Circular Dichroism Spectroelectrochemical Investigations on the Fluxional Diamagnetic and Paramagnetic Organometallic Complexes $[Mo(His\text{-}N_\epsilon\text{-}C_2H_4COOCH_3)(2\text{-}R\text{-}allyl)(CO)_2]^{n+}$ (R = H, Me; His = *O*,*N*,N_δ-L-Histidinate; *n* = 0, 1)

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The optical and chiroptical properties of $Mo(His\text{-}N_\epsilon\text{-}C_2H_4COOCH_3)(allyl)(CO)_2$ (**1**) and $Mo(His\text{-}N_\epsilon\text{-}C_2H_4COOCH_3)(2\text{-}methylallyl)(CO)_2$ (**2**) (His = *O*,*N*,N_δ-L-histidinate, allyl = η-C_3H_5) and their one-electron-oxidized derivatives $\mathbf{1}^+$ and $\mathbf{2}^+$ are presented. The trends observed in the UV−vis and CD spectra of **1** and **2** in MeOH and MeCN are related to the ratio between the regioisomers **a** and **b**, which differ in the position of the allyl ligand relative to the facially coordinating His ligand. Increase of the ratio in favor of **a** leads to a bathochromic shift of the MLCT transition in the UV−vis spectra. In addition, an increase in the abundance of isomer **a** leads to a decrease in intensity of the negative Cotton effect around 320 nm and a simultaneous increase in intensity of the negative Cotton effect around 410 nm. CD and UV−vis spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ in MeCN were acquired via spectroelectrochemical measurements. The electronic transitions observed in the UV−vis spectrum of $\mathbf{2}^+$ at 335 and 546 nm appear to correspond to the negative Cotton effects observed in the CD spectrum at 345 and 553 nm. Similarly, the electronic transition in the UV−vis spectrum of $\mathbf{1}^+$ at 348 nm appears to be related to the negative Cotton effect at 352 nm. To the best of our knowledge, this is the first CD spectroscopic study on paramagnetic organometallic compounds.

Introduction

Ultraviolet−visible (UV−vis) spectroscopy is a well-established technique for the study of transition-metal complexes. The spectra provide insight into electronic structure and yield information on the symmetry environment around the metal ion.[1,2] Circular dichroism (CD) spectra of transition-metal complexes can be informative as well, but this optical technique is restricted to compounds that possess an element of chirality.[3] A classical example is the discrimination of the Λ and Δ isomers of $[Co(en)_3]^{3+}$ (en = ethylenediamine).[4]

We have studied organometallic molybdenum carbonyl complexes [5−7] and their application for the labeling of biomolecules.[5,8,9] Recently, we elucidated the fluxional behavior of the complexes $Mo(His\text{-}N_\epsilon\text{-}C_2H_4COOCH_3)(allyl)(CO)_2$ (**1**) and $Mo(His\text{-}N_\epsilon\text{-}C_2H_4COOCH_3)(2\text{-}methylallyl)(CO)_2$ (**2**) both in their neutral diamagnetic form and in their one-electron-oxidized paramagnetic state.[6,7] The results are summarized in Scheme 1. Both **1** and **2** exist as an equilibrium mixture of regioisomers **a** and **b** in the neutral form. These conformers differ in the relative orientation of the allyl or 2-methylallyl ligand. In isomer **a**, the allyl or 2-methylallyl ligand is in a position trans to the histidine N_δ atom, whereas the allyl or 2-methylallyl ligand is trans relative to a carbonyl ligand in isomer **b**. In both isomers, the allyl or 2-methylallyl ligand is in an exo orientation with the terminal C atoms pointing toward the carbonyl ligands.

