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# Electrochemical Oxidation–Reduction of Carbamato-carbonyl-η-cyclopentadienyl-iron(II), $(\eta\text{-}C_5H_5)Fe(CO)(XYCNMe_2)$ (XY = SeSe, SeS, SS) and $(\eta\text{-}C_5H_5)Fe(CO)_2(XC(Y)NMe_2)$ (X(Y) = Se(Se), S(Se), S(S), Se(O), S(O))

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*A series of iron(II) complexes of the* $(\eta\text{-}C_5H_5)Fe(CO)(XYCNMe_2)$ *and* $(\eta\text{-}C_5H_5)Fe(CO)_2(XC(Y)NMe_2)$ *types (XY = SeSe(1), SeS(2), SS(3); X(Y) = Se(Se)(4), S(Se)(5), S(S)(6), Se(O)(7), S(O)(8)) were prepared. The carbamate ligands of the monocarbonyl complexes are coordinated to iron in a bidentate manner, while those of the dicarbonyl complexes in a unidentate manner. The electrochemical behavior of these complexes has been studied both in acetonitrile and in dichloromethane using dc cyclic voltammetry and coulometry. All the complexes undergo one-electron oxidation to afford the* $[(\eta\text{-}C_5H_5)Fe(CO)(XYCNMe_2)]^+$ *or* $[(\eta\text{-}C_5H_5)Fe(CO)_2(XC(Y)NMe_2)]^+$ *species. Anodic peak potentials are shifted anodically on going from 1 to 3 for the monocarbonyl complexes, and from 4 to 8 for the dicarbonyl complexes. Thus, ligating selenium donates more electronic charges to iron than sulfur and oxygen. Of the complexes, 1 undergoes a reversible oxidation–reduction in acetonitrile while each of 1–3 in dichloromethane exhibits a quasi-reversible oxidation–reduction wave. Complex 6 in acetonitrile displays a pair of anodic and cathodic waves; its multicyclic voltammogram reveals that the oxidation reaction is accompanied by the elimination of one molecule of carbon monoxide from iron, followed by the coordination of solvent acetonitrile to the electron deficient iron(III) species, affording* $[(\eta\text{-}C_5H_5)Fe(CO)(SC(S)NMe_2)(MeCN)]^+$*, which may be produced also by the oxidation of 3 in acetonitrile. This oxidized species undergoes one-electron reduction to liberate coordinated acetonitrile, regenerating 3. Other dicarbonyl complexes exhibit an anodic wave, followed by a cathodic one which is very weak in acetonitrile and hardly discernible in dichloromethane, suggesting that their oxidized species are fairly unstable in solution.*

## Introduction

Although a number of bidentate dithiocarbamate complexes of metal have been characterized, the isolation of metal complexes with unidentate dithiocarbamate are limited to those of ruthenium, rhodium, and iron [1]. Diseleno- and selenothiocarbamate anions also tend to coordinate to metal cations in a bidentate manner [2, 3]; no metal complex with unidentate diseleno- or selenothiocarbamate is known so far. On the other hand, seleno- and thiocarbamate anions prefer to act as unidentate ligands to metal ions rather than as bidentate ones [4, 5].

Electrochemical studies for metal complexes with dichalcogenocarbamate have been limited to those having bidentate dithiocarbamate as ligands [6, 7]. Martin *et al.* reported the electrochemical studies on a variety of dithiocarbamato–metal complexes [8, 9]. The results have shown that anodic peak potentials of the complexes of a given metal ion depend on both steric and inductive effects of the substituents on the carbamate nitrogen atom. No electrochemical study on metal complexes with unidentate dithiocarbamate or other dichalcogenocarbamate has been reported.

The present work was undertaken to elucidate the electrochemical behavior of a series of unidentate and bidentate dichalcogenocarbamate complexes of carbonyl-η-cyclopentadienyliron(II). This paper reports the preparation of complexes of the $(\eta\text{-}C_5H_5)Fe(CO)(XYCNMe_2)$ and $(\eta\text{-}C_5H_5)Fe(CO)_2(XC(Y)NMe_2)$ types (XY = SeSe, SeS, SS; X(Y) = Se(Se), S(Se), S(S), Se(O), S(O)) and their electrochemical behavior in acetonitrile and in dichloromethane.

