

The Molecular and Electronic Structure of the Electron Transfer Series $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{R}_2)_3]^z$ ($z = 0, -1, -2$; R = phenyl, *p*-tolyl, *p*-*tert*-butylphenyl)[†]

Prasanta Ghosh, Eckhard Bill, Thomas Weyhermüller, and Karl Wieghardt*

Max-Planck-Institut für Bioanorganische Chemie, Stiftstrasse 34-36, D-45470 Mülheim an der Ruhr, Germany

Received November 23, 2006

Three dinuclear (nitrosyl)iron complexes containing three 1,2-di(phenyl)ethylene-1,2-dithiolate ligands have been prepared ($[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{R}_2)_3]^0$ (R = phenyl, **1a**; *p*-tolyl, **2a**; (4-*tert*-butyl)phenyl, **3a**). Each of these compounds represents the first member of a three-membered electron-transfer series: $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{R}_2)_3]^z$ ($z = 0, -1, -2$). The salt $[\text{Co}(\text{Cp})_2][\text{Fe}_2(\text{NO})_2(\text{L}^3)_3]$ has also been isolated. The molecular structures of **2a** and **3a** have been determined by X-ray crystallography. Both neutral complexes contain two nearly linear FeNO units, one of which is S,S'-coordinated to two dithiolene ligands yielding a square-based pyramidal Fe(NO)S₄ polyhedron; the second FeNO moiety forms two (μ_2 -S)-bridges to the first unit and is S,S'-coordinated to a third dithiolate radical yielding also a square-based pyramidal Fe(NO)S₄ polyhedron. The electronic structures of the neutral, monoanionic, and dianionic species have been elucidated spectroscopically (UV-vis, IR, EPR, Mössbauer): $[\{\text{Fe}^{\text{II}}(\text{NO}^+)\}(\text{L}^*)\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}(\text{L})_2]^0$ ($S = 0$); $[\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}(\text{L})\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}(\text{L})_2]^{1-}$ ($S = 1/2$); and $[\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}(\text{L})\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}(\text{L})_2]^{2-}$ ($S = 0$), where (L)²⁻ represents the corresponding closed-shell dithiolate dianion and (L*)⁻ is its monoanionic radical.

1. Introduction

Locke, McCleverty, Wharton, and Winscom reported in 1967 the synthesis of a dinuclear (nitrosyl)iron complex containing three 1,2-di(phenyl)ethylene-1,2-dithiolate ligands,¹ $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{Ph}_2)_3] \cdot \text{CHCl}_3$ (**1a**). This compound was obtained from the reaction of the neutral dinuclear complex,² $[\text{Fe}^{\text{III}}_2(\text{S}_2\text{C}_2\text{Ph}_2)_4]$ (**1**), with NO gas in cold chloroform. From cyclic voltammetry it was deduced that (**1a**) undergoes two reversible, successive, one-electron-transfer reductions generating a dinuclear mono- and a dianion.¹ The zero-field Mössbauer spectrum of neutral **1a** revealed the presence of two distinct iron sites in a 1:1 ratio with isomer-shift values vs α -Fe at 298 K of -0.01 and 0.29 mm s^{-1} and quadrupole-splitting parameters of 1.57 and 1.26 mm s^{-1} , respectively.³ Since the structure of **1a** is not known to date, its electronic structure remained elusive.

Here we report the synthesis and structural characterization of the analogous dinuclear species $[\text{Fe}_2(\text{NO})_2(\text{L}^2)_3]$ (**2a**) and $[\text{Fe}_2(\text{NO})_2(\text{L}^3)_3]$ (**3a**). The ligands and complexes and their respective abbreviations are shown in Scheme 1.^{4,5} The electronic structures of neutral **2a**⁰, its mono-, **2a**⁻, and the dianion, **2a**²⁻, have been elucidated by infrared, UV-vis, and Mössbauer spectroscopy.

2. Experimental Section

2.1. The preparation of the dinuclear complexes $[\text{Fe}^{\text{III}}(\text{L}^1)(\text{L}^1)]_2$ (**1**), $[\text{Fe}^{\text{III}}(\text{L}^{2*})(\text{L}^2)]_2$ (**2**), and $[\text{Fe}^{\text{III}}(\text{L}^3)(\text{L}^3)]_2$ (**3**) has been described in refs 2 and 4. (L¹)²⁻ represents the dianion 1,2-di(phenyl)ethylene-1,2-dithiolate, (L²)²⁻ is 1,2-di(*p*-tolyl)ethylene-1,2-dithiolate, and (L³)³⁻ is the 1,2-di(4-*tert*-butylphenyl)ethylene-1,2-dithiolate. The abbreviations (L^{n*})⁻ ($n = 1-3$) represent the respective radical monoanion. The two diaryl-based dithiolate ligands, namely, (L²)²⁻ and (L³)²⁻ (Scheme 1), were prepared in

* To whom correspondence should be addressed. Tel: 49-208-306 3609. Fax: 49-208-306 3952. E-mail: wieghardt@mpi-muelheim.mpg.de.

[†] Dedicated to Professor E. I. Solomon on the occasion of his 60th birthday.

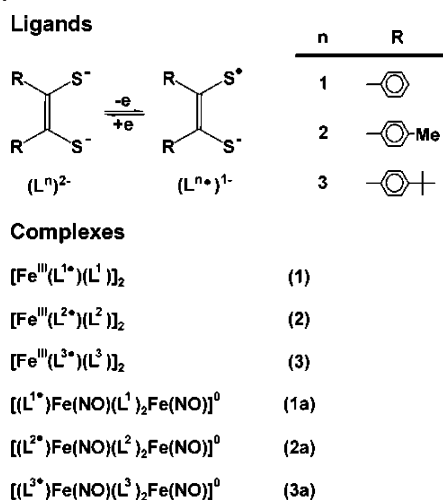
(1) (a) Locke, J.; McCleverty, J. A.; Wharton, E. J.; Winscom, C. J. *Chem. Commun.* **1967**, 1289. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (c) McCleverty, J. A.; Ratcliff, B. *J. Chem. Soc. A* **1970**, 1627. (2) Schrauzer, G. N.; Mayweg, V. P.; Finck, H. W.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 4604.

