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Journal of Organometallic Chemistry 484 (1994) 47–51

Journal of Organometallic Chemistry

Redox reactivity of azathiaferrocenophane complexes with copper(II) and palladium(II)

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Received 15 February 1994; in revised form 1 April 1994

Abstract

To further probe the influence of coordinated metal ions on the electrochemical behavior of azathiaferrocenophane ligands, a series of palladium(II) and copper(II) complexes with both cyclic and acyclic ferrocenophanes has been prepared, spectroscopically characterized and examined by cyclic voltammetry. New complexes of *N*,*N*-didecyl-2,8-diaza-5-thia[9](1,1′) ferrocenophane (**1**) are [**1**]$\mathrm{HPd(CH_3CN)(BF_4)_3}$, [**1**]$\mathrm{Pd(PPh_3)_2(BF_4)_2 \cdot CH_2Cl_2}$, [**1**]$\mathrm{Pd(AsPh_3)_2(BF_4)_2 \cdot 1.5CH_2Cl_2}$, [**1**]$\mathrm{Pd(C_6O_4Cl_2) \cdot (HN(C_2H_5)_3)_2(BF_4)_2 \cdot H_2O}$ and [**1**]$\mathrm{H_2Pd(bpy)(BF_4)_4}$. Copper(II) compounds reported include [**2**]$\mathrm{Cu(CH_3CO_2)_2 \cdot 2H_2O}$ (**2** = 1,5-bis(ferrocenyl)-3-thia-1,5-diaminopentane), [**3**]$\mathrm{Cu(CH_3CO_2)_2}$ (**3** = 1,8-bis(ferrocenyl)-3,6-dithia-1,8-diaminooctane) and $\mathrm{Cu(bas)(CH_3CO_2)_2}$ (bas = 3-thia-1,5-diaminopentane). The [**1**]$\mathrm{HPd(CH_3CN)^{3+}}$ cation ($E_{1/2}(\mathrm{Fe^{III/II}}) = 0.59$ V versus NHE in $\mathrm{CH_2Cl_2}$, 0.1 M TBAP, 25.0°C) is characterized by tridentate $\mathrm{S_2N}$ ferrocenophane ligation, leaving one coordination position open to the $\mathrm{CH_3CN}$ ligand and a protonated aza nitrogen atom uncoordinated. In contrast, **1** ligates $\mathrm{Pd^{II}}$ only through its pair of thioether sulfur atoms in [**1**]$\mathrm{Pd(PPh_3)_2^{2+}}$ ($E_{1/2} = 0.58$ V) and [**1**]$\mathrm{Pd(AsPh_3)_2^{2+}}$ ($E_{1/2} = 0.59$ V). The $\mathrm{Pd^{II}}$–chloranilate interaction in [**1**]$\mathrm{Pd(C_6O_4Cl_2) \cdot (HN(C_2H_5)_3)_2(BF_4)_2 \cdot H_2O}$ is too weak to disrupt ferrocenophane tridentate chelation or to restore the $\mathrm{Fe^{II}}$–S bonding previously documented for [**1**]$\mathrm{Pd(C_6O_4Cl_2)}$, which was prepared by another synthetic route. Electronic spectra of [**2**]$\mathrm{Cu(CH_3CO_2)_2 \cdot 2H_2O}$ and [**3**]$\mathrm{Cu(CH_3CO_2)_2}$ are consistent with tridentate $\mathrm{S_2N}$ and tetradentate $\mathrm{S_2N_2}$ ligation of $\mathrm{Cu^{II}}$, respectively, and a finding of $E_{1/2} = 0.48$ V for both complexes is in accord with expectations for the electrostatic influence of a bivalent cation on the $\mathrm{Fe^{III/II}}$ couple. Although cyclic voltammetric waves for the $\mathrm{Cu^{II,I}}$ couple were not observed, the redox reactivity of [**2**]$\mathrm{Cu^{2+}}$ towards reduction was evaluated through a kinetic study of electron transfer within its mercaptoacetate adduct.

