Redox investigation and X-ray diffraction structure of the dimeric rhodium maleonitriledithiolate complex [Cp*Rh(mnt)]₂. Confirmation of bridging and chelating mnt ligands in the solid-state structure

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Abstract

The reaction between the pentamethylcyclopentadienyl complex [Cp*RhCl₂]₂ and disodium maleonitriledithiolate (Na₂mnt) in CH₂Cl₂ solvent affords the mnt-substituted compound Cp*Rh(mnt) in moderate yield. Cp*Rh(mnt) has been isolated and characterized in solution by IR and ¹H NMR spectroscopy, and by isopiestic molecular weight measurements, which confirm the monomeric nature of this complex. However, the solid-state structure has been re-determined by X-ray diffraction analysis, revealing the presence of a dimeric structure for Cp*Rh(mnt) that possesses both bridging and chelating mnt ligands. The relationship of dimeric [Cp*Rh(mnt)]₂ to the previously reported monomeric structure for Cp*Rh(mnt) [R. Ziessel, M.-T. Youinou, F. Balegroune, D. Grandjean, J. Organomet. Chem. 441 (1992) 143] is discussed. The electrochemical properties of Cp*Rh(mnt) in CH₂Cl₂ and MeCN have been explored, and the redox chemistry is further discussed relative to the results obtained from extended Hückel molecular orbital calculations on monomeric CpRh(mnt). © 1997 Elsevier Science B.V.

Keywords: Pentamethylcyclopentadienyl rhodium complex; Bridging ligand; Chelating ligand

1. Introduction

The chemistry of transition-metal substituted dithiolate compounds has been extensively explored with regards to biologically important redox reactions and as potential light harvesting devices; the latter area of interest makes use of the intrinsic luminescent activity associated with this genre of compound [1–5]. While there are many different types of dithiolate ligands known, the two most studied dithiolate ligands are undoubtedly the maleonitriledithiolate (mnt) and 1,3-di-thiole-2-thione-4,5-dithiolate (dmit) ligand systems [6–25]. Our contribution to this area of research has dealt with the synthesis and redox investigation of the following compounds: Cp*Ru(NO)(S–S) [where S–S = mnt [26], tdas (1,2,5-thiadiazole-3,4-dithiol) [27], dmit [28], i–mnt [29]] and Cp*IrL(mnt) (where L = PMe₃, PPh₃, CNBuᵗ) [30].

Of interest to us was the recent paper by Ziessel et al., dealing with the properties and solid-state structure of Cp*Rh(mnt) [31], which bears many similarities to our Cp*IrL(mnt) compounds. The X-ray structure of Cp*Rh(mnt) was reported to have a flattened basket shape based on the 49.2(2)° angle formed by the Cp* ring carbons and the mnt ligand; the nature of this unusual ligand arrangement was ascribed to steric repulsion between the Cp* ligand and the lone electron pairs associated with sulfur atoms. This reported inner plane angle of 49.2(2)° is virtually identical to the same angle found in the three-legged piano stool complexes Cp*Ir(PPh₃)(mnt) [49.4(2)°] and Cp*Ir(CNBuᵗ)(mnt) [49.1(3)°] reported by us [30], suggesting the existence of some unusual behavior in the case of Cp*Rh(mnt).

Accordingly, we have re-examined the molecular structure of Cp*Rh(mnt) and have determined that the solid-state structure is actually composed of the dimeric compound [Cp*Rh(mnt)]₂. The dimer does not exist to any measurable extent in solution based on molecular weight measurements conducted in CH₂Cl₂ and MeCN solvents. The redox properties of Cp*Rh(mnt) (monomer) have also been explored by cyclic voltammetry

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and the observed $0/1^+$ and $0/1^-$ redox couples are discussed relative to the data obtained from extended Hückel calculations on the model compound CpRh(mnt). The monomer–dimer dichotomy is discussed in terms of a pyramidalization of the mnt ligand from its orthogonal positioning relative to the Cp* ligand in the monomer as a result of sulfur atom attack between Cp*Rh(mnt) units.

