kortus, H. Lang, Organometallics 31 (2012) 6761-6771.

[11] A.R. Pike, L.C. Ryder, B.R. Horrocks, W. Clegg, B.A. Connolly, A. Houlton, Chem. Eur. J. 11 (2005) 344-353.

[12] F. Spanig, C. Kolvacs, F. Hauke, K. Ohlubo, F. Fukuzumi, D. Guldi, A. Hirsch, J. Am. Chem. Soc. 131 (2009) 8180-8195.

[13] J. Conradie, J.C. Swarts, Organometallics 28 (2009) 1018-1026.

[14] T.G. Vosloo, W.C. du Plessis, J.C. Swarts, Inorg. Chim. Acta 331 (2002) 188-193.

[15] (a) C.E.J. van Rensburg, E. Kreft, J.C. Swarts, S.R. Dalrymple, D.M. Macdonald, M.W. Cooke, M.A.S. Aquino, Anticancer Res. 22 (2002) 889-892;

(b) J.T. Chantson, M.V.V. Falzacappa, S. Crovella, N. Metzler-Nolte, J. Organomet. Chem. 690 (2005) 4564-4572;

(c) R.F. Shago, J.C. Swarts, E. Kreft, C.E.J. van Rensburg, Anticancer Res. 27 (2007) 3431-3434;

(d) J.C. Swarts, T.G. Vosloo, S.J. Cronje, W.C. Du Plessis, C.E.J. van Rensburg, E. Kreft, J.E. van Lier, Anticancer Res. 28 (2008) 2781-2784;

(e) I. Ott, K. Kowalski, R. Gust, J. Maurer, P. Mücke, R.F. Winter, Bioorg. Med. Chem. Lett. 20 (2010) 866-869;

(f) A. Gross, N. Hüsken, J. Schur, L. Raszeja, I. Ott, N. Metzler-Nolte, Bioconjug. Chem. 23 (2012) 1764-1774;

(g) M. Maschke, M. Lieb, N. Metzler-Nolte, Eur. J. Inorg. Chem. (2012) 5953-5959.

[16] (a) I. Fernández, M.J. Mancheño, M. Gómez-Gallego, M.A. Sierra, Org. Lett. 5 (2003) 1237-1240;

(b) R. Martínez-Álvarez, M. Gómez-Gallego, I. Fernández, M.J. Mancheño, M.A. Sierra, Organometallics 23 (2004) 4647-4654;

(c) D.I. Bezuidenhout, W. Barnard, B. van der Westhuizen, E. van der Watt, D.C. Liles, Dalton Trans. 40 (2011) 6711-6721;

(d) D.I. Bezuidenhout, S. Lotz, D.C. Liles, B. van der Westhuizen, Coord. Chem. Rev. 256 (2012) 479-524.

[17] B. van der Westhuizen, P.J. Swarts, I. Strydom, D.C. Liles, I. Fernández, J.C. Swarts, D.I. Bezuidenhout, Dalton Trans. 42 (2013) 5367 -5378.

[18] B. van der Westhuizen, P.J. Swarts, L.M. van Jaarsveld, D.C. Liles, U. Siegert, J.C. Swarts, I. Fernández, D.I. Bezuidenhout, Inorg. Chem. 52 (2013) 6674-6684.

[19] (a) J.A. Connor, E.M. Jones, J.P. Lloyd, J. Organomet. Chem. 24 (1970) C20-C23;
(b) J.G. López-Cortés, L.F. Contreras de la Cruz, M.C. Ortega-Alfaro, R.A. Toscano, C. Alvarez-Toledano, H. Rudler, J. Organomet. Chem. 690 (2005) 2229 – 2237.

[20] D.I. Bezuidenhout, E. van der Watt, D.C. Liles, M. Landman, S. Lotz, Organometallics 27 (2008) 2447 -2456 .

[21] H. Meerwein, Org. Synth. 46 (1966) 113-116.

[22] (a) R.R. Gagne, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854 – 2855;
(b) G. Gritzner, J. Kuta, J. Pure Appl. Chem. 56 (1984) 461 – 466.

[23] Leading references describing the electrochemical activity and behavior of ferrocene and decamethylferrocene in a multitude of organic solvents are: (a) N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877-910;
(b) J. Ruiz, D. Astruc, C.R. Acad. Sci., Ser. IIc 1, Paris, 1998, 21;
(c) I. Noviandri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters, L. Phillips, J. Phys. Chem. B 103 (1999) 6713 – 6722;
(d) R.J. Aranzaes, M.C. Daniel, D. Astruc, Can. J. Chem. 84 (2006) 288 – 299;
(e) E. Fourie, J.C. Swarts, I. Chambrier, M.J. Cook, Dalton Trans. (2009) 1145 - 1154.

[24] Gaussian 09, Revision B.1, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J.

Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[25] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789;
(b) A.D. Becke, J. Chem. Phys., 1993, 98, 5648-5661.

[26] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 7 (2005) 3297-3305.

[27] (b) J.P. Perdew, Phys. Rev. B 33 (1986) 8822-8824;
(a) A.D. Becke, Phys. Rev. A 38 (1988) 3098-3100.

[28] N.C. Handy, A. Cohen, J. Mol. Phys. 99 (2001) 403-412.

[29] H. Sünkel, S.J. Bernhartzeder, J. Organomet. Chem. 696 (2011) 1536 - 1540.

[30] J.A. Connor, E.M. Jones, J.P. Lloyd, J. Organomet. Chem. 24 (1970) C20-C22 .

[31] M.S. Inkpen, S. Du, M. Driver, T. Albrecht, N.J. Long, Dalton Trans. 42 (2013) 2813 - 2816.