Keywords: Iron; Copper; Palladium; Ferrocenophanes; Electrochemistry

1. Introduction

Our interest in azathiaferrocenophanes was prompted by the observation of $\mathrm{Fe^{II}}$–S bonding in *N*,*N*-didecyl-2,8-diaza-5-thia[9](1,1′)ferrocenophane (**1**), as demonstrated by an unexpectedly positive ferrocenium/ferrocene half-wave reduction potential (+727 mV versus NHE in $\mathrm{CH_3CN}$) [1]. We subsequently showed that this $\mathrm{Fe^{II}}$–S interaction is highly sensitive to solvent polarity, the size of the *N*-alkyl substituent and the presence of palladium(II), which bonds to the $\mathrm{N_2S_2}$ donor atom set [2]. Although [**1**]$\mathrm{PdCl_2}$ exhibits an $E_{1/2}$ value (+441 mV) only slightly more positive than that of free **1** in $\mathrm{CH_2Cl_2}$ (+361 mV), oxidation of the closely related [**1**]Pd(CA) derivative ($\mathrm{CA^{2-}}$ = chloranilate dianion) is shifted anodically by more than 200 mV under the same conditions ($E_{1/2} = +650$ mV in $\mathrm{CH_2Cl_2}$ and 705 mV in $\mathrm{CH_3CN}$) [2]. Thus, it was proposed that $\mathrm{Fe^{II}}$–S bonding is retained by N, S ligation of $\mathrm{Pd^{II}}$ in the latter complex, while complexation of palladium by both thioether sulfur atoms precludes such an interaction in the former compound [2]. The [**1**]Pd(CA) complex isolated from the reaction of **1** with $\mathrm{[Pd(CA)(CH_3CN)_2]}$ could be a kinetic rather than a thermodynamic product, however, bringing into question the contribution of $\mathrm{Fe^{II}}$–S bond strength to the

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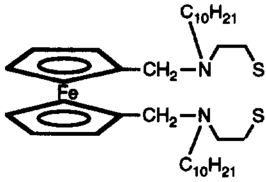

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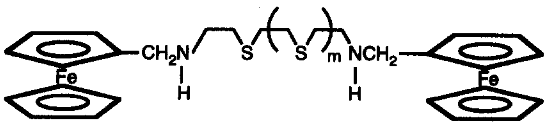

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driving force of azathiaferrocenophane complexation reactions. Coordination compounds containing N_2S_2-donor macrocyclic ligands often exhibit stereochemical rigidity such that several slowly interconverting isomers are present in solution [3]. Crown thioether ligands favor exodentate conformations with S atoms oriented out of the macrocyclic cavity [4,5]. Azathia macrocyclic ligands have received considerable attention as models for the blue copper proteins [6–8], although the duplication of metalloprotein physical properties has proved to be quite challenging.

To further probe the influence of coordinated metal atoms on the electrochemistry of azathiaferrocenophane ligands, we now describe the synthesis of $[\mathbf{1}]HPd(CH_3CN)(BF_4)_3$, in which the ferrocenophane functions as a tridentate (S_2N) ligand, and its reaction products with PPh_3, $AsPh_3$, 2,2′-bipyridine (bpy) and CA^{2-}. Also reported are copper(II) complexes of two acyclic ferrocenophanes, 1,5-bis(ferrocenyl)-3-thia-1,5-diaminopentane (**2**) and 1,8-bis(ferrocenyl)-3,6-dithia-1,8-diaminooctane (**3**).

