Journal of Organometallic Chemistry, 443 (1993) 123–129

JOM 23022

Solvent, *N*-alkyl substituent and coordination effects on the electrochemistry of 2,11-diaza-5,8-dithia[12](1,1′)ferrocenophanes

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(Received March 23, 1992)

Abstract

The synthesis of *N*,*N*-diethyl-2,11-diaza-5,8-dithia[12](1,1′)ferrocenophane (**6**), cyclic voltammetric studies of diazadithiaferrocenophanes in ten organic solvents and the electrochemical characteristics of four diazadithiaferrocenophane complexes with palladium(II) are reported with the objective of better understanding the factors which govern Fe–S bonding in such compounds. As compared with the *N*-decyl analog **7** ($E_{1/2}(\mathrm{Fe}^{III/II}) = 727$ mV *vs.* SHE), the half-wave reduction potential of **6** (388 mV) in acetonitrile solution (25°C, 0.1 M $N(^nBu)_4ClO_4$) is displaced by 0.34 V to more negative potential. However, the $E_{1/2}$ values for **6** and **7** are essentially identical (average of 0.39 ± 0.02 V) in butyronitrile, benzonitrile, dichloromethane, *N*,*N*-dimethylformamide, acetone and methanol. On this basis it is concluded that conformations which permit Fe^{II}–S bonding in **7** are supported by hydrophobic attractions between the *N*-decyl substituents. The perturbation of Fe–S bonding by coordination of S and/or N atoms to Pd^{II} was examined by preparing [**7**]$PdCl_2$, [**6**]$PdCl_2 \cdot 2HCl$, [**6**]Pd(CA)·$2H_2O$ and [**7**]Pd(CA), where CA^{2-} = 2,5-dioxo-3,6-dichloro-1,4-benzoquinone (chloranilate dianion). Electrochemical and ^{13}C NMR findings suggest that both ferrocenophane sulfur atoms ligate Pd^{II} in the former three complexes, while [**7**]Pd(CA) prefers ligation through both N and S donor atoms, leaving one thioether S to interact with the Fe^{II} center.

1. Introduction

We have recently reported the synthesis and electrochemistry of ferrocenyl thioacetal crown compounds [1], thiaoxaferrocenophanes [2,3], thiaazaferrocenophanes [4] and corand quinones [5]. Electrochemical studies of *N*,*N*-didecyl-2,8-diaza-5-thia[9](1,1′)ferrocenophane and *N*,*N*-didecyl-2,11-diaza-5,8-dithia[12](1,1′)ferrocenophane yielded $\mathrm{Fe}^{III,II}$ half-wave potentials of 705 and 727 mV vs. SHE (25°C, acetonitrile, 0.1 M $N(^nBu)_4ClO_4$) respectively, shifted to more positive potential by approximately 0.3 V as compared with acyclic analogs and *N*,*N*-didecyl-2,11-diaza-5,8-dioxa[12](1,1′)ferrocenophane (369 mV) [4]. On this basis, stabilization of the Fe^{II} oxidation state by iron–sulfur bonding within azathiaferrocenophanes was proposed [4]. To further probe the factors which influence Fe–S bonding in such compounds, we have now examined the effects of changing the *N*-alkyl substituent, varying the solvent and introducing a coordinated Pd^{II} substituent. We report here the synthesis of *N*,*N*-diethyl-2,11-diaza-5,8-dithia[12](1,1′)-ferrocenophane, cyclic voltammetric studies of diazadithiaferrocenophane oxidation reactions in ten organic solvents covering a wide polarity range and the electrochemical characteristics of four palladium(II)-diazadithiaferrocenophane complexes in which Fe–S bonding must compete with the ligation of Pd^{II} by thioether sulfur atoms.

2. Results and discussion

The synthetic route to *N*,*N*-didecyl-2,8-diaza-5,8-dithia[12](1,1′)ferrocenophane (**7**) reported previously [4] was adapted for the preparation of the diethyl analog **6** (Scheme 1). The structures of new compounds **2**, **3**, **5** and **6** were verified by elemental analyses and by IR and NMR spectra.

