Preparation of Functionalized *p*-Phenylenediamine Derivatives Using Arene−Iron Chemistry

Anthony J. Pearson* and Ann M. Gelormini

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Marye Anne Fox and Diana Watkins

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712−1167

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Selective displacement of chloride from cyclopentadienyl(1,4-dichlorobenzene)iron(1+) by a series of cyclic secondary amine nucleophiles is described. This selectivity, in combination with further manipulation of the complexes, allows access to a series of unsymmetrical and/or functionalized tetraalkyl-*p*-phenylenediamine complexes. A series of demetalated phenylenediamines were shown by CV to have redox potentials distributed over a range of 320 mV, as a consequence of remote functionality. Preliminary fluorescence studies on a series of electron acceptor-substituted phenylenediamines indicated quenching of the phenylenediamine fluorescence, attributable to rapid electron transfer.

Introduction

Transition-metal activated nucleophilic aromatic substitution is beginning to play a role in various polymer and materials applications.[1−3] While triaryl-diether and polyphenylene oxide derivatives that are accessible from these complexes have been thoroughly investigated,[1−4] other derivatives, such as N-substituted phenylenediamines, have seen far less attention. While several well known methods for the construction of the arene−nitrogen bond may be found, these reactions either proceed via a benzyne intermediate, and suffer the attendant regiocontrol problems,[5] or they require high temperatures (Ullmann conditions) or the presence of specific functionality on the ring (traditional S_NAr reactions). The alternative $S_{RN}1$ pathway is complicated by the presence of a dimethylamino substituent on the ring.[6]

We are interested in applying arene−iron chemistry to the synthesis of unsymmetrical and/or functionalized "Wurster's Blue" derivatives. The parent *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) is a powerful electron donor, and has been extensively studied.[7] However, unsymmetrical or functionalized derivatives, which might be incorporated into molecular electronic devices, have not been widely explored. This may be because any synthesis from *p*-phenylenediamine or from *p*-nitroaniline would require functional group manipulation or protection/deprotection sequences which are incompatable with the phenylene diamine functionality. Conventional syntheses for the few derivatives which have been reported in the open literature are quite low yielding.[8] A recent report has disclosed a palladium-based cross-coupling reaction which has been applied to the synthesis of some simple tetraalkyl derivatives in good yields.[9] We[4a,b] and others[10] have described the use of secondary amines as nucleophiles for arene−iron complexes.

We report herein a protocol for the use of arene−iron chemistry in the synthesis of unsymmetrical and functionalized Wurster's Blue derivatives, our solutions to the problems inherent in the critical decomplexation step, and the synthesis of functionalized Wurster's Blue derivatives containing a covalently linked electron-acceptor functionality. In this work, the FeCp moiety serves in a three-fold capacity. Complexation of *p*-dichlorobenzene to $[FeCp]^+$ facilitates S_NAr reactions, allows them to be conducted chemoselectively, and renders the arene sufficiently electron poor that neighboring functionality can be manipulated without the risk of oxidation of the target phenylenediamine.

Results and Discussion

Synthesis and Decomplexation Studies. The symmetrical *p*-phenylenediamine−FeCp cations **2**−**5** were prepared in 80−96% yields by double nucleophilic displacement reactions on the *p*-dichlorobenzene−FeCp complex **1** (Scheme 1**)**. The reaction conditions are quite straightforward, consisting of stirring a THF solution of **1** and an excess of the appropriate nucleophile, in the presence of K_2CO_3, for 12−24 h at room temperature. The

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(2) (a) Abd-El-Aziz, A. S.; Schreimer, D. C.; de Denus, C. R. *Organometallics* **1994**, *13*, 374−384. (b) Abd-El-Aziz, A. S.; de Denus, C. R. *J. Chem. Soc., Chem. Commun.* **1994**, 663−665. (c) Abd-El-Aziz, A. S.; Epp, K.; de Denus, C. R. *Organometallics* **1994,** *13*, 2299.

(3) (a) Dembek, A. A.; Burch, R. R.; Fiering, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2087−2088. (b) Dembek, A. A. ; Burch, R. R. Fiering, A. E. *Macromolecules* **1993**, *26*, 2992−2994. (c) Segal, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1338-1339.

(4) (a) Pearson, A. J.; Gelormini, A. M. *J. Org Chem.* **1995**, *60*, 281−284. (b) Pearson, A. J.; Park, J. G.; Zhu, P. Y. *J. Org. Chem.* **1992**, *57*, 3583−3589. (c) Park, J. G.; Yang, Y. S.; Chuang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1363−1364.

(5) Razzuk, A.; Biehl, E. R. *J. Org. Chem.* **1987**, *52*, 2619−2622.

(6) For examples of each of the described cases, see March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992 and references cited therein.

(7) For a review, see Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1969.

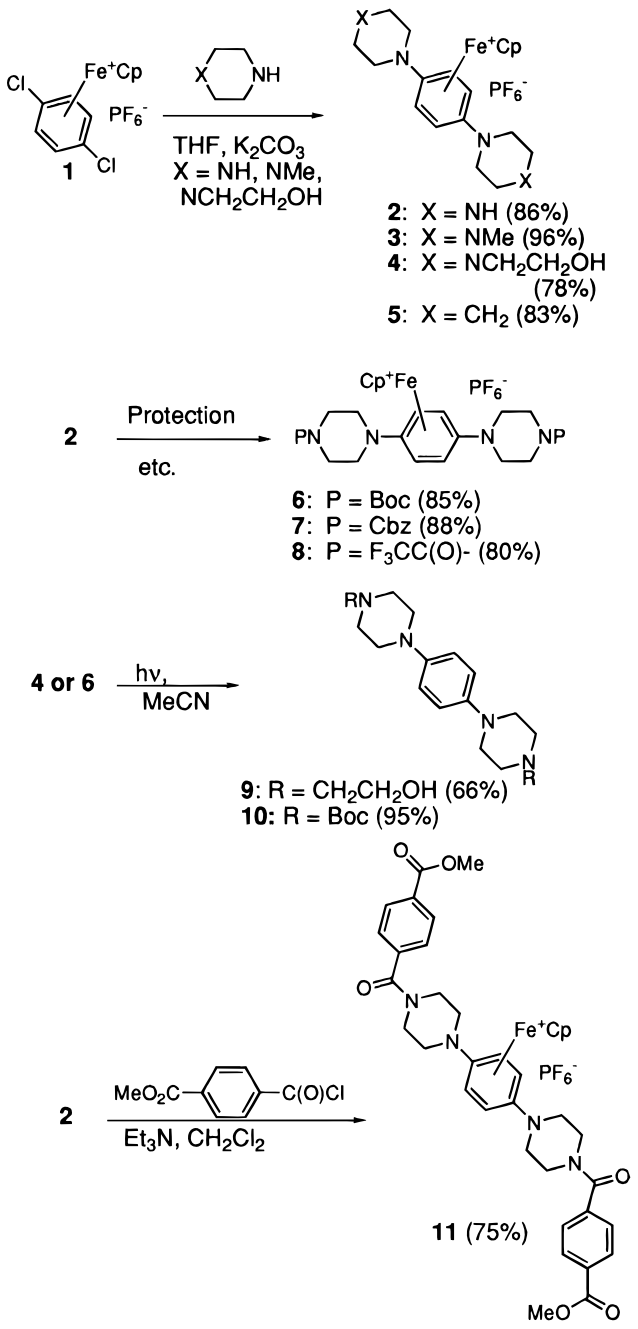
(8) For example, Nelsen, S. F.; Yunta, M. J. R. *J. Phys. Org. Chem.* **1994**, *7*, 55 describes the synthesis of compounds structurally similar to several of our derivatives. In no case is the yield of any step higher than 20%. A few recent patent applications have appeared (e.g. Muto, N.; Myamoto, E.; Nakazawa, S. Jpn. Kokai Tokkyo Koho JP 01,118,-141 [89,118,1411] Chem. Abstr. **1989**, 111, 184160s and Yoshikawa, M.; Suzuki, T.; Kojima, A.; Masayuki, S. Jp. Kokai Tokkyo Koho JP 01,154,571 [89,154,571] Chem. Abstr. **1990**, 112, 29317a) which employ such derivatives in thin-film photoconductive photoreceptors.

(9) Guram, A. S.; Buchwald, S. L *J. Am. Chem. Soc.* **1994**, *116*, 7901−7902.

(10) Abd-El-Aziz, A. S.; Piórko, A.; Lee, C. C.; Sutherland, R. G. *Can. J. Chem.* **1989**, *67*, 1618−1623.

0022-3263/96/1961-1297$12.00/0

Scheme 1



purification is likewise simple; the cationic product is precipitated by addition of ether to a concentrated dichloromethane solution of the crude reaction mixture.

