Formation of a Novel Dipyrrolopyrrole Mediated by a 1,4-Diaza-1,3-diene Complex of Iron

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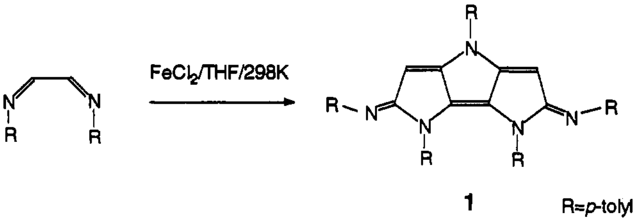
The dipyrrolopyrrole 2,6-bis(*p*-tolylimino)-4,7-dihydro-1,4,7-tri-*p*-tolyl-1*H*-dipyrrolo[3,2-*b*:2′,3′-*d*]pyrrole (**1**) was obtained from the reaction of a 1,4-diaza-1,3-diene, glyoxal bis(*p*-tolylimine), in the presence of $FeCl_2$. Crystals of **1**, $C_{43}H_{32}N_5$, are triclinic, space group, $P\bar{1}$, with $a = 10.014(3)$ Å, $b = 13.212(3)$ Å, $c = 13.710(3)$ Å, $\alpha = 106.31(2)°$, $\beta = 95.79(2)°$, $\gamma = 105.77(2)°$, $V = 1644$ Å^3, $Z = 2$, $D_{calcd} = 1.211$ g cm^{-1}, $R = 0.026$, and $R_w = 0.057$. The compound is thought to result from a series of metal-mediated condensations of the 1,4-diaza-1,3-diene precursor.

Introduction

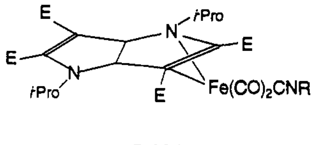
Complexes of transition metals in low oxidation states with 1,4-diaza-1,3-diene ligands, particularly complexes of Fe and Ni, act as precursors for a variety of highly selective and substrate specific catalytic reactions. The 1,4-diaza-1,3-diene (DAD) ligands contain the -N═C—C═N- group which forms the coordinating backbone. The -N═C—C═N- functional group is synthesized by the condensation of aromatic or aliphatic amines with α-diketones and α-dialdehydes, *e.g.* gyloxal or biacetyl.[1] Metal complexes of 1,4-diaza-1,3-dienes have been reported with a range of metals, including vanadium,[2] copper,[3] nickel,[4,5] ruthenium,[6–10] and iron.[11,12]

Iron complexes containing DAD groups as directive ligands catalyze [4 + 2] cycloadditions of simple dienes with nonterminal alkynes at room temperature.[13] Complexes of the type $FeCl_2$(DAD) have outstanding catalytic activity in the cyclodimerization of 1,3-dienes,[14,15] and chirality transfer from systems assembled with chiral DAD ligands has also been observed.[16] In general, C–H,[17] C–C,[18,19] and C–N[20] coupling reactions have been observed in both monometallic and bimetallic complexes of 1,4-diaza-1,3-dienes.

Scheme 1



Coordination of the DAD ligands to one or more metal centers can result in activation of the α-diimine skeleton itself. Keijsper *et al.*[18] showed that C–C coupling of two DAD ligands could occur on Mn metal centers and also that C–C coupled dimers could form on Ru metal centers.[19] 1,3-Dipolar cycloaddition of alkynes to the diazadiene fragments coordinated to Fe and Ru occurs with the formation of bicyclic pyrrole compounds where the pyrrole remains bound to the metal, *e.g.* **2**.[21] Bimetallic complexes of C–C coupled DAD ligands have also been isolated, *e.g.* **3**.[18] For FeL_3DAD complexes, N—C and C—C addition across the N═C bond of the metal-bound DAD ligand enables formation of metal-bound pyrrole–pyrrole species. Depending on the nature of the ligand L, the bipyrrole product can be displaced from the metal center, bringing about "catalytic" formation of the polycyclic organic product.[21,22] In the course of our investigations of iron(II) complexes of 1,4-diaza-1,3-dienes, we have uncovered a unique, metal-assisted oligomerization of the glyoxal bis(*p*-tolylimine) ligand. The product of this oligomerization was a tricyclic dipyrrolopyrrole, 2,6-bis(*p*-tolylimino)-4,7-dihydro-1,4,7-tri-*p*-tolyl-1*H*-dipyrrolo[3,2-*b*:2′,3′-*d*]pyrrole (**1**) (Scheme 1), and is probably a product of a series of electrocyclic reactions involving four 1,4-diaza-1,3-diene ligands.



