following Zweifel's procedure.[15] The product pentylidinecyclohexane was purified by distillation: 1.28 g (60% yield); bp 94–96 °C (12 mmHg).

Application of Lithium Dicyclohexylborohydride. The Zweifel Cis Olefin Synthesis. Dicyclohexylborane was generated from a THF solution of lithium dicyclohexylborohydride (10 mmol) at 0 °C by using methyl iodide (15 mmol). Hydroboration of 1-hexyne (12 mmol) with this reagent produced the vinylborane. The product was treated with iodine following Zweifel's procedure.[16] There was produced *cis*-1-cyclohexyl-1-hexene, purified by distillation: 1.13 g (68% yield); bp 93–95 °C (12 mmHg).

Acknowledgment. We thank the National Science Foundation for support by Grant CHE 79-18881.

Registry No. LDEA, 19582-13-9; LMEA, 26522-31-6; LiR_2BH_2 (R = *n*-butyl), 84280-32-0; LiR_2BH_2 (R = *n*-hexyl), 91389-03-6; LiR_2BH_2 (R = 2-methyl-1-propyl), 91389-04-7; LiR_2BH_2 (R = 3-methyl-2-butyl), 67813-43-8; LiR_2BH_2 (R = cyclohexyl), 67813-27-8; LiR_2BH_2 (R = tetramethylene), 34571-55-6; LiR_2BH_2 (R = pentamethylene), 91389-05-8; R_2BOMe (R = *n*-butyl), 2344-21-0; R_2BOMe (R = *n*-hexyl), 2344-22-1; R_2BOMe (R = 2-methyl-1-propyl), 17832-17-6; R_2BOMe (R = 3-methyl-2-butyl), 43209-69-4; R_2BOMe (R = cyclohexyl), 32705-46-7; R_2BOMe (R = tetramethylene), 6166-10-5; R_2BOMe (R = pentamethylene), 38050-70-3; 4-vinylcyclohexene, 100-40-3; disiamylborane, 1069-54-1; borinane, 289-53-2; 1-iodo-1-hexyne, 1119-67-1; dicyclohexylborane, 1568-65-6; 1-hexyne, 693-02-7; 2-(4-cyclohexenyl)ethanol, 18240-10-3; pentylidinecyclohexane, 39546-79-7; *cis*-1-cyclohexyl-1-hexene, 17301-35-8.

Synthesis from Diamines of Mono- and Dinuclear Cyclopentadienyliron Dicarbonyl Carbamoyl Compounds. Crystal and Molecular Structure of (μ-$CONH(CH_2)_2NHCO)[CpFe(CO)_2]_2$

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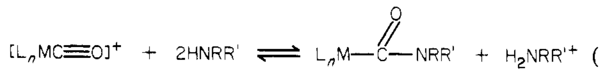
The cationic complex $[CpFe(CO)_3]PF_6$ exhibits three types of reactivity toward diamines. It reacts with the unsymmetrical primary diamine $H_2NCH_2CMe_2NH_2$ to give the mononuclear cationic carbamoyl complex $[CpFe(CO)_2(CONHCH_2CMe_2NH_3)]PF_6$ (**1**); spectroscopic studies indicate relatively strong intermolecular hydrogen bonding between the carbamoyl oxygen and an NH_3^+ group. Complex **1** is readily deprotonated to yield its neutral analogue $CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (**2**) that can be further deprotonated in the presence of $[CpFe(CO)_3]PF_6$ to form the first reported dinuclear "dicarbamoyl-bridged" complex (μ-$CONHCH_2CMe_2NHCO)[CpFe(CO)_2]_2$ (**3**). In addition, $[CpFe(CO)_3]PF_6$ reacts with the unsymmetrical primary/tertiary diamine $H_2N(CH_2)_2NMe_2$ and with $H_2N(CH_2)_2OH$ to form exclusively $CpFe(CO)_2(CONH(CH_2)_2NMe_2)$ (**4**) and $CpFe(CO)_2(CONH(CH_2)_2OH)$ (**5**), respectively. Finally, $[CpFe(CO)_3]PF_6$ reacts with symmetrical primary and secondary diamines such as $RHN(CH_2)_xNHR$ (R = H, x = 2, 3; R = Me, x = 2) and the cyclic diamine piperazine $HN(CH_2CH_2)_2NH$ to yield exclusively the dinuclear dicarbamoyl-bridged complexes (μ-$CONR(CH_2)_xNRCO)[CpFe(CO)_2]_2$ (R = H, x = 2 (**6**); R = H, x = 3 (**7**); R = Me, x = 2 (**8**)) and (μ-$CON(CH_2CH_2)_2NCO)[CpFe(CO)_2]_2$ (**9**). The molecular structure of complex **6** was determined by X-ray diffraction. The crystals are triclinic of space group $P\bar{1}$ with two crystallographically independent molecules per unit cell, each having an inversion center, and with cell constants of a = 9.504 (7) Å, b = 8.435 (5) Å, c = 12.989 (9) Å, α = 101.20 (5)°, β = 104.80 (5)°, and γ = 100.49 (5)°. The structure was refined to R = 0.043 and R_w = 0.047 for 1485 independent observed reflections having $I \geq 3.0\sigma(I)$. The dimensions of the two crystallographically independent molecules do not differ significantly; the average Fe–C(carbamoyl) distance of 1.99 Å is significantly longer than the average Fe–C(CO) distance of 1.76 Å. The overall geometry of the structure shows the metal centers to be in a transoid orientation about the bridging ligand as dictated by the inversion center, and the central part of the structure adopts a gauche–trans–gauche conformation. Each molecule is connected through weak hydrogen bonds to two others.

Introduction

Many cationic, and to a lesser extent neutral, metal carbonyl complexes are known to react directly with nucleophiles such as ammonia and primary and secondary amines to yield carbamoyl complexes[1-3] (eq 1).



$$[L_nMC\equiv O]^+ + 2HNRR' \rightleftharpoons L_nM-\overset{O}{\overset{\|}{C}}-NRR' + H_2NRR'^+ \quad (1)$$

R, R′ = H and/or alkyl

Although an extensive range of amines has been studied in this reaction, no reports involving the analogous reactions with diamines have been noted. In this paper, we report the reaction of $[CpFe(CO)_3]PF_6$[4] with 2-aminoethanol and a range of diamines to yield both neutral and cationic monomeric carbamoyl complexes, as well as neutral dinuclear dicarbamoyl-bridged compounds. Some of the neutral monomeric complexes have "dangling" NH_2

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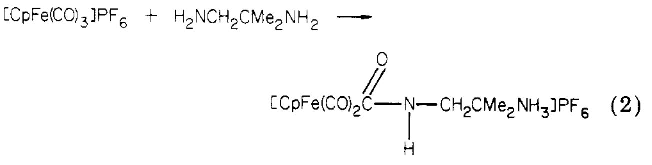
or OH functionalities and thus have the potential for forming homo- or heterobimetallic dicarbamoyl-bridged or mixed alkoxycarbonyl/carbamoyl-bridged compounds.

The present study also constitutes the first structural characterization of a dinuclear carbamoyl complex in which the two metal centers are linked via a dicarbamoyl bridge, i.e., the $(CONH(CH_2)_2NHCO)$ moiety in $(\mu\text{-}CONH(CH_2)_2NHCO)[CpFe(CO)_2]_2$ (**6**). An understanding of the conformational and stereochemical characteristics of such compounds may prove valuable in explaining their reactivities, especially since, as several authors[5,6] have recently noted, interactions between two metal reaction sites in close proximity may profoundly affect the chemical properties of their coordinated organic moieties.