2. Results and discussion

2.1. Synthesis of Cp*Rh(mnt) and X-ray diffraction structure of [Cp*Rh(mnt)]₂

Treatment of Na₂mnt [32] and [Cp*RhCl₂]₂ [33] with CH₂Cl₂, followed by stirring for 24 h, afforded the soluble product Cp*Rh(mnt) in moderate to good yields after chromatographic purification over silica gel. Solution characterization of Cp*Rh(mnt) by IR and ^{1}H NMR spectroscopy furnished spectral data in full agreement with the proposed product and the previously reported data [31]. Isopiestic molecular weight measurements carried out in both CH₂Cl₂ and MeCN confirmed only the presence of the monomer Cp*Rh(mnt) in solution [34]. Scheme 1 illustrates this reaction and the conditions responsible in determining the final composition of Cp*Rh(mnt), (where the Cp ring = Cp*).

The solid-state structure of Cp*Rh(mnt) was redetermined by X-ray crystallography. The X-ray data collection and processing parameters and the final fractional coordinates for Cp*Rh(mnt) found by us are identical to those data reported by Ziessel et al. [31], and do not
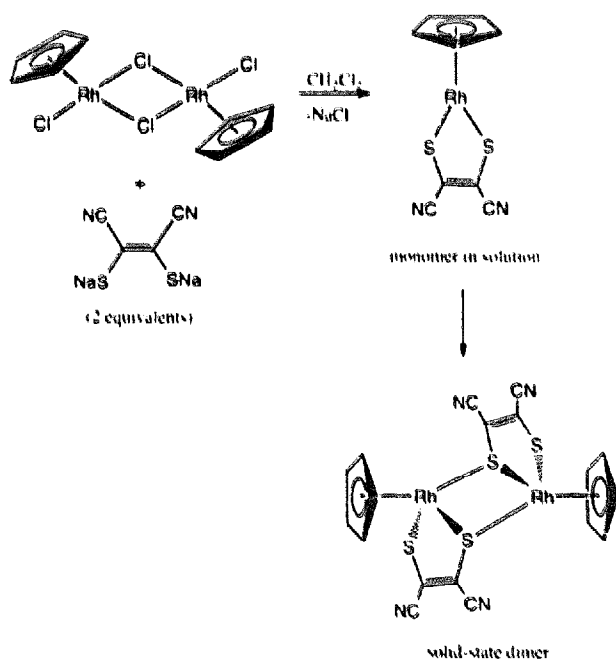
Scheme 1.

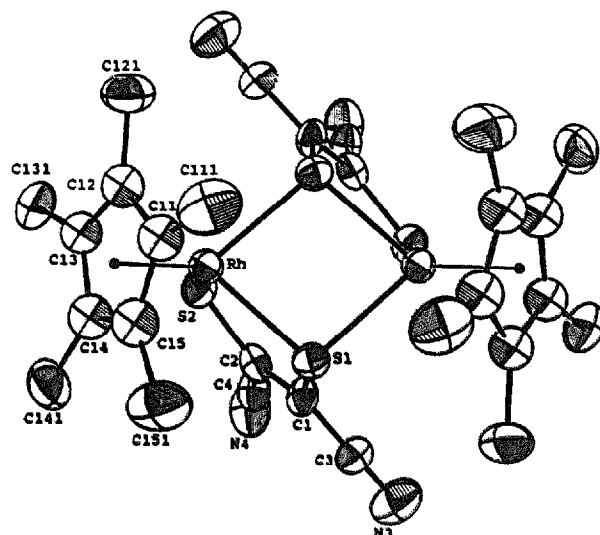Fig. 1. ORTEP drawing of the nonhydrogen atoms of [Cp*Rh(mnt)]₂ showing the thermal ellipsoids at the 50% probability level.

require reproduction here (see supplementary material). The ORTEP diagram in Fig. 1 shows that the molecule is dimeric, consisting of two Cp*Rh(mnt) units that are related by a crystallographic two-fold axis. The effect of this axis had been overlooked in the original report. Table 1 gives the selected bond distances and angles for [Cp*Rh(mnt)]₂.