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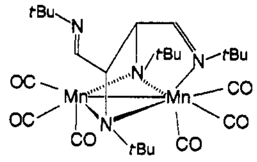

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Experimental Section

All synthetic manipulations involving reactions of anhydrous iron dichloride with *N,N′*-*p*-tolylglyoxal diimine were carried out under an

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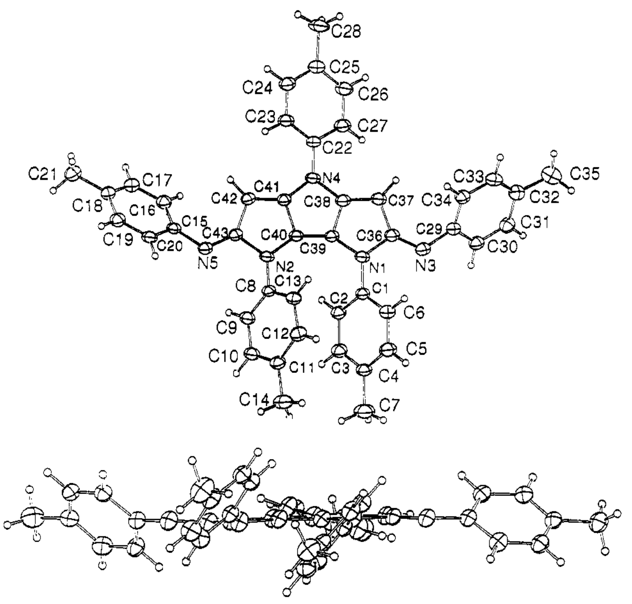

Figure 1. ORTEP plots of the complex: (a, top) view perpendicular to the N4 plane, giving the crystallographic atom numbering; (b, bottom) view in the N4 plane, perpendicular to the C(40)–C(39) bond. The 30% probability ellipsoids are shown.

inert atmosphere of argon, in an argon filled dry box. Diethyl ether and hexane were dried over sodium wire before distillation. Acetonitrile (AR grade) and isopropanol (AR grade) were used without further purification. Solvents required for air sensitive reactions were degassed prior to use via 3–5 freeze-pump-thaw cycles. Anhydrous iron chloride was prepared by heating iron(II) chloride tetrahydrate under vacuum (kugelrohr) at 50 °C for 6 h.

Melting points were recorded in air and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX400 spectrometer. Chemical shifts were internally referenced to solvent residual peaks.

Preparation of Glyoxal Bis(*p*-tolylimine).[4] Glyoxal bis(*p*-tolylimine) was prepared following a modification of the published procedure.[4] Glyoxal (30% aqueous solution, 12 mL, 0.06 mol) was added dropwise to a solution of *p*-toluidine (10.7 g, 0.01 mol) in 2-propanol (50 mL) at 0 °C over approximately 1 h. After addition was complete, the mixture was allowed to stir for 1 h at 0 °C. The mixture was filtered and recrystallized immediately from 2-propanol to give glyoxal bis(*p*-tolylimine) as a yellow crystalline solid (5.1 g, 44%, mp 159–162 °C). ^1H NMR spectrum ($CDCl_3$): δ 8.42 (s, 2H, N=C*H*–), 7.23 (s, 8H, aromatic H), 2.51 (s, 6H, *p*-CH_3). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 300 K): δ 159.8 (N=CH), 148.3, 138.9, 130.8, 122.0 (aromatic C), 21.9 (*p*-CH_3). IR, ν_{max} (Nujol): 2970 (w), 1609 (w), 1503 (m), 1219 (s) cm^{-1}. Mass spectrum, *m/z* (%): 235 (49) ($C_{16}H_{16}N_2$), 221 (95) ($C_{15}H_{12}N_2$), 118 (65) (C_8H_8N), 91 (100) (C_7H_7), 65 (39).