While **4** could be decomplexed using established methodology[1] (stirring a solution of the complex in acetonitrile, under a sunlamp, for 2−4 h), attempts to decomplex **2** and **3** in this manner failed and starting material was not recovered. We obtained, instead, an orange-brown precipitate which gave positive qualitative tests for the presence of iron and a Wurster's Blue derivative (red coloration on addition to aqueous phenanthroline and blue coloration of a solution in 10% HCl). Very little free phenylenediamine remained in the acetonitrile solution. If the precipitate was treated with aqueous base and then neutralized, iron hydroxide precipitated; however, this procedure also resulted in substantial oxidation of the amine. The desired product was obtained only in low yield and was accompanied by several impurities. We initially reasoned this behavior to be the result of amine coordination of the liberated iron.[11]

To circumvent this, the Boc (*tert*-butoxycarbonyl) protected derivative **6** was synthesized and decomplexed in 95% yield to give **10**; however, attempted deprotections were unsuccessful. Protection of **2** as its Cbz- (benzyloxycarbonyl) and trifluoroacetate derivatives (**7, 8**) or its derivatization to the bis-terephthalamide **11** also proceeded without incident; however, once again, the decomplexations were problematic, indicating that there were additional complications besides iron ligation. Performing the decomplexation under room lighting for extended periods (36−48 h) afforded a partial solution to the problem, as is evidenced in Table 1, indicating that amine photooxidation could be a competing problem.[12]

The above constraints required that we select reaction conditions that are at most mildly photolytic and which allow us to irreversibly remove the metal from participation, once it is freed from the arene. Pyrolytic sublimation is one decomplexation technique that would fit these requirements;[13] however, this method is tedious, and the arene must be stable at the required temperatures (>200 °C). Attempts to pyrolytically sublime **2** and the bis-terephthalamide **11** failed.

Another approach is to introduce stronger iron ligators than acetonitrile to the reaction mixture, in anticipation that this would promote decomplexation and more efficiently sequester the iron once it is removed. While the reaction would still require photoinitiation, intense and prolonged irradiation could be avoided. Decomplexation of these complexes using acetylacetone[14] and 1,10-phenanthroline[15] as competing ligands have been described; however, the focus of those studies was on the resulting metal complexes. No attention was given to the liberated organic ligand and no attempts were made to isolate the arene or to develop this into a useful synthetic method. Conceptually, however, this approach was appropriate for our complexes. Owing to the inherent advantages of phenanthroline (a very strong donor ligand, the possiblity of following the reaction spectrophotometrically, the need to eliminate only an ionic solid byproduct) we began our investigations there and have optimized conditions for this decomplexation method.

In our initial approach to the phenanthroline-assisted demetalations, the complex was stirred with an acetonitrile/water solution containing a modest excess of phenanthroline·HCl·H_2O, in the presence of room light, for 24−36 h. The excess was used to ensure complete capture of the iron. Although the reaction appeared to be reaching completion by UV-vis spectrophotometry, severe losses were incurred in attempting to separate the excess phenanthroline. This procedure was then modified to employ phenanthroline as the limiting reagent (2.9:1), The yields were increased, often dramatically, by this adjustment.

In this manner, we were able to prepare a series of protected or functionalized *p*-phenylenedipiperazines and

(11) Bertoncello, K.; Fallon, G. D.; Hodgkin, J. D.; Murray, K. S. *Inorg. Chem.* **1988**, *27*, 4750−4758.
(12) For example, see Albrecht, A. C. *J. Am. Chem. Soc.* **1960**, *82*, 3813−1816.
(13) For an example, see Sutherland, R. G.; Piorko, A.; Gill, U. S.; Lee, C. C. *J. Heterocycl. Chem.* **1982**, *19*, 801−803.
(14) Razuvaev, G. A.; Domrachev, G. A.; Suvorova, O. N.; Abakumova, L. G. *J. Organomet. Chem.* **1971**, *32*, 113−120.
(15) (a) McNair, A. M.; Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633−2640. (b) Brown, R. A.; Fernando, S. I. S.; Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 1* **1994**, 197−201.

Table 1. Comparison of Yields from Photolytic and Phenanthroline-Assisted Decomplexation Methods

complex	decomplexation product	phenanthroline-assisted decomplexation, %	*hν*-assisted decomplexation, %	decomplexation under room light, %
2	**17**	0 (separation problem)	5−10	
3	**15**	67	0	
4	**9**	25 (separation problem)	66	
5	**16**	51		
6	**10**	Not attempted	95	
7	**12**	94	24	
8	**13**	39	trace, deprotection	
11	**14**	75	20	39
25	**31**	42		
26	**32**	82		52
27	**33**	78		
28	**34**	72		30
29	**35**	81		
30	**36**	77 (over two steps)		
37	**38**	53		

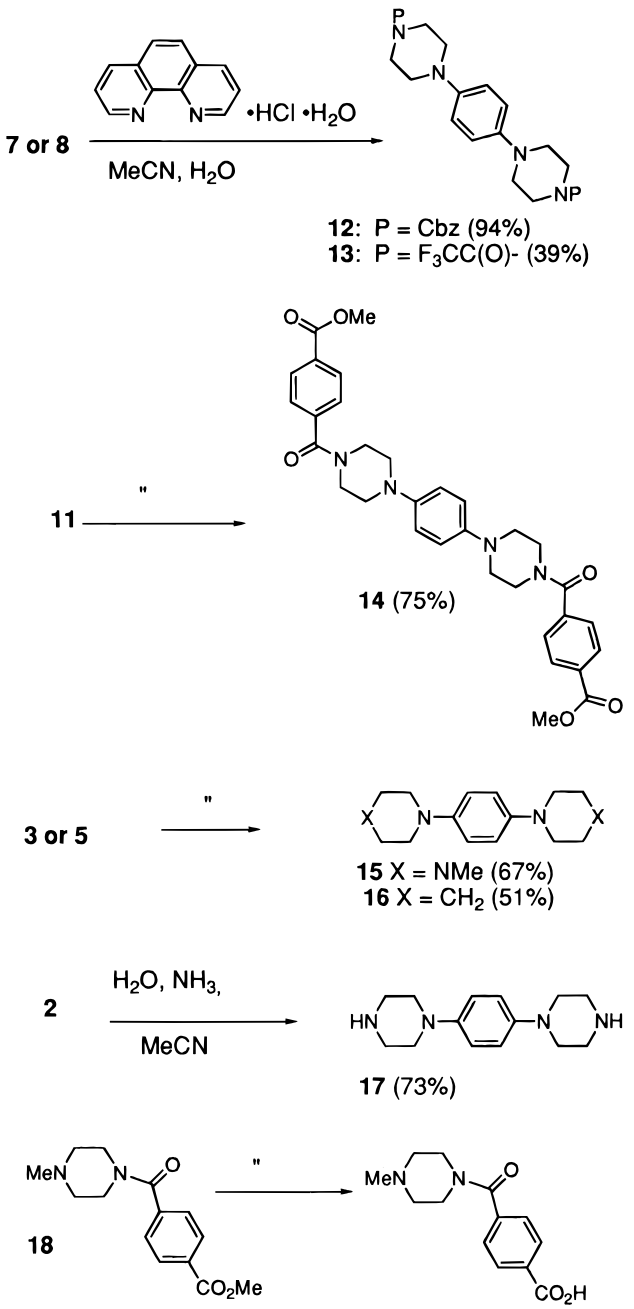
related molecules, (Scheme 2); however, the free diamine **17** remained elusive. While evidence for decomplexation was obtained, it was not possible to separate the $[Fe(Phen)_3]^{2+}$ from the liberated diamine. Attempts to deprotect the benzyloxycarbonyl derivative were unsuccessful, presumably due to catalyst poisoning by the diamine. The trifluoroacetate derivative was not obtained in good yield and was therefore not pursued further. Attempted decomplexation using imidazole as a competing ligand was again accompanied by a separation problem. We were, however, able to recover the imidazole nearly quantitatively after the decomplexation. This led us to speculate that increasing the basicity of the reaction mixture causes precipitation of iron hydroxide and drives the reaction to completion. Decomplexation of **2** in dilute, aqueous ammonia, under room lighting, followed by extraction of the product into chloroform, provided a pathway to **17** in yields of *ca*. 75%. This method is potentially more straightforward in terms of purification than the phenanthroline-assisted decomplexation and would be adequate as long as no hydrolytically unstable functionality is present. For example, treatment of the model compound **18** under identical conditions resulted in complete ester hydrolysis.

