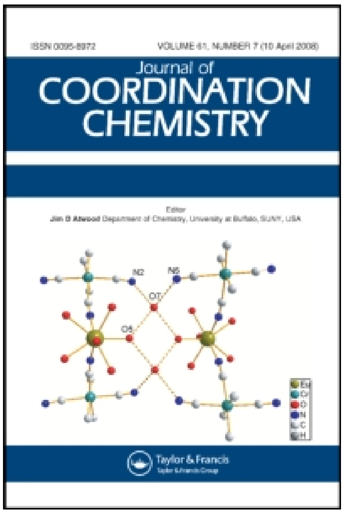

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REACTION OF $Cp^*Ru(NO)Cl_2$ WITH 2,2-DICYANO-1,1-ETHYLENEDITHIOLATE (i-mnt). REDOX CHEMISTRY AND X-RAY DIFFRACTION STRUCTURE OF $Cp^*Ru(NO)[S_2C=C(CN)_2]$

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The reaction of the disodium salt of 2,2-dicyano-1,1-ethylenedithiol (i-mnt) with the cyclopentadienyl compound $Cp^*Ru(NO)Cl_2$ in methanol gives the new piano-stool compound Cp*Ru(NO)(i-mnt), (**1**), in high yield. **1** has been isolated and characterized in solution by IR and NMR (^1H and ^{13}C NMR) spectroscopic methods, and the solid-state structure has been confirmed by X-ray diffraction analysis. Cp*Ru(NO)(i-mnt) crystallizes, as the CH_2Cl_2 solvate, in the orthorhombic space group Pbcm, a = 9.8872(6) Å, b = 13.5269(8) Å, c = 15.0557(8) Å, V = 2013.6(2) $Å^3$, Z = 4, d_{calc} = 1.621 $g \cdot cm^{-3}$; R = 0.0330, R_w = 0.0353 for 1068 observed reflections with $I > 3\sigma(I)$. The observed Ru-N-O bond angle of 168.9(7)° in the X-ray structure of **1** confirms the near linear nature of the nitrosyl linkage. The oxidation/reduction properties of **1** have been explored by cyclic voltammetry, which revealed the presence of a *quasi*-reversible one-electron reduction ($0/1^-$) and an irreversible oxidation. A comparison of the electrochemical data for Cp*Ru(NO)(i-mnt) with the isomeric compound Cp*Ru(NO)(mnt) is also presented.

KEYWORDS: dithiolate, ruthenium, nitrosyl

INTRODUCTION

The chemistry of transition-metal compounds that are substituted with dithiolate ligands remains of topical interest due to the possibility of producing novel electrical and magnetic materials.[1] Numerous examples of dithiolate compounds that exhibit interesting solution and solid-state properties are known, many of which are based on the ligands maleonitriledithiolate (mnt) and 1,3-dithiole-2-thione-4,5-dithiolate (dmit).[2,3]

Our groups have been involved in the synthesis and structural characterization of pentamethylcyclopentadienylruthenium(nitrosyl) compounds having the general form Cp*Ru(NO)(S-S) (where S-S = dithiolate).[4,5] In our first contribution to this area, we reported our data on the preparation and X-ray structural characterization of the compound Cp*Ru(NO)(mnt) (where mnt = 1,2-dicyano-1,2-ethylenedi-

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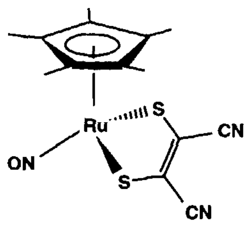
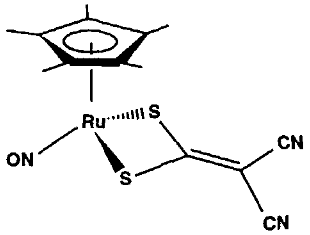
* Authors for correspondence.

thiolate). The redox properties and the nature of the HOMO and LUMO in Cp*Ru(NO)(mnt) were also discussed in detail in the initial report.