Results and Discussion

Synthesis and Characterization of $[CpFe(CO)_2(CONHCH_2CMe_2NH_3)]PF_6$ (1), $CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (2), and $(\mu\text{-}CONHCH_2CMe_2NHCO)[CpFe(CO)_2]_2$ (3). The reaction of an excess of the unsymmetrical primary diamine $H_2NCH_2CMe_2NH_2$ with a suspension of $[CpFe(CO)_3]PF_6$ in diethyl ether leads to the formation of the insoluble yellow complex 1 in nearly quantitative yield (eq 2). The



$$[CpFe(CO)_3]PF_6 + H_2NCH_2CMe_2NH_2 \longrightarrow [CpFe(CO)_2C(=O)\text{—}N(H)\text{—}CH_2CMe_2NH_3]PF_6 \quad (2)$$

1

formulation of this complex is clearly established by mass spectrometry (parent ion, M^+, m/e 293), elemental analysis, and its conductivity [Λ (1×10^{-3} M) = 150 Ω^{-1} cm^2 mol^{-1} in acetone]. An ^1H NMR spectrum in CD_3CN (Table I) unambiguously demonstrates the presence of only one isomer, complex 1, in solution since only one Cp ring resonance at δ 5.03 is observed, and the methylene group of the diamine is observed as a doublet at δ 3.15 ($^3J_{HH}$ = 5.9 Hz) due to spin–spin coupling from the carbamoyl NH proton. It is presumed that steric requirements of the CMe_2 group dictate the formation of only isomer 1. A more detailed spectroscopic discussion of complex 1 is deferred until later.

Complex 1 is readily deprotonated by an excess of K_2CO_3 in CH_3CN to give the bright yellow highly soluble compound $CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (**2**). This is a sharp-melting, nonconducting compound that displays a mass spectrum which contains no parent ion, M^+, but does show m/e 264 ($M^+ - CO$), 236 ($M^+ - 2CO$), 208 ($M^+ - 3CO$). As expected, an ^1H NMR spectrum of complex 2 in CD_3CN (Table I) shows Cp ring, CH_2, and Me resonances at slightly higher field than those of its precursor, complex 1. Neither the NH resonance at δ 6.00 nor the NH_2 resonance at δ 1.30 is markedly concentration dependent; i.e., they both shift by less than 0.05 ppm over a range of 0.30–0.03 M. The NH resonance of complex 1 shows a very similar trend, i.e. a shift of less than 0.03 ppm on decreasing the concentration from 0.15 to 0.03 M. However, over the same concentration range, the NH_3^+ resonance shifts by 1.00 ppm, decreasing from δ 5.87 to 4.87, thus suggesting that the NH_3^+ group is participating in at least moderately strong intermolecular hydrogen bonding.[7,8]

Table I. ^1H NMR Spectra[a,b] of Complexes 1–9

complexes	solv	NH	Cp	CONCH$_2$	Me	others
$[CpFe(CO)_2(CONHCH_2CMe_2NH_3)]PF_6$ (1)	CD_3CN	6.73	5.03	3.15 (d, $^3J_{HH}$ = 5.9)	1.29	5.87 (NH_3^+)
$CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (2)	CD_3CN	6.00	4.99	2.98 (d, $^3J_{HH}$ = 6.1)	0.98	1.30 (NH_2)
	$CDCl_3$	5.74	4.92	3.08 (d, $^3J_{HH}$ = 5.9)	1.05	1.26 (NH_2)
$(\mu\text{-}CONHCH_2CMe_2NHCO)[CpFe(CO)_2]_2$[c] (3)	CD_3CN	6.66, 6.46	5.01, 4.97	3.01 (d, $^3J_{HH}$ = 6.4)	1.21	
$CpFe(CO)_2(CONHCH_2CH_2NMe_2)$ (4)	$CDCl_3$	5.83	4.93	3.31 (q, $^3J_{HH}$ = 6.4)	2.22	2.34 (t, $^3J_{HH}$ = 6.4, CH_2)
$CpFe(CO)_2(CONHCH_2CH_2OH)$[d] (5)	CD_3CN	6.19	4.98	3.17 (q, $^3J_{HH}$ = 5.4)		3.45 (t, $^3J_{HH}$ = 5.4, CH_2)
$(\mu\text{-}CONH(CH_2)_2NHCO)[CpFe(CO)_2]_2$[e] (6)	CD_2Cl_2	6.09	4.96	3.22 (t, $^3J_{HH}$ = 5.0, $^4J_{HH}$ = 2.5)		
$(\mu\text{-}CONH(CH_2)_3NHCO)[CpFe(CO)_2]_2$ (7)	$CDCl_3$	5.94	4.97	3.27 (q, $^3J_{HH}$ = 6.1)		1.51 (q′, $^3J_{HH}$ = 6.1, CH_2)
$(\mu\text{-}CONMe(CH_2)_2NMeCO)[CpFe(CO)_2]_2$ (8)	$CDCl_3$		4.93	3.49	3.08	
$(\mu\text{-}CON(CH_2CH_2)_2NCO)[CpFe(CO)_2]_2$ (9)	$CDCl_3$		4.90	3.57		

[a] Chemical shift in δ and coupling constants in Hz. [b] d = doublet, t = triplet, q = quartet, q′ = quintet. All undesignated resonances are singlets. [c] Spin-tickling the highest field NH resonance collapses the CH_2 doublet to a singlet. [d] No OH resonance is observed though integration suggests it may be hidden under the δ 3.45 resonance. [e] The 1:1:1 virtually coupled triplet at δ 3.22 collapses to a singlet upon spin-tickling the NH protons.

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Table II. $^{13}C\{^1H\}$ NMR Spectra[a] of Complexes 1-7

complexes	solv	CO	CONH	Cp	CONCH$_2$	Me	CMe$_2$
1[b]	CD_3CN	214.76	207.68	86.56	50.86	23.89	58.08
2[b]	CD_3CN	216.18	193.90	86.94	53.31	28.69	51.05
	$CDCl_3$	213.93	194.02	85.41	52.12	28.11	49.78
3[b,c]	CD_3CN	216.26, 215.92	198.32, 194.08	86.96	52.35	24.88	58.60
4[d]	$CDCl_3$	214.36	194.90	85.81	39.10, $\underline{58.60}$	45.25	
5[d]	CD_3CN	216.09	197.46	87.11	45.25, $\underline{63.10}$		
6	CD_2Cl_2	214.84	195.77	86.13	42.97		
7[d]	$CDCl_3$	214.27	195.63	85.73	$\underline{30.94}$, 37.62		

[a] Chemical shifts in δ_C. [b] ^{13}C NMR resonances for CH_2 and CMe_2 are assigned on the basis of proton coupled spectra. [c] Uncertain $^{13}C\{^1H\}$ NMR assignment of CONH resonances due to low signal to noise ratio. [d] Underlined resonances are assigned to other CH_2 groups in the complexes.