A comparison of $\mathrm{Fe}^{III,II}$ half-wave reduction potentials for **6** and **7** in ten organic solvents is presented in Table 1. Ferrocenophane **6** exhibited quasi-reversible,

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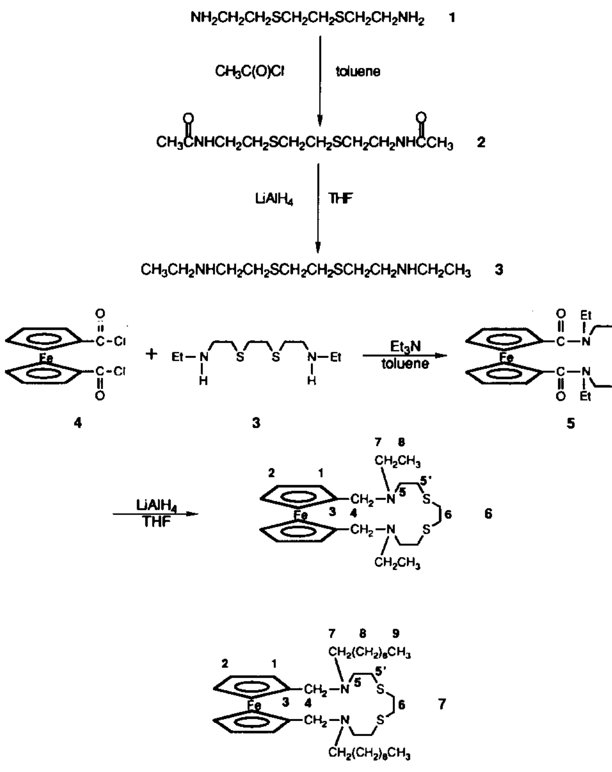

Scheme 1.

one-electron oxidation waves in all solvents examined with $E_{1/2}$ values covering a narrow range from 372 to 440 mV vs. SHE. The finding of $E_{1/2} = 388$ mV *vs.* SHE for **6** in acetonitrile solution contrasts sharply with the value of 727 mV reported previously for **7** under the same conditions [4]. Thus, the replacement of decyl substituents by ethyl groups results in a shift of 0.34 V to more negative potential. However, the half-wave potentials of **6** and **7** are essentially *identical* in all other solvents examined, including two with the nitrile functional group (butyronitrile and benzonitrile).

An unsuccessful effort was made to find a highly polar solvent besides acetonitrile in which **7** exhibits an unusually positive half-wave potential. Although cyclic voltammograms of **6** in dimethyl sulfoxide, propylene carbonate and nitromethane follow the quasi-reversible pattern typical of ferrocenophanes, electrochemical complications prevented the determination of $E_{1/2}$ values for **7** in these solvents. The solubility of **7** in highly polar solvents is very small, although adequate for the detection of cyclic voltammetric waves. No oxidation wave for **7** was observed in dimethyl sulfoxide solution from 0 mV to the solvent cutoff at 810 mV. Either a positively-shifted wave or exceptionally slow electrode kinetics could account for this negative result. Cyclic voltammograms of **7** in propylene carbonate and nitromethane lacked distinct anodic current peaks, but exhibited anodic shoulders and cathodic current peaks as described in Table 1. Precipitation of an oxidation product on the working electrode was observed subsequent to steady-state voltammograms of **7** in acetonitrile, propylene carbonate and nitromethane, which necessitated frequent electrode cleaning.