Synthesis of Donor−Acceptor Systems. The possibility of obtaining unsymmetrically substituted arenes by sequential, chemoselective S_NAr reactions on dichlorobenzene FeCp cations is well precedented.[1,2,4] We have applied this methodology to the preparation of the unsymmetrical phenylenediamine complexes **23** and **24**. Unfortunately, we were not able to obtain acceptable selectivity with piperazine as the first nucleophile. We obtained almost complete selectivity, however, by using nearly stoichiometric amounts of either *N*-methylpiperazine or piperidine as the first nucleophile. The morpholine adducts **19** and **22** have been described previously.[1b]

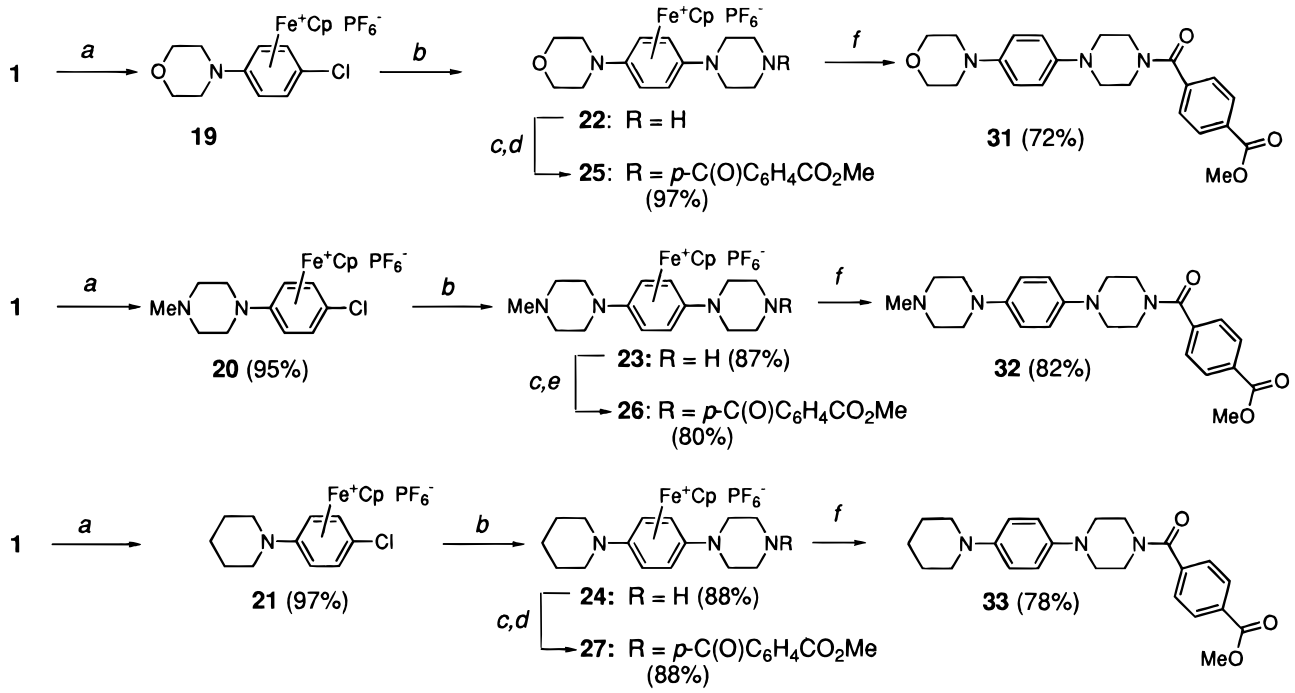
Following a second substitution with piperazine as the nucleophile, we were in possession of three electronically differentiated tetraalkyl-*p*-phenylenediamine complexes **22**−**24**, each with the secondary piperazine nitrogen as a point for further functionalization. Treatment of these complexes with the acid chloride of mono-methyl terephthalate gave the corresponding amides **25**−**27**, each with a potential electron acceptor incorporated into the structure (Scheme 3). Complex **24** was also allowed to react with the acid chlorides of 2-naphthoic acid and anthraquinone-2-carboxylic acid to give compounds **28** and 29. The amidations proceeded in 80−97% yields.

We were also able to use **24** in a conventional S_NAr reaction, with *p*-nitrofluorobenzene (refluxing glyme, 24 h, K_2CO_3), to give **30** and then **36** in 77% overall yield (Scheme 4). Complex **30** was isolated in 66% yield; however, its synthesis is accompanied by some decom-

Scheme 2



Scheme 3[a]



[a] Reagents and conditions: (a) amine nucleophile, K_2CO_3, THF, 12-24 h, rt; (b) piperazine, K_2CO_3, THF, 12 h, rt; (c) monomethyl terephthalate, oxalyl chloride, pyridine, CH_2Cl_2, rt; (d) **20** or **22**, product of c, K_2CO_3, CH_2Cl_2, rt. (e) **21**, prodcut of c, Et_3N, CH_2Cl_2 rt; (f) phenanthroline ·HCl·H_2O, MeCN−H_2O, room light, 24 h, rt.

plexation. Therefore, in order to maximize the yield of **36**, the crude product mixture was usually taken forward to the decomplexation step. Surprisingly, attempts to prepare **30** directly from **21** and the commercially available 4-(4-nitrophenyl)piperazine were unsucessful. Even under relatively forcing conditions (5 equiv of amine, K_2CO_3, refluxing THF, 20 h) we observed only partial (*ca.* 20%) conversion.

Phenanthroline-mediated decomplexations of these amides were straightforward, proceeding in 70−91% yields (this is quite comparable to yields obtained by standard photolytic decomplexations of compounds not presenting chelation or oxidation problems)[1,12] to give the series of donor−acceptor dyads **31**−**36**. The workup in each case consisted of adsorbing the reaction mixture onto basic alumina (adding basic alumina to the reaction mixture, removing the solvent, and drying the residue thoroughly), placing this atop a short alumina column, and washing the organic product through with chloroform. This preadsorption was necessary in order to avoid introducing polar solvents onto the column, which causes cochromatographing of the $Fe(Phen)_3^{2+}$. In most cases, the chloroform eluant was washed with 0.05 M HCl and then water and dried, the solvent removed, and the product recrystallized, usually from acetone. Further chromatographic purification was usually undertaken to obtain material suitable for sensitive physical studies (e.g. fluorescence spectroscopy).

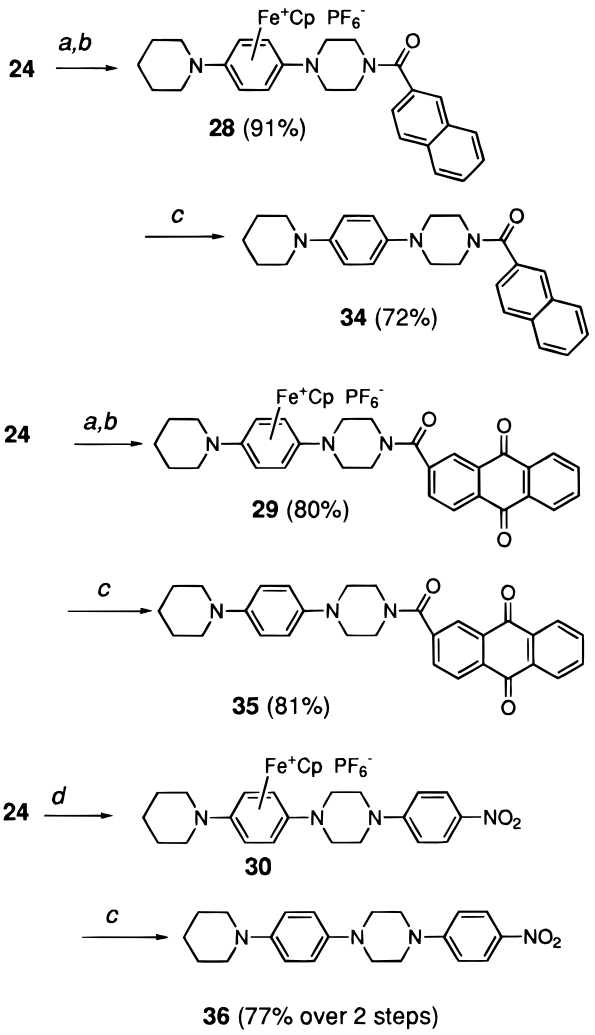
At ambient temperatures the proton and ^{13}C NMR spectra of both the complexed and free amides exhibit severe broadening of the piperazine ring signals, presumably due to slow rotation about the C−N bond as a result of amide resonance. Partial coalescence was observed at 90 °C in CD_3NO_2; however, the signals were still not well resolved. Low temperature spectroscopy in CD_2Cl_2 was therefore employed to obtain the resolved spectra reported herein. We were unable to obtain well-resolved signals for the coresponding atoms of any metalated compounds.

Cyclic Voltammetry. In acetonitrile, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine exhibits a fully reversible first oxidation wave at 120 mV vs SCE .[16] The latitude of nucleophile and substituent control available by using arene-metal chemistry provides a potential method for preparing derivatives of TMPD with attenuated oxidation potentials. "Tuning devices" (inductively electron-withdrawing or sterically demanding groups) can be incorporated as heteroatoms in the cyclic secondary amine nucleophile or introduced by further reaction at the secondary piperazine nitrogen(s) in e.g. **2**, and **22**−**24**, or can be present on the starting dichlorobenzene complex, such as with complex **37** (Figure 1). Several of the compounds presented above were analyzed by CV in acetonitrile, and the results are tabulated in Table 2. The increase in redox potential from TMPD to **16** is presumably the result of the different steric requirements for the planarization of the system which accompanies oxidation. We observed an additional attenuation of the redox potential which was dependent on the inductive electron-withdrawing ability of remote substituents, which covered a range of 320 mV. The most dramatic effects were seen by tuning devices incorporated in the heterocyclic nucleophiles. As expected, only minor adjustments were induced by more remote functionality. With the exception of compounds with a tertiary aliphatic amine remote from the arene, the oxidation waves observed were either fully or quasireversible over a range of 0 to +1.00 V.

Compound **38** is interesting in that the *o*-methyl substituent results in an increased oxidation potential, presumably due to steric inhibition of resonance domi-

(16) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702−711.

