Synthesis and isomerization behavior of cyano-vinyl ferrocenes

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ABSTRACT

The reaction of Z-FcC(Cl)=CHC(O)H (Fc = Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)) with KI/ZnO/NH$_2$OH·HCl gave Z-FcC(Cl)=CHC≡N, which on further treatment with ROH/KOH (R = Me, Et, ^{i}Pr, OCH$_2$CH$_2$OH) or H$_2$NCH$_2$Ph produced Z-FcC(OR)=CHC≡N, E-FcC(NHCH$_2$Ph)=CHC≡N and FcC(OCH$_2$)$_2$CH$_2$C≡N. However, the use of the sterically demanding O^{t}Bu group resulted in the elimination of HCl giving 3-ferrocenylpropynenitrile. Complex [PtCl$_2$(N≡CCH=C(Cl)Fc)$_2$], as a mixture of E/Z and $cis/trans$ isomers, was accessible by the addition of [PtCl$_2$] to Z-FcC(Cl)=CHC(O)H. When Z-FcC(OR)=CHC≡N (R = Me; Et; ^{i}Pr) was reacted with [PtCl$_2$] in the molar ratio of 2:1, solely $trans$-[PtCl$_2$(E-N≡CCH=C(OR)Fc)$_2$] was formed with isomerization of the C,C double bond from Z to E. These are the first examples for the entirely conversion of Z to E isomers of coordinated acrylonitriles. The stereochemistry of Z-FcC(OR)=CHC≡N is maintained, when the Pt source is excluded, while a combination of heat and light treatment resulted in the partial isomerization. The electrochemical properties of the chloro- and the methoxy-functionalized vinyl ferrocene were studied. In the corresponding Pt complexes an anodic shift of the ferrocenyl units is observed due to an electron density transfer towards the Pt atom. Spectroelectrochemical studies of the Pt complexes allowed no definite verification that an electronic interaction between the redox-active ferrocenyl/ferrocenium termini occurs even when high ΔE_p values in the cyclic indicate that two individual oxidation processes might take place in a close potential range.

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1. Introduction

Recently, the research on "molecular wire molecules" in organometallic chemistry has become important, due to the increasing demand for miniaturization in microelectronics. In this respect, transition metal complexes featuring π-conjugated bridging units, including sp- and sp^2-hybridized carbon chains like polyynes (−C≡C−)$_n$ (n = 1 − 8) [1−4] and polyenes (−CH=CH−)$_n$ (n = 1 − 6) [5−8], connecting the appropriate redox-active metal centers, received great interest. Such complexes possess high potential as components in molecular electronics. [7,9−13]. The electron transfer between the corresponding terminal metal fragments depends on the number [2,14−16] and variety [16−22] of the linking groups. In particular, comprehensive investigations of the influence of the ethylene connectivity on the electronic interactions were reported [23−26]. As terminal redox-active building blocks mainly sandwich and half-sandwich moieties were established due to their excellent electrochemical behavior [27−30].

In 1976, Taube and Krentzien reported about the first use of the N≡C−C≡N structural motif, as verified in ^{t}butylmalononitrile, as an excellent electron conducting bridge between the ruthenium ions in homobimetallic ruthenium complexes [31]. Later Taube, Henri and Lewis reported in 1981 on the example of the heteronuclear complex $trans$-[Ru(NH$_3$)$_5$(N≡C−CH=CH−Fc)]$^{2+}$, in which a ferrocenyl and a Ru(II)(NH$_3$)$_5$ units are bridged by a CH=CH−C≡N connectivity, where an electronic interaction in the mixed-valent species between the iron(II) and the ruthenium(III) ions takes place [32]. The electron transfer was confirmed by the observation of a small IVCT (= Inter-Valence Charge Transfer) band in the NIR spectrum classifying this compound as a weakly coupled mixed-valence system [16,33].

This prompted us to use acrylonitrile derivatives as π-conjugated connectivities in platinum(II) complexes featuring terminal, redox-active ferrocenyls. We here describe the synthesis, properties, structure and bonding of complexes of type Z-FcC(X)=CHC≡N (X = Cl, OMe, OEt, O^{i}Pr; Fc = Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)), E-FcC(NHCH$_2$Ph)=CHC≡N, FcC(OCH$_2$)$_2$CH$_2$C≡N, [PtCl$_2$(N≡CCH=C(Cl)Fc)$_2$] (isomeric mixture) and $trans$-[PtCl$_2$(E-N≡CCH=C(OR)Fc)$_2$] (R = Me, ^{i}Pr).

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2. Material and methods

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Toluene and dichloromethane were dried using a MBraun MB SPS-800 system (double column solvent filtration, working pressure 0.5 bar).