Table III. Selected Solution[a] and Solid[b] Infrared Stretching Frequencies for Complexes 1-9[c]

complex	ν_{NH}, cm^{-1}	$\nu_{C\equiv O}$, cm^{-1}	$\nu_{C=O}$, cm^{-1}	ν_{OH}, cm^{-1}
1[d]		2030 (s), 1973 (vs)		
	[3461 (m) (CONH), 3266 (w, br) (NH_3^+)]	[2028 (s), 1976 (vs)]	[1513 (m)]	
2	3458 (w), 3335 (w, br) (CONH + NH_2)	2020 (s), 1961 (vs)	1592 (m, br)	
	[3350 (w, sh), 3290 (m, br) (CONH + NH_2)]	[2018 (s), 2007 (s), 1962 (vs), 1930 (w)]	[1567 (m)]	
3	3459 (w), 3340 (w, br)	2019 (s), 1963 (vs)	1602 (m), 1596 (m)	
	[3380 (m), 3305 (w)]	[2018 (s), 2003 (m), 1970 (s), 1948 (vs)]	[1593 (m), 1561 (m)]	
4	3430 (m, br)	2018 (s), 1963 (vs)	1590 (m)	
	[3317 (m)]	[2018 (s), 2008 (s), 1963 (vs)]	[1575 (s)]	
5	3460 (m)	2022 (s), 1965 (vs)	1590 (m)	3605 (w)
	[3345 (m)]	[2016 (s), 1956 (vs)]	[1540 (m)]	[3224 (m, br)]
6	3364 (w)	2021 (s), 1963 (vs)	1584 (m, br)	
	[3368 (w), 3320 (w)]	[2023 (s), 1974 (vs), 1956 (s)]	[1566 (s)]	
7[e,f]		2019 (s), 1960 (vs)	1581 (m, br)	
8[g]		2022 (s), 1962 (vs)	1538 (m, br)	
		[2016 (s), 1962 (s), 1955 (s), 1944 (s)]	[1538 (s)]	
9[g]		2024 (s), 1965 (vs)	1545 (m)	
		[2019 (s), 1949 (vs)]	[1546 (s)]	

[a] CH_2Cl_2 solutions except for complex 1 (CH_3CN). [b] Nujol mull in brackets. [c] w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad. [d] ν_{NH} (CONH and NH_3^+) and $\nu_{C=O}$ are masked by CH_3CN solvent bands. [e] ν_{NH} not observed in CH_2Cl_2 solution. [f] Not isolated as a solid. [g] Complexes do not contain N-H bonds, and consequently no ν_{NH} bands are observed.

Comparing the $^{13}C\{^1H\}$ NMR spectra of complexes 1 and 2 in CD_3CN (Table II), it is obvious that all the resonances associated with the carbamoyl ligand are different in the two complexes. The "crossover" of the CMe_2 and CH_2 resonance positions from complex 1 to complex 2 is readily understandable in terms of the loss of deshielding from the $CMe_2NH_3^+$ resonance upon deprotonation of the NH_3^+ group. Whereas the CONH resonance of complex 2 occurs at δ_c 193.90 [δ_c 194.02 in $CDCl_3$], well within the range delimited by the "normal values" (δ_c 193.0–195.2 in $CDCl_3$)[9] for complexes of this type and roughly comparable to those of the other neutral complexes in Table II, the CONH resonance of complex 1 occurs at the considerably lower field of δ_c 207.68. This shift to lower field may be attributed to deshielding of the carbamoyl carbon due to its being more positively charged through intermolecular hydrogen bonding[10] of the carbamoyl oxygen with the protons from an NH_3^+ group on a neighboring molecule.

Further evidence for hydrogen bonding is obtained from IR data (Table III). Solution spectra in the ν_{NH}(CONH), $\nu_{NH}(NH_3^+)$, and $\nu_{C=O}$(CONH) regions could not be obtained for complex 1 (due to insolubility in a suitable solvent); however, a Nujol mull spectrum shows a very low $\nu_{C=O}$ of 1513 cm^{-1} (cf. 1540–1590 cm^{-1} for other Nujol mull $\nu_{C=O}$ values in Table III) that clearly attests to the strength of the –N—H···O=C– hydrogen-bonding interaction. The high ν_{NH}(CONH) of 3461 cm^{-1} in the solid phase (cf. 3300–3380 cm^{-1} for other ν_{NH}(CONH) values in the solid phase in Table III) suggests that it has little or no participation in hydrogen bonding. The relatively modest increase in $\nu_{C=O}$ on changing from the solid state to solution in complex 2 is consistent with weak hydrogen bonding.[11]

The compound $CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (2) is readily deprotonated (eq 3) by a fivefold excess of K_2CO_3

$$\underset{2}{CpFe(CO)_2(CONHCH_2CMe_2NH_2)} + CpFe(CO)_3^+ + K_2CO_3 \rightarrow \underset{3}{(\mu\text{-}CONHCH_2CMe_2NHCO)[CpFe(CO)_2]_2} + KHCO_3 + K^+ \quad (3)$$

in the presence of 1 equiv of $[CpFe(CO)_3]PF_6$ in CH_3CN to give a 66% yield of the first reported dinuclear dicarbamoyl-bridged complex (μ-$CONHCH_2CMe_2NHCO$)$[CpFe(CO)_2]_2$ (3). The other organometallic product formed in this reaction is $[CpFe(CO)_2]_2$ that is produced

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through a competitive reduction of $[CpFe(CO)_3]PF_6$ by K_2CO_3.

Complex 3 has been fully characterized by elemental analysis, mass spectrometry [m/e 468 ($M^+ - CO$), 440 ($M^+ - 2CO$), 412 ($M^+ - 3CO$), and 384 ($M^+ - 4CO$)] and NMR and IR spectroscopies. An ^1H NMR spectrum in CD_3CN shows positional characteristics very similar to complexes 1 and 2; however, now two NH and Cp ring resonances are observed (Table I). A $^{13}C\{^1H\}$ NMR spectrum in the same solvent shows only one Cp ring resonance but two CO resonances at δ_c 216.26 and 215.92. Low signal to noise ratio, due to insolubility, makes an assignment of the CONH resonances difficult. The remaining CH_2, CMe_2, and Me resonances are at positions that are close to those of complexes 1 and 2 (Table II). Infrared spectra in solution and in the solid state show two $\nu_{C=O}$ bands (Table III). The moderate increase in ν_{NH} and $\nu_{C=O}$ on changing from the solid state to solution is, as in complex 2, compatible with the presence of weak intermolecular hydrogen bonding.[11]

Synthesis and Characterization of $CpFe(CO)_2(CONH(CH_2)_2NMe_2)$ (4) and $CpFe(CO)_2(CONH(CH_2)_2OH)$ (5). Reacting a diethyl ether suspension of $[CpFe(CO)_3]PF_6$ with an excess of the unsymmetrical primary/tertiary diamine $H_2N(CH_2)_2NMe_2$ produces the bright yellow neutral complexes $CpFe(CO)_2(CONH(CH_2)_2NMe_2)$ (4) in 86% yield (eq 4). This sharp-melting

$$CpFe(CO)_3^+ + 2H_2N(CH_2)_2E \rightarrow CpFe(CO)_2(CONH(CH_2)_2E) + H_3^+N(CH_2)_2E \quad (4)$$

$$E = NMe_2\ (4)\ \text{or}\ OH\ (5)$$

complex displays mass spectral evidence in agreement with its formulation, i.e., m/e 264 ($M^+ - CO$), 236 ($M^+ - 2CO$), and 208 ($M^+ - 3CO$). Unambiguous assignments of ^1H NMR resonances of complex 4 in $CDCl_3$ are shown in Table I. A $^{13}C\{^1H\}$ NMR spectrum of this compound in the same solvent shows CO and CONH resonances at the normal values[9] of δ_c 214.36 and 194.40, respectively; the Me and CH_2 resonances are also at normal positions. Infrared data (Table III) are again indicative of weak intermolecular hydrogen bonding[11] since both ν_{NH} and $\nu_{C=O}$ are subject to a moderate increase in frequency upon changing from the solid phase to solution.