Scheme 4[a]



[a] Reagents and conditions: (a) ArCOOH, $(ClC(O))_2$, py, rt; (b) compound **22**, product of a, K_2CO_3, CH_2Cl_2, rt; (c) as for Scheme 3, step f; (d) glyme, K_2CO_3, reflux, 24 h.

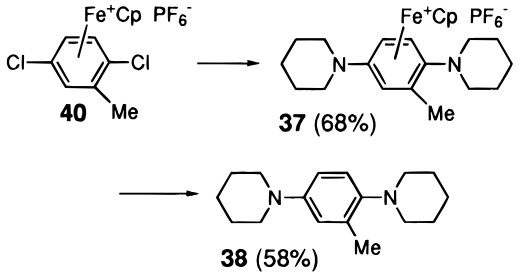


Figure 1.

nating over the inductive electron release of the methyl group. Additionally, in the corresponding complex **37**, the methyl serves as a site for further functionalization. Protons of methyl groups on arene−iron complexes show enhanced acidity owing to the ability of the FeCp fragment to stabilize the resulting carbanion, and deprotonation−alkylation sequences have been explored by Sutherland[17] and Astruc.[17]

Fluorescence Studies. In order to establish whether electronic interactions couple the chromophores in this series, low temperature emission spectra of the electron donor **15**, the donor−acceptor dyad **32**, and the acceptor−donor−acceptor triad **14** were examined. Dyad **32** could probe the effect of one donor on ET quenching of **15**, whereas triad **14** would provide information of the effects of symmetrical substituents on this emission.

Table 2. First Oxidation Potentials of Derivatized *p*-Phenylenediamines (vs NHE)

symmetrical derivatives		unsymmetrical derivatives	
compd	mV	compd	mV
16	192	**36**	272
17	246	**34**	285
9	292	**33**	291
15	299	**35**	295
14	393	**32**	343
13	443	**38**	343
		31	377

Table 3. Percent Quenching of the Triplet Emission of Phenylenediamine Units Contained in 32 and 14, Followed by Steady-State Emission Intensities

compound	% quenching I/I_o
15	0
32	95
14	99

Steady-state emission studies were carried out in MeTHF on compounds **14, 15**, and **32**. Their relative triplet emission intensities, from steady-state measurements, are collected in Table 3. Comparison of emission intensities of the unsubstituted donor to the acceptor−donor dyads indicates fluorescence quenching. From the triplet energies of the donor **15** (E_T = 2.64 eV) and the acceptor (E_T = 3.10 eV) it is clear that the acceptor is not capable of quenching the donor T_1 state. Hence we attribute steady-state quenching in the donor−acceptor dyads to rapid electron transfer quenching.

Conclusions

We have illustrated the use of arene−iron complexes in synthesizing unsymmetrical and functionalized Wurster's blue derivatives. The presence of the metal moiety renders the phenylenediamine sufficiently electron deficient that it may be manipulated conveniently. The decomplexations of these derivatives are not straightforward due to complications involving metal chelation and possible photooxidation reactions of the phenylenediamine. To circumvent this, we have developed a method for the decomplexation of these derivatives, which involves a combination of a mild light source and 1,10-phenanthroline. The phenanthroline coordinates the liberated iron, removing it from further participation in the reaction, and we have applied this procedure to the synthesis of a series of monomers (e.g. **9, 15**) and donor−acceptor systems. We have illustrated an attenuation of the first oxidation wave of these compounds, as a function of remote functionality, over a range of 350 mV, and we are presently involved in further study of their electronic properties.

Experimental Section

General. Complex **1** was prepared according to a previously published procedure.[1b] For general methods, see reference 12b. General procedures are given below and variations

(17) Sutherland, R. G.; Steele, B. R.; Demchuk, K. J.; Lee, C. C. *J. Organomet. Chem.* **1979**, *181*, 411−424.

(18) (a) Moulines, F.; Gloaguen, B. Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 458−460. (b) Fillaut, J.-L.; Boese, R.; Astruc, D. *Synlett* **1992**, 55−56. (c) Moulines, F., Djakovitch, L.; Fillaut, J.-L., Astruc, D. *Synlett* **1992**, 57−58.

are noted with the spectral data for individual compounds. Nuclear magnetic resonance spectra were recorded for solutions of complexes in acetone-d_6, and spectra for products of decomplexation reactions were taken for solutions in $CDCl_3$, at rt or at low temperatures in CD_2Cl_2 unless otherwise specified. Cyclic voltammetry studies were performed on a BAS-100 electrochemical analyzer in CH_3CN with TBAP (0.1 M) as the supporting electrolyte and a sample concentration of 1.0 mM, using a platinum electrode. Reported oxidation potentials are vs NHE and were calculated according to the formula E(vs NHE) = E_{ex}(vs SCE) − E_{Fc}(vs SCE) + 400 mV where E_{Fc} = the potential of the ferrocene/ferricinium couple taken immediately prior to the measurement of the unknown. Emission spectra were recorded at 77 K (λ = 300 nm) in a MeTHF glass, using a SLM Aminco SPF 500 spectrofluorimeter, since room temperature measurements showed no emission. All solutions were deoxygenated by bubbling with nitrogen and had an OD < 0.10 in a 1 cm cuvette. The emission spectra were measured in the ratio mode (to correct for variations in lamp intensity with time). Delayed fluorescence and phosphorescence spectra were recorded on a SLM Aminco SPF 500 spectrofluorometer with a phosphoroscope attachment that uses light baffles and a variable-speed chopper (0−10000 rpm). To prevent light scattering of the excitation wavelength from the low-temperature dewar, a 350 nm cut-off filter was inserted at the front end of the emission monochromator.

General Procedures for Double S_NAr Reactions. Complex **2** was stirred with the amine (10 mmol of amine/mmol of **2**) in the presence of K_2CO_3 (5 mmol/mmol **2**) in THF (25 mL/mmol **2**) at rt for 12 h. The reaction mixture was filtered, and the solid was washed with acetonitrile until the washings were no longer orange. The combined filtrate and washings were concentrated *in vacuo*, redissolved in a minimum of CH_2Cl_2, and added dropwise to approximately a ten-fold excess of ether. The precipitate was isolated by suction filtration and dried *in vacuo*. If the initial precipitate was an oil, the suspension was chilled overnight, the solvent was decanted, and the oil was redissolved and reprecipitated. This procedure was repeated until a solid was obtained.

(1,4-Dipiperazinobenzene)(cyclopentadienyl)iron Hexafluorophosphate (2). Two reprecipitations were usually necessary to remove residual piperazine**.** Yield: 86%. IR (KBr pellet) 3345, 3124, 2959−2843, 1569, 1517 cm^{-1}. ^{1}H NMR δ 5.76 (4H, s), 5.06 (1H, s), 3.31 (8H, t, J = 4.9 Hz), 2.97 (8H, t, J = 4.9 Hz). ^{13}C NMR δ 123.2, 74.2, 66.3, 48.5, 46.1.

[1,4-Bis(4-methylpiperazino)benzene](cyclopentadienyl)iron Hexafluorophosphate (**3**). Yield: 96%. IR (KBr pellet) 3345, 2959−2843, 1569, 1517 cm^{-1}. ^{1}H NMR δ 5.84 (4H, s), 5.14 (5H, s), 3.44 (8H, t, J = 5.1 Hz), 2.59 (8H, t, J = 5.1 Hz), 2.35 (6H, s). ^{13}C NMR (δ) 122.6, 74.4, 66.6, 55.0, 47.6, 46.2.

[1,4-Bis[4-(2-hydroxyethyl)piperazino]benzene-(cyclopentadienyl)iron Hexafluorophosphate (4). Yield: 80%. IR (film) 3380−3210, 2943−2824, 1520, 842 cm^{-1}. ^{1}H NMR δ 5.87 (4H, s), 5.15 (5H, s), 3.73 (4H, t, J = 5.6 Hz), 3.48 (8H, t, J = 5.0 Hz), 2.76 (8H, t, J = 5.0 Hz), 2.64 (4H, t, J = 5.6 Hz). ^{13}C NMR δ 122.6, 74.4, 66.6, 60.8, 59.6, 53.3, 47.8.

[1,4-Dipiperidinobenzene](cyclopentadienyl)iron Hexafluorophosphate (**5**). Yield: 83%. ^{1}H NMR δ 5.82 (4H, s), 5.07 (5H, s), 3.46 (8H, t, J = 5.5 Hz), 1.79 (8H, apparent t, J = 4.9 Hz), 1.75 (4H, t, J = 4.4 Hz). ^{13}C NMR δ 123.2, 74.4, 66.1, 48.3, 26.0, 24.1.

[1,4-Bis[4-(*tert*-butyloxycarbonyl)piperazino]benzene]-(cyclopentadienyl)iron Hexafluorophosphate (6). Complex **2** (51 mg, 0.1 mmol) and di-*tert*-butyl dicarbonate (48 mg, 0.22 mmol) were stirred in CH_2Cl_2 (2 mL) for 2 h. The mixture was filtered through a cotton plug directly into 20 mL of 1:1 ether/pentane. The solid was allowed to settle, the solvent was decanted, and the residue was rinsed with ether (5 mL) and vacuum dried to give **5** (70 mg) in 98% yield. IR (film) 3007−2962, 1691, 1518, 840 cm^{-1}. ^{1}H NMR δ 5.96 (4H, s), 5.16 (5H, s), 3.67 (8H, t, J = 4.8 Hz), 3.50 (8H, t, J = 4.8 Hz), 1.54 (18H, s). ^{13}C NMR δ 155.2, 122.3, 80.6, 74.8, 67.1, 47.4, 28.5.