Results from EPR spectroscopy and IR spectroelectrochemistry umambiguously showed that the one-electron oxidation of **1** and **2** is metal-centered.[7] Low-temperature electrochemical investigations revealed that both $\mathbf{1}^+$ and $\mathbf{2}^+$ strongly prefer the conformation in which the allyl or 2-methylallyl ligand is in a trans position relative to the carboxylate moiety.[6,7] A difference between the allyl complex $\mathbf{1}^+$ and the 2-methylallyl compound $\mathbf{2}^+$ is that the former likely exists as a mixture of endo and exo isomers, with the main com-

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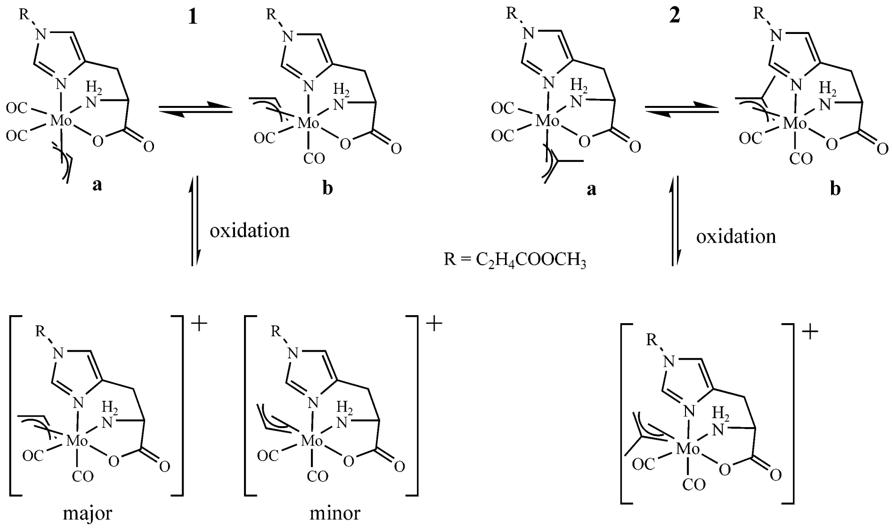
Scheme 1. Overview of the Isomeric Composition of 1, 1^+, 2, and 2^+ [a]



[a] See refs 6 and 7.

ponent being the exo isomer. Complex 2^+, on the other hand, exists exclusively in the endo conformation. These exo or endo orientations of the allyl or 2-methylallyl ligand in 1^+ and 2^+ were suggested by combining the results from EPR spectroscopy and from detailed density functional theory (DFT) calculations.[7]

Herein, we present a study on the optical and chiroptical properties of the neutral diamagnetic and one-electron-oxidized paramagnetic forms of the fluxional organometalic complexes **1** and **2**. In comparison to CD spectroscopic investigations of transition-metal *coordination* complexes, CD spectroscopic studies on *organometallic* transition-metal complexes are scarce.[10-13] Poli and co-workers have studied the electronic structure and reactivity of paramagnetic organometallic compounds quite extensively,[14-16] including a number of molybdenum allyl complexes.[17] Even if chiral paramagnetic organometallics were investigated,[18] however, these compounds were not used in an enantiomerically pure form. It should be noted that the histidinate ligand used in our studies[6,7,9] was always used as the L enantiomer and, thus, enantiomerically pure molybdenum complexes were obtained, making them suitable for CD spectroscopy. By adapting a procedure commonly used for UV−vis spectro-electrochemical investigations, CD spectra of 1^+ and 2^+ could be acquired. CD spectroelectrochemistry as an experimental technique has been reported before. However, it was mainly used for the study of biomolecules, such as proteins,[19-22] vitamins,[23,24] and hormones.[25-28] In this work, we adapt it for the study of organometallic complexes and show its use as a complementary technique to the more common UV−vis spectro-electrochemical investigations. CD spectra can often be measured on the same samples in the same cuvettes used for UV−vis spectroscopy. Provided that a cell for UV−vis spectroelectrochemistry is available, no additional instrumentation is required for CD spectroelectrochemical investigations apart from the spectrometer. As shown herein, CD spectroscopy provides valuable additional insight into the orbital situation. To the best of our knowledge, this paper presents the first example of a CD spectroscopic investigation on paramagnetic organometallic compounds.

