(100.6 MHz, $CDCl_3$, TMS): $\delta = 161.16$, 158.70 (d, $^1J(C,F) = 247.8$ Hz), 131.89 (s), 126.56 (s), 124.31 (s), 55.89 (s); ^{19}F NMR (564.7 MHz, $CDCl_3$, $CFCl_3$): $\delta = -126.26$; MS (FAB): m/z (%): 827 (100) $[M+K^+]$; elemental analysis of a sample recrystallized from $CHCl_3$: calcd for $C_{48}H_{42}N_4F_6 \cdot C_6H_2N_3O_7K \cdot 2H_2O$: C 59.39, H 4.43, N 8.98; found: C 59.47, H 4.30, N 8.93.

Crystallographic data for $K^+ \subset \mathbf{1} \cdot Pic^- \cdot 2H_2O$ ($C_{54}H_{48}N_7O_9F_6K$): $M_r = 1092.10$, $T = 23\,^\circ C$, $Mo_{K\alpha}$ (Rigaku RAXIS-IV imaging plate area detector, $\lambda = 0.71070$ Å), crystal dimensions $0.40 \times 0.30 \times 0.50$ mm^3 (yellow prism); triclinic, space group $P\bar{1}$ (no. 2), $a = 13.980(4)$, $b = 18.336(8)$, $c = 11.198(5)$ Å, $\alpha = 98.38(1)$, $\beta = 110.54(3)$, $\gamma = 102.04(2)^\circ$, $Z = 2$, $\mu_{Mo} = 1.87$ cm^{-1}, $V = 2552.6(8)$ Å^3, $\rho_{calcd} = 1.391$ g cm^{-3}, $2\theta_{max} = 55^\circ$, $F(000) = 1106$. Indexing was performed from three oscillations which were exposed for four minutes. A total of 31 oscillation images (5.00°) were collected, each being exposed for ten minutes. Of the 8043 reflections collected, 6178 were unique and 8000 were independent with $I > 3\sigma(I)$. The structure was solved by direct methods and refined on SAPI 91. Data were corrected for Lorentz and polarization effects. The data/parameter ratio was 6.86; $R = 0.071$, $Rw = 0.065$, GOF = 1.55, max./min. residual density $+0.95/-0.58$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103215. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Novel Aluminum-Containing Ring Systems: An Octanuclear Structural Analogue of a Calix[4]pyrrole**

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The study of the coordination chemistry of Group 13 alkyl derivatives to give complexes of differing nuclearities is being actively pursued, prompted by the relevance of such species to alkylaluminoxanes, $(RAlO)_n$,[1] and as single-source precursors to semiconducting and electronic materials, for example GaN.[2] In recent studies, a number of unusual aluminum-containing ring and cage structures have been described. For example, difunctional molecules such as 1,2-diaminobenzene ($1,2\text{-}(NH_2)_2C_6H_4$), salicylic acid ($1\text{-}(CO_2H)\text{-}2\text{-}(OH)C_6H_4$), and 1,2-diphosphanylbenzenes ($1,2\text{-}(PR_2)_2C_6H_4$; R = H, Me) have been shown to react with Me_3M (M = Al, Ga) to give ring and cage structures for both aluminum and gallium;[3] other ring and cage structures have been accessed from reactions involving the use of primary or secondary amines[4] and phenylhydrazine.[5]

In separate studies, gallium-mediated coupling reactions involving acetonitrile have recently been described. For example, the trimethylgallium-induced trimerization of acetonitrile, in the presence of a catalytic amount of caesium salt, was supported by the isolation and crystal structure determination of the heterocycle $[Me_2Ga\{HNC(Me)\}_2C(CN)]$;[6] further reaction with Me_3Ga/MeCN gave $[(Me_2Ga)_4(MeGa)_2\{HNC(Me)C(CN)CH(NCMe)_2\}_2]$. Here we describe two remarkable reactions of Me_3Al with 1,1-disubstituted hydrazines to give novel macrocyclic ring structures arising by reaction of Me_3Al with the hydrazine followed by insertion of acetonitrile into the so-generated Al–N bonds.