As an extension to the above mnt-substituted compound, we next decided to prepare and examine the isomeric compound bearing the branched (iso) dithiolate ligand 2,2-dicyano-1,1-ethylenedithiolate (i-mnt). The structures of both mnt Cp*Ru(NO) compounds are shown below. The presence of an isomeric mnt ligand in each of these compounds allows us the opportunity to study the electrochemical data as a function of the mnt ligand. Herein we report our results on the synthesis and X-ray diffraction structure of Cp*Ru(NO)(i-mnt), (**1**), along with the electrochemical properties exhibited by **1**. The effect of the chelating nature of the ancillary dithiolate ligand on the redox properties in both mnt-substituted compounds is described.



Cp*Ru(NO)(mnt)



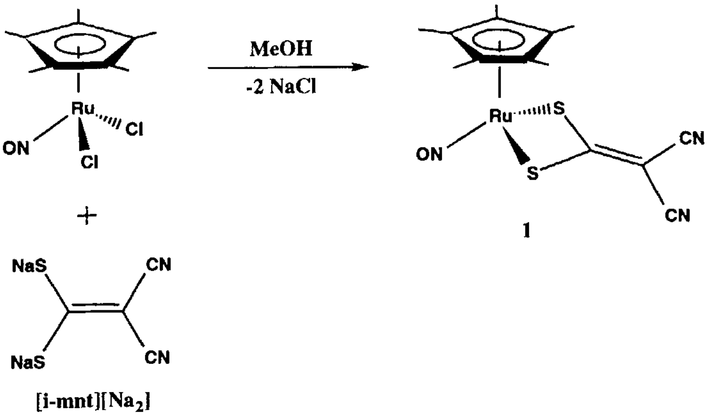
Cp*Ru(NO)(i-mnt)

RESULTS AND DISCUSSION

A. Synthesis and Spectroscopic Characterization

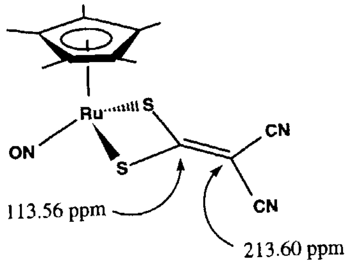
Treatment of a methanolic solution containing disodium 2,2-dicyano-1,1-ethylenedithiolate [i-mnt][Na]$_2$[6] at room temperature with Cp*Ru(NO)Cl$_2$[7] led to the new compound Cp*Ru(NO)(i-mnt) as the sole observable product by IR and TLC analysis. The desired product was isolated by chromatography over silica gel using CH_2Cl_2 as the eluant, with typical yields of Cp*Ru(NO)(i-mnt) being on the order of 80%. Compound **1** is soluble in halogenated and aromatic solvents but is much less soluble in saturated hydrocarbons such as pentane and petroleum ether. **1** appears to be relatively air-stable in the solid state; however, it does show signs of slight decomposition when kept in solution over long periods of time. The reaction leading to Cp*Ru(NO)(i-mnt) is illustrated in equation **1**.

The IR spectrum of Cp*Ru(NO)(i-mnt) in CH_2Cl_2 exhibits a strong ν(NO) band at 1782 cm^{-1}, which supports the existence of a linear (3e donor) rather than a bent (1e donor) nitrosyl ligand,[8] while the single, moderate intensity stretch observed at 2212 cm^{-1} is attributed to a ν(CN) band.[9] The ^{1}H NMR spectrum of **1** in $CDCl_3$ exhibits a single resonance at δ 1.90 that is assigned to the methyl groups of the Cp* ligand. The $^{13}C\{^1H\}$ NMR spectrum of **1** displays four resonances at δ 9.58, 109.25, 113.56, and 213.60. The former two resonances may be confidently assigned to the methyl groups and the ring carbons of the pentamethylcyclopentadienyl ligand, respectively. On the basis of related organic compounds, the remaining two resonances are ascribed to the α and β carbons of the i-mnt ligand, as shown below.[10] It should be noted that only four of the five expected resonances are observed for Cp*Ru(NO)(i-mnt). In this particular case, the nitrile carbon has not



(1)

been observed, presumably due to the quadrupolar broadening exerted on the nitrile carbon by the attached ^{14}N nucleus.[11]



B. X-Ray Diffraction Structure of $Cp^*Ru(NO)(i\text{-}mnt)\cdot CH_2Cl_2$

The molecular structure of Cp*Ru(NO)(i-mnt) was established by X-ray crystallography. The unit cell contains discrete molecules of Cp*Ru(NO)(i-mnt) with no unusually short intra- or inter-molecular contacts. Table 1 gives the X-ray data and processing parameters employed in the refinement of **1**, with the fractional coordinates and selected bond distances and angles listed in Tables 2 and 3, respectively.