Strong reinforcement of iron–sulfur bonding by hydrophobic interactions between *N*-decyl substituents is implicated by our finding that the $E_{1/2}$ of **6** is typical of model compounds which lack this structural characteristic [4]. Consistent with this hypothesis is the close correspondence between half-wave potentials of **6** and **7** in low polarity solvents for which solvation of *N*-decyl substituents presumably competes strongly with hydrophobic attractions between them. It is not clear why acetonitrile is the only solvent which promotes Fe–S bonding within **7** to such a large extent. We conclude, however, that diazadithiaferrocenophane conformations which permit Fe–S interaction are *not* stabilized primarily by a high iron–sulfur bond strength. Indeed, we previously noted that Fe^{II} dπ to thioether S dπ back-donation should have a larger impact on the $E_{1/2}$ value than sulfur-to-iron sigma donation [4].

To further document the sensitivity of diazadithiaferrocenophane conformation to solvent variations, ^1H and ^{13}C NMR spectra of **6** and **7** were taken in several media (Tables 2 and 3). Unfortunately, the low solubility of **7** in acetonitrile prevented the acquisition of its

TABLE 1. Solvent dependence of diazadithiaferrocenophane half-wave potentials [a]

Solvent	ϵ [b]	$E_{1/2}$ in mV *vs.* SHE (ΔE_p, mV)	
		7	6
Acetonitrile	35.94	727 (83)	388 (75)
Butyronitrile	24.83	384 (83)	372 (75)
Benzonitrile	25.20	402 (94)	394 (79)
Dichloromethane	8.93	361 (98)	374 (110)
N,N-dimethylformamide	36.71	387 (94)	390 (79)
Dimethyl sulfoxide	46.45	[c]	412 (79)
Acetone	20.56	400 (83)	400 (75)
Propylene carbonate	64.92	[d]	388 (75)
Methanol	32.66	428 (79)	440 (79)
Nitromethane	35.87	[e]	400 (79)

[a] 25.0°C, I = 0.1 M ($N(^nBu)_4ClO_4$). Pt working and auxiliary electrodes, saturated calomel reference electrode in 0.1 M $NaNO_3$(aq); 50 mV s^{-1} sweep rate. [b] Solvent dielectric constants from J.A. Riddick, W.B. Bunger and T.K. Sakano, *Organic Solvents*, 4th edition, Wiley-Interscience, New York, 1986. [c] No anodic or cathodic waves were observed within the interval accessible before the solvent cutoff at 810 mV *vs.* SHE. [d] An anodic shoulder near 460 mV and a cathodic wave with $E_{pc} = 363$ mV *vs.* SHE were observed. For **6**, $E_{pc} = 351$ mV. [e] An anodic shoulder near 495 mV and a cathodic wave with $E_{pc} = 377$ mV *vs.* SHE were observed. For **6**, $E_{pc} = 361$ mV.

TABLE 2. NMR spectroscopy of ferrocenophane amine **6**

C atom [a]	^{1}H NMR chemical shift, δ			^{13}C NMR chemical shift, δ		
	CD_2Cl_2	$CD_3C(O)CD_3$	$CD_3S(O)CD_3$	CD_2Cl_2	$CD_3C(O)CD_3$	$CD_3S(O)CD_3$
1	4.08–4.11, m	4.07–4.13, m	4.08, s	71.19	71.53	70.51
2	4.08–4.11, m	4.07–4.13, m	4.08, s	68.30	68.40	67.52
3				84.55	85.57	84.14
4	3.49, s	3.56, s	3.45, s	53.15	53.45	51.93
5	2.71, s	2.66–2.78, m	2.62–2.72, m	54.41 (5)	54.96 (5)	53.63 (5)
				29.83 (5′)	30.06 (5′)	28.21 (5′)
6	2.78, s	2.79, s	2.74, s	33.07	33.21	31.83
7	2.35, q	2.33, q	2.27 q	46.79	47.04	45.66
8	0.92, t	0.90, t	0.84, t	12.04	12.46	11.87

[a] See Scheme 1.