Addition of two molar equivalents of Me_3Al to 1,1-dimethylhydrazine (Me_2NNH_2) in toluene results in rapid evolution of methane and formation of a colorless solution. After removal of the solvent, the residue was dissolved in acetonitrile, warmed at 80 °C for 10 min, and then cooled to −20 °C to give large colorless prisms of complex **1**. The crystal structure[7] of **1** (Figure 1 a) shows the molecule to be made up of four five-membered AlN_3C rings linked by Me_2Al bridges, and it may be viewed as a structural analogue of the calix[4]pyrroles.[8] The molecule has non-crystallographic S_4 symmetry, adopting a 1,3-*alternate* conformation (Figure 1 b) very similar to the aforementioned calix[4]pyrroles. The four bridging aluminum atoms of the 16-membered ring are coplanar to within 0.19 Å, with the four near-planar AlN_3C rings inclined by 59–67° to this plane. The geometries at the bridging aluminum centers are only slightly

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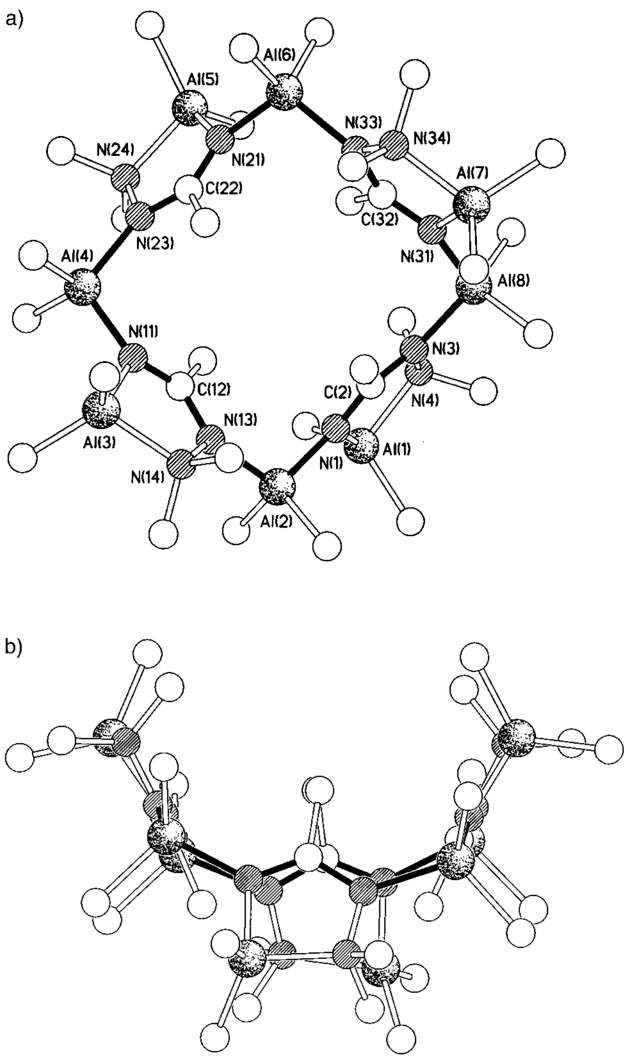
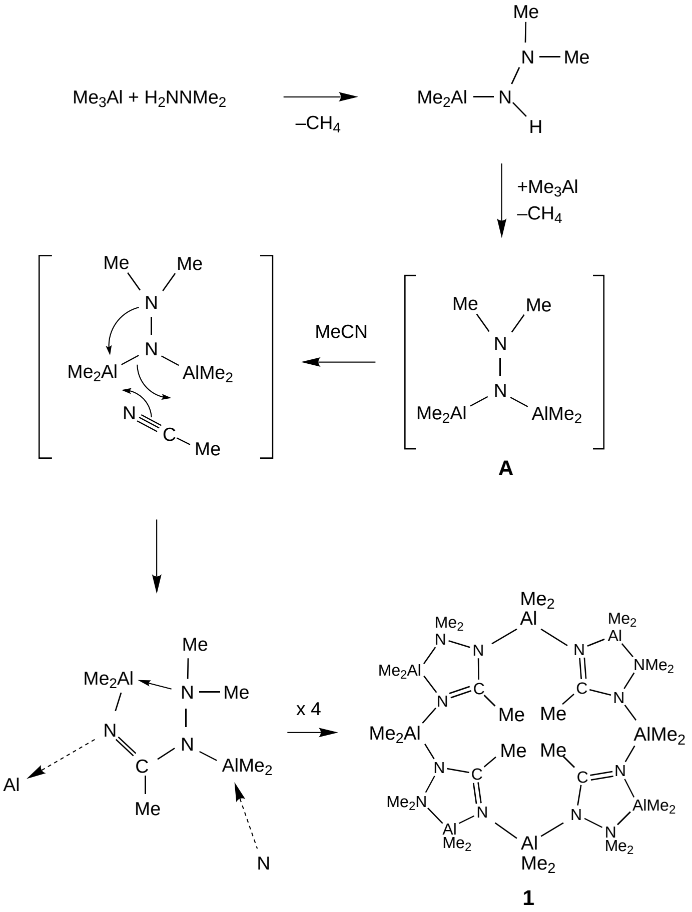