Reaction of *N,N′*-Di-*p*-tolylglyoxal Diimine with Iron(II) Dichloride. Glyoxal bis(*p*-tolylimine) (230 mg, 9.7 × 10^{-4} mol) was added to a suspension of iron(II) dichloride (90 mg, 7.1 × 10^{-4} mol) in ether (40 mL), and the mixture was stirred at room temperature for 3 days. The red/brown solution was filtered, the solvent was removed under vacuum, and the residue was extracted with hexane (3 × 20 mL). The hexane solvent was removed under vacuum to give a red glassy solid as the only isolated product (approximately 20 mg). A sample was recrystallized slowly from acetonitrile and the dipyrrolopyrrole (**1**) was obtained as a burgundy-colored crystalline solid. ^1H NMR spectrum (CD_2Cl_2, 220 K): δ 6.89, 6.76, 6.73, 6.48 (4 × m, 20H, aromatic-*H*), 5.31 (s, 2H, =C–*H*), 2.02, 1.99, 1.94 (3 × s, 3H, 6H, 6H, aromatic CH_3). Mass spectrum, *m/z* (%): 623 (100), 599 (<2), 534 (<2), 520 (<2), 426 (<2), 399 (<2), 312 (23), 208 (<2), 91 (6). High resolution mass spectrum: calculated, 623.3048; found, 623.3049. Crystals obtained by this method were suitable for X-ray diffraction.

Structure Determination. Cell constants were determined by least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table 1. Data were reduced, and Lorentz, polarization, and absorption corrections were applied using the Enraf-Nonius structure determination package (SDP).[23] The structure was solved by direct methods using SHELX-86[24] and was refined by blocked-matrix least-squares analysis with SHELX-76.[25] Hydrogen atoms were included at calculated sites (C–H, 0.97 Å) with individual isotropic thermal parameters. All other atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections were taken from the values supplied in SHELX-76. Non-hydrogen atom coordinates are listed in Table 2. Figures were drawn using the program ORTEP.[26] The atomic nomenclature is defined in Figure 1.

Table 1. Crystal Data for $C_{43}H_{32}N_5$ (**1**)

space group	$P\bar{1}$	D_{calcd}, g cm^{-3}	1.211
a, Å	10.014(3)	empirical formula	$C_{43}H_{32}N_5$
b, Å	13.212(3)	*Z*	2
c, Å	13.710(3)	abs coeff., cm^{-1}	6.45
α, deg	106.31(2)	transm coeff	0.9704–0.8712
β, deg	95.79(2)	temp, °C	21
γ, deg	105.77(2)	λ, Å	0.710 69
V, Å^3	1644	R^a	0.048
fw	618	$R_w{}^a$	0.057

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = \sum(w^{1/2}||F_o| - |F_c||)/\sum w^{1/2}|F_o|$.

Results and Discussion

The structure of **1** consists of discrete molecules. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles, and anisotropic thermal parameters have been deposited as supplementary material. Bond distances and angles are given in Tables 3 and 4, and positional parameters have been given in Table 2. Figure 1 illustrates the molecular geometry of **1**, shown in two orientations. The three fused central pyrrole rings of **1** are essentially coplanar, with an angle of 0.83° between the N(2) and N(4) ring planes, an angle of 1.65° between the N(4) and N(1) ring planes, and an angle of 0.87° between the N(2) and N(1) ring planes. The tolyl substituents on the N(2) and N(1) atoms of the pyrrole rings are parallel, but tilted relative to the plane of the central pyrrole ring, with the C(8) ring tilted at 130.19° relative to the plane of the ring N(2). The tolyl rings bound to N(5) and N(4) are not coplanar with the central pyrrole rings, with the C(15) rings tilted at an angle of 40.10° relative to the N(2) ring and the C(29) ring plane at an angle of 131.64° relative to the plane of ring N(1). The unique tolyl group bound to N(4) does, however, lie almost in the same plane as the central pyrrole ring, with the angle between the planes of the N(4) and C(22) rings being 18.25°. The tilting of the tolyl C(1) and C(8) rings relative to the pyrrole ring plane are probably due to steric factors, whereas the orientation of the C(29) and C(15) rings would maximize conjugation.