[1,4-Bis[4-(benzyloxycarbonyl)piperazino]benzene]-(cyclopentadienyl)iron Hexafluorophosphate (7). Complex **2** (513 mg, 1.0 mmol) was stirred with benzyl chloroformate (425 mg, 357 μL, 2.5 mmol) and K_2CO_3 (690 mg, 5.0 mmol) in CH_2Cl_2 (25 mL) for 2 h at rt. Water (1.0 mL) was added, and the mixture was stirred for an additional 0.5 h. The mixture was diluted to 50 mL with CH_2Cl_2, filtered through Celite, and washed through with additional CH_2Cl_2. The combined filtrate and washings were washed with 50% saturated aqueous NH_4PF_6 (10 mL), 0.1 M NaOH (2 × 10 mL), and water (10 mL). The organic layer was dried over $MgSO_4$, concentrated to ca. 10 mL, and added dropwise to 100 mL ether. The precipitate was isolated by suction filtration, rinsed with ether (10 mL), and dried *in vacuo* to give **6** in 88% yield (686 mg). ^{1}H NMR δ 7.43−7.36 (10 H, m), 5.90 (4H, s), 5.17 (4H, s), 5.10 (5H, s), 3.67 (8H, t, J = 6.0 Hz), 3.45 (8H, t, J = 6.0 Hz). ^{13}C NMR δ 155.5, 137.8, 129.1, 128.8, 122.0, 74.2, 67.1, 47.3, 43.5. Two quaternary carbons were not detected.

[1,4-Bis[4-(trifluoroacetyl)piperazino]benzene]-(cyclopentadienyl)iron Hexafluorophosphate (8). Compound **2** (205 mg, 0.4 mmol) was stirred with trifluoroacetic anhydride (336 mg, 226 μL, 1.6 mmol) and pyridine (1.0 mmol, 79 mg, 81 μL) in CH_2Cl_2 (10 mL) for 4 h at rt. The solution was diluted to 30 mL, washed with saturated $NaHCO_3$ (10 mL) and water (2 × 10 mL), dried over $MgSO_4$, and isolated as usual in 80% yield (226 mg). IR (film) 2957−2830 (weak), 1697, 1521, 840 cm^{-1}. ^{1}H NMR (δ) 5.99 (4H, s), 5.16 (5H, s), 3.87 (8H, t, J = 5.0 Hz), 3.65 (8H, t, J = 5.0 Hz). ^{13}C NMR (δ) 121.6, 75.0, 67.4, 47.1, 46.8, 45.3, 42.9.

[1-Chloro-4-piperidinobenzene](cyclopentadienyl)-iron Hexafluorophosphate (**21**). Complex **1** (6.20 g, 15.0 mmol) was stirred with K_2CO_3 (2.07 g, 15.0 mmol) in THF (100 mL). To this suspension was added piperidine (1.70 g, 20.0 mmol), and the reaction was allowed to stir at room temp for 20 h. An additional 272 mg piperidine and 220 mg K_2CO_3 were then added, and the mixture was stirred an additional 12 h. The mixture was filtered and the solid washed thououghly with CH_2Cl_2. The combined washings and filtrate were concentrated *in vacuo* to approximately 20 mL and were added dropwise to ether (200 mL). The precipitate was isolated by suction filtration, washed with ether, and dried *in vacuo* to give the product in 97% yield (6.72 g). ^{1}H NMR (δ) 6.60 (2H, d, J = 7.2 Hz), 6.13 (2H, d, J = 7.2 Hz), 5.22 (5H, s), 3.59 (4H, t, J = 5.6 Hz), 1.79 (6H, br m). ^{13}C NMR (δ) 127.7, 102.3, 86.7, 78.1, 66.6, 48.2, 25.7, 24.0.

[1-Chloro-4-(4-methylpiperazino)benzene](cyclopentadienyl)iron Hexafluorophosphate (**20**). The procedure was as for **21** except that 2 equiv of the amine was used initially and a second portion was not added. Yield: 95%. ^{1}H NMR (δ) 6.45 (2H, d, J = 6.9 Hz), 6.01 (2H, d J = 6.9 Hz), 5.13 (5H, s), 3.40 (2H, t, J = 5.1 Hz); 2.49 (4H, t, J = 5.1 Hz); 2.27 (3H, s). ^{13}C NMR (δ) 126.3, 102.9, 86.8, 78.2, 68.1, 54.4, 46.9, 45.5.

[1-(4-Methylpiperazino)-4-piperazinobenzene](cyclopentadienyl)iron Hexafluorophosphate (**23**). Complex **18** (800 mg, 1.7 mmol) was stirred with piperazine (577 mg, 6.7 mmol) and K_2CO_3 (464 mg, 3.4 mmol) in THF (20 mL) for 12 h at rt. The resulting orange solution was filtered, and the solid was washed with MeCN until it was no longer orange. The combined filtrate and washings were concentrated to approximately 10 mL and added dropwise to 150 mL of ether. The resulting precipitate was isolated by suction filtration and dried *in vacuo* to give the product in 87% yield (799 mg). IR (film) 3325−3195, 3121, 2948−2804, 1565, 1520, 840 cm^{-1}. ^{1}H NMR (δ) 5.76 (4H, s), 5.06 (5H, s), 3.37 (4H, t, J = 5.1 Hz), 3.30 (3H, t, J = 5.2 Hz), 2.96 (4H, t, J = 5.2 Hz), 2.53 (4H, t, J = 5.1 Hz), 2.29 (3H, s). ^{13}C NMR (δ) 123.3, 122.5, 74.3, 66.6, 66.2, 55.0, 48.5, 47.6, 46.7, 46.1.

[1-Piperazino-4-piperidinobenzene](cyclopentadienyl)-iron Hexafluorophosphate (24). The procedure was as for **21**, giving the product in 88% yield. IR (film) 3352−3325, 3118, 2942, 2855, 1567, 1519, 840 cm^{-1}. ^{1}H NMR δ 5.74 (4H, s), 5.02 (5H, s), 3.39 (4H, t, J = 5.4 Hz), 3.30 (4H, t, J = 4.6 Hz), 2.99 (4H, br m), 1.74−1.66 (6H, br m). ^{13}C NMR δ 123.6, 122.8, 74.4, 66.5, 66.1, 48.5, 48.4, 46.1, 26.0, 24.1.

General Procedure for Amidations. The appropriate

carboxylic acid was stirred with pyridine (1.1 equiv) in CH_2Cl_2 (10−15 mL/mmol of acid). A solution of oxalyl chloride (1.0 equiv) in CH_2Cl_2 (5 mL/mmol) was added dropwise to the mixture, from a pressure equalizing dropping funnel. After stirring for 0.5 h, the solvent was removed by rotary evaporation, and the residue was dried *in vacuo* for 1 h. The residue was then redissolved in CH_2Cl_2 (10 mL/mmol) and stirred with K_2CO_3 (1.0 equiv). To this was added a solution of the selected complex in dichloromethane (5 mL/mmol, 0.5 equiv relative to the acid), and the mixture was stirred for 2−4 h. The mixture was diluted with 2 volumes CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, 1.0 M NaOH, and water, dried over $MgSO_4$, and concentrated to ∼10 mL by rotary evaporation. This was added dropwise to ether, and the precipitate was collected by suction filtration and dried under vacuum.

(Cyclopentadienyl)[1,4-bis[4-[4-(methoxycarbonyl)-benzoyl]piperazino]benzene]iron Hexafluorophosphate (11). Terephthalic acid monomethyl ester (2.05 g, 11.4 mmol) and complex **2** (1.48 g, 2.9 mmol) were used. At the conclusion of the reaction, the mixture was diluted with 1:1 CH_2Cl_2/MeCN and worked up as usual to give the product in 78% yield (1,79 g). IR (KBr pellet) 3109, 3004−2849, 1718, 1638, 1575, 1513, 843 cm^{-1}. ^1H NMR δ 8.09 (4H, d, J = 8.3 Hz), 7.57 (4H, d, J = 8.3 Hz), 5.56 (4H, s), 4.87 (5H, s), 3.90 (6H, s) overlapping 3.88 (4H, br), 3.86−3.23 (12H, br m). ^{13}C NMR δ 169.8, 167.1, 141.1, 132.4, 130.5, 128.2, 122.2, 75.0, 67.4, 52.9, 47.6, 47.5, 47.7, 47.2.

[1-Morpholino-4-[4-[4-(methoxycarbonyl)benzoyl]piperazino]benzene] (cyclopentadienyl)iron Hexafluorophosphate (25). Complex **22** (512 mg) and terephthalic acid monomethyl ester gave 756 mg of the product (97%) as an orange microcrystalline powder. IR (KBr pellet) 1718, 1640, 1517 cm^{-1}. ^1H NMR δ 8.08 (2H, d, J = 7.9 Hz), 7.64 (2H, d, J = 7.9 Hz), 5.83 (4H, s), 5.11 (5H, s), 3.92 (5H, s), 3.82 (6H, br s), 3.54 (2H, br s), 3.63 (2H, br s), 3.36 (4H, br s). ^{13}C NMR δ 169.4, 166.6, 141.2, 132.0, 130.3, 128.3, 122.6, 122.2, 74.8, 67.5, 66.9, 66.6, 52.7, 47.7, 41.9.