Figure 1. a) The molecular structure of **1** (top view). Selected bond lengths [Å]: Al(1)–N(1) 1.877(3), Al(1)–N(4) 2.042(3), Al(2)–N(1) 1.899(3), Al(2)–N(13) 1.972(3), N(1)–C(2) 1.313(4), C(2)–N(3) 1.356(4); b) Side view of **1**.

distorted from tetrahedral, with angles ranging between 107 and 115°. By contrast, the aluminum atoms within the five-membered rings have pseudo-trigonal-pyramidal geometries with the Me_2N moiety occupying the apical position and with the aluminum atoms lying between 0.37 and 0.39 Å out of the basal plane.[9] This geometry, coupled with the noticeably long Al–N(apical) linkages (2.020(3) – 2.042(3) Å), is comparable to that observed in related $Al-NR_3$ systems[10] and reflects the formal dative character of these bonds; the other Al–N distance within the five-membered rings is about 0.14 Å shorter (av 1.886 Å). The bridging Al–N distances alternate in length, with those to N(1), N(11), N(21), and N(31) (av 1.893 Å) being significantly shorter than those to N(3), N(13), N(23), and N(33) (av 1.975 Å); in each case the shorter distance is to the nitrogen atom involved in a double bond to the ring carbon atom (av 1.308 Å). The Al–Me distances are unexceptional (1.952(4) – 1.981(4) Å). The presence of the bulky methyl substituents results in an essential self-filling of the potential macrocyclic cavity, there being no significant free pathway through the ring center.

Any mechanism for the synthesis of **1** has to account for (after the loss of methane) the presence of two extra carbon atoms and a nitrogen atom in each of the five-membered rings. A plausible sequence is shown in Scheme 1, where the first two steps involve loss of methane and formation of a bridged hydrazido(2 –) species **A**. This intermediate is then postulated to react by insertion of acetonitrile into an Al–N bond to afford the five-membered ring structural motif found in **1**.



Scheme 1. Proposed mechanism for the formation of **1**.

The macrocycle **1** displays broadened signals in the ^1H NMR spectrum ([D$_8$]toluene, 500 MHz) for the Me_2N ($\delta = 2.31$; $\omega_{1/2} = 80$ Hz) and Me_2Al groups ($\delta = -0.43$, -0.58; $\omega_{1/2} = 60$ Hz) at ambient temperature. At the low temperature limit (265 K) each of the broadened resonances is resolved into two signals of approximately equal intensity. The $\Delta G^{\neq}$ value for this fluxional process, which we attribute to being a flipping of the five-membered rings in the 1,3-*alternate* conformation, is calculated to be 64 kJ mol^{-1} ($T_c = 295$ K, rate constant $k = 27$ s^{-1}). On warming to 325 K all signals are sharp. In the ambient-temperature ^{13}C NMR spectrum, the Me_2N group appears as two broadened resonances ($\delta = 47.5$, 49.0), while the Me_2Al units give rise to two sets of broadened signals ($\delta = -9.7$, -8.4 and -4.9, -2.3). All three sets coalesce to singlet resonances on warming ($T_c = 350$ K).