Fused bicyclic and tricyclic pyrrole ring systems are known, although no crystal structures of tricyclic pyrrole ring systems have been reported. The structure of the bicyclic pyrrole **4** reported by Dieck *et al.*[27] has two coplanar fused pyrrole rings which is similar to the three-ring system reported here. The bicyclic dihydropyrrolopyrrole **5**,[28] which has substituents at the C-2 positions on both pyrrole rings, is not planar and has an angle of 66.9° between the two pyrrole ring planes. When still coordinated to a metal atom,[21,22] the bicyclic pyrrolopyrrole ring

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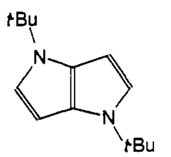
Table 2. Positional Parameters (×10^4)

	x	*y*	*z*
N(1)	1977(3)	1755(2)	1450(2)
N(2)	3179(3)	−273(2)	2240(2)
N(3)	1329(3)	2979(2)	709(2)
N(4)	2787(3)	−366(2)	−362(2)
N(5)	3886(3)	−1724(2)	2522(2)
C(1)	2179(3)	2430(2)	2499(2)
C(2)	3425(3)	2674(2)	3173(2)
C(3)	3593(4)	3316(3)	4188(3)
C(4)	2565(4)	3764(3)	4545(2)
C(5)	1333(4)	3512(3)	3851(3)
C(6)	1131(4)	2850(3)	2834(2)
C(7)	2782(5)	4477(3)	5655(3)
C(8)	2825(3)	129(2)	3227(2)
C(9)	3804(3)	428(3)	4128(2)
C(10)	3482(4)	904(3)	5073(2)
C(11)	2192(4)	1097(2)	5143(2)
C(12)	1222(4)	764(3)	4233(3)
C(13)	1520(3)	276(3)	3282(2)
C(14)	1888(4)	1659(3)	6176(3)
C(15)	4275(3)	−2696(2)	2226(2)
C(16)	5166(3)	−2916(3)	1536(2)
C(17)	5522(3)	−3889(3)	1334(2)
C(18)	4996(3)	−4674(2)	1803(2)
C(19)	4132(3)	−4443(3)	2513(3)
C(20)	3797(3)	−3469(3)	2728(2)
C(21)	5347(4)	−5725(3)	1558(3)
c(22)	2791(3)	−905(2)	−1407(2)
C(23)	2773(4)	−1998(3)	−1744(2)
C(24)	2739(4)	−2513(3)	−2771(2)
C(25)	2684(3)	−1982(3)	−3501(2)
C(26)	2720(4)	−890(3)	−3158(2)
C(27)	2787(4)	−359(3)	−2127(2)
C(28)	2584(5)	−2563(3)	−4642(3)
C(29)	1013(3)	3356(3)	−124(2)
C(30)	1571(3)	4485(3)	26(3)
C(31)	1268(3)	4918(3)	−738(3)
C(32)	391(3)	4254(3)	−1681(3)
C(33)	−185(4)	3137(3)	−1815(3)
C(34)	121(3)	2692(3)	−1053(2)
C(35)	26(4)	4768(4)	−2480(3)
C(36)	1659(3)	2090(2)	580(2)
C(37)	1896(3)	1307(3)	−325(2)
C(38)	2367(3)	581(2)	11(2)
C(39)	2433(3)	837(2)	1108(2)
C(40)	2845(3)	55(2)	1403(2)
C(41)	3085(3)	−693(2)	493(2)
C(42)	3530(3)	−1470(2)	763(2)
C(43)	3599(3)	−1237(2)	1877(2)

systems are not coplanar, *e.g.* **2**, and the pyrrole ring itself is not planar when coordinated to the metal atom. In **1**, the exocyclic



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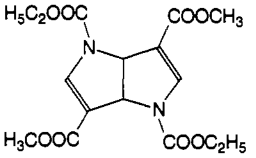

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C=N bond lengths (C(43)–N(5) and C(36)–N(3) are significantly shorter (1.282(5) and 1.276(5) Å) than the C–N bond lengths within the pyrrole rings (1.387(4)–1.423(4) Å). The exocyclic C=N bond lengths are very similar to the equivalent C=N bond (1.29(1) Å) observed in a bipyrrole formed from *tert*-butyl isonitrile and norbornene under high pressure.[29] In **1**, the C–N bond lengths within the fused pyrrole rings are equivalent to those observed in two known bicyclic pyrroles,[27,28] even where the substituents bound to the N atoms are significantly different.