2. Experimental section

Compounds **1**, **2**, **3**, $[\mathbf{1}]PdCl_2$ and $[Pd(CA)(CH_3CN)_2]$ were available from previous work [1,9]. The $AgBF_4$, PPh_3, $AsPh_3$, 2,2′-bipyridine and chloranilic acid were purchased from Aldrich and the dicyclohexylammonium mercaptoacetate was kindly donated by Professor Harvey Schugar. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Infrared and electronic spectra were acquired on Perkin-Elmer Model 267 and Shimadzu Model UV-260 spectrophotometers, respectively. ^1H and broad-band decoupled ^{13}C NMR resonances (Bruker 300-MHz spectrometer) are reported in parts per million (δ) downfield from tetramethylsilane, while ^{31}P chemical shifts are referenced to 85% H_3PO_4. Cyclic voltammetric measurements employed Pt working and auxiliary electrodes in the working compartment (0.1 M $N(^nBu)_4ClO_4$ in CH_2Cl_2, CH_3CN or CH_3OH) and an aqueous saturated calomel electrode in the reference compartment (0.1 M $NaNO_3$). Half-wave potentials were derived as the mean of anodic and cathodic peak potentials at a sweep rate of 50 mV s^{-1} and converted to the NHE scale by use of hydroxyethylferrocene as an internal calibrant [1,2]. Anaerobic kinetic studies of copper(II)–mercaptoacetate redox reactions were carried out at 400 nm on a Durrum D-110 stopped flow spectrophotometer with initial Cu^{II} and dicyclohexylammonium mercaptoacetate concentrations of 0.14 and 0.10 mM, respectively [10]. Reported first-order rate constants are the average of three independent determinations at 25.0°C.

2.1. Preparation of $[1]HPd(CH_3CN)(BF_4)_3$

$AgBF_4$ (0.2605 g, 1.06 mmol) was slowly added to 450 mg of $[\mathbf{1}]PdCl_2$ (0.53 mmol) in 100 ml of CH_3CN, resulting in a color change from orange to brown with precipitation of AgCl. Subsequent to stirring of the solution for 3 h at room temperature, the precipitated AgCl was removed by filtration through a fine frit with celite. The product was isolated by evaporation of the supernatant, washed with diethyl ether and vacuum-dried. Yield: 320 mg (63%). Anal. Calcd for $[\mathbf{1}]HPd(CH_3CN)(BF_4)_3$ ($C_{40}H_{70}N_3S_2B_3F_{12}FePd$): C, 44.49; H, 6.53; N, 3.89. Found: C, 44.75; H, 6.49; N, 3.87. ^1H NMR ($CDCl_3$): δ 0.90, 1.29 (decyl). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.64, 26.50, 27.03, 29.27, 29.49, 31.85 (decyl). IR (deposit from a $CHCl_3$ solution on a NaCl plate): 2924s, 2853m, 1466m, 1066vs, 1027vs cm^{-1}. UV-VIS (CH_3CN): λ_{max} 418 nm (ε 1.6×10^3 M^{-1} cm^{-1}); 260, sh (1.1×10^4).

