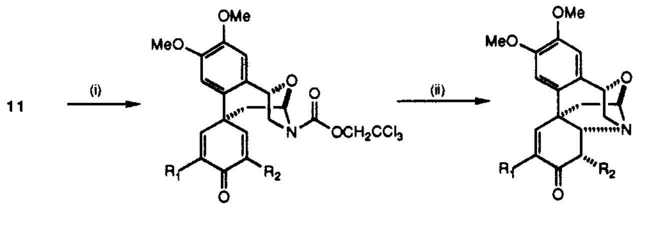
Scheme II[a]



12, R_1 = OMe, R_2 = H
13, R_1 = H, R_2 = OMe

14, R_1 = OMe, R_2 = H
15, R_1 = H, R_2 = OMe

[a] (i) VOF_3, $(CF_3CO)_2O$, TFA, CH_2Cl_2, − 78 °C (44%), **12**:**13**, 5:1; (ii) Zn, MeOH, reflux (46%).

tallographic analysis (Figure 1).[14] As expected, when the trans (2*S*,5*S*) isomer of **7** ($[\alpha]_D$ +24.8°) was exposed to VOF_3, no intramolecular phenolic coupling occurred. Reductive removal of the (trichloroethoxy)carbonyl group from **8** resulted in spontaneous addition of the liberated amine to the dienone in a process analogous to that observed previously.[15] The structure of the cyclization product **9**, which was also determined by X-ray crystallographic analysis (Figure 1),[16] possesses the cis-fused perhydroindole subunit in a configuration characteristic of the hasbanane alkaloids.[17]

With the aim of determining which of two diastereomeric products would predominate from oxidative coupling of a substrate in which the benzyl ring of the oxazolidine contained an additional substituent, a parallel sequence to that of Scheme I was initiated from homovanillic acid (**10**). This route led to cis oxazolidine **11** in excellent yield, which underwent phenolic coupling[18] to give **12** and **13** in the ratio 5:1, respectively (Scheme II). After deprotection, these diastereomeric dienones gave structurally isomeric pentacyclic amines **14** and **15**, which were readily distinguished on the basis of their ^1H NMR spectra.[19] Thus, the major stereoisomer **12** from phenolic coupling of **11** possesses a secoisosalutaridine framework antipodal to that found in most natural morphinans.

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Supplementary Material Available: Spectroscopic data (IR, ^1H NMR, ^{13}C NMR, MS), optical rotations ($[\alpha]_D$), and combustion analyses (or HRMS) for **2**–**12** and **14** (4 pages). Ordering information is given on any current masthead page.

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(14) Compound **8** crystallized in a monoclinic space group ($P21/c$) with four molecules located within a unit cell of the following dimensions: a = 10.589 (8) Å, b = 19.221 (5) Å, c = 11.112 (5) Å; β = 104.72 (4)°; V = 2187 (2) Å^3. The structure was solved by using 927 observed unique reflections [$I > 3\sigma(I)$] for $2\theta \leq 40°$ with MITHRIL (Gilmore, G. J. *J. Appl. Crystallogr.* **1984**, *17*, 42), DIRDIF (Beurskens, P. T. Technical Report 1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegan, The Netherlands, 1984), and successive analysis of difference maps. Anisotropic full-matrix least-squares refinement of all non-hydrogen atoms afforded residuals of R = 0.043 and R_w = 0.042 with S = 1.29.

(15) White, J. D.; Chong, W. K. M.; Thirring, K. *J. Org. Chem.* **1983**, *48*, 2300.

(16) Crystals of **9** were triclinic ($P\bar{1}$), having two molecules located within a unit cell of the following dimensions: a = 9.648 (3) Å, b = 9.874 (2) Å, c = 8.791 (2) Å; α = 100.72 (2)°, β = 112.63 (2)°, γ = 84.22 (2)°; V = 759.1 (3) Å^3. The structure was solved by using MITHRIL,[14] DIRDIF,[14] and successive analysis of difference maps with 1750 observed unique reflections [$I > 3\sigma(I)$] and $2\theta \leq 50°$. Anisotropic full-matrix least-squares refinement of all non-hydrogen atoms afforded residuals of R = 0.042 and R_w = 0.048 with S = 1.53.