The ORTEP diagram in Figure 1 shows the molecular structure of Cp*Ru(NO)(i-mnt) and confirms the identity of this new compound. The ruthenium center is **1** is best described as octahedral, provided that the Cp* ligand is viewed as a three-coordinate ligand. The idealized crystallographically imposed C_s symmetry displayed by **1** is in agreement with other three-legged piano-stool compounds that contain two equivalent legs.[4,5,12]

The observed Ru-S bond length of 2.373(2) Å in **1** compares well with the mean distance of 2.340 Å for the two Ru-S bonds in Cp*Ru(NO)(mnt)[4] and other metal-sulfur compounds.[13] The corresponding S-Ru-S' bond angle of 72.5(1)° is slightly less than the idealized octahedral angle of 90° but is not exceptional for the

Table 1 X-ray crystallographic data and processing parameters for Cp*Ru(NO)(i-mnt)·CH_2Cl_2

space group	Pbcm, orthorhombic
a, Å	9.8872(6)
b, Å	13.5269(8)
c, Å	15.0557(8)
V, Å^3	2013.6(2)
mol formula	$C_{15}H_{17}Cl_2N_3ORuS_2$
fw	491.43
formula units per cell (Z)	4
ρ, g·cm^{-3}	1.621
abs coeff (μ), cm^{-1}	12.38
λ (Mo Kα), Å	0.71073
collection range, deg	$2.0 \leq 2\theta \leq 44.0$
max scan time, s	120
scan speed range, deg·min^{-1}	0.8–8.0
tot. no. of data collcd	1452
no. of indep data, $I > 3\sigma(I)$	1068
R	0.0330
R_w	0.0353
weights	$[0.04F^2 + (\sigma F)^2]^{-1}$

Table 2 Positional parameters for the non-hydrogen atoms in Cp*Ru(NO)(i-mnt)·CH_2Cl_2 with estimated standard deviations in parentheses*

atom	*x*	*y*	*z*	*B*, Å^2
Ru	0.15428(7)	0.02792(5)	0.250	2.99(1)
Cl	0.2574(3)	0.3577(3)	0.0138(3)	14.5(1)
S	-0.0240(2)	0.0829(1)	0.34323(9)	3.86(3)
O	0.3540(7)	0.1833(5)	0.250	7.1(2)
N	0.2657(7)	0.1289(5)	0.250	3.9(2)
N(3)	-0.3791(5)	0.1612(5)	0.3962(4)	6.3(1)
C(1)	-0.1215(8)	0.1046(5)	0.250	3.4(2)
C(1s)	0.343(1)	0.250	0.000	10.4(4)
C(2)	-0.2537(8)	0.1329(6)	0.250	3.5(2)
C(3)	-0.3231(6)	0.1489(4)	0.3306(4)	4.4(1)
C(11)	0.0858(8)	-0.1274(5)	0.250	3.3(2)
C(12)	0.1705(6)	-0.1143(4)	0.1728(4)	3.4(1)
C(13)	0.3010(6)	-0.0880(4)	0.2030(4)	4.0(1)
C(111)	-0.0581(9)	-0.1576(6)	0.250	4.3(2)
C(121)	0.1270(7)	-0.1304(5)	0.0791(4)	5.3(2)
C(131)	0.4216(7)	-0.0713(5)	0.1451(5)	6.2(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

bite angle of the i-mnt ligand. The Ru-C(Cp*) distances range from 2.207(7) Å to 2.253(5) Å, with a mean length of 2.237 Å. These values are in good agreement with other structurally characterized Cp*Ru compounds.[14] A Ru-N(nitrosyl) bond length of 1.755(7) Å agrees well with the distance reported for other linear nitrosyl compounds,[15] and the angle of 168.9(7)° found for the Ru-N-O moiety in **1** agrees with the 3e (*i.e.*, linear) description of the nitrosyl ligand.[8,14] Similar angular deviations on the order of 10–15° from the expected linear Ru-N-O bond angle have been observed in selected nitrosyl compounds.[8]