(3) (a) Birchall, T.; Greenwood, N. N.; McCleverty, J. A. *Nature* **1967**, *215*, 626. (b) Birchall, T.; Greenwood, N. N. *J. Chem. Soc. A* **1969**, 286.

(4) Patra, A.; Bill, E.; Weyhermüller, T.; Stobie, K.; Bell, Z.; Ward, M. D.; McCleverty, J. A.; Wieghardt, K. *Inorg. Chem.* **2006**, *45*, 6541.

(5) Patra, A.; Bill, E.; Chlopek, K.; Neese, F.; Weyhermüller, T.; Stobie, K.; Ward, M. D.; McCleverty, J. A.; Wieghardt, K. *Inorg. Chem.* **2006**, *45*, 7877.

Scheme 1



situ from their dithiophosphoric esters according to literature procedures^{2,6} and were used for the synthesis of dinuclear complexes (1–3) without preceding isolation.

$[Fe_2(NO)_2(L^2)_3]$ (2a). Through a vigorously stirred suspension of **1** (200 mg, 0.16 mmol) in CH_2Cl_2 (40 mL) was passed a stream of Ar for ~5 min, after which time a stream of NO gas was bubbled through the solution for 90 s at 20 °C followed by an Ar stream. To the dark brown solution was added dry methanol (20 mL), and the volume of the solution was reduced to ~30 mL under reduced pressure. Black microcrystals of the neutral, mononuclear species $[Fe(NO)(L^2)_2]^0$ precipitated and were then filtered off. The filtrate was allowed to slowly evaporate by slowly passing a stream of Ar through the solution. Within 4–5 days, black crystals of the desired dinuclear product had precipitated. Yield: 30 mg (~18%). Anal. Calcd for $C_{48}H_{42}N_2O_2S_6Fe_2$: C, 58.64; H, 4.30; N, 2.85; S, 19.57. Found: C, 58.6; H, 4.4; N, 2.8; S, 19.6.

$[Fe_2(NO)_2(L^3)_3]$ (3a). This complex has been prepared as described above for **2a**⁰ by using dinuclear **3** (160 mg, 0.10 mmol) as starting material. It is noted that mononuclear $[Fe(NO)(L^3)_2]^0$ was not obtained as crystalline material in this instance. Yield: 95 mg (73%). Anal. Calcd for $C_{66}H_{78}N_2O_2S_6Fe_2$: C, 64.16; H, 6.36; N, 2.27; S, 15.57; Fe, 9.04. Found: C, 64.3; H, 6.5; N, 2.2; S, 15.5; Fe, 9.1.

$[Co(Cp)_2][Fe_2(NO)_2(L^3)_3][Co(Cp)_2]$ [3a]. To a stirred solution of **3a**⁰ (100 mg, 0.08 mmol) in *n*-hexane (40 mL) under an Ar blanketing atmosphere was added 16 mg (0.08 mmol) of cobaltocene, $[Co(Cp)_2]$. After stirring the solution for 10 h at 20 °C, a light green solid precipitated which was filtered off and dried under Ar. Yield: 70 mg (60%). Anal. Calcd for $C_{76}H_{88}N_2O_2S_6Fe_2Co$: C, 64.08; H, 6.23; N, 1.97. Found: C, 64.2; H, 6.2; N, 1.9.

2.2. X-ray Crystallographic Data Collection and Refinement of the Structures. Dark brown single crystals of **2a** and **3a** were coated with perfluoropolyether, picked up with nylon loops, and were mounted in the nitrogen cold stream of the diffractometer. A Nonius Kappa-CCD diffractometer equipped with a Mo-target, rotating-anode X-ray source, and a graphite monochromator (Mo $K\alpha$, $\lambda = 0.71073$ Å) was used. Final cell constants were obtained from least-squares fits of all measured reflections. Intensity data were corrected for absorption using intensities of redundant reflections.

Table 1. Crystallographic Data for **2a** and **3a**

	[2a]	[3a]
chemical formula	$C_{48}H_{42}Fe_2N_2O_2S_6$	$C_{66}H_{78}Fe_2N_2O_2S_6$
fw	982.90	1235.36
space group	$C2/c$, No. 15	$P2_1/c$, No. 14
<i>a</i> , Å	37.1295(8)	19.0256(6)
<i>b</i> , Å	11.0515(2)	29.5816(9)
<i>c</i> , Å	24.1369(4)	12.0932(3)
β , deg	109.212(3)	101.446(4)
<i>V</i> , Å ³	9352.7(3)	6670.8(3)
<i>Z</i>	8	4
<i>T</i> , K	100(2)	100(2)
ρ calcd, g cm ⁻³	1.396	1.230
refl. collected/ $2\theta_{max}$	81 005/60.00	76 038/55.00
unique refl./ $I > 2\sigma(I)$	13 609/11 286	15 313/12 312
no. of params/restr	547/0	725/25
λ , Å/ μ (Mo $K\alpha$), cm ⁻¹	0.71073/9.28	0.71073/6.65
$R1^a$ /GOF ^b	0.0320/1.088	0.0627/1.184
wR2 ^c ($I > 2\sigma(I)$)	0.0672	0.1059
residual density, e Å ⁻³	+0.44/−0.26	+0.54/−0.35

^a Observation criterion: $I > 2\sigma(I)$. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^bGOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. ^cwR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

The structures were readily solved by direct methods and subsequent difference-Fourier techniques. The Siemens ShelXTL⁸ software package was used for solution and artwork of the structure; ShelXL97⁹ was used for the refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic data of the compounds are listed in Table 1.