2.2. Reactions of $[1]HPd(CH_3CN)(BF_4)_3$ with triphenylphosphine, triphenylarsine and 2,2′-bipyridine

$[\mathbf{1}]HPd(CH_3CN)(BF_4)_3$ (100 mg, 0.093 mmol) was combined with triphenylphosphine (60.6 mg, 0.231 mmol) in 2.0 ml of CH_3CN. The reaction mixture was stirred, at room temperature for 10 h and evaporated *in vacuo*. The dark brown product was washed with diethyl ether to remove the excess triphenylphosphine and recrystallized from CH_2Cl_2. Yield: 140 mg (93%). Anal. Calcd for $[\mathbf{1}]Pd(PPh_3)_2(BF_4)_2 \cdot CH_2Cl_2$ ($C_{75}H_{98}B_2F_8N_2S_2P_2Cl_2FePd$): C, 57.73; H, 6.33; N, 1.80. Found: C, 57.51; H, 5.85; N, 2.09. ^1H NMR ($CDCl_3$): δ 0.88, 1.20, 1.25 (decyl), 7.46–7.70 (m, phenyl). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.59, 26.10, 28.80, 29.18, 29.31, 29.38, 31.78 (decyl), 128.36–134.54 (m, phenyl). ^{31}P NMR ($CDCl_3$): 27.63, 29.55, 32.76, 33.20, 33.78. IR (deposit from a $CHCl_3$ solution on a NaCl plate): 2925m, 2854w, 1466w, 1437m, 1163w, 1062vs, 914w, 748w, 723m, 695s cm^{-1}. UV-VIS (CH_3CN): λ_{max} 405 nm (ε 1.8×10^3 M^{-1} cm^{-1}); 305, sh (1.1×10^4). $[1]Pd(AsPh_3)_2(BF_4)_2 \cdot 1.5CH_2Cl_2$ was prepared by the same procedure with PPh_3 replaced by $AsPh_3$. Anal. Calcd for $C_{74}H_{96}B_2F_8N_2S_2As_2FePd \cdot 1.5CH_2Cl_2$: C, 53.63; H, 5.90; N, 1.66. Found: C, 53.87; H, 5.94; N, 1.70. ^1H NMR ($CDCl_3$): δ 0.88, 1.20, 1.25 (decyl) 7.06–7.69 (m, phenyl). ^{13}C NMR ($CDCl_3$): δ 14.10, 22.63, 27.09, 28.83, 29.20, 29.35, 31.81 (decyl), 128.64–134.37 (m, phenyl). IR (deposit from a $CHCl_3$ solution on a NaCl plate): 2924m, 2853w, 1466w, 1435m, 1066vs, 1024vs, 738m, 723m, 694s cm^{-1}. UV-VIS (CH_3CN): λ_{max} 308 nm (ε 5.9×10^3 M^{-1} cm^{-1}). $[1]HPd(CH_3CN)(BF_4)_3$ (0.1002 g, 0.093 mmol) was combined with 2,2′-bipyridine (0.170 g, 0.096 mmol) in 50 ml of CH_3CN. The crude product that precipitated within 1 h was recrystallized from CH_3CN. Yield: 56 mg (54%). Anal. Calcd for $[1]H_2Pd(bpy)(BF_4)_4$ ($C_{48}H_{76}N_4S_2$-$B_4F_{16}FePd$): C, 44.95; H, 5.97; N, 4.37. Found: C, 44.83; H, 5.65; N, 4.81. IR (KBr): 2923s, 2849m, 1602w, 1466m, 1384w, 1296w, 1243w, 1083vs, 808w, 766m, 522m cm^{-1}. UV-VIS (CH_3CN): λ_{max} 285 nm (ε 1.5×10^4 M^{-1} cm^{-1}).

2.3. *Preparations of $[1]Pd(C_6O_4Cl_2) \cdot (HN(C_2H_5)_3)_2$-$(BF_4)_2 \cdot H_2O$ and $[2]Pd(C_6O_4Cl_2) \cdot 3H_2O$*

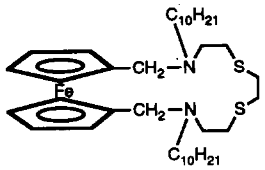
In an attempt to prepare a chloranilate complex, $[1]HPd(CH_3CN)(BF_4)_3$ (30 mg, 0.031 mmol) was combined with chloranilic acid (6.6 mg, 0.031 mmol) and triethylamine (6.4 mg, 0.063 mmol) in 1.0 ml of CH_3CN. After 10 h the reaction mixture was filtered to remove a small amount of gray solid and the brown filtrate was evaporated *in vacuo*. Anal. Calcd for $[1]Pd(C_6O_4Cl_2) \cdot (HN(C_2H_5)_3)_2(BF_4)_2 \cdot H_2O$ ($C_{56}H_{100}N_4S_2B_2F_8O_5Cl_2$-FePd): C, 48.73; H, 7.30; N, 4.06. Found: C, 48.65; H, 7.47; N, 4.00. ^1H NMR ($CDCl_3$): δ 0.89, 1.22, 1.28 (decyl). IR (deposit from a $CHCl_3$ solution on a NaCl plate): 2924s, 2853m, 1529s (C=O) 1466m, 1062vs (BF_4^-) 848w (C–Cl) cm^{-1}. UV-VIS (CH_3CN): λ 330, sh nm (ε 6.5×10^3 M^{-1} cm^{-1}). The complex $[2]Pd(C_6O_4Cl_2) \cdot 3H_2O$ was prepared from **2** and $[Pd(CA)(CH_3CN)_2]$ by the method described for [1]Pd(CA) [2]. Anal. Calcd for $[2]Pd(C_6O_4Cl_2) \cdot 3H_2O$ ($C_{34}H_{42}N_2S_2Cl_2O_7Fe_2Pd$): C, 43.27; H, 4.49; N, 2.97. Found: C, 43.22; H, 3.89; N, 3.11.