## Experimental

### *Starting Materials*

Bromodicarbonyl-η-cyclopentadienyliron(II), $(\eta\text{-}C_5H_5)Fe(CO)_2Br$ [10], and acetonedicarbonyl-η-cyclopentadienyliron(II) tetrafluoroborate, $[(\eta\text{-}C_5H_5)Fe(CO)_2(OCMe_2)][BF_4]$ [11], were prepared according to the literature methods. Bis(dimethyldiselenocarbamato)dimethyltin(IV), $Me_2Sn(Se_2CNMe_2)_2$ [2], bis(dimethylselenothiocarbamato)dimethyltin(IV), $Me_2Sn(SeSCNMe_2)_2$ [3], and

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dimethylselenothiocarbamatodimethylchlorotin(IV), $Me_2SnCl(SeSCNMe_2)$ [3], were prepared as described previously. Dimethylammonium dimethyldiselenocarbamate, $[Me_2NH_2][Se_2CNMe_2]$, was obtained by the reaction of carbon diselenide with dimethylamine by the procedure similar to that for $Na[Se_2CNMe_2]$ [12]. Dimethylammonium-dimethylselenocarbamate, $[Me_2NH_2][SeC(O)NMe_2]$ [13], and -dimethylthiocarbamate, $[Me_2NH_2][SC(O)NMe_2]$ [14], were obtained by the methods described elsewhere.

### *Dimethyldiseleno-, -selenothio-, and -dithiocarbamato-carbonyl-η-cyclopentadienyliron(II), (η-C₅H₅)-Fe(CO)(XYCNMe₂) (XY = SeSe(1), SeS(2), SS(3))*

A benzene (50 $cm^3$) solution containing $(\eta\text{-}C_5H_5)Fe(CO)_2Br$ (0.52 g, 2.0 mmol) and $Me_2Sn(Se_2CNMe_2)_2$ (0.59 g, 1.0 mmol) was refluxed with stirring for 2 h. After cooling to room temperature, the solution was filtered and the filtrate shaken with water to remove formed $Me_2SnBr_2$. The benzene layer was separated and dried over $CaCl_2$, followed by evaporation to dryness under reduced pressure. The product obtained was recrystallized from a mixture of dichloromethane and hexane to give dark red crystals of 1 in a 55% yield. Similarly, red crystals 2 and brown crystals 3 were obtained in 60% and 65% yields by the reactions of $(\eta\text{-}C_5H_5)Fe(CO)_2Br$ with $Me_2SnCl(SeSCNMe_2)$ and $[Me_2NH_2][S_2CNMe_2]$, respectively, in benzene.

### *Dimethyldiseleno- and -dithiocarbamatodicarbonyl-η-cyclopentadienyliron(II), (η-C₅H₅)Fe(CO)₂(XC(Y)-NMe₂) (X(Y) = Se(Se)(4), S(S)(6))*

Dark red crystals 4 and brown crystals 6 were prepared in 70% and 75% yields by the reactions of $[(\eta\text{-}C_5H_5)Fe(CO)_2(OCMe_2)][BF_4]$ with small excess amounts of $[Me_2NH_2][Se_2CNMe_2]$ and $[Me_2NH_2][S_2CNMe_2]$, respectively, in acetone by the procedure similar to that for 1.

### *Dimethylselenothiocarbamatodicarbonyl-η-cyclopentadienyliron(II), (η-C₅H₅)Fe(CO)₂(SC(Se)NMe₂) (5)*

To a diethylether (25 $cm^3$) solution of $Me_2Sn(SeSCNMe_2)_2$ (1.5 g, 3.1 mmol) was added $LiAlH_4$ (0.12 g, 3.1 mmol) in diethylether (25 $cm^3$) at 0 °C under argon atmosphere, followed by stirring for 2 h at this temperature. To the solution was added dropwise an acetone (30 $cm^3$) solution of $[(\eta\text{-}C_5H_5)Fe(CO)_2(OCMe_2)][BF_4]$ (1.9 g, 6.0 mmol) at 0 °C. The mixture was stirred for an additional 20 min at ambient temperature, followed by evaporation to dryness under reduced pressure. The product obtained was dissolved in dichloromethane and the solution was shaken with water. The dichloromethane layer was separated and dried over $CaCl_2$. To the solution thus obtained was added a small amount of hexane, and the mixture was concentrated to a half volume under reduced pressure to give red crystals in a 40% yield.