Experimental Section

The complexes $Mo(His\text{-}N_{\epsilon}\text{-}C_2H_4COOCH_3)(\eta\text{-}2\text{-}R\text{-}allyl)(CO)_2$ (**1**, R = H; **2**, R = CH_3; His = l-O,N,N_{δ}-histidinate) were prepared as reported previously.[6,7] UV−vis spectra were recorded on a Hewlett-Packard HP 8452A diode array spectrophotometer. CD spectra were recorded on a Jasco J-715 spectropolarimeter, equipped with a Hamamatsu R376 photomultiplier (185−850 nm) using a bandwidth of 1 nm. Controlled-potential coulometry spectroelectrochemical measurements were performed by using an EG&G 273A potentiostat/galvanostat. A three-electrode cuvette cell having a path length of 0.5 cm was employed with a Pt grid as a working electrode, a Pt brush separated from the working electrode compartment by a Vycor frit as an auxiliary electrode, and an $Ag/AgNO_3$ (0.01 M $AgNO_3$ in MeCN) working electrode. For

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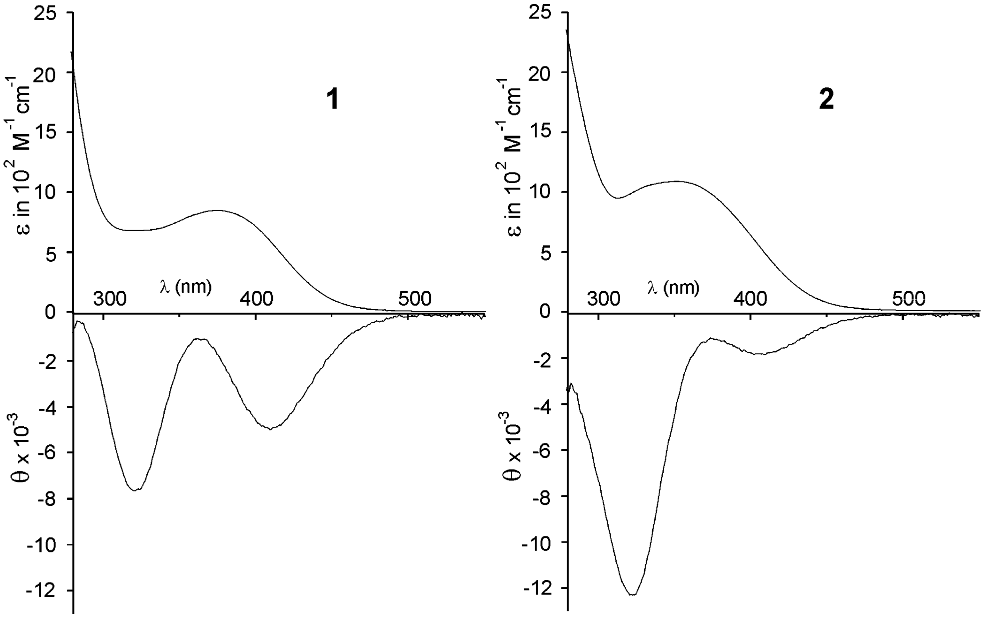

Figure 1. Selected regions from the UV−vis and CD spectra of **1** and **2** in MeCN.

Table 1. Selected UV−vis and CD Spectroscopic Data for 1, 2, 1⁺, and 2⁺ in MeOH and MeCN

		a/b	UV−vis		CD	
complex	solvent	ratio[a]	λ_{max}[b]	$\epsilon(\lambda_{max})$[c]	λ_{max}[b]	$\theta(\lambda_{max})$[d]
1	MeOH	79/21	385	820	322 413	-3.9×10^3 -6.7×10^3
1	MeCN	53/47	375	840	320 409	-7.7×10^3 -5.0×10^3
2	MeOH	55/45	366	940	324 411	-8.7×10^3 -5.0×10^3
2	MeCN	21/79	353	1080	323 410	-12.2×10^3 -1.7×10^3
$\mathbf{1}^+$	MeCN		348 622	1370 70	352	-2.7×10^2
$\mathbf{2}^+$	MeCN		ca. 335[e] 546	n.d.[e] 64	345 553	-2.9×10^2 -2.8×10^3

[a] Determined by ^{1}H NMR spectroscopy in ref 7. [b] In nm. [c] In L mol^{-1} cm^{-1}. [d] In deg L mol^{-1} cm^{-1}. [e] Could not be determined reliably; see text.

the spectroelectrochemical investigations, the complex concentration was about 5×10^{-4} M and NBu_4PF_6 (0.1 M) was used as the supporting electrolyte. All electrochemical experiments were carried out at 0 °C. Oxidations were exhaustive to exactly one electron per molecule (100 ± 2%). All spectroelectrochemical experiments were completely reversible, not only by electrochemical criteria by also by comparison of the respective spectra before and after the experiments.

