Corrolocenes: Corrole Sandwich Complexes

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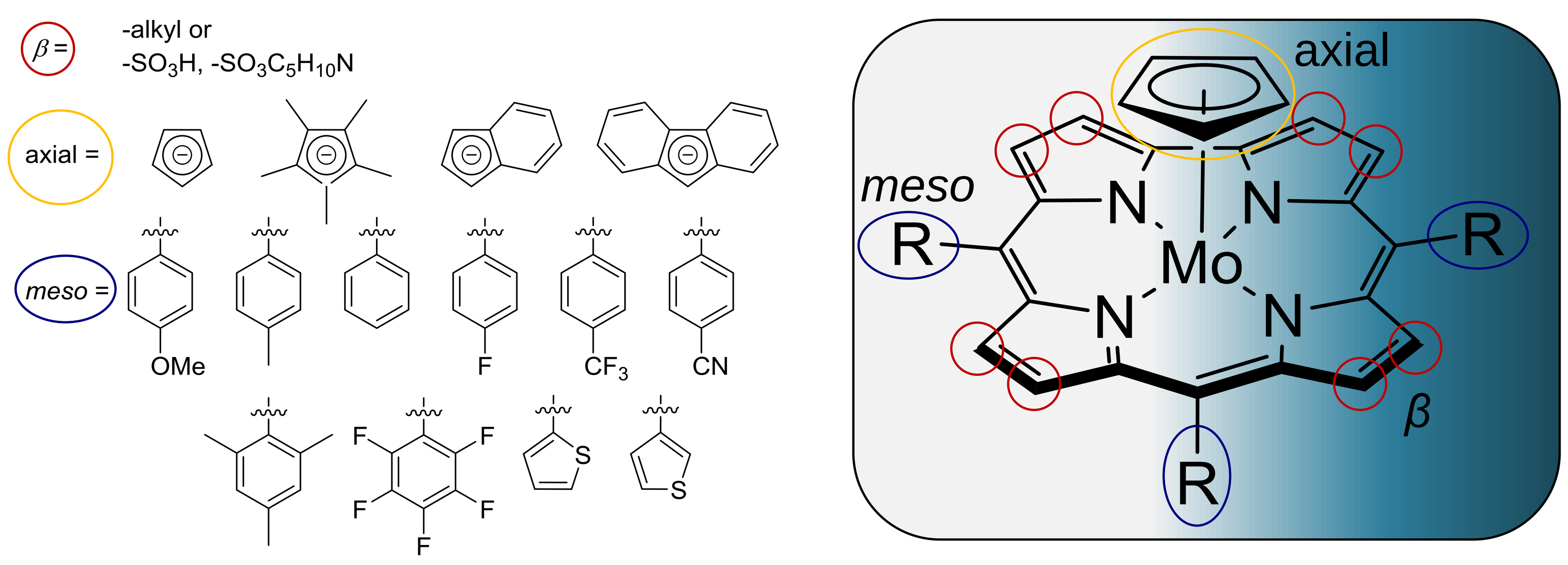
Introduction

Corrolocenes are half-sandwich complexes in which the central metal atom is coordinated by one corrole, which is a ring contracted porphyrinoid and one cyclopentadienyl ligand.[1,2] This novel, organometallic substance class constitutes a conceptual link between the research fields of porphyrinoids and sandwich complexes, and archetypical issues from both worlds, like electron transfer and catalysis, are interesting objects of study for corrolocene derivatives.