### *Dimethylseleno- and -thiocarbamatodicarbonyl-η-cyclopentadienyliron(II), (η-C₅H₅)Fe(CO)₂(XC(O)-NMe₂) (X = Se(7), S(8))*

To a tetrahydrofuran (25 $cm^3$) solution of $[Me_2NH_2][XC(O)NMe_2]$ (0.75 g, 3.8 mmol for X = Se; 0.53 g, 3.7 mmol for X = S) was added $[(\eta\text{-}C_5H_5)Fe(CO)_2(OCMe_2)][BF_4]$ (1.1 g, 3.4 mmol). The solution was refluxed for 2 h, followed by evaporation to dryness *in vacuo*. The product obtained was recrystallized from a mixture of dichloromethane and hexane to yield dark red crystals of 7 or 8 in a 70% yield.

### *Electrochemistry*

Electrochemical measurements were carried out by the use of a Hokuto Denko PS-500B potential stat, a Nikko Keisoku NPS-2 potential sweeper, and a Riken Denshi F-3DP X-Y recorder. Cyclic voltammetry was performed in a cell consisting of a Beckman platinum working electrode, an auxiliary electrode of a 4 $cm^2$ platinum plate, and a Ag wire/$AgNO_3$ ($1.0 \times 10^{-2}$ mol $dm^{-3}$) electrode in acetonitrile or a standard calomel electrode (SCE) in dichloromethane at ambient temperature. The reference electrode was separated from the cell by a KCl bridge. In the case of coulometry, a working electrode of a 12 $cm^2$ platinum plate was separated from an auxiliary electrode of a platinum plate with the same size by a glass frit. The anode compartment required 30 $cm^3$ of solutions, which was stirred with a magnetic stirrer.

A sample solution containing a metal complex ($1.0 \times 10^{-3}$ mol $dm^{-3}$) and a supporting electrolyte ($1.0 \times 10^{-1}$ mol $dm^{-3}$) was deaerated with argon or dry nitrogen prior to measurements. Tetraethyl- and tetrabutylammonium perchlorates were used as supporting electrolytes in acetonitrile and in dichloromethane, respectively. Acetonitrile was purified by distillation over calcium hydride, and dichloromethane was distilled over phosphorus pentoxide. The potentials in the cyclic voltammetry were swept at the rates of 0.2–0.02 V $s^{-1}$. The number of coulombs used in the electrolysis was calculated according to the method of MacNevin *et al.* [15].

### *Spectra*

Infrared spectra were recorded in dichloromethane on a Hitachi-Perkin Elmer 225 spectrophotometer with 0.5 mm KRS-5 cells. Mass spectra were obtained with a Hitachi RMU-6E spectrometer.

TABLE I. Analysis and Physical Properties of the Complexes.

| | Complex | mp[a] °C | %C | %H | %N | $\nu(\mathrm{C}\equiv\mathrm{O})$[b] | $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ or $\nu(\mathrm{C}=\mathrm{O})$[b] | $k(\mathrm{C}\equiv\mathrm{O})$[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | $(\eta\text{-}C_5H_5)Fe(CO)(Se_2CNMe_2)$ | 145 | 29.48<br>(29.79) | 2.98<br>(3.06) | 3.79<br>(3.86) | 1926 | 1520 | 14.98 |
| 2 | $(\eta\text{-}C_5H_5)Fe(CO)(SeSCNMe_2)$ | 140 | 33.94<br>(34.21) | 3.47<br>(3.51) | 4.42<br>(4.43) | 1931 | 1515 | 15.06 |
| 3 | $(\eta\text{-}C_5H_5)Fe(CO)(S_2CNMe_2)$ | 141 | 40.18<br>(40.41) | 3.58<br>(3.73) | 4.94<br>(4.71) | 1936 | 1510 | 15.14 |
| 4 | $(\eta\text{-}C_5H_5)Fe(CO)_2(SeC(Se)NMe_2)$ | 125 | 30.42<br>(30.73) | 2.81<br>(2.84) | 3.59<br>(3.58) | 1988 2035 | (1460) | 16.34 |
| 5 | $(\eta\text{-}C_5H_5)Fe(CO)_2(SC(Se)NMe_2)$ | 129 | 34.72<br>(34.91) | 3.39<br>(3.22) | 4.10<br>(4.07) | 1986 2033 | (1460) | 16.31 |
| 6 | $(\eta\text{-}C_5H_5)Fe(CO)_2(SC(S)NMe_2)$ | 127 | 39.93<br>(40.17) | 4.03<br>(4.12) | 5.23<br>(5.21) | 1933 2040 | (1475) | 16.42 |
| 7 | $(\eta\text{-}C_5H_5)Fe(CO)_2(SeC(O)NMe_2)$ | 93 - 94 | 36.40<br>(36.63) | 3.27<br>(3.38) | 4.26<br>(4.27) | 1980 2030 | 1600 | 16.24 |
| 8 | $(\eta\text{-}C_5H_5)Fe(CO)_2(SC(O)NMe_2)$ | 90 | 42.28<br>(42.73) | 3.87<br>(3.95) | 4.74<br>(4.98) | 1985 2033 | 1590 | 16.30 |