Table 3. Bond Lengths (Å) for **1**

C(1)–N(1)	1.424(3)	C(36)–N(1)	1.419(5)
C(39)–N(1)	1.387(4)	C(8)–N(2)	1.426(4)
C(40)–N(2)	1.379(4)	C(43)–N(2)	1.423(4)
C(29)–N(3)	1.409(5)	C(36)–N(3)	1.276(5)
C(22)–N(4)	1.411(4)	C(38)–N(4)	1.406(5)
C(41)–N(4)	1.392(4)	C(15)–N(5)	1.406(4)
C(43)–N(5)	1.282(5)	C(2)–C(1)	1.377(4)
C(6)–C(1)	1.375(5)	C(3)–C(2)	1.378(4)
C(4)–C(3)	1.386(6)	C(5)–C(4)	1.379(5)
C(7)–C(4)	1.504(5)	C(6)–C(5)	1.383(4)
C(9)–C(8)	1.383(4)	C(13)–C(8)	1.378(5)
C(10)–C(9)	1.384(4)	C(11)–C(10)	1.391(5)
C(12)–C(11)	1.381(4)	C(14)–C(11)	1.507(5)
C(13)–C(12)	1.385(5)	C(16)–C(15)	1.391(5)
C(20)–C(15)	1.393(5)	C(17)–C(16)	1.388(5)
C(18)–C(17)	1.382(5)	C(19)–C(18)	1.392(5)
C(21)–C(18)	1.515(5)	C(20)–C(19)	1.377(5)
C(23)–C(22)	1.382(5)	C(27)–C(22)	1.376(5)
C(24)–C(23)	1.374(4)	C(25)–C(24)	1.378(5)
C(26)–C(25)	1.375(5)	C(28)–C(25)	1.517(4)
C(27)–C(26)	1.376(4)	C(30)–C(29)	1.390(4)
C(34)–C(29)	1.380(4)	C(31)–C(30)	1.372(6)
C(32)–C(31)	1.389(4)	C(33)–C(32)	1.381(5)
C(35)–C(32)	1.506(7)	C(34)–C(33)	1.383(6)
C(37)–C(36)	1.464(4)	C(38)–C(37)	1.344(5)
C(39)–C(38)	1.437(4)	C(40)–C(39)	1.353(5)
C(41)–C(40)	1.445(4)	C(42)–C(41)	1.349(5)
C(43)–C(42)	1.462(4)		

Table 4. Bond Angles (deg) for **1**

C(36)–N(1)–C(1)	124.4(3)	C(39)–N(1)–C(1)	125.8(3)
C(39)–N(1)–C(36)	107.5(2)	C(40)–N(2)–C(8)	124.1(3)
C(43)–N(2)–C(8)	126.3(3)	C(43)–N(2)–C(40)	108.0(2)
C(36)–N(3)–C(29)	122.0(3)	C(38)–N(4)–C(22)	125.9(3)
C(41)–N(4)–C(22)	128.1(3)	C(41)–N(4)–C(38)	105.8(2)
C(43)–N(5)–C(15)	122.6(3)	C(2)–C(1)–N(1)	120.2(3)
C(6)–C(1)–N(1)	119.7(3)	C(6)–C(1)–C(2)	120.1(3)
C(3)–C(2)–C(1)	119.3(3)	C(4)–C(3)–C(2)	122.0(3)
C(5)–C(4)–C(3)	117.3(3)	C(7)–C(4)–C(3)	120.9(3)
C(7)–C(4)–C(5)	121.7(4)	C(6)–C(5)–C(4)	121.6(4)
C(5)–C(6)–C(1)	119.7(3)	C(9)–C(8)–N(2)	120.7(3)
C(13)–C(8)–N(2)	119.6(3)	C(13)–C(8)–C(9)	119.6(3)
C(10)–C(9)–C(8)	119.8(3)	C(11)–C(10)–C(9)	121.5(3)
C(12)–C(11)–C(10)	117.4(3)	C(14)–C(11)–C(10)	120.5(3)
C(14)–C(11)–C(12)	122.0(3)	C(13)–C(12)–C(11)	121.8(3)
C(12)–C(13)–C(8)	119.8(3)	C(16)–C(15)–N(5)	125.9(3)
C(20)–C(15)–N(5)	116.5(3)	C(20)–C(15)–C(16)	117.5(3)
C(17)–C(16)–C(15)	120.8(3)	C(18)–C(17)–C(16)	121.3(3)
C(19)–C(18)–C(17)	118.0(3)	C(21)–C(18)–C(17)	121.4(3)
C(21)–C(18)–C(19)	120.6(3)	C(20)–C(19)–C(18)	120.8(3)
C(19)–C(20)–C(15)	121.5(3)	C(23)–C(22)–N(4)	121.2(3)
C(27)–C(22)–N(4)	120.7(3)	C(27)–C(22)–C(23)	118.1(3)
C(24)–C(23)–C(22)	120.1(3)	C(25)–C(24)–C(23)	122.1(3)
C(26)–C(25)–C(24)	117.4(3)	C(28)–C(25)–C(24)	122.2(3)
C(28)–C(25)–C(26)	120.3(4)	C(27)–C(26)–C(25)	121.0(4)
C(26)–C(27)–C(22)	121.3(3)	C(30)–C(29)–N(3)	117.4(2)
C(34)–C(29)–N(3)	124.4(3)	C(34)–C(29)–C(30)	118.0(3)
C(31)–C(30)–C(29)	120.7(3)	C(32)–C(31)–C(30)	121.7(3)
C(33)–C(32)–C(31)	117.2(4)	C(35)–C(32)–C(31)	120.1(3)
C(35)–C(32)–C(33)	122.5(3)	C(34)–C(33)–C(32)	121.5(3)
C(33)–C(34)–C(29)	120.8(3)	N(3)–C(36)–N(1)	119.6(3)
C(37)–C(36)–N(1)	107.5(3)	C(37)–C(36)–N(3)	132.7(3)
C(38)–C(37)–C(36)	106.9(3)	C(37)–C(38)–N(4)	140.7(3)
C(39)–C(38)–N(4)	109.2(3)	C(39)–C(38)–C(37)	110.1(3)
C(38)–C(39)–N(1)	107.9(3)	C(40)–C(39)–N(1)	144.0(3)
C(40)–C(39)–C(38)	107.9(3)	C(39)–C(40)–N(2)	144.2(3)
C(41)–C(40)–N(2)	108.2(3)	C(41)–C(40)–C(39)	107.5(3)
C(40)–C(41)–N(4)	109.5(3)	C(42)–C(41)–N(4)	141.3(3)
C(42)–C(41)–C(40)	109.2(3)	C(43)–C(42)–C(41)	107.7(3)
N(5)–C(43)–N(2)	118.7(3)	C(42)–C(43)–N(2)	107.0(3)
C(42)–C(43)–N(5)	134.3(3)		