The 4-*tert*-butylphenyl entity attached to C62 in crystals of **3a** was found to be disordered. The group was split on two sites with an occupation ratio of about 65:35. Corresponding atoms of the two parts were refined with equivalent thermal displacement parameters and restrained geometry using EADP, SADI, and SAME instructions of ShelXL97.

3. Results

3.1. Syntheses and Structures of Complexes. McCleverty et al.^{1a,b} have reported that from the reaction of dinuclear **1** with NO in chloroform two products are isolable, the mononuclear neutral species $[Fe(NO)(S_2C_2Ph)_2]^{1a,7}$ and the dinuclear complex $[Fe_2(NO)_2(S_2C_2Ph)_3]$ (**1a**).^{1a} In a similar fashion we have succeeded in synthesizing the corresponding dinuclear complexes **2a** and **3a** (Scheme 1) in CH_2Cl_2 . The three complexes possess an $S_t = 0$ ground state as determined from variable temperature SQUID measurements on solid samples of **1a**, **2a**, and **3a**.

Figure 1 shows the structure of a neutral molecule in crystals of **2a** and **3a**, respectively, as determined by X-ray crystallography at 100 K. Table 2 gives selected bond lengths.

Both molecules possess the same dinuclear core where both iron ions are each coordinated to a single NO ligand. One iron ion is S,S' -bound to two bidentate dithiolate dianions, $(S_2C_2R_2)^{2-}$, whereas the second iron ion is S,S' -

(6) (a) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483. (b) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *Inorg. Chem.* **1965**, *4*, 1615.

(7) McCleverty, J. A.; Atherton, N. M.; Locke, J.; Wharton, E. J.; Winscom, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 6082.

(8) *ShelXTL*, V.5; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

(9) Sheldrick, G. M. *ShelXL97*; University of Göttingen: Göttingen, Germany, 1997.

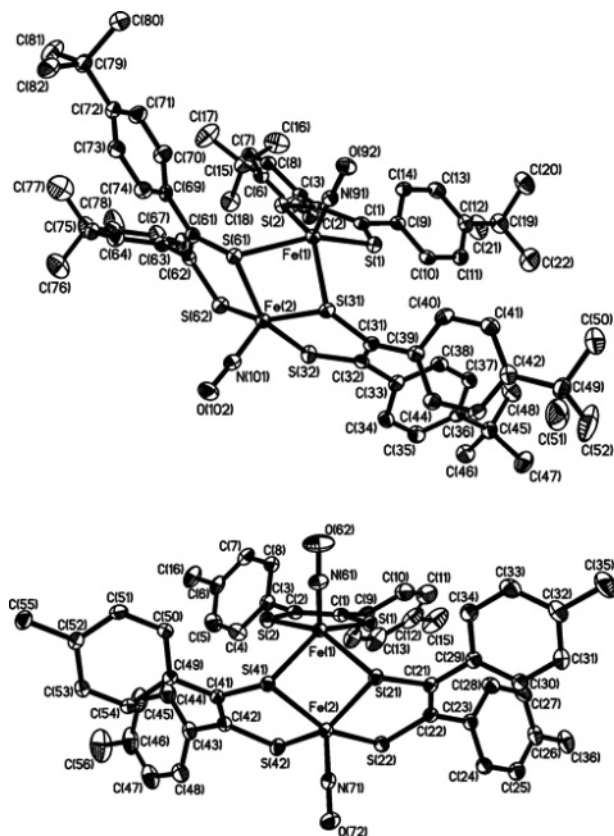


Figure 1. Structure of the neutral molecule in crystals of **[3a]** (top) and **[2a]** (bottom).

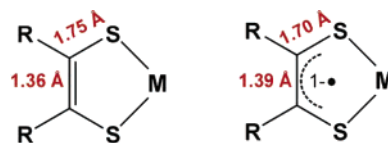
Table 2. Selected Bond Distances (Å) and Angles (deg)

Complex [2a] ⁰			
Fe1–N61	1.661(1)	Fe2–N71	1.632(1)
Fe1–S1	2.1761(4)	Fe2–S42	2.2133(4)
Fe1–S2	2.1838(4)	Fe2–S21	2.2193(4)
Fe1–S21	2.3400(4)	Fe2–S22	2.2235(4)
Fe1–S41	2.3452(4)	Fe2–S41	2.2388(4)
S1–C1	1.700(2)	S2–C2	1.698(2)
C1–C2	1.400(2)	S21–C21	1.750(2)
C21–C22	1.371(2)	S22–C22	1.723(2)
S41–C41	1.755(2)	C41–C42	1.368(2)
S42–C42	1.725(2)	Fe1···Fe2	2.8404(3)
Fe1–N61–O62	171.6(1)	N61–O62	1.170(2)
Fe2–N71–O72	172.2(1)	N71–O72	1.165(2)
Complex [3a] ⁰			
Fe1–N91	1.666(2)	Fe2–N101	1.628(3)
Fe1–S2	2.1547(8)	Fe2–S61	2.2074(8)
Fe1–S1	2.1812(8)	Fe2–S32	2.2254(8)
Fe1–S31	2.3398(8)	Fe2–S62	2.2305(8)
Fe1–S61	2.3719(8)	Fe2–S31	2.2342(8)
S1–C1	1.704(3)	S2–C2	1.695(3)
C1–C2	1.405(4)	S31–C31	1.747(3)
S32–C32	1.724(3)	C31–C32	1.369(4)
S61–C61	1.753(3)	S62–C62	1.727(3)
C61–C62	1.370(4)	Fe1···Fe2	2.8063(6)
Fe1–N91–O92	168.9(2)	O102–N101–Fe2	177.0(3)

bound to only one radical dithiolate monoanion, $(S_2C_2R_2)^{\cdot -}$; each dianion is $(\mu-S)$ -bound via a single bridging sulfur atom to both iron sites. Thus the two iron sites in **2a** and **3a** are not identical despite the fact that both iron ions are five-coordinate and both possess a square-base pyramidal $Fe(NO)_4$ coordination polyhedron.

