Spectroelectrochemical investigation of $Bu_4N[Fe(CO)_3(NO)]$: identification of a reversible EC-mechanism

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All spectroscopic studies were performed using $BuN_4[Fe(CO)_3(NO)]$ (TBA*Fe*). TBA*Fe* was prepared as reported previously.[1]

Details Cyclic Voltammetry and IR Spectroelectrochemistry

IR spectra were obtained using a Nicolet 6700 FTIR instrument. Cyclic voltammetry was carried out in 0.1 M Bu_4NPF_6 solutions using a three-electrode configuration (glassy-carbon or Pt working electrode, Pt counter electrode, Ag wire as pseudoreference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc+) couple served as internal reference. Spectroelectrochemistry was performed using an optically transparent thin-layer electrode (OTTLE) cell.[2]

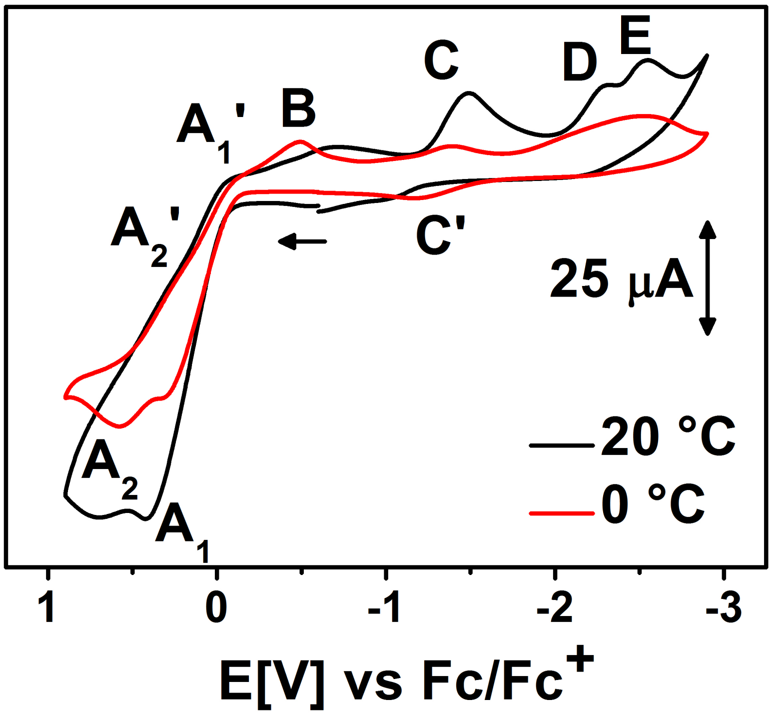

Figure S1: Cyclic voltammogram of $Bu_4N[Fe(CO)_3NO]$ (**1**) (at different temperatures) in THF / 0.1 M Bu_4PF_6 measured at 100 mV /s at 295 K. Ferrocene/ferrocenium was used as an internal standard).