Results and Discussion

Selected UV−vis spectroscopic data for the complexes **1** and **2** in MeOH and MeCN are listed in Table 1. Selected regions from the UV−vis spectra of **1** and **2** in MeCN are depicted in Figure 1 as representative examples.

The general appearances of the UV−vis spectra of **1** and **2** are very similar, differing significantly only in the position of λ_{max}. In addition to maxima around 280 nm owing to the $\pi-\pi^*$ transition of the imidazole ring, the spectra of **1** and **2** display an MLCT band around 370 nm. For both the allyl and the 2-methylallyl compounds it appears that the position of λ_{max} for this MLCT transition depends on the ratio of isomers **a** and **b** and, consequently, is solvent-dependent. The absorbance maximum of this transition is red-shifted when the abundance of isomer **a** increases. Isomer **a** has the N_δ nitrogen atom in a trans position relative to the allyl or 2-methylallyl ligand, whereas the N_δ nitrogen atom of isomer **b** is trans relative to a carbonyl ligand. Both the allyl (or 2-methylallyl) ligand and the carbonyls are ligands that only form stable complexes when the binding of these is stabilized by back-bonding. It is expected that, in either conformational isomer, the metal d orbitals are orientated suitably for d$-\pi^*$ transitions (MLCT), because back-bonding takes place in all three directions (x, y, z; chosen arbitrarily). Apparently, this MLCT transition requires less energy when the imidazole is trans relative to the allyl or 2-methylallyl ligand. Furthermore, it also seems that the molar extinction coefficient of the MLCT absorption band is higher when the λ_{max} of this band is at higher energy, but this effect might also be due to the fact that the intraligand $\pi-\pi^*$ transitions contribute to the absorption in that region. The exact identity of the MLCT transition in the UV−vis spectra of **1** and **2** is not clear, because the imidazole moiety, the carbonyl ligands, and the allyl (or 2-methylallyl) ligand all have π^* orbitals that are relatively low in energy and might act as π acceptors.

Circular dichroism spectra of complexes **1** and **2** were recorded in MeOH and MeCN, and the results are summarized in Table 1. As representative examples, the CD spectra of **1** and **2** in CH_3CN are depicted in Figure 1. Complexes **1** and **2** exhibit two negative Cotton effects in MeOH and MeCN, with the maxima located around 320 and 410 nm. The molecular ellipticity at the two maxima varies with the ratio between the isomers **a** and **b** and consequently with the solvent. For example, in the CD spectrum of **1** in MeOH, the negative Cotton effect at 322 nm is weaker than the Cotton effect at the higher wavelength. The situation is reversed in the CD spectrum of **1** in MeCN, in which the Cotton effect at the lower wavelength displays a higher negative maxi-

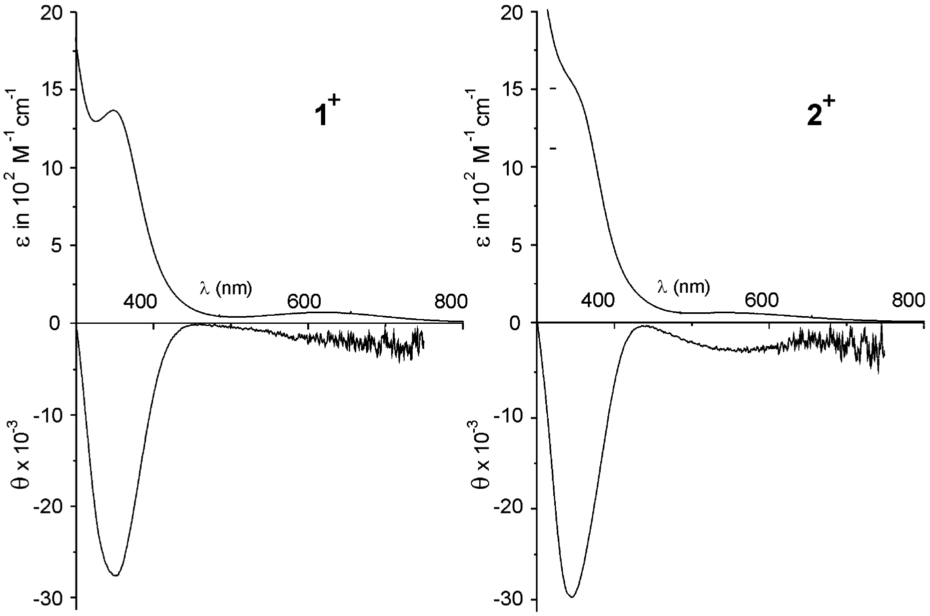

Figure 2. Selected regions from the UV−vis and CD spectra of 1^+ and 2^+ in MeCN generated by controlled-potential coulometry (0.1 M NBu_4PF_6).