As pointed out previously,^{4,5} the oxidation level of a given coordinated dithiolene ligand in a coordination compound

can be determined by X-ray crystallography via the average C–S and “olefinic” C–C bond distances. These distances are as shown below in a dianionic di(aryl)ethylene-1,2-dithiolate and its radical monoanion metal complex (the C–S and C–C bond distances are given in Å)



It is therefore unambiguous that Fe(1) is coordinated to a single radical monoanion in **2a** and **3a**, respectively, since the average C–S distance is short at 1.70 ± 0.006 Å and the corresponding C–C bond is long at 1.40 ± 0.006 Å. In contrast, these distances in the two dianionic dithiolate ligands at Fe(2) in **2a** and **3a** are distinctly different: the average (av) distance of C–S is 1.74 ± 0.006 Å and that of C–C is 1.37 ± 0.006 Å. They are quite typical for coordinated, closed-shell dianions $(L^n)^{2-}$ ($n = 1-3$).

Since **1a–3a** are neutral complexes, it follows from the above charge distribution of $(5-)$ for the three dithiolene ligands that the two $\{FeNO\}^n$ moieties must carry a $5+$ charge which is only possible if $n = 6$ for one iron ion and $n = 7$ for the other. The $\{FeNO\}^6$ unit carries then a $3+$ charge, whereas it is $2+$ for $\{FeNO\}^7$. The quality of the structure determination of **3a** allows one to discriminate between an $\{Fe^{II}(NO^+)_6$ and an $\{Fe^{II}(NO^{\cdot -})_7$ ($S = 1/2$) moiety, although we note that these descriptions represent limiting electron distributions. The observed Fe1–N91 distance at 1.666 ± 0.006 Å is significantly longer than the corresponding distance of Fe2–N101 at 1.628 ± 0.009 Å. Concomitantly, the Fe1–N91–O92 unit is slightly bent at $168.9 \pm 0.9^\circ$, whereas the unit Fe2–N101–O102 is nearly linear at 177.0° as one would expect for an $\{FeI(NO)\}^7$ and an $\{Fe2-(NO)\}^6$ moiety. Note that in this structure the two NO ligands do not display any disorder. The structure of **2a** is of slightly lower quality. Nevertheless, the Fe1–N61 and Fe2–N71 distances at 1.661 ± 0.004 and 1.632 ± 0.004 Å exhibit the same trend as above. Oxygen atom O62 displays a large isotropic thermal parameter, U_{eq} , which is significantly larger than those for N71 (21) and O72 (30). This indicates some disorder in the Fe1–N61–O62 group, $\{FeNO\}^7$, and does not allow a precise determination of the Fe–N–O bond angle. The Fe2–N71–O72 group does not display disorder problems and is nearly linear ($172.2(1)^\circ$), indicating an $\{FeNO\}^6$ group.

It is noteworthy that the two $(\mu-S)$ bridges are not symmetric. The two Fe–S distances of Fe1–S41 and Fe1–S21 are long (av 2.342 ± 0.001 Å) but shorter for Fe2–S41 and Fe2–S21 (av 2.229 ± 0.001 Å). If one heterolytically cleaves the two weak Fe–S bonds, one obtains a dication $[Fe^{II}(NO^+)(L^{\cdot -})]^{2+}$ ($S = 1/2$) and a dianion $[Fe^{II}(\dot{N}O)(L^n)_2]^{2-}$ ($S = 1/2$), where the former contains an $\{FeNO\}^6$ and the latter an $\{FeNO\}^7$ unit. The two paramagnetic units could then be envisioned to couple their spins intramolecularly antiferromagnetically, yielding the observed $S = 0$ ground state.

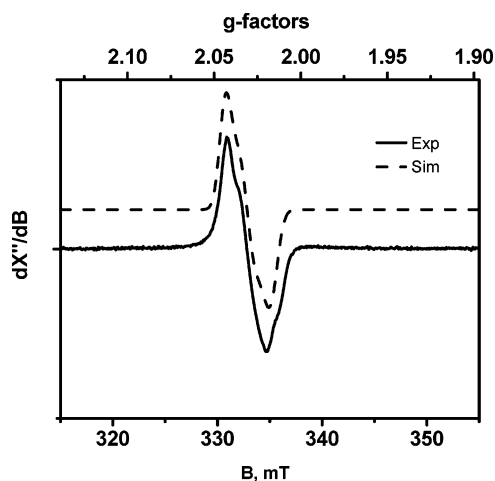


Figure 2. X-Band EPR spectrum of $[\text{Cp}_2\text{Co}][\mathbf{3a}]$ in frozen CH_2Cl_2 at 30 K. (Conditions: frequency, 9.43 GHz; power, 2.5×10^{-6} mW; modulation, 8.0 G).

Table 3. Infrared Spectroscopic Data of Complexes Recorded as Solids (KBr Disk) and (in Parentheses) in CH_2Cl_2 Solution at -25°C

complex	$\nu_{\text{NO}}(^{14}\text{N}^{16}\text{O}), \text{cm}^{-1}$ ^a	$\nu_{\text{NO}}(^{15}\text{N}^{18}\text{O}), \text{cm}^{-1}$ ^a
[2a]	1809, 1754	1726, 1681
[3a]	1809, 1763, 1744 (1810, 1768)	1727, 1687 (1736, 1695)
[Co(Cp) ₂][3a]	1758, 1733 (1734, 1689)	n.m. (1667, 1609)
[N(<i>n</i> -Bu) ₄] ₂ [3a]	(1638)	(1570)

^a (N–O) stretching frequency, *b* = broad.