Assuming that the Cp* ligand functions as a three-coordinate ligand, each rhodium center may be viewed as six-coordinate and formally belonging to the family of three-legged piano stool compounds. Coordination of one additional sulfur atom to each rhodium center as a result of Cp*Rh(mnt) dimeri. .tion is clearly responsible for the observed flattened basket shape reported for Cp*Rh(mnt) [31]. The Rh–S(1') bond involved in the dimerization exhibits a distance of 2.414(2) Å, which is slightly longer than the other Rh–S (chelating mnt) single bond lengths [Rh–S(1) = 2.350(2) Å and Rh–(S) = 2.351(2) Å]. Under these conditions each mnt ligand effectively functions in a bimodal fashion as a chelating and bridging ligand. Neglecting the Cp* ligand for a moment, it is seen that each rhodium center attains a near octahedral geometry on the basis of the S(1)–Rh–S(1'), S(1)–Rh–S(2'), and S(1)–Rh–S(2) angles of 82.40(9)°, 99.30(9)°, and 86.80(9)°, respectively. Thus, the originally reported flattened basket shape for Cp*Rh(mnt) may now be correctly viewed as arising from the ligation of a third sulfur atom to each monomeric Cp*Rh(mnt) unit. Similar bridging interactions in dimerization reactions of other dithiolates have also been reported [35,36]. That the bridging Rh–S interactions are weak is supported by the solution molecular weight data that point only to the presence of monomeric Cp*Rh(mnt). The remaining bond distances and angles are unexceptional and do not require any comment.

While the solid-state structure of [Cp˙Rh(mnt)]₂ definitely possesses coordinatively saturated rhodium centers as a result of the coordination of the extra sulfur atom, the nature of the monomeric Cp˙Rh(mnt) may be viewed as either a 16e or 18e complex, depending upon the absence or presence of lone-electron pair donation from the sulfurs to the rhodium center. Our extended Hückel MO calculations (vide infra) clearly support the existence of an electronically saturated monomer as a result of sulfur $3p$ orbital overlap with a suitable rhodium acceptor orbital. The canonical resonance forms **B–D** shown below would thus serve as the major resonance contributors to the structure of Cp˙Rh(mnt). Unfortunately this multiple Rh–S bonding cannot be confirmed by X-ray crystallography due to facile dimerization of Cp˙Rh(mnt).
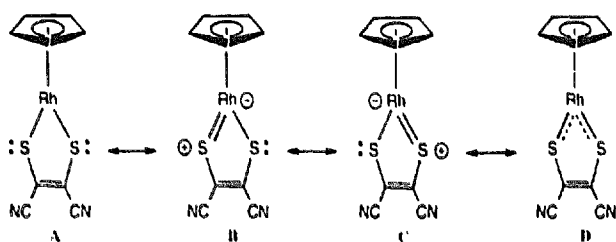
2.2. Cyclic voltammetric studies on Cp˙Rh(mnt)

The redox properties of Cp˙Rh(mnt) in MeCN and CH₂Cl₂ were studied by cyclic voltammetry at a platinum electrode, with TBAP (0.2 M) added as the supporting electrolyte. Fig. 2 shows the CV of Cp˙Rh(mnt) recorded in MeCN solvent at a scan rate of 0.5 V s⁻¹ over the potential range of 1.2 to −1.4 V. Two well-defined electrochemical responses are observed at $E_{1/2}$ = −0.99 and 0.90 V, assignable to the 0/1⁻ and 0/1⁺ redox couples. Application of the standard electrochemical criteria indicate that the reduction process is a fully reversible, diffusion-controlled process [37,38]. Removal of an electron from Cp˙Rh(mnt) affords a quasi-reversible oxidation couple, on the basis of a current ratio (I_p^c/I_p^a) of ca. 0.8. Constant-potential coulometry (vide infra) and calibration of the peak currents against the known one-electron standard Cp₂⁺Fe (internally added), taking into account the differences in the diffusion currents of the two complexes, confirmed the electron stoichiometry of both redox processes in Cp˙Rh(mnt). Routine CVs of Cp˙Rh(mnt) (not shown) were next recorded CH₂Cl₂ because this solvent represents an ideal choice for the CPC studies (vide infra). The 0/1⁻ redox couple at $E_{1/2}$ = −0.98 remained unaffected in comparison to that data obtained in MeCN, while the 0/1⁺ oxidation process ($E_{1/2}$ = 1.21) actually became more irreversible, on the basis of a current

ratio (I_p^c/I_p^a) of ca. 0.3. A new, irreversible CV wave at E_p^a = 1.00 V was also found when the oxidation potential was switched at 1.4 V and scanned back to 0.0 V. No further effort was expended on the study of the oxidation couple.