NMR spectra in this solvent. In the ^{1}H NMR spectra, ferrocenyl protons 1 and 2 appear as a complex multiplet in CD_2Cl_2 and $CD_3C(O)CD_3$, but as a singlet in $CD_3S(O)CD_3$. The 5 and 5′ protons resonate as a singlet in dichloromethane, but as second-order multiplets in the other two solvents. For **6** in $CD_3C(O)CD_3$, the 14-line multiplet between 2.66 and 2.78 ppm approximately fits an AA′BB′ spin system with $J_{AB} = 7$

TABLE 3. NMR spectroscopy of ferrocenophane amine **7** and Pd^{II}-**7** complexes

C atom [a]	^{1}H NMR chemical shift for **7**, δ		^{13}C NMR chemical shift, δ			
			7		[**7**]$PdCl_2$	[**7**]Pd(CA)
	CD_2Cl_2	$CD_3C(O)CD_3$	CD_2Cl_2	$CD_3C(O)CD_3$)	CD_2Cl_2	CD_2Cl_2
1	4.06–4.10, m	4.09–4.13, m	71.21	71.59	71.37	72.48
					72.34	
					72.50	
					74.17	
					75.86	
2	4.06–4.10, m	4.09–4.13, m	68.21	68.38	68.17	71.43
					68.47	
					69.30	
					70.31	
3			84.75	85.66	86.78	
4	3.48, s	3.57, s	53.64	54.00	54.75	
5	2.70, s	2.68–2.79, m	55.00 (5)	55.51 (5)	59.11 (5)	55.42 (5)
			29.99 (5′)	30.06 (5′)	29.96 (5′)	29.78 (5′)
6	2.77, s	2.81, s	33.12	33.30	33.32	40.08
					33.58	
					33.86	
					35.91	
7	2.26, t	2.30, t	53.13	53.25	53.08	53.08
8	1.18–1.37, m	1.19–1.37, m	23.06	23.30	23.04	23.04
			27.34	27.83	26.74	26.79
			27.64	29.03	27.47	27.42
			29.70	29.29	27.62	29.30
			29.84	29.54	28.79	29.64
			32.29	29.80	29.67	32.22
				30.23	29.82	
				30.28	29.86	
				30.33	32.26	
				30.58		
				32.61		
9	0.88, t	0.88, t	14.27	14.35	14.25	14.26

[a] See Scheme 1.

TABLE 4. Comparison of diazadithiaferrocenophane palladium(II) complex half-wave potentials [a]

Complex	$E_{1/2}$ (mV *vs.* SHE)	ΔE_p (mV)
[7]PdCl$_2$	441	150
[6]PdCl$_2$·2HCl	455	134
	713 [b]	98 [b]
[7]Pd(CA)	650	126
	705 [c]	146 [c]
[6]Pd(CA)·2H$_2$O	495	95

[a] 25.0°C, 0.1 M N(^{n}Bu)$_4$ClO$_4$ supporting electrolyte in dichloromethane unless otherwise stated. Pt working and auxiliary electrodes, saturated calomel reference electrode in 0.1 M NaNO$_3$(aq); 50 mV s^{-1} sweep rate. [b] Minor second wave corresponding to the oxidation of [6]PdCl$_2$H$_2^{2+}$. [c] 25.0°C, 0.1 M N(^{n}Bu)$_4$ClO$_4$ supporting electrolyte in CH$_3$CN; 200 mV s^{-1}sweep rate. A well-resolved anodic wave was not resolved at sweep rates smaller than 200 mV s^{-1}, but $E_{1/2}$ is independent of sweep rate at larger sweep rates. An anodic shoulder near 550 mV and a second broad cathodic wave at 353 mV were also observed.

ppm and $J_{AB'} = 4$ ppm. In general, ^{1}H and ^{13}C NMR spectra of **6** and **7** are similar in CD$_3$C(O)CD$_3$ and CD$_2$Cl$_2$. A notable difference is the deshielding of the ^{13}C signal for carbon 7 in **7** by 6.3 ppm in CD$_2$Cl$_2$, consistent with increasing p orbital character in the bond from C7 to N and decreasing the H–C7–N bond angle when the N-alkyl substituent is changed from ethyl to decyl. Also noteworthy is the resolution of 11 distinct C8 absorptions for **7** in CD$_3$C(O)CD$_3$, but only 6 lines in the less polar solvent, CD$_2$Cl$_2$.