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(18) The diminished yield of **12** and **13** is due to subsequent dienone–phenol rearrangement (Kupchan, S. M.; Kim, C.-K. *J. Am. Chem. Soc.* **1975**, *97*, 5623).

(19) **14**: δ 6.09 (s, 1 H). **15**: δ 7.20 (d, J = 11 Hz, 1 H), 6.11 (d, J = 11 Hz, 1 H).

Carbon Monoxide Dependent Solid-State Electrochemistry of Ferrocenylferraazetine: En Route to a Molecule-Based Carbon Monoxide Sensor

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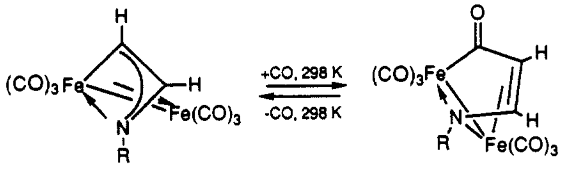
We report the solid-state reaction of CO with a ferrocenylferraazetine complex, **1a**, showing a possible entry into a new class of molecule-based CO detectors. Ferraazetine complexes **1b**,**c** show facile, reversible CO insertion to form ferrapyrrolinone complexes **2b**,**c**, eq 1.[1] Complex **1a** was synthesized with the aim of demonstrating a reversible redox active molecule that undergoes CO insertion to give a product with a different redox potential. Like **1b** and **1c**, **1a** does insert CO to form a ferrocenylferrapyrrolinone complex, **2a**, in the dark. Importantly, while **1a** is photosensitive, **1a** at 25 °C is chemically inert to 1 atm of the following gases: air (not containing CO), pure H_2, O_2, or CO_2. Using a microelectrode array,[2] the solid ionic conductor MEEP (poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene]),[3] and compound **1a**, we have been able to investigate the solid-state electrochemistry of **1a** and **2a**, Scheme I. Such solid-state microelectrochemical systems have been pioneered by Murray and coworkers.[4]



(1)

1a R = ferrocene
1b R = t-butyl
1c R = phenyl

2a, b, c

Complex **1a** was isolated as a microcrystalline solid from the reaction of ferrocenylphosphinimine, $(FcN{=}PPh_3)_2$,[5] and $Fe_2(\mu\text{-}CH_2)(CO)_8$[6] and has spectral features similar to those of **1b**

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(5) $FcN{=}PPh_3$: Anal. Calcd: C, 72.89; H, 5.26. Found: C, 72.95; H, 5.25. MS (EI): m/z 461 (M^+). ^1H NMR ($CDCl_3$): δ 7.46–7.43 (m, Ph, 15 H), 3.78 (m, CpH, 2 H), 3.75 (m, CpH, 5 H), 3.73 (m, CpH, 2 H). $E_{1/2}$ = 170 mV vs $AgNO_3/Ag$. Yield = 98%.

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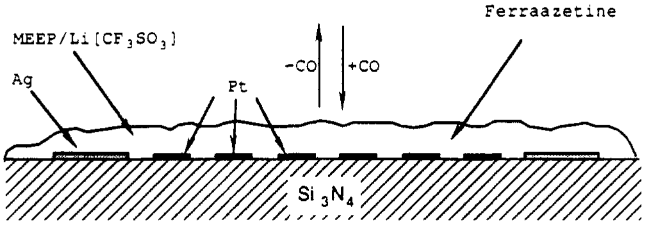
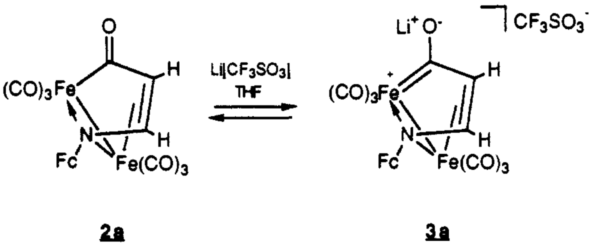
Scheme I. Cross-Sectional View of a MEEP/Li[CF_3SO_3]-Coated Microelectrode Array