From the reaction of neutral **3a** with 1 equiv of cobaltocene in *n*-hexane, a light green precipitate of $[\text{Co}(\text{Cp})_2][\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{R}_2)_3]$ ($\text{R} = 4\text{-tert-butylphenyl}$), $[\text{Co}(\text{Cp})_2][\mathbf{3a}]$ was obtained. This salt is paramagnetic ($S = 1/2$) as was established by its X-band EPR spectrum in CH_2Cl_2 solution at 30 K shown in Figure 2. From the simulation the following parameters were deduced: $g_x = 2.0371$; $g_y = 2.0109$; $g_z = 2.0244$; and $g_{\text{iso}} = 2.0241$. These values in conjunction with the small *g*-anisotropy and the lack of ^{14}N -hyperfine splitting point to the presence of an S-centered ligand radical (L^{\cdot})[–] rather than to an $\{\text{FeNO}\}^7$ ($S = 1/2$) moiety with an unpaired electron in a π^* orbital of an NO ligand.^{4,5} An electronic structure as in $[(\text{NO})\text{Fe}^{\text{II}}(\text{L}^{\cdot})_2\text{Fe}^{\text{II}}(\text{NO})(\text{L}^{\cdot})]^-$ would account for this observation if it is assumed that the two $\{\text{FeNO}\}^7$ ($S = 1/2$) units couple strongly intramolecularly antiferromagnetically.

This interpretation is corroborated by the infrared spectra of solid samples (KBr disks) of **3a** and $[\text{Co}(\text{Cp})_2][\mathbf{3a}]$ (Table 3). The neutral complexes **2a** and **3a** both exhibit two ν_{NO} stretching frequencies of which the first at 1810 cm^{-1} is characteristic for an $\{\text{FeNO}\}^6$ moiety and the second at $\sim 1755 \text{ cm}^{-1}$ must then represent an $\{\text{FeNO}\}^7$ ($S = 1/2$) unit.^{10–14} In conjunction with the X-ray structures (Figure

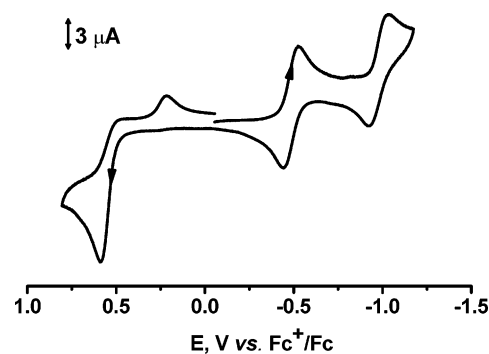
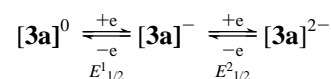


Figure 3. Cyclic voltammogram of $[\mathbf{3a}]^0$ in CH_2Cl_2 at 20°C (0.20 M $[\text{N}(\text{n-Bu})_4]\text{PF}_6$ supporting electrolyte; glassy carbon working electrode; scan rate 100 mV s^{-1}).

1), Fe1 would then correspond to an $\{\text{FeNO}\}^7$ and Fe2 to an $\{\text{FeNO}\}^6$ moiety. Thus, one electron reduction of **3a** yielding $[\mathbf{3a}]^-$ involves the process $\{\text{FeNO}\}^6 \rightarrow \{\text{FeNO}\}^7$ since the observed two ν_{NO} stretching frequencies at 1758 and 1733 cm^{-1} are very close in energy (and low in energy) and, therefore, belong to two $\{\text{FeNO}\}^7$ moieties. These data are in accord with an electronic structure of $[\text{Fe}^{\text{II}}(\text{NO})(\text{L}^{\cdot})\text{Fe}^{\text{II}}(\text{NO})(\text{L}^{\cdot})_2]^-$.

3.2. Electro- and Spectroelectrochemistry. The cyclic voltammogram of **3a** in CH_2Cl_2 (0.20 M $[\text{N}(\text{n-Bu})_4]\text{PF}_6$ supporting electrolyte, glassy carbon working electrode; scan rate 100 mV s^{-1}) recorded at 20°C is shown in Figure 3. All redox potentials are referenced vs the ferrocenium/ferrocene couple (Fc^+/Fc).

At potentials of $<0.0 \text{ V}$ two successive, reversible, one-electron-transfer waves are observed at $E_{1/2}^1 = -0.49 \text{ V}$ and $E_{1/2}^2 = -1.00 \text{ V}$, generating a monoanion $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{R}_2)_3]^-$ and the corresponding dianion $[\text{Fe}_2(\text{NO})_2(\text{S}_2\text{C}_2\text{R}_2)_3]^{2-}$ ($\text{R} = 4\text{-tert-butylphenyl}$), respectively, as deduced from coulometric measurements of **3a** at appropriately fixed potentials by:



At more positive potential, an irreversible peak is observed at $E_{\text{p,red}} = 0.22 \text{ V}$ and $E_{\text{p,ox}} = 0.61 \text{ V}$ indicating that the oxidation of **3a** leads to decomposition of the dinuclear species, with probable generation of a mononuclear species $[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^0$. The electrochemistry of **1a** in CH_2Cl_2 in the lower potential region was reported in 1966¹ ($E_{1/2}^1 = -0.37 \text{ V}$; $E_{1/2}^2 = -1.00 \text{ V}$ vs Fc^+/Fc); these data are very similar to those reported here for **3a**.

In CH_2Cl_2 solution at -25°C (0.20 $[\text{N}(\text{n-Bu})_4]\text{PF}_6$) the neutral species $[\mathbf{3a}]^0$ and its electrochemically generated mono- and dianion are sufficiently stable to allow recording of their infrared and UV–vis absorption spectra. Figure 4 displays the infrared spectral changes observed during the

(10) (a) Hauser, C.; Glaser, T.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2000**, *122*, 4352. (b) Serres, R. C.; Grapperhaus, C. A.; Bothe, E.; Bill, E.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *J. Am. Chem. Soc.* **2004**, *126*, 5138.

(11) Li, M.; Bonnet, D.; Bill, E.; Neese, F.; Weyhermüller, T.; Blum, N.; Sellmann, D.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 3444.

(12) Sellmann, D.; Blum, N.; Heinemann, F.; Hess, B. A. *Chem.–Eur. J.* **2000**, *7*, 1874.