2.1. Reagents

3-Chloro-3-ferrocenylpropenenitrile (*Z*-**2**) and 3-ferrocenylpropynenitrile (**5**) were synthesized according to published procedures [34].

2.2. Instruments

Infrared spectra were recorded with a Thermo Nicolet 200 FT-IR spectrometer using the KBr press technique for sample preparation. NMR spectra were recorded with a Bruker Avance III 500 FT NMR spectrometer (^{1}H NMR at 500.303 MHz, ^{13}C{^{1}H} NMR at 125.813 MHz) at ambient temperature, unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane using the solvent as internal reference (CDCl$_3$: ^{1}H NMR δ 7.26 ppm; ^{13}C{^{1}H} NMR δ 77.16 ppm) [35]. Coupling constants (*J*) are reported in Hertz (Hz) and integrations are reported in numbers of protons. The following abbreviations were used to describe peak patterns: s = singlet, d = doublet, pt = pseudo-triplet, q = quartet, sp = septet. The melting points (sealed off in argon-flushed capillaries) were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed with a Thermo FLASHEA 1112 Series instrument. High-resolution mass spectra were recorded with a Bruker micrOTOF QII equipment with an Apollo II ESI source.

2.3. Electrochemistry

Electrochemical measurements were conducted in 1.0 mmol L^{-1} solutions of anhydrous dichloromethane containing 0.1 mol L^{-1} of [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte under an atmosphere of argon at 25 °C, utilizing a Voltalab PGZ 100 radiometer electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode, and an Ag/AgCl (0.01 mol L^{-1} [AgNO$_3$]) reference electrode, mounted on a Luggin capillary was applied. The working electrode was pretreated by polishing on a Buehler microcloth first with a 1 μm and then with a 0.25 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mol L^{-1} of [AgNO$_3$] and 0.1 mol L^{-1} of [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] in acetonitrile in a Luggin capillary with a porous Vycor tip. This Luggin capillary was inserted into a second Luggin capillary with porous Vycor tip filled with a 0.1 mol L^{-1} of a [N^{n}Bu$_4$][B(C$_6$F$_5$)$_4$] dichloromethane solution. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within ±5 mV. Experimental potentials were referenced against an Ag/AgCl reference electrode but results are presented referenced against ferrocene or decamethylferrocene (Fc*) as an internal standard, as required by IUPAC [36]. To achieve this, since the ferrocene couple FcH/FcH$^+$ (Fc = Fe(η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$)) interferes with the ferrocenyl signals, each experiment was first performed in the absence of any internal standard and then repeated in the presence of 1 mmol L^{-1} of ferrocene. Data were then manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH$^+$ couple to 0.0 V [36]. Under our conditions the Fc*/Fc*$^+$ couple was at −614 mV *vs* FcH/FcH$^+$ (ΔE_p = 60 mV), while the FcH/FcH$^+$ couple itself was at 220 mV *vs* Ag/AgCl

(ΔE_p = 61 mV) [37].

2.4. Single crystal X-ray diffraction

Diffraction data for *Z*-**2**, *Z*-**3a**,**c**, *E*-**3d**, **4**, *cis-Z/Z*-**6**, *trans-E/Z*-**7a** and *trans-E/E*-**7a** were collected with an Oxford Gemini S diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (*E*-**3d**, **4**, *cis-Z/Z*-**6**, *trans-E/Z*-**7a** and *trans-E/E*-**7a**) or Cu Kα radiation (λ = 1.54184 Å) (*Z*-**2**, *Z*-**3a**,**c**) using oil-coated shock-cooled crystals. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 [38,39]. Graphics of the molecular structures have been created by using SHELXTL [39] and ORTEP [40].

Crystal data of *Z*-2: C$_{13}$H$_{10}$ClFeN, M = 271.52 g mol^{-1}, dark red prism, 0.7 × 0.08 × 0.08 mm, space group *Pca*2$_1$, orthorhombic, a = 40.125(3) Å, b = 5.9531(5) Å, c = 18.8762(16) Å, V = 4509.0(6) Å^3, Z = 16, ρ_{calcd} = 1.600 g cm^{-3}, T = 115 K, θ range 3.21–62.95°, 7735 reflections collected, 5190 independent reflections, R_{int} = 0.0566, R_1 = 0.0990, wR_2 = 0.2461 ($I > 2\sigma(I)$), absolute structure parameter [41] 0.014(9).