2.4. *Preparations of copper(II) complexes*

Stoichiometric quantities of $Cu(CH_3CO_2)_2 \cdot H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ and bis(2-pyridylmethyl)amine (dmpa, Nepara), 3-thia-1,5-diaminopentane (bas) [11], **2** or **3** were mixed in CH_3OH (bas and dmpa) or CH_3CN (**2** and **3**) at room temperature. After the reaction mixtures had been stirred for 3 h at room temperature, essentially quantitative yields of copper(II) complexes were isolated by slow evaporation of the solvent. Anal. Calcd for $Cu(bas)(CH_3CO_2)_2$ ($C_8H_{18}N_2SO_4Cu$): C, 31.83; H, 6.01; N, 9.28. Found: C, 31.57; H, 6.13; N, 9.15. IR (KBr): $\nu_{as}(CO_2^-)$ 1560, $\nu_s(CO_2^-)$ 1400 cm^{-1}. UV-VIS (CH_3OH): λ_{max} 649 nm (ε 7.0×10^1 M^{-1} cm^{-1}); 324 (1.18×10^3); 240 (1.75×10^4). Anal. Calcd for $Cu(dmpa)(ClO_4)_2$ ($C_{12}H_{13}N_3Cl_2O_8Cu$): C, 31.22; H, 2.84; N, 9.10. Found: C, 30.77; H, 3.33; N, 8.61. Anal. Calcd for $[2]Cu(CH_3CO_2)_2 \cdot 2H_2O$ ($C_{30}H_{42}N_2$-SO_6Fe_2Cu): C, 49.09; H, 5.77; N, 3.82. Found: C, 49.28; H, 5.58; N, 3.66. IR (KBr): $\nu_{as}(CO_2^-)$ 1560, $\nu_s(CO_2^-)$ 1410 cm^{-1}. UV-VIS (CH_3OH) λ_{max} 648 nm (ε 2.45×10^2 M^{-1} cm^{-1}); 445 (3.90×10^2); 310, sh (3.9×10^3). Anal. Calcd for $[3]Cu(CH_3CO_2)_2$ ($C_{32}H_{42}N_2S_2O_4Fe_2Cu$): C, 50.70; H, 5.58; N, 3.70. Found C, 50.96; H, 5.68; N, 3.82. IR (KBr): $\nu_{as}(CO_2^-)$ 1580, $\nu_s(CO_2^-)$ 1380 cm^{-1}, UV-VIS (CH_3OH): λ_{max} 561 nm (ε 2.65×10^2 M^{-1} cm^{-1}); 463 (3.05×10^2); 324 (3.54×10^3).

3. Results and discussion

To permit maximal ligation of Pd^{II} by the diazadithiaferrocenophane N,S donor atoms of **1**, the chloride ligands of $[1]PdCl_2$ were removed as AgCl by treatment with $AgBF_4$ in CH_3CN, to afford a product whose analysis fits the formula $[1]HPd(CH_3CN)(BF_4)_3$. The structural formulation of the cation proposed in Fig. 1 is consistent with the spectroscopic data and the observation of a quasi-reversible (ΔE_p = peak-to-peak separation = 0.15 V) ferrocene/ferrocenium oxidation wave with $E_{1/2}$ = 0.59 V versus NHE, shifted positively by 0.23 V relative to the parent ferrocenophane and 0.15 V versus the neutral $[1]PdCl_2$ precursor. Thus, the ferrocenophane is thought to function as a tridentate



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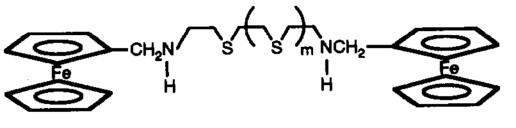

Fig. 1. Proposed structure of the complex cation in $[1]HPd(CH_3CN)$-$(BF_3)_3$.