(13) López, J. P.; Heinemann, F. W.; Prakash, R.; Hess, B. A.; Horner, O.; Jeandey, C.; Oddou, J.-L.; Latour, J.-M.; Grohmann, A. *Chem.–Eur. J.* **2002**, *8*, 5709.

(14) (a) Gonzales, M. C.; Scherlis, D. A.; Esiú, G. L.; Olabe, J. A.; Estrin, D. A. *Inorg. Chem.* **2001**, *40*, 4127. (b) Wanner, M.; Scheiring, T.; Kaim, W.; Slep, L. D.; Baraldo, L. M.; Olabe, J. A.; Zalis, S.; Baerends, E. J. *Inorg. Chem.* **2001**, *40*, 5704.

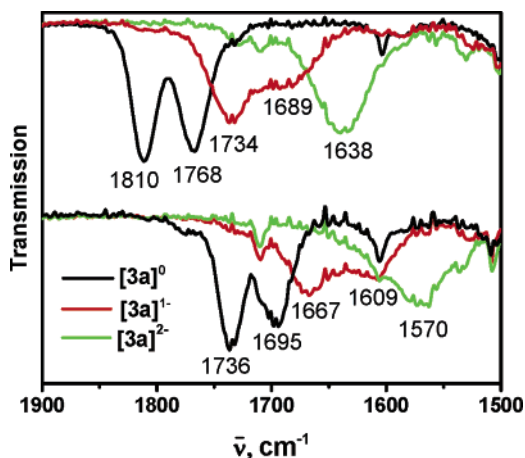


Figure 4. Infrared spectral changes observed at $-25\text{ }^{\circ}\text{C}$ during the electrochemical reduction of $[3a]^0$ (black) to the corresponding mono- (red) and dianion (green) in CH_2Cl_2 solutions (0.10 M $[\text{N}(n\text{-Bu})_4][\text{PF}_6]$). (Top) $^{14}\text{N}^{16}\text{O}$ isotopomers; (bottom) $^{15}\text{N}^{18}\text{O}$ isotopomers.

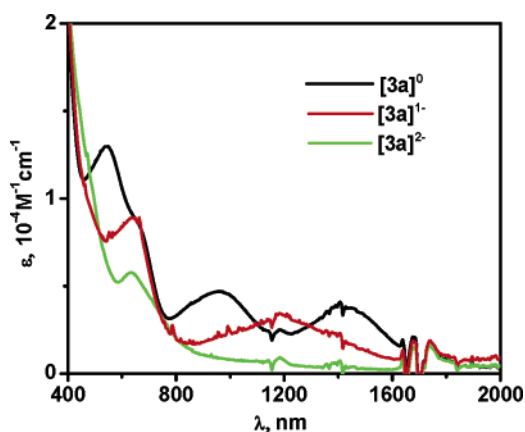


Figure 5. Electronic spectra of $[3a]^0$ (black) and of the electrochemically generated mono- (red) and dianion (green) in CH_2Cl_2 (0.20 M $[\text{N}(n\text{-Bu})_4][\text{PF}_6]$) at $-25\text{ }^{\circ}\text{C}$.

reduction of **3a**. The NO stretching frequencies are summarized in Table 3.

The neutral species **3a** displays two $\nu(\text{NO})$ frequencies at 1810 and 1768 cm^{-1} ; the monoanion also displays two such bands at 1734 and 1689 cm^{-1} , whereas the dianion displays only a single but broad band at 1638 cm^{-1} . The assignment of these as ν_{NO} stretching frequencies is clearly supported by the spectra of the corresponding $^{15}\text{N}^{18}\text{O}$ isotopomers (Figure 4 (bottom)). The corresponding ν_{NO} bands are shifted by $\sim 72\text{ cm}^{-1}$ to lower energies in the $^{15}\text{N}^{18}\text{O}$ isotopomers as expected from a simple harmonic oscillator model (calcd $68\text{--}73\text{ cm}^{-1}$).

These data indicate that the diamagnetic dianion, $[3a]^{2-}$, possesses a structure where both $\{\text{FeNO}\}^n$ units are (electronically) identical. We propose an electronic structure with two $\{\text{FeNO}\}^7$ ($S = 1/2$) units and three closed-shell dithiolate $^{(2-)}$ ligands, $(\text{L}^3)^{2-}$: $[(\text{NO})\text{Fe}^{\text{II}}(\text{L}^3)_2\text{Fe}^{\text{II}}(\text{NO})(\text{L}^3)]^{2-}$. The two $\{\text{FeNO}\}^7$ ($S = 1/2$) parts are strongly antiferromagnetically coupled, yielding the observed $S_{\text{T}} = 0$ ground state of the dinuclear dianion.

The electronic spectra of **3a** and its electrochemically generated mono- and dianion are shown in Figure 5. Table 4 summarizes the spectra. Interestingly, the spectrum of **3a**

Table 4. Electronic Spectra of Complexes

complex	λ_{max} , nm (ϵ , $10^4\text{ M}^{-1}\text{ cm}^{-1}$)
[2a]	548(0.9), 670,sh(0.6), 985(0.5), 1440(0.25)
[3a]	545(1.3), 666,sh(0.91), 981(0.5), 1460(0.4)
$[\text{N}(n\text{-Bu})_4][3a]$	650(0.9), 1190(0.3)
$[\text{N}(n\text{-Bu})_4]_2[3a]$	634(0.6)

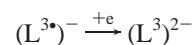
Table 5. Mössbauer Parameters at 80 K of Dinuclear Complexes

complex	δ , mm s^{-1} ^b	ΔE_{Q} , mm s^{-1} ^c	ref
1a^{II}	-0.01	1.57	3
	0.29	1.26	
2a^{II}	0.07	1.75	this work
	0.22	1.16	
3a^{II}	0.07	1.73	this work
	0.23	1.06	
$[\text{Co}(\text{Cp})_2][3a]$	0.25	0.96	this work

^a Two subspectra of equal intensity (50:50) were observed. ^b Isomer shift vs $\alpha\text{-Fe}$ at 298 K. ^c Quadrupole splitting.

displays two intense maxima in the near-infrared region (NIR) at 960 and 1430 nm, whereas the monoanion displays only one such band at 1190 nm, and the dianion does not show any absorption $> 800\text{ nm}$.