The formation of the neutral complex 4 rather than a cationic complex of type 1 may be due to the strict constraints imposed by the two methyl groups on nitrogen that prevent the formation of a hydrogen bond stabilized ammonium complex. The instability of the ammonium complex $[CpFe(CO)_2(CONH(CH_2)_2NHMe_2)]SO_3CF_3$ (δ 5.03 (Cp ring) and 2.81 (Me) in CD_3CN; cf. complex 4 δ 4.97 (Cp ring) and 2.16 (Me) in the same solvent), generated in situ in an NMR tube by addition of an equimolar amount of HSO_3CF_3 to a CD_3CN solution of complex 4, is shown by its rapid decomposition to give $[CpFe(CO)_2]_2$ and unknown organic products.

The reaction of an excess of 2-aminoethanol with an acetonitrile solution of $[CpFe(CO)_3]PF_6$ generates a deep yellow solution from which yellow crystals of $CpFe(CO)_2(CONH(CH_2)_2OH)$ (5) are isolated in 63% yield. Although 2-aminoethanol has the potential to form a complex with a carbamoyl, an alkoxycarbonyl, or both groups, even a cursory evaluation of the NMR and IR data, presented in Tables I–III, leaves no doubt that under these reaction conditions only the carbamoyl complex 5 is formed. The increases in ν_{NH}, $\nu_{C=O}$, and particularly ν_{OH} on changing from the solid phase to solution (Table III) again imply intermolecular hydrogen bonding.[11]

Synthesis and Characterization of (μ-$CONR(CH_2)_xNRCO)[CpFe(CO)_2]_2$ (R = H, x = 2 (6); R = H, x = 3 (7); R = Me, x = 2 (8)) and (μ-$CON(CH_2CH_2)_2NCO)[CpFe(CO)_2]_2$ (9). Stirring a diethyl ether suspension of $[CpFe(CO)_3]PF_6$ with an excess of the symmetric primary diamines $H_2N(CH_2)_2NH_2$ or $H_2N(CH_2)_3NH_2$ leads to the exclusive formation of the dinuclear dicarbamoyl-bridged complexes (μ-$CONH(CH_2)_xNHCO)[CpFe(CO)_2]_2$ (x = 2, 6, and x = 3, 7, respectively) (eq 5). Similarly, the treatment of an CH_3CN

$$2CpFe(CO)_3^+ + 3HRN(CH_2)_xNHR \rightarrow (\mu\text{-}CONR(CH_2)_xNRCO)[CpFe(CO)_2]_2 + 2H_2RN^+(CH_2)_xNHR \quad (5)$$

$$R = H,\ x = 2\ (6);\ R = H,\ x = 3\ (7);\ R = Me,\ x = 2\ (8)$$

solution of $[CpFe(CO)_3]PF_6$ with an excess of the symmetric secondary diamine $MeHN(CH_2)_2NHMe$ or the cyclic symmetric diamine piperazine $HN(CH_2CH_2)_2NH$ leads to the immediate precipitation of the highly insoluble dinuclear dicarbamoyl-bridged complexes (μ-$CONMe(CH_2)_2NMeCO)[CpFe(CO)_2]_2$ (8) and (μ-$CON(CH_2CH_2)_2NCO)[CpFe(CO)_2]_2$ (9), respectively.

Although complex 7 has not been isolated as a solid, its solution characteristics (Tables I–III) clearly demonstrate its dinuclear nature. Complexes 6, 8, and 9 are yellow nonconducting compounds that have been characterized by elemental analysis and mass spectrometry as well as NMR and IR spectroscopies. These three complexes exhibit ^1H NMR spectra (Table I) that are entirely compatible with the above formulations. Complex 6 displays a $^{13}C\{^1H\}$ NMR spectrum (Table II) that is again fully consistent with a symmetric dinuclear structure. Both complexes 8 and 9 are too insoluble to obtain $^{13}C\{^1H\}$ NMR spectra.

A solid-state IR spectrum of complex 6 shows two ν_{NH} bonds at 3320 and 3368 cm^{-1} and a $\nu_{C=O}$ bond at 1566 cm^{-1} that become single bands at 3464 and 1584 cm^{-1}, respectively, in CH_2Cl_2 solution (Table III). These observations are interpreted in terms of weak intermolecular hydrogen bonding in the solid,[11] an interpretation which is established by an X-ray structure determination (vide infra) which shows that in the solid-state complex 6 exists as an extended sheet composed of molecules that are connected by two different types of intermolecular hydrogen bonding. The $\nu_{C=O}$ stretching frequencies of tertiary carbamoyl compounds such as 8 and 9 are both expected, and observed, to be independent of the physical state since hydrogen bonding is no longer possible.

The formation of the dinuclear complexes 6–9 presumably occurs in an analogous manner to that of dinuclear species 3, i.e., coupling of $[CpFe(CO)_3]PF_6$ and a neutral complex of the general type $CpFe(CO)_2(CONRCR'_2CR''_2NHR)$ in the presence of base. Since each of these reactions is carried out in the presence of excess diamine, the requirement of the presence of base is always fulfilled. Thus, the formation of a protonated species like complex 1 vs. the formation of dinuclear complexes such as 3 and 6–9 represents a competition between the reactions of the NHR group of $CpFe(CO)_2(CONRCR'_2CR''_2NHR)$ with H^+ or $[CpFe(CO)_3]PF_6$. An appraisal of the basicity of the various coordinated diamines is virtually impossible, since as has been previously noted[8,12] amine base strength is generally more dependent upon solvation phenomena than steric or electronic factors. Thus, little of value can be definitively stated concerning the individual influences that promote or retard the re-

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Table IV. Crystallographic Parameters for (μ-CONH$(CH_2)_2$NHCO)[CpFe$(CO)_2]_2$ (6)

space group	$P\bar{1}$
cell parameters	
a, Å	9.504 (7)
b, Å	8.435 (5)
c, Å	12.989 (9)
α, deg	101.20 (5)
β, deg	104.80 (5)
γ, deg	100.49 (5)
cell vol., Å^3	957 (1)
density	
exptl,[a] g/cm^3	1.64
calcd (Z = 2), g/cm^3	1.62
linear abs coeff μ, cm^{-1}	15.93
Mo Kα radiatn wavelength λ, Å	0.710 69

[a] Measured by flotation in CCl_4/CH_3I.