[1-[4-[4-(Methoxycarbonyl)benzoyl]piperazino]-4-(4-methylpiperazino)benzene](cyclopentadienyl)iron Hexafluorophosphate (26). Triethylamine replaced potassium carbonate in this reaction. Complex **23** (1.94 g, 3.8 mmol) and terephthalic acid monomethyl ester gave 2.14 g of the product amide (80%). IR (film) 3110, 2947−2802, 1718, 1635, 1612, 1565, 1518, 840 cm^{-1}. ^1H NMR δ 8.08 (2H, d, J = 8.2 Hz), 7.63 (2H, d, J = 8.2 Hz), 5.82 (2H, d, J = 7.2 Hz), 5.79 (2H, d, J = 7.2 Hz), 5.08 (5H, s), 3.92 (5H, s), 3.90 (2H, br s), 3.52 (2H, br s), 3.38 (4H, t, J = 5.0 Hz), 3.11 (2H, br s), 2.54 (4H, t, J = 5.0 Hz), 2.29 (3H, s). ^{13}C NMR δ 169.3, 166.7, 141.2, 132.0, 130.3, 128.3, 122.8, 122.0, 74.7, 67.5, 66.6, 54.9, 52.6, 47.5, 46.1, 42.0.

[1-[4-[4-(Methoxycarbonyl)benzoyl]piperazino]-4-piperidinobenzene](cyclopentadienyl)iron Hexafluorophosphate (27). Complex **24** (1.05 g, 2.1 mmol) and terephthalic acid monomethyl ester (815 mg, 4.2 mmol) gave 1.38 g of **27** (88%) yield. IR (film) 3114, 3001−2858, 1716, 1635, 1520, 840 cm^{-1}. ^1H NMR δ 8.09 (2H, d, J = 8.2 Hz), 7.64 (2H, d, J = 8.2 Hz), 5.81 (4H, dd, J = 12.6, 7.6 Hz), 6.06 (5H, s), 3.96 (2H, br s), 3.92 (3H, s), 3.65 (2H, br s), 3.52 (2H, br s), 3.41 (4H, t, J = 5.6 Hz, overlapping 2H, br s), 1.71 (6H, m). ^{13}C NMR δ 169.3, 166.6, 141.2, 132.0, 130.3, 128.3, 124.0, 121.5, 74.7, 67.6, 66.0, 52.6, 48.4, 47.6, 41.8, 25.9, 24.1.

Complex 28. Complex **24** (1.80 g, 3.5 mmol) and 2-naphthoic acid (1.19 g, 7.0 mmol) gave 2.10 g (91%) of the corresponding amide. IR (film) 3108−3060, 2940, 2857, 1778, 1700, 1635, 1635, 1520, 841 cm^{-1}. ^1H NMR δ 8.07−7.96 (4H, m), 7.65−7.59 (3H, m), 5.87 (2H, d, J = 7.6 Hz), 5.82 (2H, d, J = 7.6 Hz), 5.09 (5H, s), 3.86 (4H, br s), 3.55 (4H, br s), 3.42 (4H, t, J = 4.9 Hz), 1.75 (6H, br m). ^{13}C NMR δ 134.7, 134.1, 133.6, 129.3, 129.0, 128.7, 128.0, 127.8, 127.6, 125.5, 124.0, 121.7, 74.7, 67.6, 66.0, 48.4, 47.8, 26.0, 24.1.

Complex 29. This reaction was conducted with only 1 equiv of the acid chloride. Complex **24.** (512 mg, 1.0 mmol) and anthraquinone-2-carboxylic acid (252 mg, 1.0 mmol) gave 599 mg (80%) of the amide. IR (film) 3110, 2940−2859, 1702, 1676, 1639, 1591, 1517, 840 cm^{-1}. ^1H NMR δ 8.41 (1H, d, J = 8.0 Hz), 8.37 (1H, s), 8.35 (2H, dd, J = 5.8, 3.3 Hz), 8.09 (1H, dd, J = 8.0, 1.6 Hz), 8.03, (2H, dd, J = 5.8, 3.3 Hz), 5.89 (2H, d, J = 7.3 Hz), 5.84 (2H, d, J = 7.3 Hz), 5.13 (5H, s), 4.03 (2H, br s), 3.81 (2H, br s), 3.63 (4H, br s), 3.46 (4H, t, J = 4.9 Hz), 1.80 (6H, br s). ^{13}C NMR δ 183.0, 182.9, 168.5, 142.4, 135.4, 134.7, 134.5, 134.3, 133.5, 128.2, 127.8, 126.5, 123.9, 121.5, 74.7, 67.6, 66.0, 48.3, 47.4 (br), 41.9 (br), 25.9, 24.1.

Complex 30. Complex **24** (102 mg, 0.2 mmol), was stirred with 4-fluoronitrobenzene (141 mg, 106 μL, 1.0 mmol) and K_2CO_3 (55 mg, 0.4 mmol) in refluxing 1,2-dimethoxyethane (1.0 mL) in an aluminum foil-wrapped flask, for 24 h. The solution was cooled, filtered through a cotton plug, and added dropwise to ether (20 mL). The precipitate was isolated by suction filtration, redissolved in CH_2Cl_2, and reprecipitated from ether. This precipitate was isolated by suction filtration and dried *in vacuo* to give the product in 75% yield (95 mg). IR (film) 3117, 2941, 2856, 1596, 1569, 1515, 839 cm^{-1}. ^1H NMR δ 8.13 (2H, d, J = 9.22 Hz), 5.85 (4H, dd, J = 15.38, 7.14 Hz), 5.06 (5H, s), 3.79 (4H, t, J = 5.0 Hz), 3.68 (4H, t, J = 5.0 Hz), 3.42 (4H, t, J = 5.4 Hz), 1.74 (6H, br m). ^{13}C NMR δ 155.4, 139.2, 126.4, 123.8, 121.6, 113.7, 74.7, 67.3, 66.1, 48.4, 46.9, 46.8, 26.0, 24.1.

General Procedure for Phenanthroline-Assisted Decomplexations. To an acetonitrile solution of the organometallic complex (0.4 mmol/20 mL) was added 2.9 equiv of 1,10-phenanthroline·HCl·H_2O. Water sufficient to dissolve the phenanthroline was added, and the mixture was allowed to stir in the presence of room lighting for 24 h. Basic alumina (Brockman I) was added to the now intensely red solution. The solvent was removed by rotary evaporation and the alumina/residue dried *in vacuo*. This was placed atop a short basic alumina column, and the amide was washed off by passing chloroform through the column. Any remaining phenanthroline was then removed by washing the chloroform eluant with 0.05 M aqueous HCl and water and then drying over $MgSO_4$. Recrystallization from hot acetone, unless otherwise specified, gave a product that was pure by ^1H and ^{13}C NMR, in the yield specified.

1,4-Bis[4-(benzyloxycarbonyl)piperazino]benzene (12). The chloroform solution was washed with dilute HCl until the washings were no longer red, the organic layer was dried over $MgSO_4$, the solvent was removed *in vacuo*, and the residue was recrystallized from hot acetone to give the product in 83% yield. Mp (evacuated) 168−169 °C. TLC (Al_2O_3, $CHCl_3$) R_f = 0.24. IR (KBr pellet) 3059−3026, 2950−2817, 1696, 1521, 1499 cm^{-1}. ^1H NMR (δ) 7.15−7.09 (5H, m), 6.66 (4H, s), 4.94 (4H, s), 3.43 (8H, t, J = 5.0 Hz), 2.81 (8H, t, J = 5.0 Hz). ^{13}C NMR (δ) 155.2, 145.6, 136.6, 128.5, 128.1, 127.9, 118.3, 67.2, 50.4, 43.9. HRMS calcd for $C_{30}H_{34}N_4O_4$ 514.2580. Found 514.2566.

1,4-Bis[4-(trifluoroacetyl)piperazino]benzene (13). This compound was recrystallized from $CHCl_3$/hexane. Yield: 39%. Mp 115−116 °C. TLC (Al_2O_3, $CHCl_3$) R_f = 0.16. IR (KBr pellet) 3048−2810, 1685, 1517 cm^{-1}. ^1H NMR δ 6.67 (4H, s), 3.60 (4H, t, J = 5.1 Hz), 3.52 (4H, t, J = 5.1 Hz), 2.90 (8H, t, J = 5.1 Hz). ^{13}C NMR δ 144.9, 118.1, 50.2, 49.7, 45.4, 42.9. HRMS calcd for $C_{18}H_{20}F_6N_4O_2$ 438.1490. Found 438.1494.