[a] Decomposition temperature except for 7. [b] The wave numbers in $CH_2Cl_2$ except for those in parenthesis, which are for in hexachlorobutadiene mulls. [c] Stretching force constants in md $Å^{-1}$.

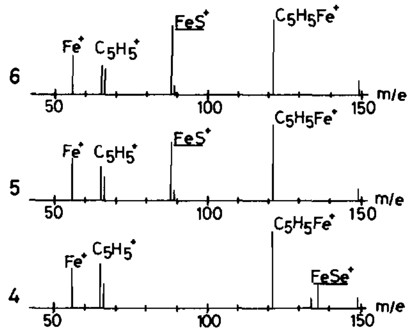


Fig. 1. Mass spectra of $(\eta\text{-}C_5H_5)Fe(CO)_2(XC(Y)NMe_2)$; X(Y) = Se(Se)(4), S(Se(5), S(S)(6).

## Results and Discussion

### *Preparation and Configuration*

The reactions of $(\eta\text{-}C_5H_5)Fe(CO)_2Br$ with the dimethyldiseleno-, -selenothio-, and -dithiocarbamate anions gave $(\eta\text{-}C_5H_5)Fe(CO)(XYCNMe_2)$ (XY = SeSe(1), SeS(2), SS(3)) with the elimination of one molecule of carbon monoxide, while these anions reacted with $[(\eta\text{-}C_5H_5)Fe(CO)_2(OCMe_2)][BF_4]$ to afford dicarbonyl complexes, $(\eta\text{-}C_5H_5)Fe(CO)_2(XC(Y)NMe_2)$ (X(Y) = Se(Se)(4), S(Se)(5), S(S)(6)), as confirmed by elemental analyses. On the other hand, dimethylseleno- and -thiocarbamate anions yielded dicarbonyl complexes of the $(\eta\text{-}C_5H_5)Fe(CO)_2(XC(O)NMe_2)$ type (X = Se(7), S(8)) in the reaction with either $(\eta\text{-}C_5H_5)Fe(CO)_2Br$ or $[(\eta\text{-}C_5H_5)Fe(CO)_2(OCMe_2)][BF_4]$, although the reaction with the former iron(II) complex has not been described in the Experimental Section.

The infrared spectra of 1–3 show a carbamate $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band around 1540 $cm^{-1}$ (Table I), suggesting the coordination of the carbamate anions in a bidentate manner [16]. Complexes 4–6, however, exhibit the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band in the 1460–1475 $cm^{-1}$ range, which is compared with those (1460–1470 $cm^{-1}$) of the dithiocarbamate ligands coordinated to some metal ions in a unidentate manner [1]. It is, therefore, assumed that 4–6 involve the unidentate diseleno-, selenothio-, and dithiocarbamate ligands, respectively.

There are two possible coordination sites of the unidentate selenothiocarbamate ligand in 5; selenium and sulfur. The mass spectrum of 5 shows the $FeS^+$ fragment peak, but no $FeSe^+$ peak, as depicted in Fig. 1. This result suggests the coordination of selenothiocarbamate to iron through the sulfur atom with the free selenocarbonyl group. This is compatible with the mass spectra of 4 and 6 giving the fragment peaks of $FeSe^+$ and $FeS^+$, respectively (Fig. 1), the former of which was accompanied with several weak peaks arising from the selenium isotopes, but some of them are not given in Fig. 1.