Table 3 Selected bond distances (Å) and angles (deg) in $Cp^*Ru(NO)(i\text{-}mnt)\cdot CH_2Cl_2$[a]

Bond Distances			
Ru-S	2.373(2)	Ru-C(11)	2.207(7)
Ru-C(13)	2.250(5)	S-C(1)	1.728(5)
N(3)-C(3)	1.144(9)	C(2)-C(3)	1.411(7)
C(11)-C(111)	1.48(1)	C(12)-C(121)	1.492(8)
C(13)-C(131)	1.494(9)	Ru-N	1.755(7)
Ru-C(12)	2.253(5)	Cl-C(1s)	1.697(7)
O-N	1.14(1)	C(1)-C(2)	1.36(1)
C(11)-C(12)	1.443(7)	C(12)-C(13)	1.413(8)
C(13)-C(13')	1.415(8)	Ru-Cp*(centroid)	1.889(6)
Bond Angles			
S-Ru-S'	72.5(1)	S-Ru-C(11)	94.0(2)
S-Ru-C(12')	90.9(1)	S-Ru-S(13')	120.7(1)
N-Ru-C(12)	128.3(2)	C(11)-Ru-C(12)	37.7(2)
C(12)-Ru-C(12')	62.1(2)	C(12)-Ru-C(13')	61.4(2)
Ru-S-C(1)	89.3(2)	S-C(1)-S'	108.7(1)
C(1)-C(2)-C(3)	120.7(4)	Ru-C(11)-C(12)	72.9(4)
Ru-C(12)-C(11)	69.4(3)	Ru-C(13)-C(12)	71.8(3)
S-Ru-N	102.8(2)	S-Ru-C(12)	128.7(1)
S-Ru-C(13)	152.0(1)	N-Ru-C(11)	159.0(3)
N-Ru-C(13)	97.9(2)	Ru-N-O	168.9(7)
S-C(1)-C(2)	125.7(2)	N(3)-C(3)-C(2)	179.5(7)
Ru-C(12)-C(13)	71.6(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The observed distances and angles associated with the Cp* methyl groups and the i-mnt ligand are within normal ranges for these ligands and require no comments.

C. Electrochemistry

The electrochemical behavior of Cp*Ru(NO)(i-mnt) was examined by cyclic voltammetry at a platinum electrode in MeCN containing 0.1 M TBAP as the supporting electrolyte. The cyclic voltammogram (CV) of Cp*Ru(NO)(i-mnt) displays two well-defined redox responses at room temperature and a scan rate (v) of 0.1 V/s, as shown in Figure 2a. A *quasi*-reversible reduction is observed at $E_{1/2} = -0.99$ V that may be assigned to the $0/1^{-}$ redox couple for Cp*Ru(NO)(i-mnt). The peak-to-peak separation (ΔE_p) of 84 mV for this couple is comparable to that of internally added ferrocene ($\Delta E_p = 80$ mV) and supports a rapid heterogeneous charge transfer (*i.e.*, k_{het} is fast). Calibration of the forward peak current of **1** against that of ferrocene, using Walden's Rule,[16] firmly establishes the one-electron stoichiometry of this redox couple. At this particular scan rate, the $0/^{1-}$ redox couple exhibits a current ratio less than unity ($I_pa/I_pc = 0.83$), a situation that signals the presence of a competitive follow-up reaction that leads to the consumption of the radical anion $[Cp^*Ru(NO)(i\text{-}mnt)]^{\cdot -}$ before it can be oxidized on the reverse scan.[16,17] Similar electrochemically promoted behavior has been observed in $CpM(CO)_2(NO)$ (where M = Cr, Mo)[18] and Cp*Ru(NO)(S-S) (where S-S = mnt, tdas).[4,5] Here the CV behavior is modulated by a linear-to-bent nitrosyl conversion (3e → 1e) that originates from the radical anion of **1**. Scheme 1 shows this nitrosyl transformation. Assuming that the rate constants k_1 and k_{-1} are faster than the employed scan rate (v), it is predicted that the CV will appear reversible. Only when