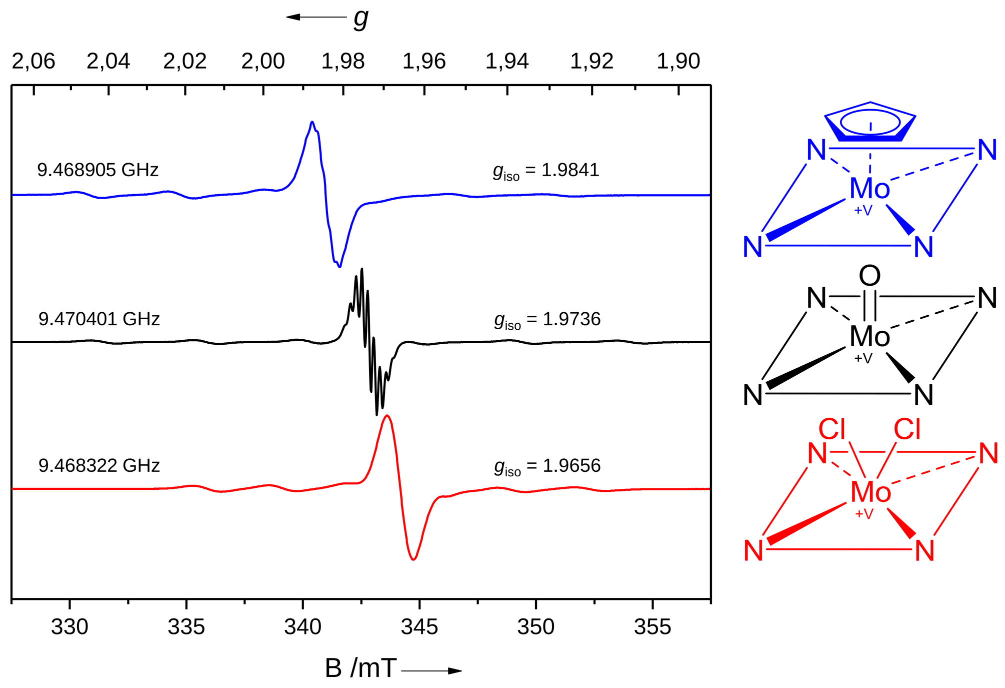
For molybdenum, corrolocenes are available from inreactive oxomolybdenum(V)[3,4] precursors by a chlorination – reductive coordination sequence in excellent yields, making use of the recently developed *Viking Helmet*-corroles[2] as reactive intermediates. We have now conducted further electrochemical and spectroelectrochemical studies as well as investigations into the functionalization of such molybdenum corrolocenes.

Functionalisation and Substitutions

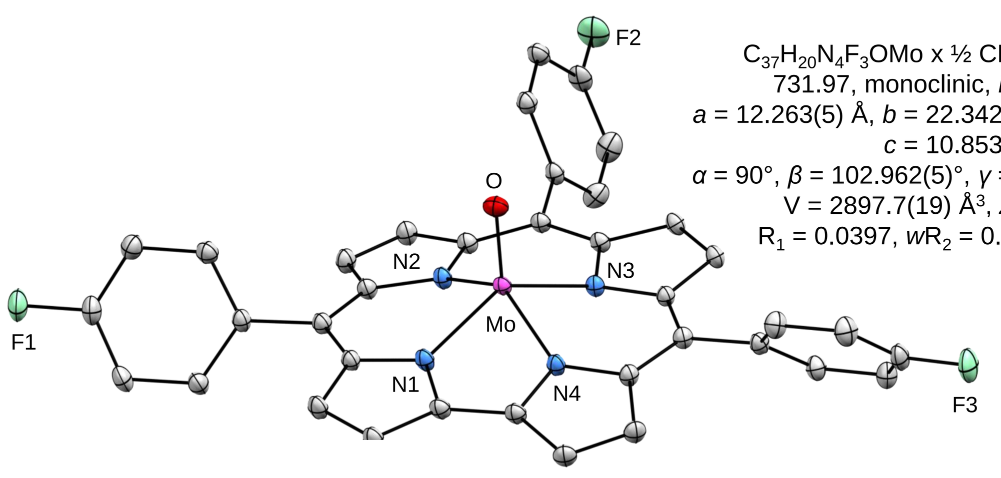


X-band EPR

Figure 1. X-band EPR studies of molybdenum(V)corrolocenium (blue), oxomolybdenum(V)corrole (black), dichloridomolybdenum(V)corrole (red) in toluene at room temperature,).



Structural analysis



$C_{37}H_{20}N_4F_3OMo$ x ½ CH_2Cl_2,
731.97, monoclinic, $P2_1/c$,
a = 12.263(5) Å, b = 22.342(5) Å,
c = 10.853(5) Å,
α = 90°, β = 102.962(5)°, γ = 90°,
V = 2897.7(19) Å³, Z = 4,
R_1 = 0.0397, wR_2 = 0.0878.

Figure 1. Molecular structure of oxo-5,10,15-(4-fluorophenyl)corrolatomolybdenum.