Coordination sites of the seleno- and thiocarbamate ligands in 7 and 8, respectively, have been determined by infrared spectroscopy. Both complexes display the $\nu(\mathrm{C}=\mathrm{O})$ band around 1600 $cm^{-1}$ (Table I), indicating the coordination of seleno- and thiocarbamates to iron through the selenium and sulfur atoms, respectively, with the free carbonyl group [4, 5].

TABLE II. Cyclic Voltammetry at the Sweep Rate of 0.2 V $s^{-1}$.

| Complex | In MeCN | | | In $CH_2Cl_2$ | | |
|---|---|---|---|---|---|---|
| | $E_{pa}$[a] | $\Delta E_p$[c] | $i_{pc}/i_{pa}$[d] | $E_{pa}$[b] | $\Delta E_p$[c] | $i_{pc}/i_{pa}$[d] |
| 1 | 150 | 60 | 1.0 | 600 | 100 | 1.0 |
| 2 | 200 | 60 | 0.68 | 660 | 140 | 1.0 |
| | | 750 | 0.21 | | | |
| 3 | 250 | 800 | 0.28 | 710 | 130 | 0.93 |
| 4 | 150 | | | 600 | | |
| 5 | 340 | | | 750 | | |
| 6 | 450 | 1000 | 0.25 | 940 | | |
| 7 | 450 | | | 900 | | |
| 8 | 600 | | | 1030 | | |

[a] Anodic peak potentials *vs.* Ag/$Ag^+$, mV. [b] Anodic peak potentials *vs.* SCE, mV. [c] Peak separations between the anodic and cathodic waves. [d] Ratios of the cathodic peak current to the anodic one.

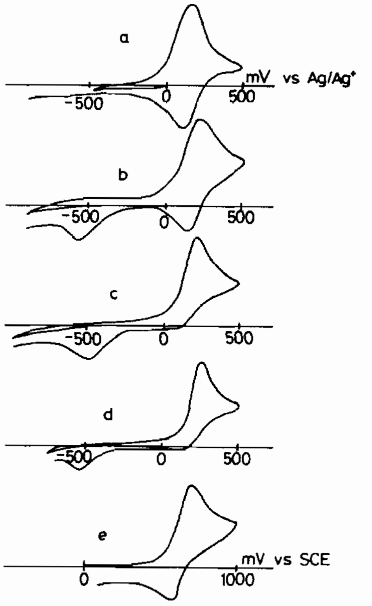


Fig. 2. Cyclic voltammograms of ($\eta$-$C_5H_5$)Fe(CO)-($XYCNMe_2$); XY = SeSe(1), SeS(2), SS(3). a: 1 in MeCN at 0.2 V $s^{-1}$, b: 2 in MeCN at 0.2 V $s^{-1}$, c: 2 in MeCN at 0.02 V $s^{-1}$, d: 3 in MeCN at 0.2 V $s^{-1}$, e: 3 in $CH_2Cl_2$ at 0.2 V $s^{-1}$.

### Electrochemistry

Figure 2 shows the cyclic voltammograms of 1–3 in MeCN or in $CH_2Cl_2$ at the sweep rate of 0.2 V $s^{-1}$ or 0.02 V $s^{-1}$. Complex 1 in MeCN displays a pair of anodic and cathodic waves (Fig. 2a), and the peak potentials were independent of the sweep rate in the range 0.2–0.02 V $s^{-1}$. The separation of these potentials, $\Delta E_p$, is 60 mV and the ratio of cathodic to anodic peak currents, $i_{pc}/i_{pa}$, is 1.0 (Table II). These results in connection with the controlled potential electrolysis (Table III) confirm that 1 in MeCN undergoes a typically reversible one-electron process. In $CH_2Cl_2$, however, the oxidation–reduction process of 1 is quasi-reversible, as evidenced from the values of $\Delta E_p$ = 100 mV and of $i_{pc}/i_{pa}$ = 1.0 (Table II).