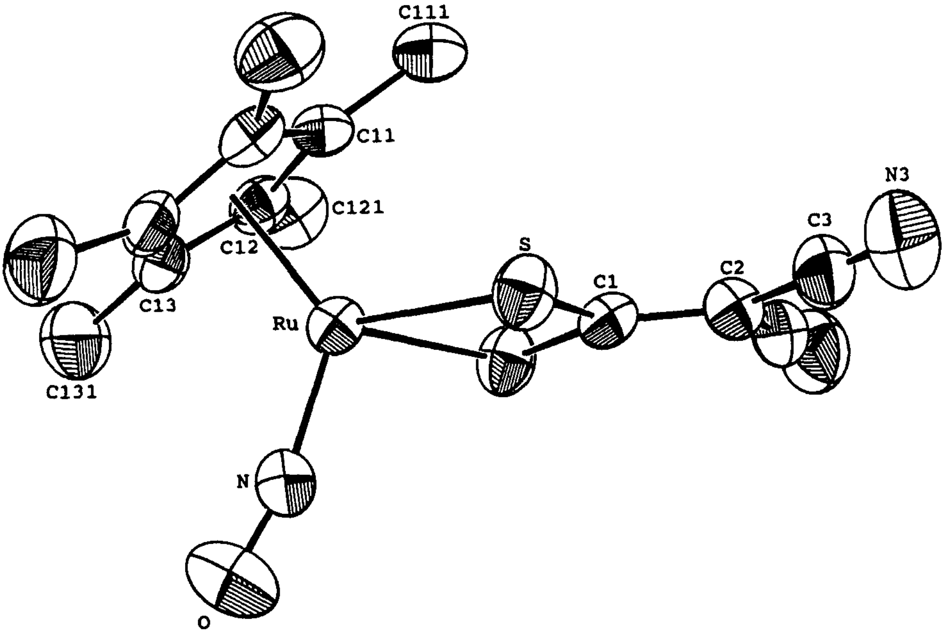


Figure 1 ORTEP diagram of the non-hydrogen atoms of Cp*Ru(NO)(i-mnt)·CH_2Cl_2 showing the thermal ellipsoids at the 50% probability level.

the scan rate (v) is faster than that of the chemical step k_{-1} will the CV display irreversible behavior. This becomes obvious at a scan rate (v) of 5.0 V/s in **1** (Figure 2b), by which time the CV of **1** has been rendered completely irreversible. Repetitive cycling over a potential of 0 V to −1.5 V did not yield any evidence for reversibility of any of the participant redox couples at the scan rates examined.

The irreversible multielectron wave observed at $E_p{}^a$ = 1.48 V in Figure 2a is assigned to the $0/1^+$ redox couple. This oxidation appears as an irreversible process, presumably the result of an EC scheme that facilitates removal of the electrochemically generated $[Cp^*Ru(NO)(i\text{-}mnt)]^{\cdot +}$ by a fast chemical reaction. The fate of the extricated $[Cp^*Ru(NO)(i\text{-}mnt)]^{\cdot +}$ remains to be established.

A redox comparison of the isomeric mnt-substituted compounds Cp*Ru(NO)(mnt) and Cp*Ru(NO)(i-mnt) provides a clear picture on how the mnt ligand affects the oxidation/reduction properties as a result of its coordination mode to the Cp*Ru(NO) moiety. The potential at which both compounds undergo reduction is very similar, as verified by the $E_{1/2}$ values of −0.92 V for Cp*Ru(NO)(mnt)[4] and −0.99 V for **1** (*vide supra*). Interestingly enough, the oxidation process in each compound displays pronounced differences. The mnt compound Cp*Ru(NO)(mnt) undergoes a reversible one-electron oxidation, unlike that of **1** with its i-mnt ligand.