Table 1
Electrochemistry of azathiaferrocenophane complexes [a]

Complex	$E_{1/2}$ (V vs. NHE)	ΔE_p(V)
[**1**] [b]	+0.36	0.10
[**1**]$PdCl_2$ [b]	+0.44	0.15
[**1**]Pd(CA) [b]	+0.65	0.13
[**1**]$HPd(CH_3CN)(BF_4)_3$	+0.59	0.15
[**1**]$Pd(PPh_3)_2(BF_4)_2 \cdot CH_2Cl_2$	+0.58	0.14
[**1**]$Pd(AsPh_3)_2(BF_4)_2 \cdot 1.5CH_2Cl_2$	+0.59	0.15
[**1**]$Pd(CA) \cdot (HN(C_2H_5)_3)_2(BF_4)_2 \cdot H_2O$	+0.37	0.22
[**1**]$H_2Pd(bpy)(BF_4)_4$	+0.79 [c]	
[**2**] [d]	+0.38	0.07
[**2**]$Pd(CA) \cdot 3H_2O$	+0.47	0.08
[**2**]$Cu(CH_3CO_2)_2 \cdot 2H_2O$ [e]	+0.48	0.08
[**3**] [d]	+0.37	0.08
[**3**]$Cu(CH_3CO_2)_2$ [e]	+0.48	0.07

[a] At 25.0°C with 0.1 M TBAP supporting electrolyte in CH_2Cl_2 and a 50 mV s^{-1} sweep rate, unless otherwise stated. [b] Data from ref. [2]. [c] The anodic-peak potential of a totally irreversible wave. [d] Data from ref. [1] in CH_3CN. [e] In CH_3OH.

S_2N ligand, leaving one coordination position open to a CH_3CN ligand and one protonated aza nitrogen atom uncoordinated. Our previous characterization of [**1**]$PdCl_2$ indicated bidentate chelation of Pd^{II} through the two thioether sulfur atoms only [2]. Attempts to prepare [**1**]$Pd(CH_3CN)(BF_4)_2$ by neutralization of the N-H group with triethylamine gave palladium metal as the primary product.

The reactions of [**1**]$HPd(CH_3CN)(BF_4)_3$ with triphenylphosphine and triphenylarsine cleanly gave products containing the [**1**]$Pd(PPh_3)_2^{2+}$ and [**1**]$Pd(AsPh_3)_2^{2+}$ cations, respectively. Only ^1H and ^{13}C signals attributable to decyl and phenyl groups were sharply resolved in the NMR spectra and five distinct ^{31}P NMR lines were observed for the former complex, suggesting the presence of several different conformers. Ferrocenophane methylene and ferrocenyl resonances for these and other Pd^{II} adducts reported here were broadened or not detected even in spectra of saturated solutions. Electrochemical results are presented in Table 1. As expected from the proximal 2+ charge of the Pd^{II} center, $E_{1/2}$ values for [**1**]Pd$(PPh_3)_2^{2+}$ and [**1**]$Pd(AsPh_3)_2^{2+}$ are essentially identical and are shifted anodically by more than 0.2 V relative to that of **1**. In addition to the ferrocenyl absorption near 400 nm in the electronic spectra, these complexes exhibit strong bands between 300 and 310 nm which may be assigned as $P \rightarrow Pd^{II}$ and $As \rightarrow Pd^{II}$ LMCT transitions. When allowed to react with 2,2′-bipyridine, [**1**]$HPd(CH_3CN)(BF_4)_3$ is converted to a doubly-protonated product, [**1**]$H_2Pd(bpy)(BF_4)_4$, whose electronic spectrum is dominated by an intraligand bpy π-π^* transition at 285 nm. Unlike all other complexes of **1** studied to date, [**1**]$H_2Pd(bpy)^{4+}$ exhibits a sharp, but totally irreversible, anodic wave at 0.79 V versus NHE (50 mV s^{-1} sweep rate). This result could be reproduced only with frequent cleaning of the Pt working electrode, which indicates that precipitation of the oxidation product is responsible for the irreversible electrochemistry.