$C_{40}H_{20}N_4Cl_2F_9Mo$ x 1 C_7H_8,
986.57, triclinic, P-1,
a = 8.1250(2) Å, b = 15.8252(4) Å,
c = 16.1608(4) Å,
α = 84.820(2)°, β = 76.444(2)°,
γ = 89.088(2)°,
V = 2011.8(9) Å³, Z = 2,
R1 = 0.0478, wR2 = 0.0996.

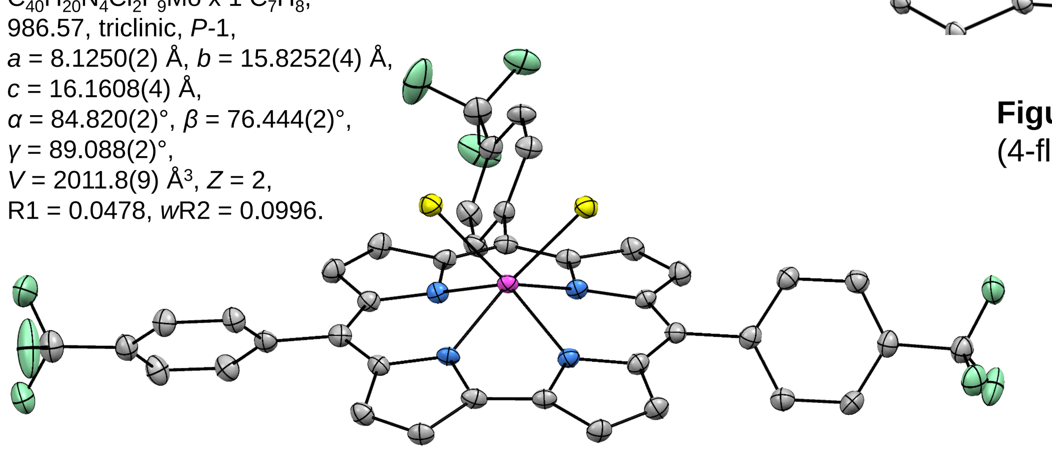
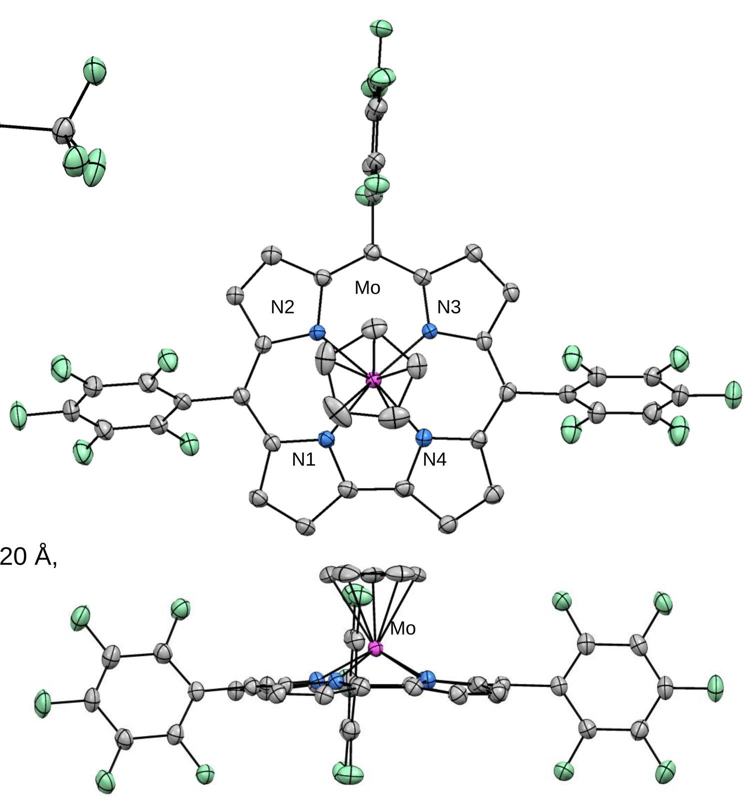
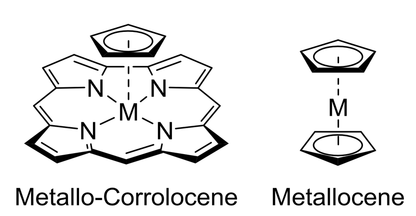


Figure 2. Molecular structure of dichlorido-5,10,15-(4-trifluoromethylphenyl)corrolatomolybdenum.