Cp˙Rh(mnt) was examined by constant-potential coulometry (CPC) (1) to unambiguously establish the one-electron nature of the reduction process and (2) to gain additional information regarding the site of elec-

Bond distances

Rh–S(1)	2.350(2)	Rh–S(1')	2.414(2)
Rh–S(2)	2.351(2)	Rh–C(11)	2.176(9)
Rh–C(12)	2.18(1)	Rh–C(13)	2.190(9)
Rh–C(14)	2.16(1)	Rh–C(15)	2.21(1)
S(1)–C(1)	1.771(9)	S(2)–C(2)	1.713(9)
N(3)–C(3)	1.13(1)	N(4)–C(4)	1.14(1)
C(1)–C(2)	1.36(1)	C(1)–C(3)	1.43(1)
C(2)–C(4)	1.42(1)	C(11)–C(12)	1.42(1)
C(11)–C(15)	1.43(2)	C(11)–C(111)	1.48(1)
C(12)–C(13)	1.40(1)	C(12)–C(121)	1.51(1)
C(13)–C(14)	1.44(1)	C(13)–C(131)	1.50(2)
C(14)–C(15)	1.40(1)	C(14)–C(141)	1.50(2)
C(15)–C(151)	1.51(2)	Rh●●●Rh	3.581(1)

Bond angles

S(1)–Rh–S(1')	82.4(9)	S(1)–Rh–S(2)	86.8(9)
S(1)–Rh–S(2')	99.3(9)	S(1)–Rh–C(11)	111.9(3)
S(1)–Rh–C(12)	149.5(3)	S(1)–Rh–C(13)	152.9(2)
S(1)–Rh–C(14)	114.5(3)	S(1)–Rh–C(15)	96.5(3)
S(1)–Rh–C(11')	95.9(3)	S(1)–Rh–C(12')	94.1(3)
S(1)–Rh–C(13')	124.0(2)	S(1)–Rh–C(14')	156.9(3)
S(1)–Rh–C(15')	129.8(3)	S(2)–Rh–C(11)	157.4(3)
S(2)–Rh–C(12)	123.6(3)	S(2)–Rh–C(13)	93.7(3)
S(2)–Rh–C(14)	97.3(3)	S(2)–Rh–C(15)	130.9(3)
Rh–S(1)–Rh'	97.52(6)	Rh–S(1)–C(1)	103.2(3)
Rh–S(1)–C(1')	105.9(3)	Rh–S(2)–C(2)	103.4(3)
S(1)–C(1)–C(2)	120.7(7)	S(1)–C(1)–C(3)	114.4(6)
C(2)–C(1)–C(3)	124.6(8)	S(2)–C(2)–C(1)	124.4(7)
S(2)–C(2)–C(4)	116.7(7)	C(1)–C(2)–C(4)	118.9(8)
N(3)–C(3)–C(1)	177(1)	N(4)–C(4)–C(2)	177(1)

Potential (Volts)

Fig. 2. Cyclic voltammogram of Cp˙Rh(mnt) (ca. 10⁻³ M; 298 K) in MeCN containing 0.2 M TBAP at 0.5 V s⁻¹.

tron accession in Cp˙Rh(mnt). The former aspect was deemed important because if Cp˙Rh(mnt) was formally coordinatively unsaturated due to the absence of sulfur–rhodium $3p–4d$ π overlap it would not be unreasonable to expect either two one-electron responses or a single two-electron reduction process. The CPC experiment was conducted in CH_2Cl_2 because this would facilitate the IR observation of the nitrile bands belonging to the mnt ligand.