and **1c**.[1,7] The ^1H NMR spectrum of complex **1a** in THF-d_8 shows resonances at δ 7.17 (d, ^1J = 1.95 Hz, 1 H) and δ 6.15 (d, ^1J = 1.95 Hz, 1 H) assigned to the metallacyclic ring H's, a resonance at δ 4.23 (s, 5 H) assigned to the five equivalent H's on the unsubstituted cyclopentadienyl ligand, and two resonances at δ 4.18 (m, 2 H) and δ 4.06 (m, 2 H) assigned to the H's on the substituted cyclopentadienyl ring. ^1H NMR and FTIR show that ~1 mM **1a** is converted rapidly ($t_{1/2} < 1$ min) and quantitatively to **2a** upon exposure to 1 atm of CO in solution, and FTIR confirms the same chemistry to occur in a thin film of MEEP/Li[CF_3SO_3] at 298 K.[7,8] The ^1H NMR spectrum of complex **2a** in THF-d_8, which results from the addition of CO to **1a**, shows two distinct resonances for the metallacyclic ring H's at δ 8.32 (d, ^1J = 2.48 Hz, 1 H) and δ 4.26 (d, ^1J = 2.48 Hz, 1 H). In addition to a resonance at δ 4.38 (s, 5 H) assigned to the unsubstituted cyclopentadienyl ring H's, there are four separate resonances assigned to the H's attached to the substituted cyclopentadienyl ligand. The four separate resonances indicate a barrier to free rotation about the bond between the N atom of the metallacycle and the C atom of the cyclopentadiene ring. Significantly, there is no effect on the ^1H NMR spectrum of **1a** upon the addition of 0.1 M Li[CF_3SO_3], whereas there is a significant effect on the ^1H NMR of **2a**. For **2a**, there is a 7.5-Hz downfield shift for the metallacyclic ring H resonance at δ 8.31 and an even greater downfield shift of 27.5 Hz for the metallacyclic ring H resonance at δ 4.26. These shifts can be attributed to the interaction of the Li^+ with the O atom of the metallacyclic ring carbonyl to form complex **3a**, eq 2.[9] Similarly, alkyl cations and H^+ are known to attack the O atom of the metallacyclic ring carbonyl of **2b** and **2c**, and the product formed from the methylation of **2b** has been crystallographically characterized.[10]



(2)

2a **3a**

The solid-state electrochemistry of **1a** and **2a** was investigated at Pt microelectrodes (144 μm long × 2 μm wide × 0.1 μm thick), Scheme I, and compared to the electrochemical behavior in THF/[n-Bu_4N]PF_6, Figure 1. Octamethylferrocene[11] has been used as an internal reference in the solid electrolyte medium. To functionalize the electrodes, 6 mg (0.012 mmol) of **1a** and 3 mg (0.010 mmol) of octamethylferrocene were dissolved in a 50% solution of 4:1 MEEP/Li[CF_3SO_3] in THF, and a film was cast on the microelectrode array. A cyclic voltammogram of a 1:1 mixture of octamethylferrocene and **1a** in a THF-saturated Ar atmosphere is shown in Figure 1A. When the atmosphere is changed to a THF-saturated CO atmosphere, a 100-mV shift in $E_{1/2}$ relative to the octamethylferrocene wave is observed in less than 1 min. A similar effect is observed for the electrochemistry of compound **1a** in the liquid electrolyte, Figure 1B. At intermediate conversion of **1a** to **2a**, the cyclic voltammogram shows signals for each complex.