The C–C bond lengths for the fused rings of two previously reported bicyclic systems, **4** and **5**,[27,28] are 1.374(3) and 1.554(3) Å, respectively, consistent with C=C double and C—C single bonds in these systems. The length of the C–C bonds between the shared C atoms of the fused rings (1.437(4) and 1.445(4) Å)

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for the tricyclic pyrrole **1** are consistent with a substantially delocalized structure for the dipyrrolopyrrole **1**.

The crystal structure of compound **1** indicates that in the solid state, the molecule lacks symmetry. However, in the ^{1}H NMR spectrum of the compound at 303 K in solution, only three sets of aromatic resonances are observed, one vinylic resonance at 5.3 ppm, and three methyl resonances, in the ratio 1:2:2. The spectrum does not change significantly at temperatures as low as 220 K. The NMR spectrum indicates that the molecule undergoes conformational averaging in solution, with rapid inversion of the phenyl rings about the C═N bonds giving the molecule an effective plane of symmetry about the N(4)–C(22) axis.

The synthesis of bicyclic pyrroles has previously been achieved by a variety of methods, including alcoholysis of 1,4-diaza-1,3-dienes in the presence of appropriate catalysts,[27] high pressure induced cycloaddition of an isonitrile and bicycloheptene,[29] and thermolysis of azido compounds.[28] It has also been found that electrocyclic reactions of metal complexes of 1,4-diaza-1,3-diene ligands can lead to the formation of bicyclic pyrroles, bound to metals, and that these can be displaced from the metal complexes as organic products.[20,22]

The stoichiometry of the reaction dictates that the reaction involves the condensation of four 1,4-diaza-1,3-diene ligands, with the loss of effectively half of one DAD fragment at some stage during the reaction. The tricyclic dipyrrolopyrrole **1** is formed only in the presence of $FeCl_2$, and although no intermediate metal complex containing the pyrrole has been isolated, it is likely that the reaction route is analogous to the 1,3-cycloaddition reaction pathways previously postulated for the formation of bicyclic pyrrolopyrroles in the presence of Fe.[20,22] Such a scheme would involve a series of cycloaddition reactions to a metal-bound 1,4-diaza-1,3-diene.

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Supplementary Material Available: Listings of atom coordinates, anisotropic thermal parameters, torsion angles, and the details of least-squares planes calculations (7 pages). Ordering information is given on any current masthead page.