Table V. Atomic Coordinates and Isotropic Thermal Parameters for (μ-CONH$(CH_2)_2$NHCO)[CpFe$(CO)_2]_2$ (6)[a]

atom[b,c]	x	y	x	B,[d] Å^2
FeA	0.5077 (1)	0.2696 (1)	0.3084 (1)	3.5 (1)
FeB	0.8209 (1)	−0.2284 (2)	0.1299 (1)	3.6 (1)
C1A	0.5396 (9)	0.2598 (12)	0.1798 (8)	5.1 (3)
C1B	0.6371 (11)	−0.2861 (10)	0.1410 (6)	3.9 (3)
C2A	0.4160 (11)	0.4324 (12)	0.3024 (8)	4.9 (3)
C2B	0.7825 (11)	−0.0708 (14)	0.0688 (8)	5.4 (4)
O1A	0.5597 (8)	0.2541 (10)	0.0971 (6)	7.7 (3)
O1B	0.5197 (7)	−0.3246 (9)	0.1464 (5)	6.4 (3)
O2A	0.3503 (8)	0.5353 (9)	0.3006 (6)	7.3 (3)
O2B	0.7572 (9)	0.0339 (10)	0.0253 (6)	7.7 (3)
C3A	0.7067 (8)	0.4319 (10)	0.3747 (6)	3.0 (3)
C3B	0.8866 (8)	−0.0626 (10)	0.2752 (6)	2.8 (3)
O3A	0.7181 (5)	0.5827 (7)	0.4094 (5)	4.2 (2)
O3B	0.9422 (6)	0.0844 (7)	0.2885 (4)	4.1 (2)
NA	0.8304 (7)	0.3758 (8)	0.3813 (5)	3.3 (2)
NB	0.8664 (7)	−0.1207 (8)	0.3622 (5)	3.1 (2)
C4A	0.9825 (8)	0.4826 (11)	0.4380 (6)	3.3 (3)
C4B	0.9157 (8)	−0.0132 (11)	0.4737 (6)	3.1 (2)
C11A	0.5643 (10)	0.1643 (12)	0.4435 (8)	4.2 (3)
C11B	1.0221 (10)	−0.2385 (13)	0.0955 (9)	5.2 (4)
C12A	0.5529 (10)	0.0518 (11)	0.3466 (8)	4.4 (3)
C12B	0.9000 (13)	−0.3460 (16)	0.0056 (8)	6.1 (4)
C13A	0.4067 (10)	0.0122 (11)	0.2748 (9)	4.7 (3)
C13B	0.8242 (11)	−0.4659 (14)	0.0428 (8)	5.5 (4)
C14A	0.3248 (10)	0.1078 (12)	0.3262 (9)	5.0 (4)
C14B	0.8963 (11)	−0.4396 (11)	0.1551 (8)	4.6 (4)
C15A	0.4216 (11)	0.2006 (12)	0.4318 (9)	4.9 (4)
C15B	1.0211 (10)	−0.3027 (12)	0.1864 (8)	4.5 (3)
H1A	0.833 (9)	0.271 (11)	0.352 (7)	3.2 (0)
H1B	0.834 (9)	−0.224 (10)	0.365 (7)	3.2 (0)
H2A	1.041 (9)	0.421 (10)	0.406 (6)	3.2 (0)
H2B	0.907 (9)	0.106 (11)	0.475 (7)	3.2 (0)
H3A	0.992 (9)	0.585 (11)	0.417 (6)	3.2 (0)
H3B	0.867 (9)	−0.081 (10)	0.521 (7)	3.2 (0)
H11A	0.649 (10)	0.222 (10)	0.503 (7)	3.2 (0)
H11B	1.087 (10)	−0.172 (11)	0.090 (8)	3.2 (0)
H12A	0.618 (10)	0.004 (10)	0.331 (7)	3.2 (0)
H12B	0.880 (10)	−0.309 (10)	−0.054 (7)	3.2 (0)
H13A	0.378 (9)	−0.058 (11)	0.200 (7)	3.2 (0)
H13B	0.741 (10)	−0.545 (10)	0.012 (7)	3.2 (0)
H14A	0.230 (10)	0.118 (10)	0.296 (7)	3.2 (0)
H14B	0.862 (10)	−0.512 (11)	0.195 (7)	3.2 (0)
H15A	0.389 (9)	0.273 (10)	0.484 (7)	3.2 (0)
H15B	1.077 (9)	−0.257 (10)	0.254 (7)	3.2 (0)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figure 1. [c] A refers to molecule A and B to molecule B. [d] B is the isotropic average of the anisotropic temperature factors.

actions of CpFe$(CO)_2$(CONRCR$'_2$CR$''_2$NHR) with H^+ or [CpFe$(CO)_3]^+$ and thus the formation of a protonated complex of type **1** or dinuclear complexes of type **3** and **6–9**.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) of (μ-CONH$(CH_2)_2$NHCO)[CpFe$(CO)_2]_2$ (6) and Comparison with *N*,*N'*-Ethylenedibenzamide,[21] PhC(O)NH$(CH_2)_2$NHC(O)Ph [C][a,b]

	molecule A	molecule B	[C]
	(a) Distances		
Fe-C1	1.762 (8)	1.777 (7)	
Fe-C2	1.759 (8)	1.723 (8)	
Fe-C3	1.990 (6)	1.991 (6)	
Fe-C11	2.110 (8)	2.084 (8)	
Fe-C12	2.083 (8)	2.104 (9)	
Fe-C13	2.118 (8)	2.110 (8)	
Fe-C14	2.098 (8)	2.089 (8)	
Fe-C15	2.107 (8)	2.110 (8)	
C1-O1	1.131 (10)	1.128 (9)	
C2-O2	1.159 (10)	1.165 (11)	
C3-O3	1.239 (7)	1.216 (7)	1.235 (6)
C3-N	1.335 (8)	1.358 (8)	1.343 (6)
N-C4	1.472 (8)	1.460 (8)	1.445 (6)
C4-C′4[c]	1.516 (9)	1.529 (9)	1.522 (6)
N-H1	0.897 (68)	0.877 (67)	0.89 (3)
C4-H2	0.949 (65)	1.025 (68)	1.02 (3)
C4-H3	0.949 (65)	1.055 (66)	0.98 (3)
	(b) Angles		
C1-Fe-C2	94.75 (35)	93.50 (36)	
C1-Fe-C3	87.15 (30)	90.65 (28)	
C2-Fe-C3	91.14 (31)	88.23 (33)	
Fe-C1-O1	180.00 (69)	178.47 (62)	
Fe-C2-O2	176.23 (69)	178.93 (76)	
M-C3-O3[d]	121.70 (45)	123.36 (45)	121.5 (4)
M-C3-N[d]	118.71 (44)	116.73 (42)	117.7 (4)
N-C3-O3	119.58 (56)	119.88 (54)	120.8 (4)
C3-N-C4	122.90 (51)	122.03 (50)	122.4 (4)
N-C4-C′4[c]	111.56 (51)	110.98 (50)	112.0 (4)
	(c) Torsional Angles		
C3-N-C4-C′4[c]	75.5	−79.4	88.8
N-C4-C′4-N′	−180	−180	180
M-C3-N-C4[c]	−174.1	177.4	179.2
O3-C3-N-C4	6.1	−2.8	−0.7

(d) Intermolecular Hydrogen Bonding

D-H· · ·A[b]	angle	D· · ·A	H· · ·A	D-H
NA-H1A· · ·O3B[e]	153 (6)	3.012 (7)	2.18 (7)	0.90 (7)
NB-H1B· · ·O3A[f]	158 (6)	2.894 (7)	2.06 (7)	0.88 (7)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figure 1. [c] For molecule A, the symmetry code relating primed and nonprimed atoms is $2 - x, 1 - y, 1 - z$; for molecule B, it is $2 - x, -y, 1 - z$. [d] M is iron in molecules A and B and carbon in [C]. [e] Symmetry code: x, y, z. [f] Symmetry code $x, -1 + y, z$.