1,4-Bis[4-[4-(methoxycarbonyl)benzoyl]piperazino]-benzene (14). Yield: 75%. Mp 257−259 °C (d). TLC (SiO_2, EtOAc, R_f = 0.20; Al_2O_3, $CHCl_3$, R_f = 0.33). IR (KBr pellet) 2828, 1725, 1630 cm^{-1}. ^1H NMR δ 8.10 (4H, dm, J = 8.3 Hz), 7.49 (4H, dm, J = 8.3 Hz), 7.26 (4H, s), 3.95 (6H, s) overlapping 3.94 (4H, br), 3.53 (4H, br), 3.17 (4H, br), 3.03 (4H, br). ^{13}C NMR δ 169.3, 166.3, 145.5, 139.9, 131.3, 129.9, 127.1, 118.4, 52.4, 50.9, 50.5, 47.6, 42.2. HRMS calcd for $C_{32}H_{34}N_4O_6$ 572.2635. Found 572.2586.

1,4-Bis(4-methylpiperazino)benzene (15). The chloroform solution of the compound was concentrated *in vacuo* and the residue rechromatographed (flash SiO_2, 10% MeOH in $CHCl_3$, increasing to 50% MeOH in $CHCl_3$ after collection of the residual phenanthroline and then to 100% MeOH. The solvent was removed and the residue dried to give the product in 67% yield. For fluoresence studies, the compound was vacuum sublimed at 120 °C. Mp 165−166 °C. TLC (Al_2O_3, 1% MeOH/$CHCl_3$), R_f = 0.30. IR (KBr pellet) 2961−2687, 1516 cm^{-1}. ^1H NMR (δ) 6.85 (4H, s), 3.07 (8H, t, J = 5.0 Hz), 2.53

(8H, t, J = 5.0 Hz), 2.30 (6H, s). ^{13}C NMR (δ) 145.3, 117.6, 55.2, 50.2, 46.1. HRMS calcd for $C_{16}H_{26}N_4$ 274.2157. Found 274.2144.

1,4-Dipiperidinobenzene (16). The chloroform solution of the compound was concentrated in vacuo and the residue rechromatographed (flash SiO_2, $CHCl_3$ R_f = 0.7) to give the product in 51% yield. ^{1}H NMR δ 6.85 (4H, br s), 2.98 (8H, br s), 1.67 (8H, quint, J = 5.5 Hz), 1.50 (4H, s). ^{13}C NMR δ 146.2, 118.1, 51.9, 26.1, 24.2. HRMS calcd for $C_{16}H_{24}N_2$ 244.1939. Found 244.1942.

1-Morpholino-4-[4-[4-(methoxycarbonyl)benzoyl]piperazino]benzene (31). 72% Yield. Mp 186−187 °C. TLC (Al_2O_3, $CHCl_3$,R_f = 0.31). IR (KBr pellet, cm^{-1}) 3050−2813, 1725, 1632, 1514. ^{1}H NMR δ 8.08, (2H, d, J = 8.2 Hz), 7.49 (2H, d, J = 8.2 Hz), 6.87 (4H, s), 3.92 (5H, s), 3.83 (4H, t, J = 4.8 Hz), 3.51 (2H, br s), 3.14 (2H, br s), 3.06 (4H, t, J = 4.8 Hz), 2.99 (2H, br s). Low temperature ^{1}H NMR (CD_2Cl_2, −30 °C) δ 7.92 (2H, dd, J = 8.2, 1.8 Hz), 7.34 (2H, dd, J = 8.2, 1.8 Hz), 6.73 (4H, s), 3.75 (3H, s, overlapping 2H, t, J = 4.9 Hz), 3.65 (4H, t, J = 4.6 Hz), 3.36 (2H, t, J = 4.9 Hz), 2.98 (2H, t, J = 4.9 Hz), 2.87 (4H, t, J = 4.6 Hz), 2.82 (2H, t, J = 4.9 Hz). ^{13}C NMR δ 169.3, 166.3, 146.1, 144.8, 139.9, 131.2, 129.9, 127.0, 118.5, 117.2, 67.0, 52.4, 51.0, 50.7, 50.2, 47.6, 42.2. HRMS calcd for $C_{23}H_{27}N_3O_4$ 409.2001. Found 409.1993.

1-[4-[4-(Methoxycarbonyl)benzoyl]piperazino]-4-(4-methylpiperazino)benzene (32). The acid wash must be omitted from this workup. Chromatography (Al_2O_3, CH_2Cl_2, R_f = 0.20), followed by recrystallization, gave the product in 82% yield. Mp 188-189 °C. TLC (Al_2O_3, $CHCl_3$), R_f = 0.38. IR (KBr pellet) 2963−2740, 1729, 1631, 1609, 1519 cm^{-1}. ^{1}H NMR δ 8.08 (2H, d, J = 8.1 Hz), 7.48 (2H, d, J = 8.1 Hz), 6.87 (4H, s), 3.91 (5H, s), 3.50 (2H, br s), 3.11 (4H, t, J = 4.9 Hz), 2.98 (2H, br s), 2.56 (4H, t, J = 4.9 Hz), 2.33 (3H, s). Low temperature ^{1}H NMR (CD_2Cl_2, −30 °C) δ 7.92 (2H, dd, J = 8.2, 1.9 Hz), 7.34 (2H, dd, J = 8.2, 1.9 Hz), 6.72 (4H, s), 3.76 (3H, s, overlapping 2H, t, J = 5.0 Hz), 3.35 (2H, t, J = 5.0 Hz), 2.98 (2H, t, J = 5.0 Hz), 2.92 (4H, t, J = 4.9 Hz), 2.82 (2H, t, J = 5.0 Hz), 2.38 (4H, t, J = 4.9 Hz), 2.14 (3H, s). ^{13}C NMR δ 169.3, 166.3, 146.1, 144.6, 140.0, 131.2, 129.9, 127.1, 118.5, 117.5, 55.2, 52.3, 51.1, 50.7, 49.9, 47.7, 46.1, 42.2. HRMS calcd for $C_{24}H_{30}N_4O_3$ 422.2318. Found 422.2318.

1-[4-[4-(Methoxycarbonylbenzoyl)piperazino]-4-piperidinobenzene (33). Chromatography (SiO_2, 2.5% MeOH/$CHCl_3$, R_f = 0.25) in lieu of recrystallization gave **28** in 78% yield. Mp 135−6 °C. TLC (Al_2O_3, $CHCl_3$), R_f = 0.40. IR (KBr pellet) 2927−2825, 1725, 1628, 1515 cm^{-1}. ^{1}H NMR δ 8.02 (2H, d, J = 8.2 Hz), 7.41 (2H, d, J = 8.2 Hz), 8.61 (4H, dd, J = 19.8, 9.2 Hz), 3.85 (3H, s, overlapping 2H, br), 3.44 (2H, br s), 3.07 (2H, br s), 2.97 (4H, t, J = 5.5 Hz overlapping 2H, br s), 1.61 (4H, apparent t, J = 5.5 Hz), 1.46 (2H, apparent q, J = 5.5 Hz). Low temperature ^{1}H NMR (CD_2Cl_2, −30 °C) δ 7.92 (2H, dd, J = 8.2, 1.7 Hz), 7.34 (2H, dd, J = 8.2, 1.7 Hz), 6.72 (4H, s), 3.76 (3H, s, overlapping 2H, t, J = 4.9 Hz), 3.36 (2H, t, J = 4.9 Hz), 2.97 (2H, t, J = 4.9 Hz), 2.85 (4H, t, J = 5.4 Hz overlapping 2H, t, J = 4.9 Hz), 1.51 (4 H, apparent quint, J = 5.4 Hz), 1.36 (2H, apparent quint, J = 5.4 Hz). ^{13}C NMR δ 169.3, 166.3, 147.1, 144.3, 139.9, 131.2, 129.8, 127.0, 118.4, 118.1, 52.3, 51.7, 51.1, 50.7, 47.7, 42.2, 25.9, 24.1. HRMS calcd for $C_{24}H_{29}N_3O_3$ 407.2209. Found 407.2214.

Naphthoate Derivative 34. Yield: 72%. Mp (evacuated) 163−165 °C. TLC (Al_2O_3, $CHCl_3$), R_f = 0.16. IR (KBr pellet) 3053−2808, 1623, 1609, 1515 cm^{-1}. ^{1}H NMR δ 7.92−7.83 (4H, m), 7.55−7.48 (3H, m), 6.89 (2H, d, J = 0.4 Hz), 6.88 (2H, d, J = 0.4 Hz), 3.96 (2H, br s), 3.59 (2H, br s), 3.10 (4H, br s) overlapping 3.03 (4H, t, J = 5.4 Hz), 1.69 (4H, quint, J = 5.6 Hz), 1.52 (2H, m). ^{13}C NMR δ 170.4, 147.2, 144.4, 133.7, 133.0, 132.7, 128.4, 127.8, 127.1, 127.0, 126.7, 124.3, 118.4, 118.1, 50.9, 47.9, 42.4, 26.0, 24.2. HRMS calcd for $C_{26}H_{29}N_3O$ 399.2310. Found 399.2310.