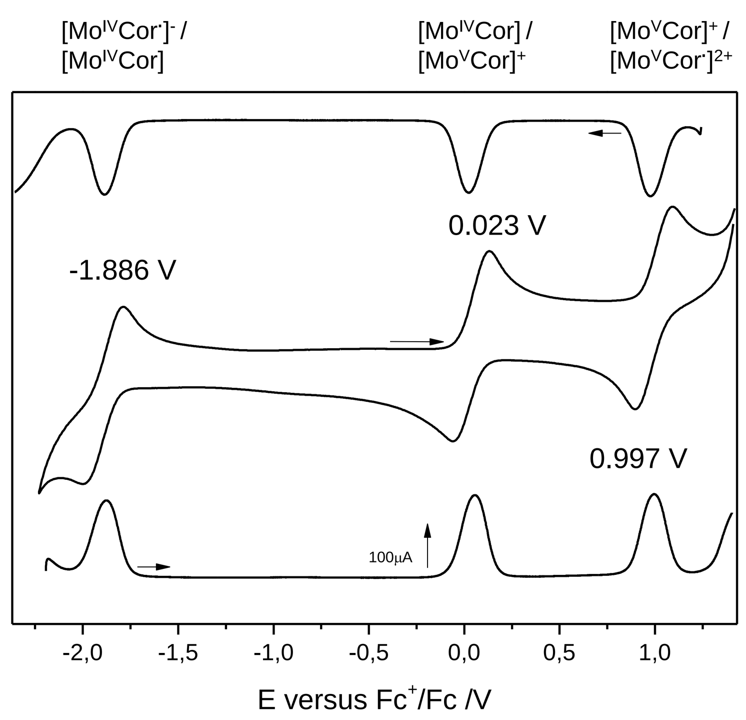


Metallo-Corrolocene Metallocene

$C_{42}H_{13}N_4F_{15}Mo$,
954.50, monoclinic, $P2_1$,
a = 14.8666(10) Å, b = 10.0120 Å,
c = 15.0160(10) Å,
α = 90°, β = 116.1140(10)°,
γ = 90°,
V = 2006.89(2) Å³, Z = 2,
R1 = 0.0251, wR2 = 0.0643.

Figure 1. Top and sideview of the molecular structure of cyclopentadienyl-5,10,15-(4-fluorophenyl)corrolatomolybdenum.