Crystal and Molecular Structure of (μ-CONH$(CH_2)_2$NHCO)[CpFe$(CO)_2]_2$ (6). The dinuclear dicarbamoyl-bridged complex **6** crystallizes in centrosymmetric space group $P\bar{1}$. The unit cell comprises two crystallographically centrosymmetric independent molecules (Tables IV–VI). The dimensions and conformations of the two independent half-molecules do not differ significantly from each other, and, in the discussion that follows, appropriate mean values are quoted.

Bond Distances and Angles. (a) Around the Fe Atoms. Figure 1 shows that each Fe atom is coordinated to a planar Cp ring, two CO ligands, and a planar carbamoyl moiety. Like other carbamoyl complexes of this type, e.g., CpRu$(CO)_2(CONH_2)$[13] and CpMn(CO)(NO)$(CONH_2)$,[14] the bond angles between the monodentate ligands at the metal atom are close to the octahedral value of 90° (Table VI).

The mean Fe–C(Cp ring) distance of ca. 2.10 Å (Fe–C-

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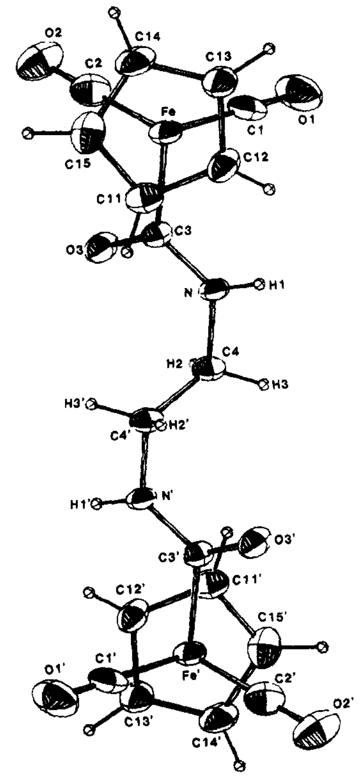

Figure 1. ORTEP drawing of the coordination about each Fe atom in (μ-CONH$(CH_2)_2$NHCO)$[CpFe(CO)_2]_2$ (**6**). The thermal ellipsoid boundaries are at the 30% probability level except for those of the H atoms that are represented by spheres of a fixed arbitrary radius.

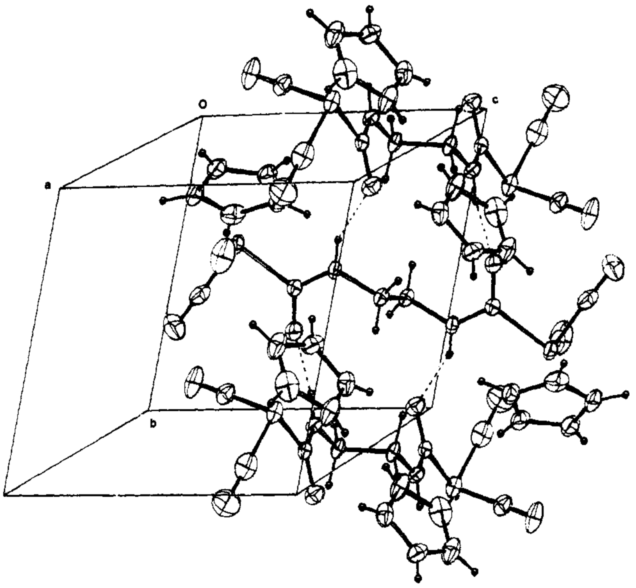

Figure 2. A perspective view of the unit cell of (μ-CONH$(CH_2)_2$NHCO)$[CpFe(CO)_2]_2$ (**6**) showing intermolecular hydrogen bonding as broken lines (---).

(Cp ring) [center of gravity] = 1.73 Å) and the average C–C ring distance of 1.403 Å are within the limits described by $[CpFe(CO)_2]_2$[15] (Fe–C(Cp) = ca. 2.11 Å and C–C = ca. 1.37 Å) and Cp_2Fe[16] (Fe–C(Cp) = ca. 2.05 Å and C–C = ca. 1.43 Å). The Cp rings are planar, deviating by less than 0.02 Å from the best plane.

The Fe–C(CO) and C–O distances and the Fe–C–O angles (Table VI) are comparable to those of other dinuclear compounds such as (μ-$(PhO)_2P(CH_2)_2P(OPh)_2$)[CpFe(CO)I]$_2$,[5] (μ-$(PhO)_2P(CH_2)_2P(OPh)_2$)$Me_2Si[\eta^5$-C_5H_4Fe(CO)I]$_2$,[5] and (μ-S_x)$[CpFe(CO)_2]_2$ (x = 3, 4).[17]

(b) Around the Dicarbamoyl Bridge Moiety. In common with other carbamoyl complexes such as $CpRu(CO)_2(CONH_2)$,[13] $CpW(CO)_2(NH_2Me)(CONHMe)$,[18] $CpMn(CO)(NO)(CONH_2)$,[14] and $Mn(CO)_4(NH_2Me)(CONHMe)$[19] as well as organic amides[20] and diamides,[21] the carbamoyl carbon atoms of complex **6** are sp^2 hybridized; i.e., all the bond angles around the carbon atom of the Fe—C(=O)N moiety are nearly 120° (Table VI) and the sum of the angles at carbon is 359.99°.

The C–N and C–O bond distances of complex **6** are the same, i.e., within the 3σ criterion, as those compounds mentioned above. The Fe–C (carbamoyl) distance in complex **6** is considerably longer (ca. 0.24 Å) than the terminal Fe–C(CO) distances. However, the 1.991 (6) Å length of the Fe–C(carbamoyl) distance is in excellent agreement with other Fe–C(sp^2 hybridized) bond distances, i.e., 1.99–2.03 Å.[22-26] The apparent slight contraction of the metal–carbamoyl bond noted in an early review[1] of carbamoyl chemistry is not clearly manifested in the present complex. The remaining atoms of the bridging unit of the iron dicarbamoyl bridged complex adopt very similar bond angles and distances to those of its organic analogue, *N,N'*-ethylenedibenzamide, PhC(O)NH$(CH_2)_2$NHC(O)Ph[21] (Table VI).

Dihedral and Torsion Angles. (a) Dihedral Angles. The plane formed by the Cp ring is tilted at an average angle of 36.9° away from the amide plane. The angle between the Cp ring plane and the normal vector ON of the amide moiety is, on average, 16.8° (the Cp ring plane is closer to the carbamoyl N atom than the O atom). The dihedral angle between the amide plane and that formed by the $NHCH_2CH_2NH$ moiety is, on average, 100.1° which is close to the 91.5° observed for *N,N'*-ethylenedibenzamide.[21]

(b) Torsion Angles. Palmer and Brisse[21] have shown through a conformational analysis of *N,N'*-ethylenedibenzamide that this compound adapts a gauche–trans–gauche conformation of the central C3–N–C4–C4'–N'–C3' group. Table VI shows that the torsion angles of this central group in both *N,N*-ethylene dibenzamide and complex **6** are very similar; hence, the latter too adopts a gauche–trans–gauche conformation. Palmer and Brisse[21] found that the conformation adopted by their molecule to be less energetically favorable than several other conformations. However, they argued that the adoption of the gauche–trans–gauche conformation is probably due to the stabilizing influence of intermolecular hydrogen-bonding.