Cp˙Rh(mnt) was reduced at room temperature at −1.30 V, and the total charge passed upon completion of the reduction was calculated to be $Q = 1.04$ C/mol of Cp˙Rh(mnt), in total agreement with the one-electron stoichiometry determined by using CV criteria. IR analysis of the catholyte revealed the presence of two ν(CN) bands at 2210 (w) and 2192 (s) cm^{-1}. These two ν(CN) bands of [Cp˙Rh(mnt)]$^{-\bullet}$ are shifted by 12 and 20 cm^{-1}, respectively, to lower energy relative to the neutral monomer Cp˙Rh(mnt). The magnitude of these frequency shifts indicates that little of the odd-electron density is associated with the two nitrile groups and that the reduction is largely confined to the rhodium center. Parallel reduction experiments conducted with the known one-electron reducing agent Cp_2Co (1.0 mol equiv) also afforded [Cp˙Rh(mnt)]$^{-\bullet}$ in quantitative yield. The IR spectra of [Cp˙Rh(mnt)]$^{-\bullet}$ obtained by chemical reduction were identical to those data obtained by bulk electrolysis. We attempted to grow single crystals of [Cp˙Rh(mnt)][Cp$_2$Co] in order to probe for any noticeable structural changes attendant upon reduction; however, all solutions of [Cp˙Rh(mnt)][Cp$_2$Co] decomposed over the course of several hours, depositing a black solid that proved to be insoluble in all common solvents. Given the absence of prominent nitrile bands in the IR (KBR) of this black solid, we have tentatively assigned it as some form of rhodium sulfide. No further effort was expended in the characterization of this particular material.

2.3. Extended Hückel molecular orbital calculations

The composition of the important HOMO and LUMO levels of Cp˙Rh(mnt) was determined by carrying out extended Hückel calculations on the model complex CpRh(mnt). Fig. 3 shows the three-dimensional CA-CAO drawings of these orbitals.

The HOMO of CpRh(mnt) occurs at −11.54 eV and is best described as a rhodium-based orbital (81%), whose d_{z^2} parentage is immediately discerned. The antibonding overlap between the d_{z^2} orbital and the lone-electron pair orbitals (p_y character) belonging to the sulfur atoms (17%) accounts for the remaining significant contribution to the HOMO. The nodal pattern and energy of this HOMO are similar to the HOMO level found in the related dithiolate complexes Cp˙Ru(NO)(mnt) and Cp˙Ru(NO)(tdas) already examined by us [26,27].

CpRh(mnt) exhibits a LUMO level at −9.50 eV and consists of an antibonding overlap involving the rhodium d_{xz} orbital and the sulfur p_x lone-electron pairs. This MO may be viewed as CpRh based (84%), with the sulfur p_x lone-electron pairs contributing ca. 15% to the LUMO. It is gratifying to find that the MO calculations support our contention concerning the population of a rhodium-based orbital during formation of [Cp˙Rh(mnt)]$^{-\bullet}$. The small amount of nitrile π contribution (< 1%) to the LUMO is in full agreement with the IR data found for [Cp˙Rh(mnt)]$^{-\bullet}$.

The question regarding the electron count at the rhodium center in Cp˙Rh(mnt) still exists. An earlier X-ray study on the related complex CpCo(mnt) by Churchill et al. has revealed that the olefinic bond of the mnt group was not coordinated to the cobalt atom [39]. Bond length arguments and conventional electron-counting rules suggest that the cobalt center in CpCo(mnt) is coordinatively unsaturated (16e). Of interest to us was the possibility of metal-sulfur $d\pi–p\pi$ overlap, the type expressed by the canonical resonance structures B–D (vide supra), which have been shown to exist in other metal dithiolate systems [26–28,40,41]. Indeed, a later paper went on the report that CpCo(mnt) was a bona fide 16e monomer given the rapid addition of PPh$_3$ to the monomer to give CpCo(PPh$_3$)(mnt) [42].

Accordingly, a thorough MO study examining the important valence orbitals of CpRh(mnt) was carried in order to probe for the existence of metal-sulfur $d\pi–p\pi$
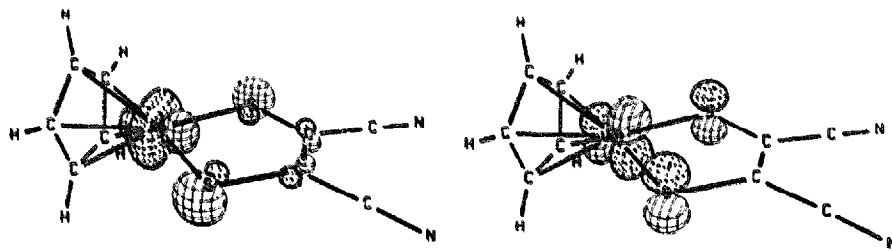