In the complex [**1**]Pd(CA), which was prepared previously [2] by the reaction of **1** with $[Pd(CA)(CH_3CN)_2]$, chloranilate functions as a bidentate ligand towards Pd^{II}. Considering the surprising result that Fe-S bonding is retained in [**1**]Pd(CA), we have now attempted to prepare this complex by another route to determine whether it is a kinetic or thermodynamic product. Chloranilic acid which had been fully neutralized with triethylamine was mixed with an equimolar quantity of [**1**]$HPd(CH_3CN)(BF_4)_3$ in acetonitrile, the same solvent that was used in the original synthesis. While purple [**1**]Pd(CA) readily precipitated from solution during the reaction of **1** with $[Pd(CA)(CH_3CN)_2]$, no such precipitation was observed in the current effort. Evaporation of the reaction mixture after 10 h afforded a solid which analyzes as the double salt [**1**]$Pd(CA) \cdot (HN(C_2H_5)_3)_2(BF_4)_2 \cdot H_2O$. Monodentate ligation of Pd^{II} by chloranilate in this species is suggested by both the decrease in CA^{2-} π-π^* band intensity [12] at 330 nm relative to the analogous transition of [**1**]Pd(CA) (1.5×10^4 M^{-1} cm^{-1} at 344 nm) [2] and the finding of a $Fe^{III/II}$ half-wave potential essentially identical to that of neutral ferrocenophane **1**. Thus, it is now apparent that the Pd^{II}-chloranilate interaction is too weak to disrupt ferrocenophane tridentate S_2N chelation of Pd^{II} in [**1**]$Pd(CA) \cdot (HN(C_2H_5)_3)_2(BF_4)_2 \cdot H_2O$, the thermodynamic product, or to promote restoration of the Fe^{II}-S bonding once it is broken by preferential coordination of both thioether sulfur atoms to Pd^{II}.

Copper(II) complexes with 3-thia-1,5-diaminopentane, tridentate S_2N (**2**) or tetradentate S_2N_2 (**3**) acyclic ferrocenophane ligands were readily prepared through reactions with $Cu(CH_3CO_2)_2 \cdot H_2O$. Related coordination compounds with dinucleating ferrocenophane ligands have been reported by Beer and co-workers [13]. The close correspondence of d-d band positions for [**2**]$Cu(CH_3CO_2)_2 \cdot 2H_2O$ (649 nm) and $Cu(bas)(CH_3CO_2)_2$ (648 nm) in CH_3OH indicates the presence of S_2NO ligand fields in both complexes. Furthermore, the latter exhibits a $S \rightarrow Cu^{II}$ LMCT transition [14] at 324 nm, while the spectrum of [**2**]$Cu(CH_3CO_2)_2 \cdot 2H_2O$ has a well-defined shoulder at 310 nm. Consistent with the presence of an open coordination position, the d-d band of [**2**]Cu^{2+} red-shifts to 675 nm in CH_3CN (ε 1.72×10^2 M^{-1} cm^{-1}). The replacement of S_2NO by the stronger-field S_2N_2 ligand field of [**3**]$Cu(CH_3CO_2)_2$ is reflected in a blue-shift of the d-d band (2400 cm^{-1}) to 561 nm. For this complex, the $S \rightarrow Cu^{II}$ LMCT band is clearly resolved at 324 nm.