From our study¹⁵ of the electronic spectra of the mononuclear series $[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)]^{+,0,-2-}$, it is possible to conclude that the maximum at 1430 nm in **3a** is due to an $\{\text{FeNO}\}^6$ unit and that the 960 nm absorption is a ligand-to-ligand charge transfer between a $(\text{L}^3)^-$ radical anion and a dianion $(\text{L}^3)^{2-}$ both coordinated to an iron ion.⁵ Upon one-electron reduction of **3a**, the LLCT band at 960 nm is shifted to 1190 nm and the NIR absorption at 1430 nm in **3a** is missing in $[3a]^{1-}$. Thus, $[3a]^{1-}$ still contains at least one $(\text{L}^3)^-$ radical and a dianion $(\text{L}^3)^{2-}$. Generating the dianion is then a ligand-centered reduction



and, consequently, all absorption maxima in the NIR have disappeared.

3.3. Mössbauer Spectroscopy. Solid samples of complexes **2a**, **3a**, and $[\text{Co}(\text{Cp})_2][3a]$ have been investigated by zero-field Mössbauer spectroscopy at 80 K. The results are summarized in Table 5, and Figure 6 shows the spectra of the neutral complexes **2a** and **3a**. These spectra resemble closely that reported for **1a** in 1967.³

It is a characteristic feature of the spectra for all neutral complexes that they display two quadrupole doublets in each case in the ratio of 1:1. Both doublets exhibit significantly different isomer shift and quadrupole-splitting parameters: The doublet $\delta = -0.01\text{--}0.07\text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 1.6\text{--}1.7\text{ mm s}^{-1}$, is typical for a $\{\text{FeNO}\}^6$ moiety with a low-spin ferrous ion (Fe^{II} ; d^6 ; $S_{\text{Fe}} = 0$) and a closed-shell NO^+ ligand^{10–14} whereas the other one with $\delta = 0.22\text{--}0.29\text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 1.1\text{--}1.3\text{ mm s}^{-1}$ is characteristic for the $\{\text{FeNO}\}^7$ ($S = 1/2$) moiety with again a low-spin ferrous ion but a neutral $\dot{\text{N}}\text{O}$ ligand.^{3,10–14} In agreement with the crystal structures of **2a** and **3a** (see above), we assign Fe1 the $\{\text{FeNO}\}^7$ signal and Fe2 displays the $\{\text{FeNO}\}^6$ signal.

(15) Ghosh, P.; Stobie, K.; Bill, E.; Bothe, E.; Weyhermüller, T.; Ward, M. D.; McCleverty, J. A.; Wieghardt, K. *Inorg. Chem.*, **2007**, *46*, 522–532.

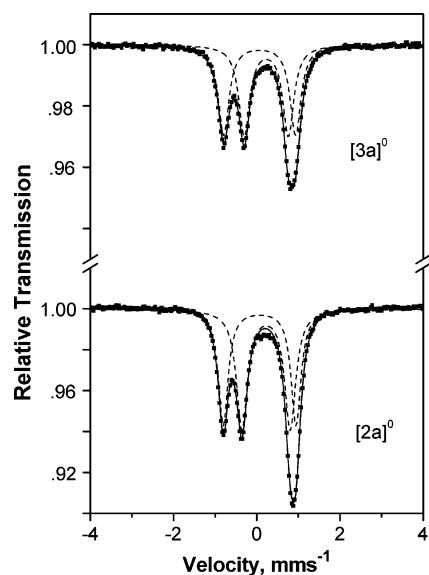


Figure 6. Zero-field Mössbauer spectra at 80 K of $[3a]^0$ (top) and $[2a]^0$ (bottom). Fit parameters are given in the text.

Interestingly, the spectrum of $[\text{Co}(\text{Cp})_2][3a]$ shows only a single doublet with $\delta = 0.25 \text{ mm s}^{-1}$, $\Delta E_Q = 0.96 \text{ mm s}^{-1}$. This is an excellent marker for the interpretation that one-electron reduction of the neutral compounds produces a monoanion with two (very similar) $\{\text{FeNO}\}^7$ ($S = 1/2$) moieties present.

4. Discussion

In a previous publication¹⁵ we reported the synthesis and spectroscopic characterization of four mononuclear members of the electron-transfer series $[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^z$ ($z = +1, 0, -1, -2$; $\text{R} = p\text{-tolyl}$). The results are shown in Scheme 2. Table 6 summarizes the observed ν_{NO} stretching frequencies and gives their corresponding zero-field Mössbauer parameters (isomer shift vs $\alpha\text{-Fe}$ at 298 K, quadrupole splitting).

It was shown that the monocation, the neutral species, and the monoanion each contain an $\{\text{FeNO}\}^6$ moiety with Mössbauer parameters in the very narrow range of $\delta = 0.01\text{--}0.07 \text{ mm s}^{-1}$, $\Delta E_Q = 1.4\text{--}1.9 \text{ mm s}^{-1}$. A number of six-coordinate nitrosyl/iron complexes containing an $\{\text{FeNO}\}^6$ unit have also been reported to display isomer shifts in this range.^{10–14} From DFT calculations,^{10b,14} it has been concluded that these complexes possess an electronic structure which is best described as low-spin ferrous coordinated to an NO^+ ligand. In the above mononuclear $\{\text{FeNO}\}^6$ series, $[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^z$ ($z = +1, 0, -1$), all redox processes are then dithiolene ligand-based: the monocation contains two $(\text{S}_2\text{C}_2\text{R}_2)^{\bullet-}$ monoanionic radicals; the neutral species only one radical and a closed-shell dianion (the ligand mixed valency is of class III (delocalized)); and the monoanionic species contains two closed-shell dithiolate⁽²⁻⁾ ligands. Interestingly, these dithiolene-based redox processes do not significantly influence the Mössbauer parameters of these three $\{\text{FeNO}\}^6$ species.