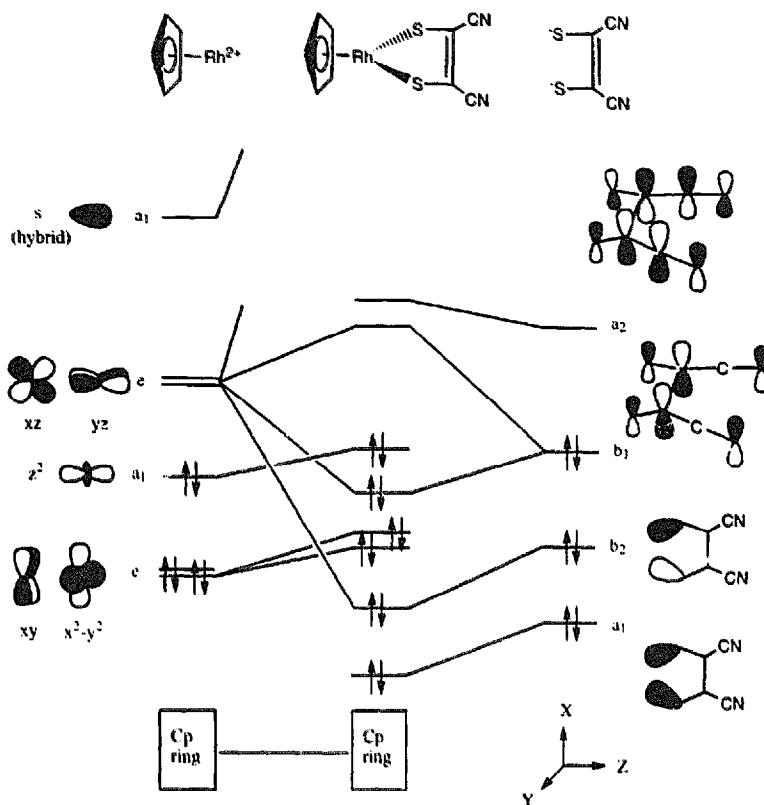Fig. 3. CACAO drawings of the HOMO (left) and LUMO (right) of CpRh(mnt).

Fig. 4. Qualitative MO diagram for CpRh(mnt) showing selected frontier orbital interactions.

overlap and to confirm the electron count at the rhodium center. Fig. 4 shows a qualitative MO diagram for CpRh(mnt) constructed from the union of $CpRh^{2+}$ and mnt^{2-} fragments. The observed low-energy block of MOs representing the π system of the Cp ligand is similar to earlier calculations performed by Hoffmann and coworkers [43], while the interaction of the rhodium d_{z^2} and d_{yz} orbitals with the a_1 and b_2 mnt orbitals, respectively, affords the two Rh–S sigma bonds present in CpRh(mnt). The crucial interaction in determining the electron count at the rhodium center involves the mnt b_1 orbital and the rhodium d_{xz}. This particular mnt orbital is composed of the p_x lone-electron pairs on the sulfur centers, with additional π contributions from the remaining portion of the mnt ligand. The in-phase interaction between the mnt b_1 and the rhodium d_{xz} orbitals affords the bonding MO immediately below the HOMO level, while the antibonding interaction between these same two orbitals gives rise to the LUMO, whose composition has already been discussed. The net effect of this $p\pi \rightarrow d\pi$ donation is the addition of two electrons to the rhodium center and relief of the unsaturation in CpRh(mnt). Maximum $p\pi \rightarrow d\pi$ donation occurs when the mnt ligand and the Cp ring adopt an orthogonal geometry, as confirmed by calculating the total energy of CpRh(mnt) as a function of mnt bending (i.e., pyramidalization of the sulfur atoms). A Walsh analysis on the bending of the mnt ligand (not shown)

has revealed that moving the mnt ligand from orthogonality by as little as 30° destabilizes CpRh(mnt) by 0.54 eV. The in-depth consequences associated with such pyramidalization in $CpML_3$ complexes have been addressed with respect to the overall electron count at the metal center [44]. Clearly this type of $p\pi \rightarrow d\pi$ donation must be soft or 'coordinatively flexible' given the uptake of the third sulfur ligand in the solid-state structure of $[CpRh(mnt)]_2$ and the ready formation of the monomeric CpRh(mnt) in solution.