TABLE III. Controlled Potential Electrolysis[a] for 3.0 × $10^{-5}$ mol of the Complex in MeCN.

| Complex | Q<br>Coulomb | n<br>e $m^{-1}$ |
|---|---|---|
| 1 | 2.98 | 1.03 |
| 2 | 3.09 | 1.07 |
| 3 | 2.54 | 0.88 |

[a] Carried out at 100 mV more positive than the anodic peak potentials.

The cyclic voltammogram of 2 in MeCN at 0.2 V $s^{-1}$ shows not only a pair of anodic and cathodic waves but also an additional cathodic one (Fig. 2b). The peak potentials of these waves are dependent on the sweep rate; when the rate is 0.02 V $s^{-1}$, the anodic and the second cathodic peak potentials shift cathodically by about 10 mV and anodically by about 100 mV, respectively, and the first cathodic wave completely disappears (Fig. 2c). These observations suggest that the oxidized species of 2, $[(\eta$-$C_5H_5)Fe(CO)(SeSCNMe_2)]^+$, is somewhat unstable in MeCN and at such a slow sweep rate as 0.02 V $s^{-1}$ it may be converted into a species which is reduced around −500 mV (*vs.* Ag/$Ag^+$) and any other species.

The cyclic voltammogram of 3 in MeCN at 0.2 V $s^{-1}$ shows a pair of anodic and cathodic waves (Fig. 2d), but they are not associated with a reversible oxidation-reduction process, because of a large peak separation and a much smaller $i_{pc}/i_{pa}$ value than unity (Table II). This is compatible with the fact that

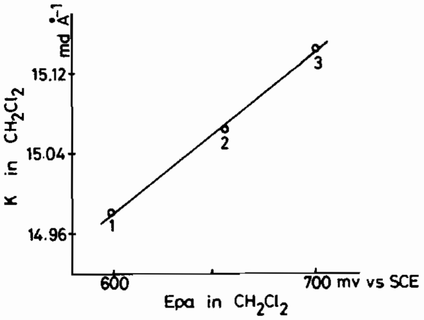


Fig. 3. Plots of the C≡O stretching force constant and the anodic peak potential of $(\eta\text{-}C_5H_5)Fe(CO)(XYCNMe_2)$ in $CH_2Cl_2$; XY = SeSe(1), SeS(2), SS(3).

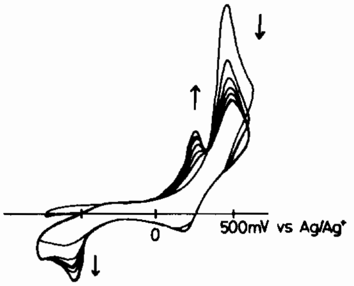
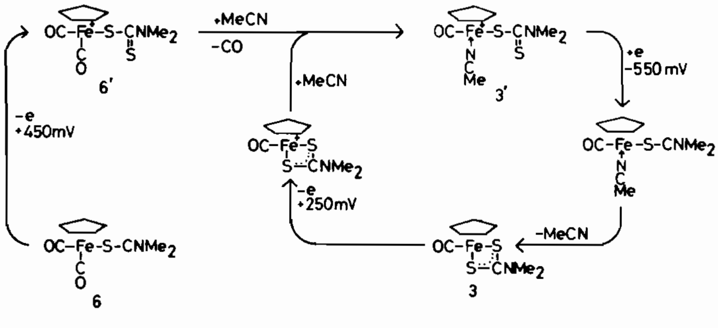


Fig. 4. The multicyclic voltammogram of $(\eta\text{-}C_5H_5)Fe(CO)_2$-$(SC(S)NMe_2)$ in MeCN at 0.2 V s$^{-1}$.

the anodic and cathodic peak potentials at 0.2 V s$^{-1}$ (Table II) were shifted cathodically by about 10 mV and anodically by about 60 mV at the sweep rate of 0.02 V s$^{-1}$, respectively. In $CH_2Cl_2$, however, 3 exhibits a quasireversible cyclic voltammogram (Fig. 2e and see also the $\Delta E_p$ and $i_{pc}/i_{pa}$ values in Table II). A similar quasireversible oxidation–reduction process was found in the cyclic voltammogram of 2 in $CH_2Cl_2$.