In addition to the *N*-alkyl substituent and solvent effects, perturbation of Fe–S bonding in diazadithiaferrocenophanes by coordination of the S and/or N atoms to Pd^{II} has been examined. Ferrocenophane amines **7** and **6** react slowly with [PdCl$_2$(CH$_3$CN)$_2$] and [Pd(CA)(CH$_3$CN)$_2$] (CA^{2-} = 2,5-dioxo-3,6-dichloro-1,4-benzoquinone; chloranilate dianion) in acetonitrile solution to give precipitates of [**7**]PdCl$_2$, [**7**]Pd(CA), [**6**]PdCl$_2$ · 2HCl and [**6**]Pd(CA) · 2H$_2$O over a three day interval. The electrochemical characteristics of these complexes in dichloromethane are summarized in Table 4. Unfortunately, precipitation of oxidation products at the Pt working electrode prevented the resolution of anodic and cathodic peak current potentials for acetonitrile solutions of these complexes except [**7**]Pd(CA) at rapid sweep rates. A compared with the free ferrocenophanes, [**7**]PdCl$_2$ and [**6**]PdCl$_2$ exhibit one-electron oxidation waves shifted moderately to a more positive potential by 80 mV and 81 mV respectively, consistent with the presence of a Pd^{II} center in close proximity to the redox-active site [5]. Replacement of two chloride ligands by a chloranilate dianion in Pd^{II}-**6** complexes yields an additional positive shift in $E_{1/2}$ (40 mV relative to [**6**]PdCl$_2$; 121 mV *vs.* free **6**). A much larger differential between $E_{1/2}$ (Pd(CA) complex) and $E_{1/2}$ (PdCl$_2$ complex) pertains for ferrocenophane **7** (209 mV).

Electronic, ^{1}H and ^{13}C NMR spectra of [**7**]PdCl$_2$ and [**7**]Pd(CA) were acquired to elucidate the structural differences between the two complexes. The possibility of Pd–Fe bonding may be ruled out since neither complex exhibits strong absorption ($\epsilon > 5 \times 10^3$ M^{-1} cm^{-1}) above 380 nm [6–9]. Thus, for [**7**]PdCl$_2$, bands at 406 nm and 310 nm are blue-shifted and more intense than the corresponding transitions of **7** at 437 nm and 325 nm. Tilting of ferrocenophane cyclopentadienyl rings by bridging groups gives rise to *bathochromic* shifts of d–d transitions [10], opposite to those reported here. The electronic spectrum of [**7**]Pd(CA) is dominated by a strong π–π^* transition of the chloranilate ligand (344 nm) in its *p*-quininoid resonance form [11,12].

Room temperature ^{1}H NMR spectra of [**7**]PdCl$_2$ and [**7**]Pd(CA) are severely broadened to the point where only decyl group signals at 0.87 ppm and 1.23–1.25 ppm are observed, along with ferrocenyl resonances at 4.09, 4.17, 4.20, 4.22, 4.25, 4.34, 4.58 (d) and 5.10 (d) for [**7**]PdCl$_2$. Coordination of sulfur atoms to transition metals increases the rate of pyramidal S inversion as a result of (p–d) π conjugation effects [13], lending fluxionality to thioether complexes. Well-resolved ^{13}C spectra were obtained for Pd^{II}-**7** complexes, however (Table 3). Several differences may be noted between the spectra of **7** and [**7**]PdCl$_2$. In the complex, ferrocenyl C1 and C2 signals are both split into several components. Although the C5 resonance is shifted downfield by 4.1 ppm, the C5′ signal remains essentially unchanged. The single C6 resonance of **7** is split into four components in [**7**]PdCl$_2$, with signals shifted downfield by 0.2–2.8 ppm, and nine distinct C8 methylene signals are observed for the complex. [**7**]Pd(CA) exhibits a distinctly different ^{13}C NMR spectrum from the PdCl$_2$ complex. Single lines are observed for C1 and C2, C5 is only slightly deshielded, the C6 signal is displaced downfield by 7.0 ppm relative to **7** and the six-line C8 pattern corresponds closely to that of the free ferrocenophane. Although [Pd(CA)(PPh$_3$)$_2$] exhibits three chloranilate ^{13}C signals at 103.3, 170.9 and 174.7 ppm (CD$_2$Cl$_2$) [14], no lines attributable to CA^{2-} were observed for [**7**]Pd(CA) in the 100–200 ppm region. The comparatively weak C3 and C4 signals of **7** are also not resolved in the chloranilate complex.

