



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



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ABSTRACT

The series $[(CO)_5Cr=C(R)Fc]$, (**1**, R = OEt; **2**, R = NHⁿBu) as well as $[(OC)_5Cr=C(R)-Fc'-(R)C=Cr(CO)_5]$, (**3**, R = OEt; **4**, R = NHⁿPr) 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 $\Delta E^{o'}$ 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) center 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 oxidized *before* Cr(0) oxidation. The ethoxycarbenes **1** and **3** also showed a carbene double bond reduction to an anion radical, $^{\ominus}Cr=C$, 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.

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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 centers [16]. From our recently published results related to an electrochemical and theoretical investigation

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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 $[(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})(\text{Ar}')\text{C}(\text{OEt})=\text{Cr}(\text{CO})_5]$ with $\text{Ar}' = \text{Th}'$ 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-bis-carbene 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 $[(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})(\text{Fc}')\text{C}(\text{OEt})=\text{Cr}(\text{CO})_5]$, where the 2,5-thiendiyl or 2,5-furadiyl linking aryl unit between the two Cr carbene functionalities was replaced by a ferrocene-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 $[\text{Cr}(\text{CO})_5=\text{C}(\text{NH}^n\text{Bu})\text{Fc}]$, **2**, and $[(\text{CO})_5\text{Cr}=\text{C}(\text{NH}^n\text{Pr})(\text{Fc}')\text{C}(\text{NH}^n\text{Pr})=\text{Cr}(\text{CO})_5]$, **4**, from the previously reported ethoxy complexes $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OEt})\text{Fc}\}]$, **1** [19], and $[(\text{CO})_5\text{Cr}\{\text{C}(\text{OEt})(\text{Fc}')\text{C}(\text{OEt})\}\text{Cr}(\text{CO})_5]$, **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: ^1H 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

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

A diethylether solution of **1** (2 mmol, 0.87 g) was stirred at room temperature (rt) and *n*-butylamine (2 mmol, 0.20 mL) was added. The color 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: 0.72 g (78%), yellow solid. *Anal.* Calc. for $\text{CrFeC}_{20}\text{H}_{19}\text{NO}_5$: C, 52.08; H, 4.16. Found: C, 52.05; H, 4.10. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 9.48 (s, 1H, NH), 4.42 (br, 4H, $\text{H}_\alpha, \text{H}_\beta$ overlapping resonances), 4.17 (s, 5H, Cp), 4.10–3.96 (m, 2H, NCH_2), 1.85 (p, $J = 7.5$ Hz, 2H, CH_2CH_2), 1.57 (s, 2H, CH_2CH_2), 1.06 (t, $J = 7.4$ Hz, 3H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 270.6 ($\text{C}_{\text{carbene}}$), 223.6 (*trans*-CO), 217.8 (*cis*-CO), 99.6 (C_{ipso}), 70.0 (C_α), 68.3 (C_β), 69.4 (Cp), 52.6 (NCH_2), 31.9 (CH_2CH_2), 20.1 (CH_2CH_2), 13.8 (CH_3). FTIR (hexane, νCO , cm^{-1}): 2053 s (A'_1), 1971 w (B), 1931 s (A'_1 overlap E).

2.2.2. $[(\text{CO})_5\text{Cr}=\text{C}(\text{NH}^n\text{Pr})(\text{Fc}')\text{C}(\text{NH}^n\text{Pr})=\text{Cr}(\text{CO})_5]$ (**4**)

Complex **3** (2 mmol, 1.27 g) was dissolved in diethylether and *n*-propylamine (2 mmol, 0.16 mL) was added at rt. The color 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: 0.96 g (68%), deep yellow crystals. *Anal.* Calc. for $\text{Cr}_2\text{FeC}_{28}\text{H}_{24}\text{N}_2\text{O}_{10}$: C, 56.82; H, 5.08. Found: C, 55.72; H, 4.90. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 9.38 (s, 2H, NH), 4.42 (m, 8H, $\text{H}_\alpha, \text{H}_\beta$ overlapping resonances), 4.01 (m, 4H, NCH_2), 1.89 (m, 4H, CH_2CH_3), 1.15 (t, $J = 7.4$ Hz, 6H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 270.6 ($\text{C}_{\text{carbene}}$), 223.2 (CO_{trans}), 217.5 (CO_{cis}), 101.4 (C_{ipso}), 70.9 (C_α), 68.7 (C_β), 54.7 (HNCH_2), 23.2 (CH_2CH_3), 11.2 (CH_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 $\text{O}_2 < 5$ ppm) as described before [17,18]. CVs were recorded from 0.5 $\text{mmol}\cdot\text{dm}^{-3}$ solutions of analyte in CH_2Cl_2 containing 0.1 $\text{mol}\cdot\text{dm}^{-3}$ $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ 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^+ , $\text{FcH} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$, $E^\circ = 0.00$ 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 $\Delta E = 72$ mV and $i_{\text{pc}}/i_{\text{pa}} = 1$ 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 $[\text{Cr}(\text{CO})_6]$ and subsequent alkylation with Et_3OBF_4 [21] yielded the known complex **1** $[(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})\text{Fc}]$, 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

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