Hydrogen Bonding. Weak intermolecular hydrogen bonding is a common feature in X-ray structure determinations of both carbamoyl complexes[13,14,19] and organic

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amides[20] and diamides.[21] Unlike the helical chain formed from a two-dimensional hydrogen bond network in $CpRu(CO)_2(CONH_2)$,[13] the hydrogen-bonding network employed in complex **6** (Figure 2 and Table VI) involves an extended sheet along the *b* axis, formed by each molecule interacting with its two nearest neighbors via two types of donor–acceptor linkages. A similar situation prevails in *N,N'*-ethylenedibenzamide; however, in this case each molecule is weakly hydrogen bonded to its four nearest neighbors since "space-saving" stacking of the phenyl rings is possible. The N–H···O angle of 167 (3)° and the N–H and H···O distances of 0.89 (3) and 1.98 (3) Å, respectively, which characterize the hydrogen bonding in *N,N'*-ethylenedibenzamide[21] are the same, within the 3σ criterion, as those of complex **6** (Table VI).

Experimental Section

General Procedures. All synthetic operations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques. Reaction products were then worked up in air. All reagents were obtained commercially and used without further purification. Methylene chloride was dried over CaH_2 and distilled under N_2. Both diethyl ether and tetrahydrofuran were distilled under N_2 in the presence of sodium benzophenone ketyl. Acetonitrile was predried with CaH_2 and twice distilled, first from P_2O_5 and then from CaH_2, under N_2. Benzene, *n*-hexane, and *n*-pentane were reagent grade and were not further purified.

Infrared spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer. The ν_{CO} frequencies were calibrated against the 1601 cm^{-1} band of polystyrene. ^1H NMR spectra were obtained on Varian EM360, JEOL FX-90Q and Nicolet NT-300 spectrometers at 60, 89.6, and 300 MHz, respectively, using deuterated solvents as internal locks. Proton-decoupled ^{13}C NMR spectra were recorded at 22.5 and 75 MHz, respectively, on JEOL FX-90Q and Nicolet NT-300 spectrometers using an internal deuterium lock. To reduce ^{13}C NMR data collection times $Cr(acac)_3$ was added to the solutions. All NMR spectra were referenced to internal Me_4Si. Electron ionization mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Melting or decomposition points (uncorrected) were determined in air using a Thomas hot-stage microscope. Prepared from $[CpFe(CO)_2]_2$ as previously described[4] was $[CpFe(CO)_3]PF_6$. All diamines and 2-aminoethanol were purchased from Aldrich Chemical Co. and used as received.

$[CpFe(CO)_2(CONHCH_2CMe_2NH_3)]PF_6$ (1). A suspension of $[CpFe(CO)_3]PF_6$ (0.50 g, 1.4 mmol) in N_2-saturated diethyl ether (50 mL) was stirred vigorously for 1 h with an excess of 1,2-diamino-2-methylpropane (0.35 mL, 3.4 mmol). The yellow powder formed was filtered, washed with diethyl ether, and recrystallized by dissolving in CH_3CN and precipitating with Et_2O at 0 °C as large yellow crystals (0.58 g, 93%): mp 90–92 °C dec; Λ (1×10^{-3} M) = 150 Ω^{-1} cm^2 mol^{-1} in acetone; EIMS, *m/e* 293 (M^+), 205 ($CpFe(CO)_3^+$). Anal. Calcd for $C_{12}H_{17}F_6FeN_2O_3P$: C, 32.90; H, 3.91; N, 6.39. Found: C, 33.02; H, 4.03; N, 6.42.

$CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (2). The complex $[CpFe(CO)_2(CONHCH_2CMe_2NH_3)]PF_6$ (**1**) (0.20 g, 0.5 mmol) was added to a stirred suspension of an excess of K_2CO_3 (0.10 g, 7.3 mmol) in N_2-saturated CH_3CN (20 mL). The yellow solution was allowed to stir for a further 10 min and filtered through Celite and the solvent evaporated to dryness. The yellow residue was then recrystallized by dissolving in Et_2O and precipitating with *n*-hexane at −20 °C as large yellow crystals (0.11 g, 83%): mp 47–48 °C; EIMS, *m/e* 264 ($M^+ - CO$), 236 ($M^+ - 2CO$), 208 ($M^+ - 3CO$). Anal. Calcd for $C_{12}H_{16}FeN_2O_3$: C, 49.34; H, 5.52; N, 9.59. Found: C, 48.08; H, 5.84; N, 9.29.

(μ-$CONHCH_2CMe_2NHCO$)$[CpFe(CO)_2]_2$ (3). An N_2-saturated solution of $[CpFe(CO)_3]PF_6$ (0.24 g, 0.7 mmol) in CH_3CN (10 mL) was added to a stirred N_2-saturated solution of $CpFe(CO)_2(CONHCH_2CMe_2NH_2)$ (**2**) (0.20 g, 0.7 mmol) in CH_3CN (20 mL) containing an excess of K_2CO_3 (0.47 g, 3.4 mmol). The two yellow solutions gave rise to a red/orange solution owing to the formation of $[CpFe(CO)_2]_2$ as a side product (due to the competitive reduction of $[CpFe(CO)_3]PF_6$ by K_2CO_3). The red/orange solution was allowed to stir for 5 min and filtered through Celite and the solvent removed under reduced pressure. The red and yellow residue was treated with diethyl ether that preferentially extracted the red component $[CpFe(CO)_2]_2$, leaving compound **3** as a bright yellow powder. This powder was dissolved in CH_2Cl_2 and filtered through Celite again in order to remove any residual inorganic salts. The bright yellow filtrate was evaporated to dryness, and the residue was recrystallized as yellow needles by dissolving in hot CH_3CN, adding Et_2O, and allowing the solution to cool to room temperature (0.23 g, 66%): mp 100 °C darkens dec; EIMS, *m/e* 468 ($M^+ - CO$), 440 ($M^+ - 2CO$), 412 ($M^+ - 3CO$), 384 ($M^+ - 4CO$). Anal. Calcd for $C_{20}H_{20}Fe_2N_2O_6$: C, 48.42; H, 4.06; N, 5.65. Found: C, 48.77; N, 4.12; H, 5.66.

$CpFe(CO)_2(CONH(CH_2)_2NMe_2)$ (4). A suspension of $[CpFe(CO)_3]PF_6$ (0.50 g, 1.4 mmol) in N_2-saturated diethyl ether (50 mL) was treated with an excess of *N,N*-dimethyl-1,2-diaminoethane (0.60 mL, 5.5 mmol) and allowed to stir for 1 h. This led to the formation of a bright yellow solution and a white solid ($Me_2HN(CH_2)_2NH_2^+PF_6^-$). The solid was removed upon filtration through Celite, and the filtrate was reduced in volume to 10 mL under reduced pressure at which point precipitation of a yellow solid occurred. The solid was filtered, dried, and recrystallized by dissolving in Et_2O and precipitating with *n*-pentane at −20 °C as large yellow crystals (0.36 g, 86%): mp 74–75 °C; EIMS, *m/e* 264 ($M^+ - CO$), 236 ($M^+ - 2CO$), 208 ($M^+ - 3CO$). Anal. Calcd for $C_{12}H_{16}FeN_2O_3$: C, 49.34; H, 5.52; N, 9.59. Found: C, 49.29; H, 5.78; N, 9.68.