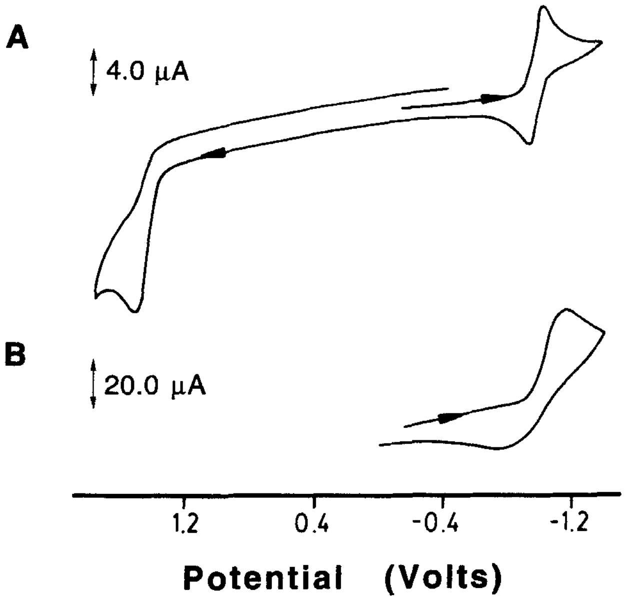


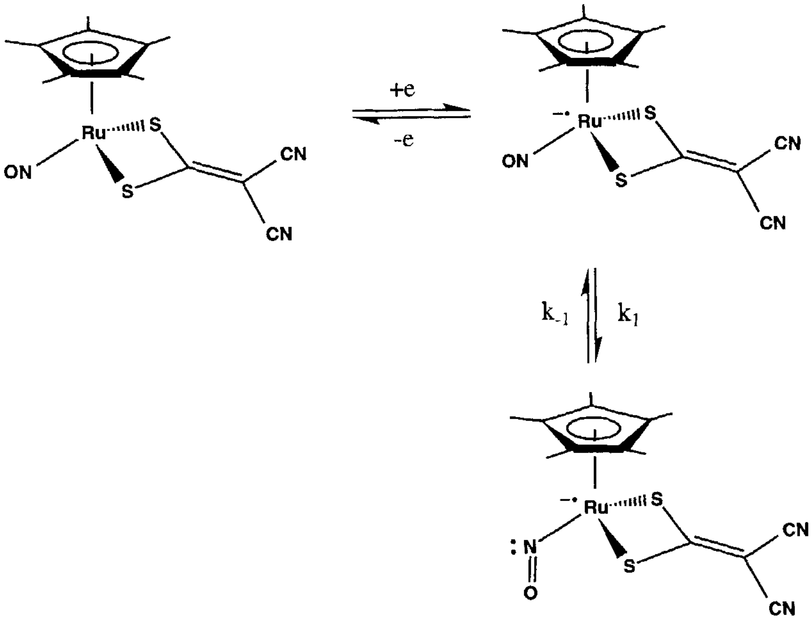
Figure 2 Cathodic scan cyclic voltammogram of *ca.* 1 × 10^{-3} M Cp*Ru(NO)(i-mnt) in MeCN containing 0.1 M TBAP at room temperature (a) 0.1 V/s and (b) 5.0 V/s.

SUMMARY

The reaction between Cp*Ru(NO)Cl_2 and [i-mnt]$^{2-}$ gives the new nitrosyl compound Cp*Ru(NO)(i-mnt). The solid-state structure was determined by X-ray crystallography, and the redox properties were investigated by cyclic voltammetry. A comparison of the redox chemistry of the isomeric compounds Cp*Ru(NO)(mnt) and Cp*Ru(NO)(i-mnt) is presented, with the results discussed relative to the chelating nature of the dithiolate ligand.