Anthraquinone Amide Derviative 35. Yield: 80%. Mp 222−224 °C dec. TLC (Al_2O_3, $CHCl_3$), R_f = 0.13. IR (KBr pellet) 3073−2808, 1675, 1630, 1595, 1517 cm^{-1}. ^{1}H NMR δ 8.39−8.27 (4H, m), 7.87−7.80 (3H, m), 6.88 (4H, s), 3.96 (2H, br s), 3.55 (2H, br s), 3.15 (2H, br s), 3.03 (2H, br s) overlapping 4H, t, J = 5.2 Hz), 1.69 (4H, m), 1.53 (2H, apparent q, J = 5.2 Hz). Low temperature ^{1}H NMR (CD_2Cl_2, −40 °C) δ 8.23−8.16 (3H, m), 7.74−7.69 (4H, m), 6.73 (4H, s), 3.79 (2H, t, J = 4.9 Hz), 3.40 (2H, t, J = 4.9 Hz), 3.02 (2H, t, J = 4.9 Hz), 2.87 (6H, m), 1.55−1.50 (4H, m), 1.42−1.38 (2H, m). ^{13}C NMR δ 182.4, 168.2, 147.4, 144.1, 141.2, 134.4, 134.0, 133.6, 133.6, 132.6, 127.9, 127.4, 125.7, 118.6, 118.0, 51.6, 51.2, 50.9, 47.8, 42.4, 26.0, 24.2. HRMS calcd for $C_{30}H_{29}N_3O_3$ 479.2209. Found 479.2209.

4-[4-(4-Piperidinophenyl)piperazino]nitrobenzene (36). Mp 201−203 °C, TLC (Al_2O_3, $CHCl_3$), R_f = 0.25. IR (KBr pellet) 2941−2780, 1588, 1513 cm^{-1}. ^{1}H NMR δ 8.12 (2H, dd, J = 9.6, 2.3 Hz), 6.90 (4H, m), 6.82 (2H, dd, J = 9.6, 2.3 Hz), 3.53 (4H, t, J = 5.1 Hz), 3.20 (4H, br s), 3.04 (4H, br s), 1.71 (4H, t, J = 4.8 Hz), 1.52 (2H, br s). ^{13}C NMR δ 154.8, 144.6, 138.6, 125.9, 118.4, 118.0, 112.8, 52.0, 50.1, 47.2, 25.8, 24.0. One quaternary carbon was not detected. HRMS calcd for $C_{21}H_{26}N_4O_2$ 366.2055. Found 366.2069.

1,4-Dipiperidino-2-methylbenzene (38). Column chromatography (SiO_2, 5% MeOH in $CHCl_3$, R_f = 0.3), gave the product as an off-white oil (71 mg, 53%). ^{1}H NMR δ 6.90 (1H, d, J = 8.7 Hz), 6.80 (1H, d, J =2.5 Hz), 6.72 (1H, dd, J = 8.7, 2.5 Hz). ^{13}C NMR δ 148.1, 145.9, 133.4, 120.1, 119.5, 114.8, 53.8, 51.6, 26.7, 26.1, 24.5, 24.3, 18.0. HRMS calcd for $C_{17}H_{26}N_2$ 258.2095. Found 258.2095.

1-(4-Piperazinophenyl)piperazine (17). Complex **2** (102 mg, 0.2 mmol) was dissolved in MeCN and added to 10 mL of 2.5 M, deoxygenated, aqueous ammonia. The mixture was allowed to stir, under room lighting, for 24 h, by which time a fine black precipitate had formed. The precipitate was removed by suction filtration, an additional 162 μL of concentrated ammonium hydroxide was added, and the mixture allowed to stir a further 24 h. The mixture was filtered again, basified (1 M NaOH), and extracted exhaustively with $CHCl_3$ to give **17** in 73% yield (36 mg). ^{1}H NMR δ 6.82 (4H, s), 3.0 (16H, m). ^{13}C NMR δ 145.9, 117.7, 51.6, 46.3. HRMS calcd for $C_{14}H_{22}N_4$ 246.1844. Found 246.1844.

General Procedure for Photolytic Decomplexations. An acetonitrile solution of the complexed phenylenediamine was stirred in the presence of a 275 W sunlamp, under argon, for 3 h. The acetonitrile was removed by rotary evaporation and the residue was dissolved in 0.5 M HCl. This dark blue soultion was immediately basified and the resulting brown precipitate removed by suction filtration and washed until addition of a small sample to dilute HCl resulted in a yellow (not blue) solution (no residual diamine is present). The filtrate was evaporated to dryness by rotary evaporation, and the residue was stirred with refluxing $CHCl_3$ for 6 h. The solution was cooled, filtered, and concentrated and the residue purified by chromatography (Al_2O_3, $CHCl_3$, MeOH as required).

1,4-Bis[4-(2-hydroxyethyl)piperazino]benzene (9). Chromatography (Al_2O_3, 2.5% MeOH/$CHCl_3$, R_f = 0.40) followed by recrystallization from acetone gave **8** in 66% yield. Mp (evacuated) 191−193 °C dec. IR (KBr pellet) 3456−3227, 2949−2730, 1513 cm^{-1}. ^{1}H NMR δ 6.86 (4H, s), 3.63 (4H, t, J = 5.3 Hz), 3.09 (8H, t, J = 4.9 Hz), 2.65 (8H, t, J = 5.3 Hz), 2.58 (4H, t, J = 5.3 Hz), 2.00 (2H, br s). ^{13}C NMR δ 145.3, 117.7, 59.3, 57.7, 52.9, 50.3. HRMS calcd for $C_{18}H_{30}N_4O_4$ 334.2369. Found 334.2369.

1,4-Bis[4-(*tert*-butoxycarbonyl)piperazino]benzene (10). As there was no complexation of iron by this compound, a traditional workup was possible. Following irradiation, the acetonitrile was removed by rotary evaporation, and the residue was chromatographed directly (SiO_2, 5% MeOH/$CHCl_3$, R_f = 0.4), to give the product in 95% yield. Mp 193−194 °C. IR (KBr pellet) 2977−2760, 1701, 1608, 1517 cm^{-1}. ^{1}H NMR δ 6.85 (4H, s), 3.53, (8H, t, J = 4.9 Hz), 2.98 (8H, t, J = 4.9 Hz), 1.43 (18H, s). ^{13}C NMR δ 118.2, 79.8, 50.5, 28.4. Two quaternary carbons were not detected. HRMS calcd for $C_{24}H_{38}N_4O_4$ 446.2893. Found 446.2897.

[(η^5-Cyclopentadienyl)(η^6-2,5-dichlorotoluene)]iron-(II) Hexafluorophosphate (39). Ferrocene (3.0 g,), $AlCl_3$ (6.0 g), and aluminum powder (400 mg) were combined under argon. To this was added freshly distilled 2,5-dichlorotoluene (20 mL), *n*-heptane (20 mL), and water (100 μL). The reaction mixture was purged of oxygen by a stream of argon and then stirred at 85 °C for 12 h. The mixture was cooled to room temperature, ice−water (50 mL) was added cautiously, and

the mixture was stirred for 10 min. The aqueous layer was separated, filtered, and washed with ether (3 × 30 mL). A saturated aqueous solution of NH_4PF_6 was added to the aqueous layer until precipitation ceased. The resulting combination of yellow solid and mother liquor was extracted into CH_2Cl_2 (3 × 30 mL), dried over $MgSO_4$, and concentrated to <20 mL. This was added dropwise to ether (200 mL), and the resulting yellow precipitate was isolated by suction filtration and dried under high vacuum to give 1.8 g (26%) shown by NMR to consist of a *ca*. 15:1 mixture of **39** and [η^6-(cyclopentadienyl)-η^5-(3-chlorotoluene)]iron(II) hexafluorophosphate. ^{1}H NMR δ 7.16 (1H, d, J = 1.7 Hz), 7.05 (1H, d, J = 6.6 Hz), 6.98 (1H, dd, J = 6.6, 1.7 Hz), 5.44 (5H, s), 2.82 (3H, s). ^{13}C NMR δ 107.6, 106.8, 103.6, 90.3, 88.9, 88.1, 82.4, 19.5.

1,4-Dipiperazino-2-methylbenzene(cyclopentadienyl)-iron Hexafluorophosphate (37). [(η^5-Cyclopentadienyl)-(η^6-2,5-dichlorotoluene)]iron(II) hexafluorophosphate (300 mg, 0.7 mmol), piperidine (595 mg, 692 μL, 7.0 mmol), and K_2CO_3 (483 mg, 3.5 mmol) were stirred in refluxing THF (10 mL) for 72 h in an aluminum foil-wrapped flask. The workup was as for **2**−**5**, to give a 9:1 mixture, by ^{1}H NMR, of **37** and the product of monodisplacement (275 mg, 75%). ^{1}H NMR δ 6.02 (1H, d, J = 2.3 Hz), 5.87 (1H, dd, J = 7.2, 2.3 Hz), 5.79 (1H, d, J = 7.2 Hz), 4.97 (5H, s), 3.50 (4H, t, J = 4.9 Hz), 3.10 (4H, m), 2.64 (3H, s), 1.93−1.67 (12H, m). ^{13}C NMR δ 125.0, 121.6, 116.5, 76.1, 70.4, 70.4, 70.0, 64.3, 53.1, 48.2, 26.8, 26.0, 24.7, 24.1, 19.4.

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Supporting Information Available: Proton and ^{13}C NMR spectra are available for all new compounds (77 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and may be ordered from the ACS; see any current masthead page for ordering information.

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