mum compared to the negative maximum around 410 nm. The following general trend can be derived from the CD spectroscopic data listed for **1** and **2** in Table 1. When the abundance of isomer **a** increases, the intensity of the Cotton effect at around 320 nm decreases and that of the Cotton effect at around 410 nm increases. It is not clear which electronic transitions give rise to the Cotton effects in the CD spectra. A comparison of the CD spectra of **1** and **2** with their UV−vis spectra reveals that the optically active transitions in the CD spectra are not situated at the same wavelength as the MLCT transitions in the UV−vis spectra. However, it is likely that bands in the UV−vis spectra which do correspond to the Cotton effects in the CD spectrum are obscured by the more intense MLCT absorption bands.

UV−vis spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ in MeCN were recorded via spectroelectrochemical measurements starting from the neutral precursors **1** and **2**. The resulting spectra are depicted in Figure 2, and the results are summarized in Table 1. In all cases, PF_6^- from the electrolyte was the counterion. After oxidation of **1**, the MLCT transition at 375 nm disappeared and a new absorption band at 348 nm with a molar extinction coefficient around 1370 M^{-1} cm^{-1} formed. Furthermore, a new band is present in $\mathbf{1}^+$ with λ_{max} 622 nm ($\epsilon \approx 70$ M^{-1} cm^{-1}).[29] This band is assigned as a transition with d−d character of an energetically low-lying orbital with d character to the half-filled orbital with d character. The compound under investigation is not a pure Werner-type coordination complex but also contains organometallic fragments. Therefore, metal d orbitals mix to some extent with π and π^* orbitals of the organometallic ligands, questioning an assignment of pure d character to most metal-centered orbitals. Upon oxidation of **2** to $\mathbf{2}^+$, a new absorption band appears in the UV−vis spectrum at around 335 nm, which is considerably stronger than the MLCT band in the UV−vis spectrum of **2**. However, the exact position of this new band as well as its molar extinction coefficient cannot be determined reliably because it overlaps with the π−π^* transition of the imidazole group. Furthermore, a new band is present after oxidation from **2** to $\mathbf{2}^+$ with λ_{max} 546 nm, with a molar extinction coefficient around 64 M^{-1} cm^{-1}. As in the UV−vis spectrum of $\mathbf{1}^+$, this new band is assigned as a transition with d−d character from a low-lying orbital to the half-filled d orbital of the metal.

The UV−vis spectra of **1** and **2** differ in the position of the λ_{max} of the MLCT transition, which is approximately 20 nm lower for **2** than for **1**. Also after the oxidation, the λ_{max} of the newly formed band around 340 nm is located about 15−20 nm lower in the UV−vis spectrum of $\mathbf{2}^+$ compared to the spectrum of $\mathbf{1}^+$. It is known from electrochemical investigations at various temperatures that both complex cations exist almost exclusively in the isomer with the allyl or 2-methylallyl ligand trans to the carboxylate oxygen atom.[6,7] However, the fact that the transition with d−d character occurs at lower wavelength for $\mathbf{2}^+$ compared to $\mathbf{1}^+$ (λ_{max} 546 and 622 nm, respectively) indicates that the energy levels of these orbitals with d character are not identical in both compounds. We have previously noticed an endo−exo equilibrium of the allyl ligand only in the case of $\mathbf{1}^+$, not $\mathbf{2}^+$. The difference of 76 nm in the low-wavelength transition between 1+ and 2+ may actually reflect this difference in fluxionality in the paramagnetic species.