Electrochemical and spectroscopic findings suggest that both ferrocenophane S atoms ligate palladium(II) in the complexes [**6**]PdCl$_2$, [**6**]Pd(CA) and [**7**]PdCl$_2$, consistent with the structures of related azathia-Pd^{II} compounds [6,7,15–17]. Ligation of Pd^{II} in [**7**]Pd(CA) could be through both N and S donor atoms, however, leaving one thioether S free to interact with Fe^{II} (Fig. 1). Thus, the ferrocenophane S atoms are thought to retain typical [18,19] *gauche, exo* orientations when both are coordinated to a square planar Pd^{II} center. In contrast, the structure proposed for [7]Pd(CA) has one *exo* S atom while the Fe-ligating S atom is *endo*, changing the relationship between the two sulfurs to *anti*. We note that such *N,S* chelation is not proven by the NMR and electrochemical results reported here, and are currently preparing other $[7]Pd^{II}$ derivatives in the hope that crystallographic structural evidence may ultimately be presented. The coordination mode of chloranilate to Pd^{II} cannot be derived from the available data, but bidentate *O,O* chelation pertains in chloranilatobis(tri-*m*-tolylphosphine)palladium(II) [20]. 1,8-Diamino-3,6-dithiaoctane and related acyclic N_2S_2 ligands are known to exhibit considerable flexibility in coordination number and geometry when bonding to Ni^{II} and Pd^{II} [21,22].

3. Experimental section

Unless specified otherwise, reagent grade chemicals and solvents were used as received. *N,N*-Didecyl-2,8-diaza-5,8-dithia[12](1,1')ferrocenophane (7) [(UV-VIS $(CH_2Cl_2)\lambda_{max}$, nm (ϵ, M^{-1} cm^{-1}): 437 (9.9×10^1), 325 (7.3×10^1), 234 (7.2×10^3)] and $[Pd(CA)(CH_3CN)_2]$ were available from earlier work [4,14]. $[PdCl_2(CH_3CN)_2]$ was purchased from Aldrich. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Electronic and infrared spectra were acquired with Shimadzu UV-260 and Perkin-Elmer 267 spectrophotometers respectively. ^1H and broad-band decoupled ^{13}C NMR spectra were recorded on a Bruker 300-MHz spectrometer; chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Signal assignments were made with the assistance of 2D, ^1H, ^1H and ^1H, ^{13}C COSY measurements. Cyclic voltammetric measurements in non-aqueous solvents followed standard protocols [1], employing Pt working and auxiliary electrodes in the working compartment (0.1 M $N(^nBu)_4ClO_4$) and an aqueous saturated calomel electrode in the reference compartment (0.1 M $NaNO_3$). Half-wave potentials were calculated as the mean of anodic and cathodic peak potentials at a sweep rate of 50 mV s^{-1} and were converted to the SHE scale by use of hydroxyethylferrocene ($E_{1/2} = 402$ mV *vs.* SHE) as an internal calibrant [1].