If, on the other hand, the monoanion is further reduced by one electron affording the corresponding dianion

Scheme 2

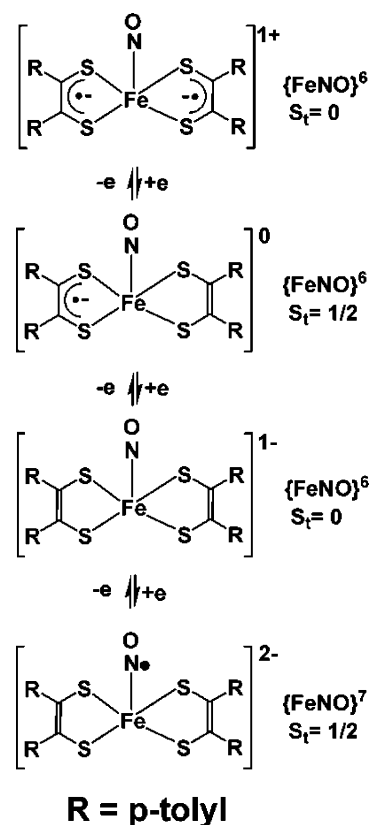


Table 6. Mössbauer Parameters of Mononuclear Complexes $[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^n$ ($n = +1, 0, -1, -2$; $\text{R} = p\text{-tolyl}$; $(\text{bdt})^{2-} = \text{benzene-1,2-dithiolate}^{(2-)}$) at 80 K and ν_{NO} Stretching Frequencies (ref 15)

complex	ν_{NO} , cm^{-1}	δ , mm s^{-1} ^a	ΔE_Q , mm s^{-1} ^b	$\{\text{FeNO}\}^n$, $n =$
$[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^+$	1833	0.07	1.40	6
$[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^0$	1800, 1783	0.06	1.70	6
$[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^{1-}$	1758	0.04	1.88	6
$[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^{2-}$	1575, 1530	0.20	1.16	7
$[\text{Fe}(\text{NO})(\text{bdt})_2]^{2-}$ ^c	1600	0.27	1.12	7
$[\text{Fe}(\text{NO})(\text{bdt})_2]^{1-}$ ^c	1800	0.01	2.48	6

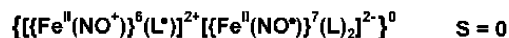
^a Isomer shift vs $\alpha\text{-Fe}$ at 298 K. ^b Quadrupole splitting. ^c Synthesis and X-ray structure: Lee, C.-M.; Chen, C.-H.; Chen, H.-W.; Hsu, J.-L.; Lee, G.-H.; Liaw, W.-F. *Inorg. Chem.* **2005**, *44*, 6670.

$[\text{Fe}(\text{NO})(\text{S}_2\text{C}_2\text{R}_2)_2]^{2-}$ with an $\{\text{FeNO}\}^7$ ($S = 1/2$) moiety which has been characterized as low-spin ferrous with a neutral $\dot{\text{N}}\text{O}$ radical ligand, the isomer shift, δ , increases significantly and the quadrupole splitting, $|\Delta E_Q|$, decreases: $\delta = 0.25\text{--}0.31 \text{ mm s}^{-1}$, $|\Delta E_Q| = 1.2\text{--}0.8 \text{ mm s}^{-1}$.

Thus, the Mössbauer parameters are clear markers for the presence of an $\{\text{FeNO}\}^6$ and/or an $\{\text{FeNO}\}^7$ moiety. The isomer-shift difference of $\sim 0.3 \text{ mm s}^{-1}$ on going from an $\{\text{FeNO}\}^7$ to an $\{\text{FeNO}\}^6$ species has been accounted for by the varying π -back-bonding ability of an $\dot{\text{N}}\text{O}$ versus an NO^+ ligand.¹¹ According to this scheme it clearly emerges that the dinuclear complexes **1a**, **2a**, and **3a** each contain one $\{\text{FeNO}\}^6$ and one $\{\text{FeNO}\}^7$ fragment in a 1:1 ratio. The dinuclear monoanion must then have two $\{\text{FeNO}\}^7$ units because only a single broad-quadrupole doublet with an isomer shift of 0.25 mm s^{-1} (80 K) is observed. For the dianion we predict similar behavior: a single quadrupole

Scheme 3

Neutral Complex



Monoanionic Complex



Dianionic Complex



doublet with an isomer shift of $\sim 0.28 \text{ mm s}^{-1}$ should indicate the presence of two $\{\text{FeNO}\}^7$ units and three closed-shell dithiolene dianions.

Using the above spectroscopic markers from the mononuclear series, one can safely assign the following electronic structures shown in Scheme 3 for the neutral, mono-, and dianionic dinuclear species:

(1) The neutral species contains one $\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O}^+)\}^6$ ($S = 0$) and one $\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}^7$ ($S = 1/2$) moiety as readily deduced

from the Mössbauer parameters and the two ν_{NO} stretching frequencies; the presence of a ligand radical $(\text{L}^{\cdot})^-$ is clearly established from the crystal structure and the electronic spectrum.

(2) The paramagnetic ($S = 1/2$) monoanionic species contains two antiferromagnetically coupled $\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}^7$ ($S = 1/2$) units (Mössbauer and IR) and a ligand π radical (electronic and EPR spectrum).

(3) The diamagnetic dianion consists of two $\{\text{Fe}^{\text{II}}(\dot{\text{N}}\text{O})\}^7$ ($S = 1/2$) units (antiferromagnetically coupled) and three closed-shell dianions $(\text{S}_2\text{C}_2\text{R}_2)^{2-}$ (Mössbauer and IR spectra).

Acknowledgment. One of us (P.G.) thanks the Max-Planck Society for financial support. We are grateful to the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: X-ray crystallographic files for compounds **2a** and **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0622306