The infrared spectra of 1–3 in $CH_2Cl_2$ show a ν(C≡O) band around 1930 cm$^{-1}$ (Table I), from which the C≡O bond stretching force constant, k, was calculated by the Cotton–Kraihanzel method [17]. The result is also listed in Table I. Plots of the k values against the anodic peak potentials of 1–3 in $CH_2Cl_2$ is depicted in Fig. 3, which indicates that the k value increases with increasing anodic peak potentials. Duffy *et al.* [18] have recently suggested that in a series of $(\eta\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ (R, R' = alkyl or aryl) electron densities mainly donated from the dithiocarbamate ligand flow into the C≡O antibonding π-orbitals through the iron center, resulting in lowering the C≡O bond stretching force constant. In our complexes 1–3, the electron donor ability of the carbamate ligands is, therefore, suggested to decrease in the order $Se_2CNMe_2 > Se\ SCNMe_2 > S_2CNMe_2$.

The cyclic voltammetry of 6 in MeCN at 0.2 V s$^{-1}$ displays a cathodic wave as well as an anodic one. However, the separation of their peak potentials is very large (Table II), and the potentials depend on the sweep rate, indicating that the oxidation of 6 may be followed by a rapid chemical reaction. Figure 4 shows the multicyclic voltammogram of 6 in MeCN at 0.2 V s$^{-1}$. The second cyclic run gives a new anodic peak at +250 mV as a shoulder of the anodic peak originally appeared at +450 mV (*vs.* Ag/Ag⁺). With repeating cyclization, the electric current of the +250 mV peak increases, while that of the +450 mV peak decreases. In addition, the potentials of the newly appeared anodic peak and the cathodic peak of 6 are identical with the anodic and cathodic peak potentials of 3 in MeCN. In view of these results, the electrochemical processes of 3 and 6 in MeCN may be formulated as Scheme 1, where 6 is oxidized at +450 mV (*vs.* Ag/Ag⁺) to give an electron deficient dicarbonyliron(III) species (6'), followed by the elimination of one CO ligand owing to decreasing π-back bonding from the Fe(III) ion to the CO ligands. The elimination of the CO ligand is probably assisted by the nucleophilic attack of solvent acetonitrile yielding the MeCN adduct with the electron deficient iron(III) species (3'). The participation of MeCN in the electrochemical process is supported



Scheme 1. Mechanisms of the oxidation-reduction of $(\eta\text{-}C_5H_5)Fe(CO)_2(SC(S)NMe_2)$ (6) and $(\eta\text{-}C_5H_5)Fe(CO)$-$(S_2CNMe_2)$ (3) in MeCN.

from the fact that 6 exhibited indiscernible cathodic wave following after the anodic wave at +940 mV (*vs.* SCE).

The MeCN adduct 3′ may be formed also by the oxidation of 3 at +250 mV (*vs.* Ag/Ag$^+$), followed by the coordination of solvent acetonitrile accompanied by the fission of a Fe–S bond. The coordination of MeCN would stabilize such an electron deficient species as $[(\eta\text{-}C_5H_5)Fe(CO)(S_2CNMe_2)]^+$. In fact, the MeCN adduct with an electron deficient Ru(IV) complex, $[(MeCN)Ru(S_2CNEt_2)_3]BF_4$, has been isolated [6]. The MeCN adduct 3′ thus formed may be reduced at –550 mV (*vs.* Ag/Ag$^+$) to give the Fe(II) complex, followed by the elimination of MeCN to regenerate 3. In contrast to 6, the electrochemically oxidized species of complexes 4, 5, 7, and 8, $[(\eta\text{-}C_5H_5)Fe(CO)_n(XC(Y)NMe_2)]^+$ (X(Y) = Se(Se), S(Se), Se(O), S(O); n = 1 or 2) may not be so stabilized as that of 3 even in MeCN, because the cathodic wave of these complexes (around –500 mV *vs.* Ag/Ag$^+$) was extremely weak in this solvent.

Finally, it should be mentioned that the anodic peak potentials of 4–8 with the unidentate $XC(Y)NMe_2$ ligand in both solvents increase in the order X(Y) = Se(Se) < S(Se) < S(S) ~ Se(O) < S(O), which is compatible with the order of increasing anodic peak potentials of the bidentate carbamato complexes described above. The selenium atom can, therefore, donate more electron densities to the iron center than sulfur or oxygen. This is responsible for greater polarizability of selenium than sulfur and oxygen.

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