In analogy to the UV−vis spectra, circular dichroism spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ in MeCN were acquired via spectroelectrochemical measurements starting from the neutral precursors **1** and **2**. The resulting spectra are shown in Figure 2. The two negative Cotton effects of **1** and **2** around 320 and 410 nm are no longer present after the oxidation. Instead, a much more intense negative Cotton effect is observed at 352 nm (for $\mathbf{1}^+$) and 345 nm (for $\mathbf{2}^+$). Interestingly, the negative maximum in the CD spectrum of $\mathbf{1}^+$ is located at nearly the

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(29) The molar extinction coefficients after the oxidation cannot be determined very reliably because of solvent effervescence as a result of degassing the solution with argon.

same wavelength as the intense band in the UV−vis spectrum of this compound (352 nm in the CD spectrum and 348 nm in the UV−vis). For $\mathbf{2}^+$, however, the position of the maxima observed in the UV−vis and CD spectra differs to some extent (345 nm vs around 335 nm, respectively).

The detector used for the CD measurements (see Experimental Section) has been specified by the manufacturer to be suitable in the range 185−850 nm, but the spectral noise already becomes relatively high at 550 nm. Despite this spectral noise, a second negative Cotton effect at 553 nm is discernible for $\mathbf{2}^+$, although with considerably weaker intensity. The position of this negative maximum is nearly identical with the λ_{max} value of the band in the UV−vis spectrum of $\mathbf{2}^+$ at 546 nm. Thus, it appears that the transition with d−d character in the UV−vis spectrum of $\mathbf{2}^+$ is also optically active. The corresponding transition in the UV−vis spectrum of $\mathbf{1}^+$ has its maximum at 622 nm. A Cotton effect associated with this electronic transition could not be detected in the CD spectrum of $\mathbf{1}^+$ because of the high spectral noise at this wavelength.

Conclusion

This work presents a study on the optical and chiroptical properties of **1** and **2** and their one-electron-oxidized counterparts $\mathbf{1}^+$ and $\mathbf{2}^+$. The general appearance of the UV−vis and CD spectra of **1** and $\mathbf{1}^+$ is quite similar to that of **2** and $\mathbf{2}^+$. This is not surprising, as these complexes only differ in the presence of a methyl group on the central carbon atom of the allyl ligand. However, small differences can be observed between the CD and UV−vis spectra of the allyl compounds **1** and $\mathbf{1}^+$ and those spectra of the 2-methylallyl compounds **2** and $\mathbf{2}^+$. The trends observed in the CD and UV−vis spectra of **1** and **2** in MeOH and MeCN can be related to the ratio between the isomers **a** and **b**. When the isomeric composition is shifted in favor of **a**, a bathochromic shift of the MLCT transition in the UV−vis spectrum is observed. Similarly, an increase in the abundance of isomer **a** leads to a decrease in intensity of the negative Cotton effect around 320 nm and an increase in intensity of the negative Cotton effect around 410 nm.

CD and UV−vis spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ in MeCN were obtained by performing spectroelectrochemical oxidations on **1** and **2**. The negative Cotton effects in the CD spectra of $\mathbf{1}^+$ and $\mathbf{2}^+$ at 352 and 345 nm, respectively, appear to correspond to transitions in the UV−vis spectra at 348 nm (for $\mathbf{1}^+$) and 335 nm (for $\mathbf{2}^+$). In addition, the CD spectrum of $\mathbf{2}^+$ displays another weak negative Cotton effect at 553 nm, which appears to be related to an absorption in the UV−vis spectrum of $\mathbf{2}^+$ at 546 nm. This optically active transition likely originates from an electronic transition from an energetically lower lying orbital with d character to the singly occupied orbital. This orbital is metal-centered with a high degree of d character. An absorption at 622 nm in the UV−vis spectrum of $\mathbf{1}^+$ could not be associated with a Cotton effect in the CD spectrum of $\mathbf{1}^+$. If this transition is optically active, its Cotton effect is probably obscured by the noise of the detector at this wavelength.

In summary, CD spectroelectrochemical investigations were performed on the fluxional organometallic complexes **1** and **2**, providing information complementary to that obtained from UV−vis spectroelectrochemical measurements. We hope that this work inspires inorganic chemists to use CD spectroelectrochemistry in combination with UV−vis spectroelectrochemistry when dealing with chiral metal complexes.

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Note Added in Proof. A recent review describes the chemistry, configurational stability, and applications of chiral organometallic half-sandwich complexes.[30]

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