$CpFe(CO)_2(CONH(CH_2)_2OH)$ (5). An N_2-saturated CH_3CN solution (20 mL) containing 2-aminoethanol (0.40 mL, 6.6 mmol) was treated with $[CpFe(CO)_3]PF_6$ (0.50 g, 1.4 mmol) and stirred for 30 min. The yellow solution formed was reduced to dryness. The residue was dissolved in CH_2Cl_2 to give a yellow solution that was filtered through Celite and then reduced in volume to near dryness to give a yellow powder that was washed with diethyl ether. This product was recrystallized from CH_3CN–diethyl ether at −20 °C as large bright yellow crystals (0.24 g, 63%): mp 81–83 °C; EIMS, *m/e* 237 ($M^+ - CO$), 209 ($M^+ - 2CO$), 181 ($M^+ - 3CO$). Anal. Calcd for $C_{10}H_{11}FeNO_4$: C, 45.32; H, 4.18; N, 5.29. Found: C, 45.06; H, 4.27; N, 5.23.

(μ-$CONH(CH_2)_2NHCO$)$[CpFe(CO)_2]_2$ (6). A suspension of $[CpFe(CO)_3]PF_6$ (0.50 g, 1.4 mmol) in N_2-saturated diethyl ether (50 mL) was treated with an excess of 1,2-diaminoethane (0.50 mL, 7.5 mmol) and allowed to stir for 5 min. The suspension rapidly formed a yellow solution and an orange oil. The solvent was then removed under reduced pressure, and the residue was treated with CH_2Cl_2 (25 mL) and vigorously stirred. The yellow solution formed was filtered through Celite to remove a white precipitate ($H_3N(CH_2)_2NH_2^+PF_6^-$). Evaporation of the solvent under reduced pressure resulted in a yellow powder that was recrystallized by dissolving in hot CH_3CN, adding Et_2O, and allowing the solution to cool to room temperature to give yellow needle crystals (0.22 g, 66%): mp 106–108 °C dec; EIMS, *m/e* 440 ($M^+ - CO$), 412 ($M^+ - 2CO$), 384 ($M^+ - 3CO$), 356 ($M^+ - 4CO$), 328 ($M^+ - 6CO$). Anal. Calcd for $C_{18}H_{16}Fe_2N_2O_6$: C, 46.19; H, 3.45; N, 5.99. Found: C, 46.39; H, 3.67; N, 5.95.

(μ-$CONH(CH_2)_3NHCO$)$[CpFe(CO)_2]_2$ (7). Repetition of the procedure used for the preparation of **6**, but substituting 1,3-diaminopropane for 1,2-diaminoethane, ultimately gave a yellow oil that was spectroscopically characterized in solution (Tables I–III).

(μ-$CONMe(CH_2)_2NMeCO$)$[CpFe(CO)_2]_2$ (8). The addition of *N,N'*-dimethyl-1,2-diaminoethane (0.40 mL, 3.8 mmol) to an N_2-saturated solution of $[CpFe(CO)_3]PF_6$ (0.50 g, 1.4 mmol) in acetonitrile (30 mL) gave an immediate bright yellow precipitate. The highly insoluble yellow solid was filtered, washed with diethyl ether, and recrystallized from hot tetrahydrofuran as microcrystalline yellow needles (0.26 g, 73%): mp 88 °C darkens dec; EIMS, *m/e* 440 ($M^+ - 2CO$), 412 ($M^+ - 3CO$). Anal. Calcd for $C_{20}H_{20}Fe_2N_2C_6$: C, 48.42; H, 4.06; N, 5.65. Found: C, 47.44; H, 3.94; N, 5.49.

(μ-$CON(CH_2CH_2)_2NCO$)$[CpFe(CO)_2]_2$ (9). Repeating the procedure in the previous synthesis, but with the saturated cyclic diamine piperazine instead of *N,N*-dimethyl-1,2-diaminoethane, gave microcrystalline yellow needles upon recrystallization from hot tetrahydrofuran (0.24 g, 68%): mp 110 °C darkens dec; EIMS,

m/e 438 ($M^+ - 2CO$). Anal. Calcd for $C_{20}H_{18}Fe_2N_2O_6$: C, 48.62; H, 3.67; N, 5.67. Found: C, 48.68; H, 3.73; N, 5.77.

Crystallographic Summary for (μ-CONH(CH_2)$_2$NHCO)[CpFe(CO)$_2$]$_2$ (6). A yellow needle crystal with approximate dimensions of 0.05 × 0.2 × 0.4 mm (see Table IV for other pertinent crystal parameters) was mounted on a glass fiber and subsequently placed on a goniometer head. Fifteen reflections ($20° < 2\theta < 35°$) were centered on a Syntex $P2_1$ automated diffractometer and indexed by an indexing program (BLIND).[27]

With use of an ω step–scan technique, 2796 independent reflections were collected within a 2θ sphere of 45° and corrected for both Lorentz–polarization and absorption effects ($0.846 \leq$ transmission ≤ 0.999) (an empirical absorption correction was made by using the method described by Karcher[28]); 1485 reflections with $I \geq 3\sigma(I)$ were retained for use in subsequent calculations. The estimated variance in each intensity was calculated by $\sigma(I)^2 = C_T + C_B + (0.03C_T)^2 + (0.03C_B)^2 + (0.03I)^2$ where C_T and C_B represent the total and background counts, respectively, and the factor 0.03 is an estimate of nonstatistical errors.

The positions of the iron atoms were obtained from an analysis of a sharpened Patterson map. All the remaining atoms including all the hydrogen atoms were found from successive structure factor and electron density map calculations. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by a combination of block-matrix/full-matrix least-squares calculations.[29] The positional parameters for the hydrogen atoms were refined with fixed isotropic temperature factors (B = 3.2 Å^2). The final conventional residual index ($R = \sum||F_o| - k|F_c||/\sum|F_o|$) was 0.043 with a corresponding weighted index ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^{\,2}]^{1/2}$ of 0.047, and the function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where w is $1/\sigma(F)^2$. The atomic scattering factors were those from the ref[30], modified for the real and imaginary parts of anomalous dispersion. The final atomic parameters are listed in Table V.

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Registry No. **1**, 91178-28-8; **2**, 91178-27-7; **3**, 91178-29-9; **4**, 91178-30-2; **5**, 91178-31-3; **6**, 91190-33-9; **7**, 91178-32-4; **8**, 91178-33-5; **9**, 91178-34-6; [CpFe(CO)$_2$(CONH(CH_2)$_2$NHMe$_2$)]SO_3CF_3, 91178-35-7; [CpFe(CO)$_3$]PF_6, 38834-26-3; $H_2NCH_2CMe_2NH_2$, 811-93-8; $H_2N(CH_2)_2NMe_2$, 108-00-9; $H_2N(CH_2)_2OH$, 141-43-5; $H_2N(CH_2)_2NH_2$, 107-15-3; $H_2N(CH_2)_3NH_2$, 109-76-2; $MeHN(CH_2)_2NHMe$, 110-70-3; $HN(CH_2CH_2)_2NH$, 110-85-0.

Supplementary Material Available: Tables of anisotropic temperature factors for non-hydrogen atoms (Tables I), complete bond distances (Table S2), complete bond angles (Table S3), and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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