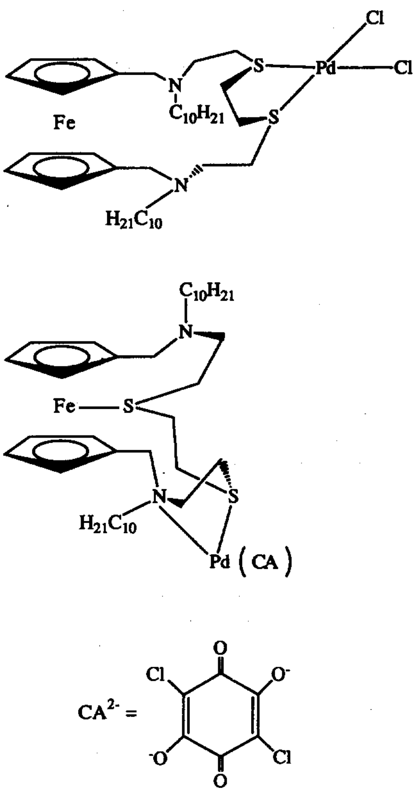

Fig. 1. Proposed structures of $[7]PdCl_2$ and [7]Pd(CA).

3.1. Preparation of diamide 2

A solution of acetyl chloride (3.50 g, 44.6 mmol) in toluene (30 ml) was added dropwise to a solution of diamine **1** [23] (4.00 g, 22.2 mmol) and triethylamine (6.32 g, 62.4 mmol) in toluene (40 ml). After stirring overnight at room temperature, the reaction mixture was filtered, the solvent was evaporated and the residue was recrystallized twice from EtOAc to produce diamide **2** (3.72 g, 63%) as white crystals with m.p. 136–138°C. ^1H NMR ($CDCl_3$): δ 1.97 (s, 6H, CH_3), 2.67 (t, 4H, CH_2S), 2.73 (s, 4H, SCH_2CH_2S), 3.41 (q, 4H, CH_2N), 6.08 (br s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ 23.48 (CH_3), 31.81 (CH_2S), 39.09 (CH_2N), 170.85 (C=O). IR (deposit from $CHCl_3$ on NaCl plate): 3270 (N–H), 1630 (C=O) cm^{-1}. Anal. Found: C, 45.31; H, 7.49. $C_{10}H_{20}N_2O_2S_2$ calcd.: C, 45.43; H, 7.62%.

3.2. Preparation of diamine 3

Diamide **2** (3.00 g, 11.3 mmol) was added to a suspension of $LiAlH_4$ (2.14 g, 56.4 mmol) in dry THF (300 ml) and the mixture was refluxed for 48 h. The reaction mixture was cooled and carefully quenched with 5% NaOH. The mixture was filtered and the solvent was evaporated to give the residue which was passed through a short bed of alumina with CH_2Cl_2 as eluent to give amine **3** (2.19 g, 82%) as a colorless liquid. ^1H NMR ($CDCl_3$): δ 1.08 (t, 6H, CH_3), 1.41 (br s, 2H, NH), 2.56–2.83 (m, 16H, $CH_2S + CH_2N$). ^{13}C NMR ($CDCl_3$): δ 15.47 (CH_3), 32.35, 32.82 (CH_2S), 44.03, 43.78 (CH_2N). Anal. Found: C, 50.62; H, 10.30. $C_{10}H_{24}N_2S_2$ calcd.: C, 50.80; H, 10.23%.

3.3. Preparation of ferrocenophane diamide 5

Solution A (210 ml) was prepared by dissolving 1,1'-bis(chlorocarbonyl)ferrocene (**4**) [24] (1.55 g, 4.98 mmol) in benzene. Triethylamine (3.5 ml) and diamine **3** (1.18 g, 4.99 mmol) were dissolved in benzene to make 210 ml of solution B. Solutions A and B were added simultaneously over 4 h to 210 ml of vigorously stirred benzene, under argon. The reaction mixture was stirred overnight at room temperature, the solvent was removed *in vacuo* and the residue was purified by column chromatography on basic alumina with EtOAc–petroleum ether (1:1) as eluent to afford diamide **5** (1.00 g, 42%) as orange crystals with m.p. 124–126°C. ^{1}H NMR ($CDCl_3$): δ 1.13 (ill-defined triplet, 6H, CH_3), 2.65–3.27 (m, 8H, CH_2S), 3.40–3.73 (m, 8H, CH_2N), 4.47 (q, 8H, Fc). ^{13}C NMR ($CDCl_3$): δ 12.85, 14.79 (CH_3), 29.34, 30.23, 30.97, 32.51, 33.11 (CH_2S), 42.33, 43.81, 44.67, 48.64 (CH_2N), 69.56, 70.52, 70.65, 72.19, 72.96, 74.65, 82.75 (Fc), 170.85 (C=O). IR (deposit from $CHCl_3$ on NaCl plate): 1608 (C=O) cm^{-1}. Anal. Found: C, 55.80; H, 6.36. $C_{22}H_{30}FeN_2O_2S_2$ calcd.: C, 55.69; H, 6.37%.