EXPERIMENTAL SECTION

The starting cyclopentadienyl compound Cp*Ru(NO)Cl_2 was synthesized from polymeric [Cp*RuCl_2]$_x$ and NO, using the procedure of Hubbard.[7] The disodium salt of 2,2-dicyano-1,1-ethylenedithiol used in this study was prepared according to the known literature procedure.[6] The malononitrile used in the synthesis of the i-mnt ligand was purchased from Aldrich Chemical Co. and used as received. The solvents CH_2Cl_2 and $CDCl_3$ were distilled from P_2O_5, while heptane was distilled from sodium/benzophenone ketyl. These particular solvents were handled under argon using Schlenk techniques.[19] Tetra-n-butylammonium perchlorate (TBAP; *caution*: strong oxidant) was purchased from Johnson-Matthey Electronics and recrystallized from ethyl acetate/petroleum ether prior to use. All purified solvents were stored in Schlenk storage vessels equipped with Teflon stopcocks. The C and H microanalysis was performed by Atlantic Microlab, Norcross, GA.



Scheme 1

Infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells, with the ^1H and ^{13}C NMR spectra being recorded in $CDCl_3$ solvent at 200 and 75 MHz, respectively, on a Varian Gemini-200 spectrometer.

*Synthesis of Cp*Ru(NO)(i-mnt)*

To a Schlenk tube containing 0.20 g (0.60 mmol) of Cp*Ru(NO)Cl_2 in 30 mL of degassed MeOH was added 0.30 g (1.6 mmol) of disodium 2,2-dicyano-1,1-ethylenedithiol. The reaction solution was stirred overnight at room temperature after which time TLC analysis (CH_2Cl_2 as the eluant) revealed complete conversion to the title compound. The solvent was removed under vacuum, and the crude solid was then purified by chromatography over silical gel, using a solvent system composed of CH_2Cl_2/acetone (95:5). The analytical sample and single crystals of **1** suitable for X-ray diffraction analysis were obtained from a CH_2Cl_2 solution of **1** that had been layered with a small amount of heptane. Yield: 0.20 g (83%). IR (CH_2Cl_2): ν 1782 (s, nitrosyl) and 2212 (m, nitrile) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.90 (s, 15 H, Cp*) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.58 (Cp* methyl group), 109.25 (Cp* ring carbons), 113.56 (dithiolate-substituted carbon), and 213.60 (dicyano-substituted carbon). *Anal.* Calcd. for $C_{14}H_{15}N_3OS_2Ru \cdot 1/8CH_2Cl_2$; C, 40.68; H, 4.09. Found: C, 40.70; H, 3.88.

*X-ray Diffraction Data for Cp*Ru(NO)(i-mnt)*

A single crystal, of dimensions 0.20 × 0.42 × 0.698 mm^3, suitable for X-ray diffraction analysis was selected and sealed inside a Lindemann capillary, followed by mounting on the goniometer of an Enraf-Nonius CAD-4 diffractometer. The radiation used was Mo Kα monochromatized by a crystal of graphite. Cell constants were obtained from a least-squares refinement of 25 reflections with $2\theta > 25°$. Intensity data in the range $2.0 \leq 2\theta \leq 44.0°$ 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 reflections (5 0 0, 0 8 0, 0 0 8) were measured after every 3600 s of exposure time in order to monitor crystal decay (< 1%). The structure was solved using a Patterson map, which revealed the position of the ruthenium atom. All non-hydrogen atoms were located with difference Fourier maps and least-squares refinement and were refined anisotropically. Refinement converted at $R = 0.0330$ and $R_w = 0.0353$ for 1068 unique reflections with $I > 3\sigma(I)$.

Electrochemical Measurements

Cyclic voltammograms were obtained with a PARC Model 273 potentiostat/galvanostat, with all electrochemical data collected by using positive feedback circuitry to reduce unwanted solution resistance. The CV cell employed was of airtight design and based on a three-electrode configuration, which enabled all CVs to be recorded free from oxygen and moisture. The CV studies utilized platinum disk (area = 0.0079 cm^2) working and auxiliary electrodes. A silver wire *quasi*-reference electrode was used in all CV experiments, and the potential data quoted in this paper are referenced to the formal potential of the Cp_2Fe/Cp_2Fe^+ (internally added) redox couple, taken to have an $E_{1/2} = 0.307$ V.[16]

Acknowledgement

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