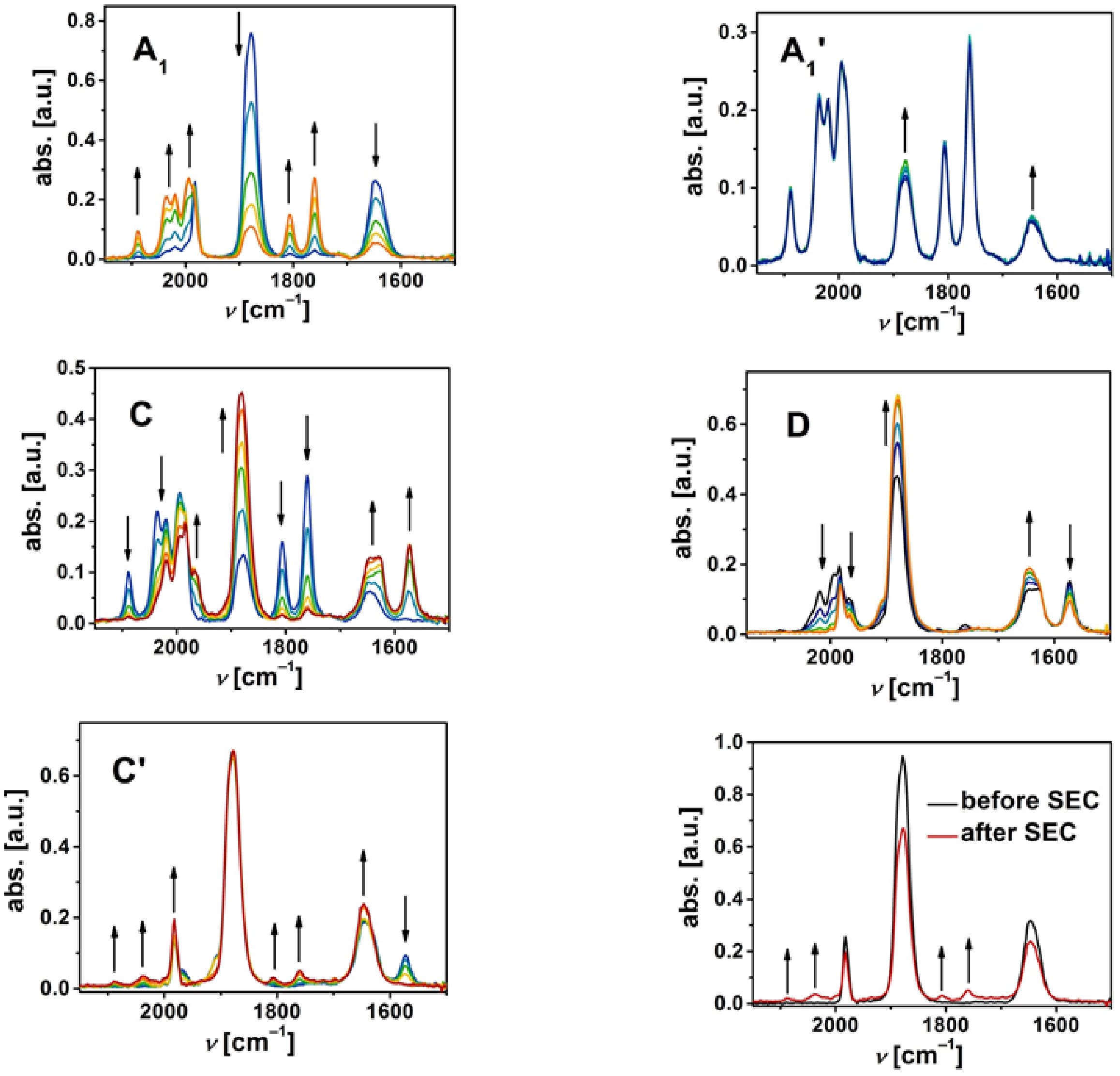

Figure 2: Changes in the IR spectrum of $Bu_4N[Fe(CO)_3NO]$ (**1**) in the absence of CO during various redox processes (see Scheme 2 for details). Measurements were carried out at 295 K in 0.1 M Bu_4NPF_6 / THF.

CV simulation parameters

The CV was simulated in three segments from 0 to 0.645 to –2.58 to 0 V at a scan rate of 0.1 V/s with potential steps of 0.005 V. The geometry of the electrode was set to planar, and the surface area was set to 0.01 cm^2. The concentration of the complex $[Fe(CO)_3(NO)]^-$ was set to 0.023 mol/L, the diffusion constants of all species were left at the standard value of 10^{-5} cm^2/s, and the diffusion was simulated as semi-infinite. The internal resistance was left at 0 Ohm, the double-layer capacity was set to 3×10^{-5} F, and the temperature was set to 298.2 K.

Equations (1)–(6) describe the simulated electrochemical processes.

$[Fe(CO)_3(NO)] + e^- \rightarrow [Fe(CO)_3(NO)]^-$ (1)
$[Fe(CO)_3(NO)]^+ + e^- \rightarrow [Fe(CO)_3(NO)]$ (2)
$[Fe(CO)_3(thf)] + e^- \rightarrow [Fe(CO)_3(thf)]^-$ (3)
$[Fe(CO)_2(NO)_2] + e^- \rightarrow [Fe(CO)_2(NO)_2]^-$ (4)
$[Fe(CO)_5] + e^- \rightarrow [Fe(CO)_5]^-$ (5)
$[Fe(CO)_2(NO)_2]^- + e^- \rightarrow [Fe(CO)_2(NO)_2]^{2-}$ (6)

All electrochemical processes were simulated as reversible, and the corresponding simulation parameters of each reaction are listed in Table S1.

Equation	E^0 [V]	α	k_s [cm/s]
(1)	+0.04	0.6	10^{-3}
(2)	+0.13	0.6	10^{-3}
(3)	–0.40	0.5	10^{-3}
(4)	–1.215	0.5	2×10^{-3}
(5)	–2.05	0.5	10^{-3}
(6)	–2.30	0.5	10^{-3}

Equations (7)–(13) describe the simulated chemical reactions.