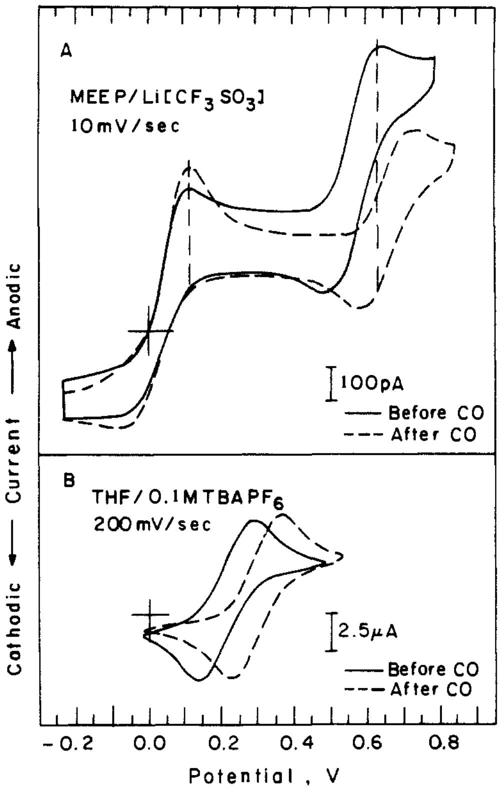


Figure 1. (A) Solid-state cyclic voltammetry at a Pt microelectrode of a 1:1 mixture of octamethylferrocene (wave at more negative potential) and ferrocenylferraazetine (waves at more positive potentials) dissolved in a 4:1 mixture of MEEP/Li[CF_3SO_3] before and after exposure to CO. (B) Cyclic voltammetry (vs $AgNO_3$/Ag) at a Pt disk (1-mm diameter) of 0.2 mM **1a** in THF/0.1 M [n-Bu_4N]PF_6 before and after the addition of CO.

In the THF/[n-Bu_4N]PF_6 medium, the conversion of **2a** back to **1a** can be effected by purging the system of CO using an Ar stream with $t_{1/2} < 1$ h at 25 °C. In the solid-state system, reversion was attempted by pulling a vacuum for 20 min on the MEEP/Li[CF_3SO_3]/**2a** mixture. $E_{1/2}$ of the ferrocenyl unit remained constant, indicating that loss of CO does not occur. In addition, FTIR of a similarly prepared sample showed that **2a** remained in the mixture with no apparent re-formation of **1a** after vacuum treatment for 20 min or upon standing for 8 h in air at 25 °C. The irreversible CO insertion to form **2a** with the resulting shift in $E_{1/2}$ results in a solid-state system that could be used to measure an accumulated exposure to CO by monitoring the growth of the electrochemical response for **2a**. The lack of reaction of **1a** with usual atmospheric gases and H_2 shows that the solid-state microelectrochemical system in Scheme I is selective for CO. Additional work is in progress to define the scope of CO insertion chemistry[9] in reversibly redox active molecules.

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(7) **1a**: Anal. Calcd: C, 42.77; H, 2.18. Found: C, 43.01; H, 2.30. MS (EI): m/z 505 (M^+). IR (THF): 2066 (m), 2024 (vs), 1989 (s), 1985 (s) cm^{-1}. IR (MEEP/Li[CF_3SO_3]): 2065 (m), 2023 (vs), 1983 (s), cm^{-1}. $E_{1/2}$ = 150 mV vs Ag/$AgNO_3$. Yield = 67% based on ferrocenylphosphinimine and $Fe_2(\mu\text{-}CH_2)(CO)_8$.

(8) $Fe_2\{\mu\text{-}C(O)CH{=}CHNFc\}(CO)_6$ (**2a**): IR (THF): 2072 (m), 2030 (vs), 2002 (s), 1993 (s), 1628 (w) cm^{-1}. IR (MEEP/Li[CF_3SO_3]): 2072 (m), 2032 (vs), 1999 (s, br) cm^{-1}.

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