3. Experimental section

The chemicals Na_2mnt [32] and $[CpRhCl_2]_2$ [33] were prepared according to the published literature procedures. The solvents CH_2Cl_2 and $CDCl_3$ were distilled under argon from P_2O_5 and stored in Schlenk storage flasks until needed. The MeCN solvent used in the CV studies was distilled from CaH_2. Schleck techniques were employed in the handling of all distilled solvents and the preparation of CV and CPC solutions [45]. The TBAP (caution: strong oxidant) used in the CV studies was purchased from Johnson Matthey Electronics and recrystallized from ethyl acetate/hexanes, followed by drying under vacuum for 72 h.

The IR spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells, while the ^{1}H

NMR spectrum was recorded on a Varian 200 VXR spectrometer.

3.1. Synthesis of [Cp*Rh(mnt)]₂

To a Schlenk tube containing 25 ml of CH_2Cl_2 under argon was added 50.0 mg (0.081 mmol) of $[Cp^*RhCl_2]_2$ and 17.0 mg (0.089 mmol) of Na_2mnt. The heterogeneous mixture was stirred overnight at room temperature, after which the solution had become dark red in color and homogeneous in nature. TLC analysis at this point revealed the presence of one spot in CH_2Cl_2 ($R_f = 0.44$). The solution was next concentrated to a volume of ca. 1.0 ml, followed by chromatographic purification over silica gel using CH_2Cl_2 as the eluant. The resulting dark red colored solution was recrystallized from CH_2Cl_2/heptane. Yield: 30.0 mg (49%) of red $[Cp^*Rh(mnt)]_2$. IR (CH_2Cl_2): $\nu(CN)$ 2222 (m, sh) and 2212 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.00 (Cp^* methyls).

3.2. X-ray diffraction data

A single crystal suitable for X-ray diffraction analysis, of dimensions $0.31 \times 0.32 \times 0.78$ mm^3, was selected from the above CH_2Cl_2/heptane solution (vide supra) and sealed inside a Lindemann capillary, followed by mounting on the goniometer of an Enraf–Nonius CAD-4 diffractometer. The radiation used was Mo $K\alpha$ monochromatized by a crystal of graphite. Cell constants were obtained from a least-squares refinement of 25 reflections with $2\theta > 36°$. Intensity data in the range of $2.0 < 2\theta < 44.0°$ were collected at room temperature using the $\theta/2\theta$-scan technique in the variable-scan-speed mode and were corrected for Lorentz, polarization, and absorption (DIFABS). Three standard reflections (1, 5, −3) were measured after every 3600 s of exposure time in order to monitor crystal decay (< 1%). The structure was solved by using standard Patterson and difference Fourier syntheses, and refined by using full-matrix least squares. With the exception of the Cp^* ring carbons, all non-hydrogen atoms were refined anisotropically, while the hydrogens were refined in idealized positions. Refinement converged at $R = 0.0297$ and $R_w = 0.0317$ for 997 unique reflections with $I > 3\sigma(I)$.

3.3. Cyclic voltammetry data

Cyclic voltammograms and CPC experiments were obtained by using a PAR Model 273 potentiostat/galvanostat. Positive feedback circuitry was employed in all CVs to compensate for iR drop. The reference electrode consisted of a silver wire quasi-reference electrode, with all potentials being reported relative to $Cp_2^*Fe/Cp_2^*Fe^+$ (internally added) redox cou-

ple, whose potential was assumed to be $E_{1/2} = -0.20$ V [46].

3.4. Extended Hückel MO calculations

The extended Hückel calculations on CpRh(mnt) were conducted with the original program developed by Hoffmann, [47,48] as modified by Mealli and Proserpio, [49] with weighted $H'_{ij}s$ [50]. The input Z matrix was constructed on a model possessing idealized C_{2v} symmetry, using Rh–S bond distances of 2.35 Å. Varying the two Rh–S bond lengths from 2.10 to 2.40 Å did not negate the overall nodal characteristics of the MOs of CpRh(mnt) and their energetic ordering in the MO diagram. All other bond distances and angles were taken from either the X-ray structure or suitable dithiolate complexes.

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