Electrochemistry



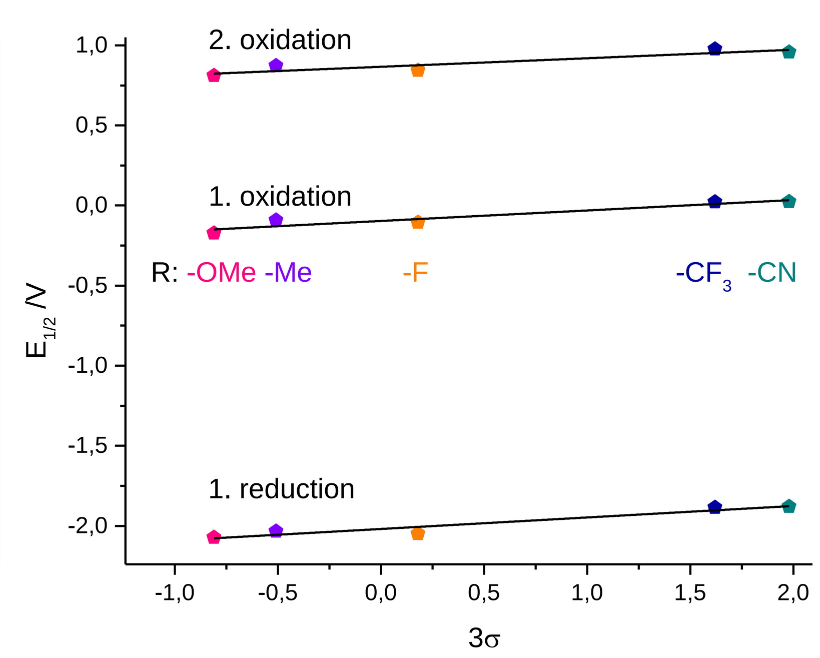
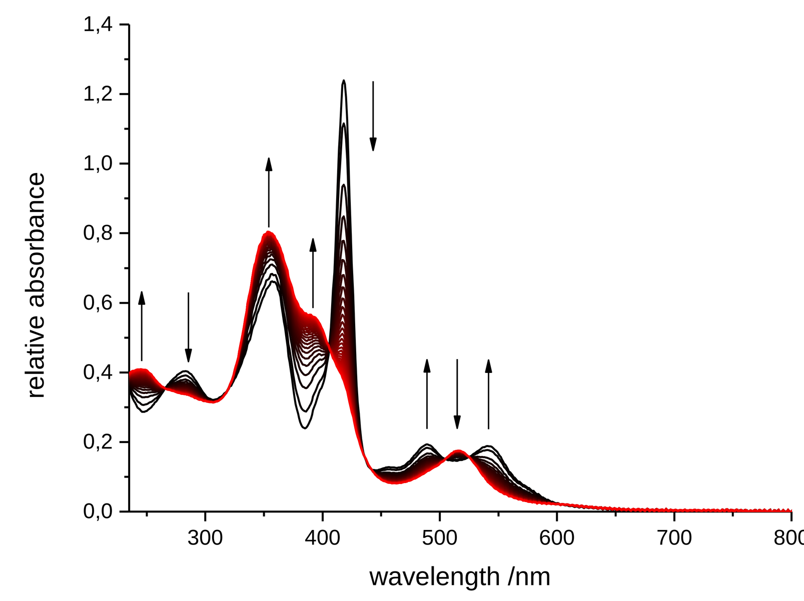


Figure 2. Cyclic voltammogram and square-wave-voltammogram of cyclopentadienyl-5,10,15-(4-tri-fluoromethylphenyl)corrolatomolybdenum (200 mV/s, 0.2 M TBAPF in CH_2Cl_2).

Figure 3. The electronic influence from the arylsubstituent of the molybdenum corrolocenes on the redoxprocesses are shown as *Hammett* plot[5].

Spectroelectrochemistry SEC



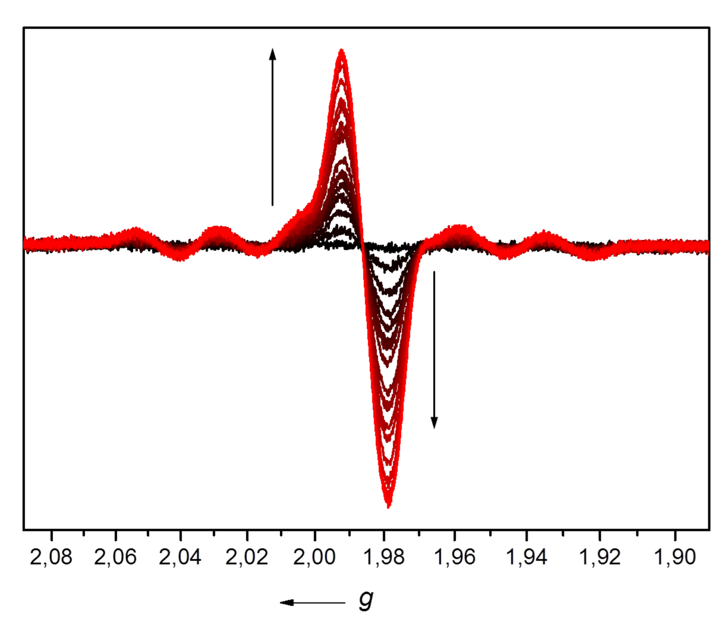


Figure 6. Optical SEC-experiment (spectro-electrochemistry) of cyclopentadienyl-5,10,15-(4-tri-fluoromethylphenyl)corrolatomolybdenum at a potential of 0.1 V in 0.2 M TBAPF in CH_2Cl_2.

Figure 7. EPR-SEC-experiment in a self-made SEC-cell of cyclopentadienyl-5,10,15-(4-tri-fluoromethylphenyl)corrolatomolybdenum at a potential of 0.2 V in 0.1 M TBAPF in CH_2Cl_2.

References

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