$[Fe(CO)_3(NO)]^+ + [Fe(CO)_3(NO)]^- \rightarrow 2[Fe(CO)_3(NO)]$(7)
$2[Fe(CO)_3(NO)] \rightarrow [Fe(CO)_4] + [Fe(CO)_2(NO)_2]$ (8)
$2[Fe(CO)_4] + thf \rightarrow [Fe(CO)_3(thf)] + [Fe(CO)_5]$ (9)
$[Fe(CO)_5]^- \rightarrow [Fe(CO)_4]^- + CO$ (10)
$[Fe(CO)_4]^- + [Fe(CO)_3(NO)]^- \rightarrow 2[Fe(CO)_3(NO)]^-$ (11)
$[Fe(CO)_3(thf)]^- \rightarrow [Fe(CO)_3(thf)]^-*$ (12)
$[Fe(CO)_2(NO)_2]^{2-} \rightarrow [Fe(CO)_2(NO)_2]^{2-}*$ (13)

The reactions of Equations (7)–(11) were simulated as reversible, the reactions of Equations (12) and (13) were simulated as irreversible, and the corresponding simulation parameters are listed in Table S2

Equation	K_{eq}	k_f	k_b
(7)	33.192	10^4 L mol^{-1} s^{-1}	301.28 L mol^{-1} s^{-1}
(8)	2×10^3	2×10^3 L mol^{-1} s^{-1}	1 L mol^{-1} s^{-1}
(9)	10^2	10 L mol^{-1} s^{-1}	0.1 L mol^{-1} s^{-1}
(10)	10	10 L mol^{-1} s^{-1}	1 L mol^{-1} s^{-1}
(11)	2×10^3	2×10^3 L mol^{-1} s^{-1}	1 L mol^{-1} s^{-1}
(12)	10	10 s^{-1}	
(13)	10	10 s^{-1}	

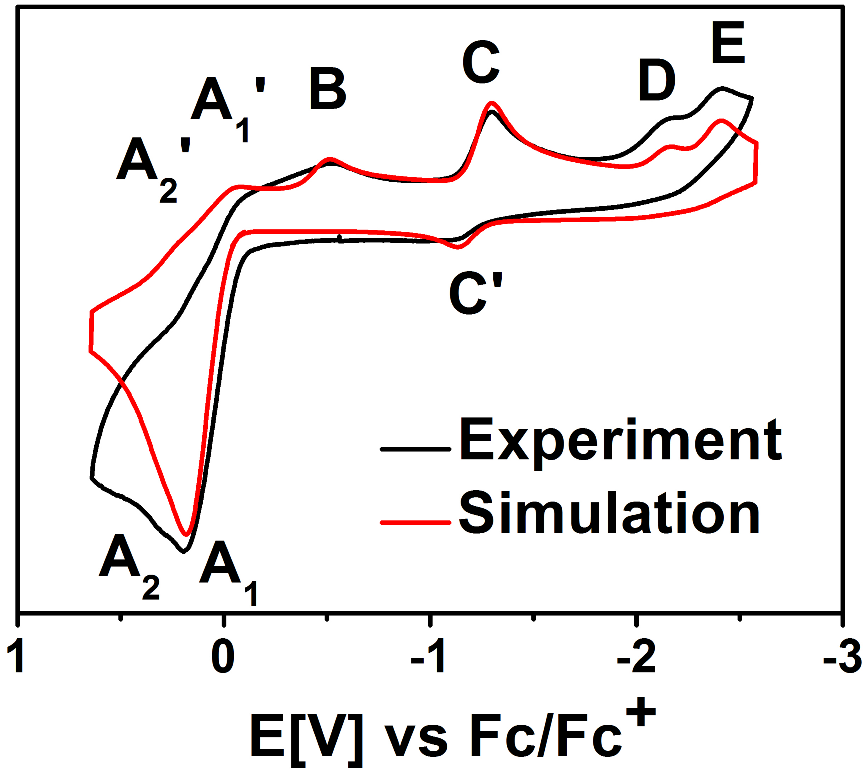

Figure S3: Cyclic voltammogram of $Bu_4N[Fe(CO)_3NO]$ (**1**) in THF / 0.1 M Bu_4PF_6 measured at 100 mV /s at 295 K together with simulation. Ferrocene/ferrocenium was used as an internal standard.

References

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[1] M. Holzwarth, A. Dieskau, M. Tabassam and B. Plietker, *Angew. Chem. Int. Ed.*, 2009, **48**, 7251.

[2] M. Krecik, M. Danek, F. Hartl, *J. Electroanal. Chem. Interfacial Electrochem.*, 1991, **317**, 179.