[32] (a) U. Klabunde, E.O. Fischer, J. Am. Chem. Soc. 89 (1967) 7141 – 7142;
(b) D.I. Bezuidenhout, D.C. Liles, P.H. van Rooyen, S. Lotz, J. Organomet. Chem. 692 (2007) 774 – 783.

[33] (a) R.D. Topsom, Acc. Chem. Res. 16 (1983) 292-298;
(b) M.L. Lage, I. Fernández, M.J. Mancheño, M.A. Sierra, Inorg. Chem. 47 (2008) 5253 - 5258.

[34] (a) D.M. Adams, Metal-Ligand and Related Vibrations, Edward Arnold Publishers Ltd., London, 1967, 98;
(b) P.S. Braterman, Metal Carbonyl Spectra, Academic Press Inc., London, 1975, 68.

[35] (a) S. Lotz, Y.M. Terblans, J. Chem. Soc., Dalton Trans. (1997) 2177 -2182;
(b) C. Crause, H. Görls, S. Lotz, Dalton Trans. (2005) 1649 -1657;
(c) S. Lotz, N.A. van Jaarsveld, D.C. Liles, C. Crause, H. Görls, Y.M. Terblans, Organometallics 31 (2012) 5371-5383.

[36] Reduction in aprotic solvents of alkenes in general and the carbene double bond, Cr=C, in particular, are known to occur at far negative applied potentials [17,18]. During a one-electron transfer process a radical anion of considerable instability is generated; follow-up chemical reactions destroy this electrochemically generated species quickly. References to general alkene reduction include: (a) A.J. Fry, Synthetic Organic Electrochemistry, 2nd ed., John Wiley and Sons, New York, 1989, 208, 232;

(b) J. Volke, F. Liska, Electrochemistry in Organic Synthesis, Springer-Verlag, Berlin, 1994, 90.

[37] This situation is usual in Fischer-type carbene complexes. See, for instance (a) M. Cases, G. Frenking, M. Duran, M. Solà, Organometallics 21 (2002) 4182-4191;

(b) G. Frenking, M. Solà, S.F. Vyboishchikov, J. Organomet. Chem. 690 (2005) 6178-6204;

(c) I. Fernández, M.A. Sierra, F.P. Cossío, J. Org. Chem. 71 (2006) 6178-6184;

(d) I. Fernández, M.A. Sierra, F.P. Cossío, J. Org. Chem. 73 (2008) 2083-2089;

(e) D.M. Andrada, A.M. Granados, M. Solá, I. Fernández, Organometallics 30 (2011) 466-476.

(f) W.I. Dzik, X.P. Zhang, B. de Bruin, Inorg. Chem. 50 (2011) 9896-9903;

(g) M. Landman, R. Liu, P.H. van Rooyen, J. Conradie, Electrochim. Acta 114 (2013) 205-214.

[38] D.I. Bezuidenhout, B. van der Westhuizen, P.J. Swarts, T. Chatturgoon, O.Q. Munro, I. Fernández, J.C. Swarts, Chem. Eur. J. 20 (2014) 4974-4985.

[39] (a) D.I. Bezuidenhout, I. Fernández, B. van der Westhuizen, P.J. Swarts, J.C. Swarts, Organometallics 32 (2013) 7334-7344;

(b) B. van der Westhuizen, J.M. Speck, M. Korb, J. Friedrich, D.I. Bezuidenhout, H. Lang, Inorg. Chem. 52 (2013) 14253-14264.

[40] (a) C. Creutz, H. Taube, J. Am. Chem. Soc. 91 (1969) 3988 – 3989;

(b) N. van Order, W.E. Geiger, T.E. Bitterwolf, A.L. Reingold, J. Am. Chem. Soc. 109 (1987) 5680 – 5690;

(c) W.E. Geiger, N. van Order, D.T. Pierce, T.E. Bitterwolf, A.L. Reingold, N.D. Chasteen, Organometallics 10 (1991) 2403 – 2411;

(d) D.T. Pierce, W.E. Geiger, Inorg. Chem. 33 (1994) 373 – 381;

(e) K.C. Kemp, E. Fourie, J. Conradie, J.C. Swarts, Organometallics 27 (2008) 353 - 362.

[41] J. March, Advanced Organic Chemistry, 4th ed., John Wiley and Sons, New York, 1992, 17-20, 263-269, 273-275.

[42] D.E. Richardson, H. Taube, Inorg. Chem. 20 (1981) 1278 -1285.

[43] (a) D.H. Evans, K.M. O'Connell, R.A. Peterson, M.J. Kelly, J. Chem. Educ. 60 (1983) 290-293;

(b) P.T. Kissinger, W.R. Heineman, J. Chem. Educ. 60 (1983) 702-706;

(c) J.J. van Benshoten, L.Y. Lewis, W.J. Heineman, J. Chem. Educ. 60 (1983) 772-776;

(d) G.A. Mobbott, J. Chem. Educ. 60 (1983) 697-702;

(e) M. J. Cook, I. Chambrier, G. F. White, E. Fourie, J. C. Swarts, Dalton Trans. (2009) 1136-1144;

(f) H.J. Gericke, N.I. Barnard, E. Erasmus, J.C. Swarts, M.J. Cook, M.A.S. Aquino, Inorg. Chim. Acta 363 (2010) 2222 – 2232.

[44] W.C. du Plessis, J.J.C. Erasmus, G.J. Lamprecht, J. Conradie, T.S. Cameron, M.A.S. Aquino, J.C. Swarts, Can. J. Chem. 77 (1999) 378 - 386.