Crystal data of *Z*-3a: C$_{14}$H$_{13}$FeNO, M = 267.10 g mol^{-1}, orange prism, 0.3 × 0.2 × 0.2 mm, space group *P*2$_1$/*c*, monoclinic, a = 9.4241(3) Å, b = 11.2877(3) Å, c = 11.5320(4) Å, β = 110.504(4), V = 1149.02(6) Å^3, Z = 4, ρ_{calcd} = 1.544 g cm^{-3}, T = 115 K, θ range 5.01–62.90°, 3225 reflections collected, 1792 independent reflections, R_{int} = 0.0380, R_1 = 0.0411, wR_2 = 0.1006 ($I > 2\sigma(I)$).

Crystal data of *Z*-3c: C$_{16}$H$_{17}$FeNO, M = 295.16 g mol^{-1}, orange prism, 0.3 × 0.2 × 0.2 mm, space group *Pbcn*, orthorhombic, a = 23.9042(5) Å, b = 9.2805(2) Å, c = 12.4218(2) Å, V = 1149.02(6) Å^3, Z = 8, ρ_{calcd} = 1.423 g cm^{-3}, T = 115 K, θ range 3.07–62.93°, 7438 reflections collected, 2195 independent reflections, R_{int} = 0.0284, R_1 = 0.0328, wR_2 = 0.0810 ($I > 2\sigma(I)$).

Crystal data of 4: C$_{15}$H$_{15}$FeNO$_2$, M = 297.13 g mol^{-1}, yellow plates, 0.4 × 0.35 × 0.02 mm, space group *Pna*2$_1$, orthorhombic, a = 19.7331(15) Å, b = 11.6817(6) Å, c = 5.7068(3) Å, V = 1315.92(14) Å^3, Z = 4, ρ_{calcd} = 1.500 g cm^{-3}, T = 110 K, θ range 3.49–25.50°, 3199 reflections collected, 1977 independent reflections, R_{int} = 0.0356, R_1 = 0.0329, wR_2 = 0.0711 ($I > 2\sigma(I)$), absolute structure parameter [41] 0.03(3).

Crystal data of *E*-3d: C$_{20}$H$_{18}$FeN$_2$, M = 342.21 g mol^{-1}, yellow prism, 0.4 × 0.4 × 0.4 mm, space group *P*$\bar{1}$, triclinic, a = 7.6575(6) Å, b = 10.3867(9) Å, c = 10.7866(14) Å, α = 69.978(9)°, β = 75.130(9), γ = 88.015(7), V = 777.74(14) Å^3, Z = 2, ρ_{calcd} = 1.461 g cm^{-3}, T = 110 K, θ range 2.99–25.48°, 4868 reflections collected, 2876 independent reflections, R_{int} = 0.0219, R_1 = 0.0329, wR_2 = 0.0722 ($I > 2\sigma(I)$).

Crystal data of *cis-Z/Z*-6: C$_{26}$H$_{20}$Cl$_4$Fe$_2$N$_2$Pt, M = 809.03 g mol^{-1}, purple needle, 0.50 × 0.10 × 0.10 mm, space group *P*$\bar{1}$, triclinic, a = 8.0064(2) Å, b = 13.2612(4) Å, c = 13.7278(4) Å, α = 61.637(3)°, β = 80.671(2)°, γ = 82.577(2)°, V = 1263.32(6) Å^3, Z = 2, ρ_{calcd} = 2.127 g cm^{-3}, T = 100 K, θ range 2.95–25.00°, 19341 reflections collected, 4442 independent reflections, R_{int} = 0.0371, R_1 = 0.0200, wR_2 = 0.0458 ($I > 2\sigma(I)$).

Crystal data of *trans-E/E*-7a: C$_{28}$H$_{26}$Cl$_2$Fe$_2$N$_2$O$_2$Pt, M = 800.20 g mol^{-1}, orange prism, 0.40 × 0.40 × 0.35 mm, space group *P*2$_1$/*c*, monoclinic, a = 6.19910(10) Å, b = 11.7030(2) Å, c = 18.0538(3) Å, β = 99.229(2)°, V = 1292.81(4) Å^3, Z = 2, ρ_{calcd} = 2.056 g cm^{-3}, T = 100 K, θ range 3.48–25.24°, 23592 reflections collected, 2314 independent reflections, R_{int} = 0.0276, R_1 = 0.0145, wR_2 = 0.0353 ($I > 2\sigma(I)$).

Crystal data of *trans-E/Z*-7a: C$_{28}$H$_{26}$Cl$_2$Fe$_2$N$_2$O$_2$Pt, M = 800.20 g mol^{-1}, orange prism, 0.30 × 0.30 × 0.20 mm, space group *P*2$_1$, monoclinic, a = 6.3894(3) Å, b = 13.7269(6) Å, c = 14.9669(7) Å, β = 95.841(4)°, V = 1305.88(10) Å^3, Z = 2, ρ_{calcd} = 2.035 g cm^{-3}, T = 110 K, θ range 2.97–25.99°, 5587