3.4. Preparation of ferrocenophane diamine 6

Diamide **5** (0.85 g, 1.79 mmol) was added to a suspension of $LiAlH_4$ (0.34 g, 9.03 mmol) in dry THF (40 ml). The mixture was stirred at room temperature for 22 h. EtOAc (20 ml) and a few drops of water were added, the organic layer was decanted, dried over anhydrous K_2CO_3, and evaporated *in vacuo*. The residue was purified by column chromatography on basic alumina with EtOAc–petroleum ether (1:1) as eluent to give ferrocenophane diamine **6** (0.65 g, 81%) as orange crystals with m.p. 81–82.5°C. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 6H, C8), 2.36 (q, 4H, C7), 2.70 (s, 8H, C5), 2.77 (s, 4H, C6), 3.48 (s, 4H, C4), 4.07 (br s, 8H, C1 & C2). ^{13}C NMR ($CDCl_3$): δ 11.97 (C8), 29.78 (C5'), 32.97 (C6), 46.79 (C7), 53.12 (C4), 54.33 (C5), 68.35 (C1), 71.13 (C2), 84.33 (C3). Anal. Found: C, 59.16; H, 7.75. $C_{22}H_{34}FeN_2S_2$ calcd.: C, 59.18; H, 7.68%.

3.5. Preparations of $PdCl_2$ and Pd(CA) complexes with 6 and 7

Palladium(II) complexes were isolated following the reactions of **6** and **7** with $[PdCl_2(CH_3CN)_2]$ and $[Pd(CA)(CH_3CN)_2]$ in acetonitrile solution. In each case, 0.15 mmol of the ferrocenophane amine was combined with equimolar palladium precursor in 25 ml of acetonitrile at room temperature. After stirring for 3 days, orange ($PdCl_2$) or purple (Pd(CA)) precipitates were collected in 40–60% yields, washed with diethyl ether and dried *in vacuo*. For [**7**]$PdCl_2$]; UV-VIS (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 406 (1.1×10^3), 310 (1.9×10^3), 244 (2.3×10^4). Anal. Found: C, 54.20; H, 8.12; N, 3.41. $C_{38}H_{66}FeN_2S_2PdCl_2$ calcd.: C, 53.81; H, 7.84; N, 3.30%. For [**7**]Pd(CA)]; UV (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 344 (1.5×10^4), 232 (2.2×10^4). Anal. Found: C, 53.30, H, 6.90; N, 2.97. $C_{44}H_{66}N_2S_2Cl_2O_4FePd$ calcd.: C, 53.69; H, 6.76; N, 2.85%. For [**6**]Pd(CA)·$2H_2O$; Anal. Found: C, 42.47; H, 4.27; N, 3.59. $C_{28}H_{38}N_2S_2Cl_2O_6FePd$ calcd.: C, 42.26; H, 4.81; N, 3.52%. A dihydrochloride was isolated from the reaction of **6** with $[PdCl_2(CH_3CN)_2]$. For [**6**]$PdCl_2$ ·2HCl; Anal. Found: C, 38.17; H, 4.88; N, 4.28. $C_{22}H_{36}N_2S_2Cl_4FePd$ calcd.: C, 37.93; H, 5.21; N, 4.02%.

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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