The two ferrocenyl units per Cu atom in [**2**]$Cu(CH_3CO_2)_2 \cdot 2H_2O$ and [**3**]$Cu(CH_3CO_2)_2$ are equivalent from an electrochemical point of view, since single cyclic voltammetric waves with $E_{1/2} = 0.48$ V versus NHE were observed for both complexes. This finding is essentially identical to that for [2]Pd(CA) · $3H_2O$, which was prepared for comparison purposes. The coordination-induced positive shift in $E_{1/2}$ of *ca.* 0.1 V for acyclic ferrocenophanes **2** and **3** is only one half of that observed for cyclic ferrocenophane **1**. To confirm the electrostatic [15] origin of this shift, cyclic voltammograms of **2** and **3** were determined in CH_3CN solutions (25.0°C, 0.1 M TBAP) to which copper or zinc acetate were added. At 1 : 1 proportions (0.5 mM), copper acetate shifted the $E_{1/2}$ values of **2** and **3** to 0.46 and 0.47 V versus NHE, while analogous findings for zinc acetate were 0.47 and 0.48 V, respectively.

In planning the syntheses of copper(II) adducts with **2** and **3**, we had hoped to find evidence for electronic communication between the Fe^{II} and Cu^{II} centers. While Cu^{II} evidently shifts the $Fe^{III/II}$ half-wave reduction potential through purely electrostatic means, an Fe^{II}–Cu^{II} interaction could strongly perturb the $Cu^{II/I}$ reduction potential as well. The cyclic voltammogram of Cu(bas)$(CH_3CO_2)_2$ in CH_3OH exhibits an $E_{1/2}$ of 0.23 V versus NHE, which was independent of sweep rate in the interval 50–300 mV s^{-1}, but with a very large ΔE_p of 400 mV even at 50 mV s^{-1}. This finding points to very slow heterogeneous electron transfer, presumably linked to the substantial change in both coordination number and geometry which typically accompanies the reduction of Cu^{II} to Cu^{I}. Unfortunately, voltammetric waves corresponding to the $Cu^{II,I}$ couple were not observed for [2]Cu$(CH_3CO_2)_2$ · $2H_2O$ and [3]Cu$(CH_3CO_2)_2$ to the solvent cutoff limit.

Although a thermodynamic measure of Cu^{II} reducibility could not be obtained by cyclic voltammetry, a kinetic criterion is available through the determination of redox decay rates for Cu^{II} adducts with mercaptoacetate [10]. In extensive kinetic studies of the factors which control Cu^{II}–thiolate S bond stability, transient, intense S → Cu^{II} LMCT absorption in the 300–400 nm region has been used to monitor the oxidations of various mercaptans to disulfides, accompanied by the formation of colorless Cu^{I} species (Eq. (1)) [10,16–18]. As a reactivity standard in these studies,

$$2\ Cu^{II} + 2\ RS^- \rightarrow 2[Cu^{II}\text{–}SR]^+ \rightarrow 2\ Cu^{I} + RS\text{–}SR \qquad (1)$$

$Cu(tmpa)^{2+}$ (tmpa = tris(2-pyridylmethyl)amine) was employed as the oxidizing agent. We now report first-order rate constants for intracomplex electron transfer reactions of mercaptoacetate adducts with $Cu(bas)^{2+}$ (7.8×10^{-2} s^{-1}), $[2]Cu^{2+}$ (1.9×10^{-1} s^{-1}) and $Cu(dmpa)^{2+}$ (1.8×10^{-2} s^{-1}) in CH_3OH at 25.0°C. By comparison, the [Cu(tmpa)(SCH_2CO_2)] redox decay rate constant is 2.3×10^{-1} s^{-1} under the same conditions [10]. On this basis, relative reactivities of the copper(II) complexes towards reduction may be ranked by ligand: tmpa (1.00) > **2**(0.83) > bas(0.34) > dmpa(0.08). Somewhat surprisingly, $[2]Cu^{2+}$ is reduced more rapidly than $Cu(bas)^{2+}$ by more than a factor of two, even though a cyclic voltammogram could only be observed for the latter. In contrast, the order of magnitude kinetic stability advantage of Cu(dmpa)(SCH_2CO_2) relative to Cu(tmpa)(SCH_2CO_2) is readily understood in terms of the ability of mercaptoacetate to chelate Cu(II) [16–18] in the former complex but not in the latter.

Acknowledgment

We thank the Welch Foundation for financial support of this research through Grants D-735 (R.A.H.) and D-775 (R.A.B.).

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