Encouraged by the successful synthesis of the novel macrocyclic ring system **1**, we then investigated the reaction of Me_3Al with methylphenylhydrazine. Slow addition of a solution of Me_3Al (2 equiv) in toluene to $MePhNNH_2$, followed by heating under reflux for 12 h in acetonitrile, afforded a pale brown solution from which colorless plates of **2** were isolated in about 55 % yield after recrystallization from hot acetonitrile. The X-ray analysis[7] reveals that the product is the C_i-symmetric macrocyclic complex illustrated in Figure 2. The 12-membered macro-ring is self-filling and comprises four aluminum atoms (two bridging and two chelating), six nitrogen atoms, and two carbon atoms. The two disubstituted chelating phenylene rings are oriented approximately axially with respect to the macro-ring plane. The geometries at Al(1) and Al(2) are distorted tetrahedral, with angles of 86.4(1) – 116.4(1)° and 99.4(1) – 115.4(1)°, respectively. There is also a marked variation in the Al–N bond lengths within the ring; the Al(2)–N(7) linkage (2.000(3) Å) is significantly longer than the others (1.909(2) – 1.961(3) Å). However, these values lie within the broad range of Al–N distances reported in the literature. The five-membered chelate rings are folded so as to produce an axial/equatorial geometry for the two methyl substituents, the aluminum atom lying 0.67 Å out of the plane of the other four ring atoms.

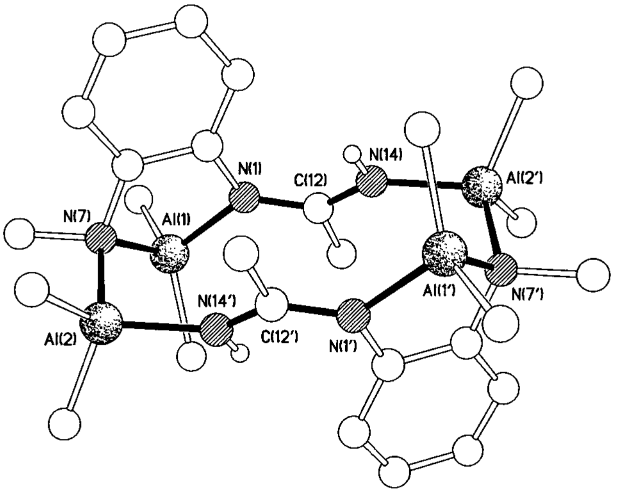


Figure 2. The molecular structure of **2**. Selected bond lengths [Å]: Al(1)–N(1) 1.930(2), Al(1)–N(7) 1.961(3), N(7)–Al(2) 2.000(3), Al(2)–N(14') 1.909(2), N(14)–C(12) 1.313(4), C(12)–N(1) 1.342(4).

The ^{1}H NMR spectrum (300 MHz) of **2** at ambient temperature shows sharp signals and consists of four singlets of equal intensity in the Al – methyl region ($\delta = -0.2$ to -0.7) together with two further singlets (again of similar intensity) at $\delta = 1.38$ and 2.57. On warming, two of the Al – methyl resonances (at ca. $\delta = -0.5$) coalesce ($T_c = 368$ K), which we attribute to wagging of the bridging Me$_2$Al groups (Al(2) and Al(2') in Figure 2); $\Delta G^{\neq} = 79$ kJ mol^{-1}, $k = 52$ s^{-1}. The mechanism of formation of **2** again clearly involves incorporation of acetonitrile, but in this case the process is accompanied by N–N hydrazine bond scission along with cleavage of one of the *ortho*-phenyl C–H bonds. The detailed pathway remains to be established.

In conclusion, these results exploiting the ready insertion of acetonitrile into aluminum – nitrogen bonds highlight a potentially powerful synthetic approach to macrocyclic aluminum-containing ring systems. Further work is in progress to explore and extend the synthetic scope of this reaction.[11]

Experimental Section

Complexes **1** and **2** were prepared by heating Me$_3$Al (50 mL, 2.0 M, 0.1 mol) and the appropriate hydrazine (0.05 mol) in toluene (30 mL) under reflux for 12 h. Volatile components were then removed in vacuo, and the products obtained by treatment with excess hot acetonitrile (50 – 60 mL). Large colorless prisms of **1** and **2** are obtained on prolonged cooling at −20 °C.

1: Yield: 3.2 g; further crops can be obtained from the mother liquor (overall yield 40 %). Elemental analysis calcd for $C_{32}H_{84}N_{12}Al_6$: C 45.1, H 9.9, N 19.7; found: C 45.1, H 9.5, N 19.9; ^{1}H NMR (500 MHz, [D$_8$]toluene, 298 K): $\delta = -0.58$ (br s, 24 H, Me–Al), −0.43 (br s, 24 H, Me–Al), 0.63 (s, 0.5 MeCN), 2.16 (s, 12 H, C(Me)), 2.31 (br s, 24 H, Me$_2$N); ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 298 K): $\delta = -9.66$, −8.42, −4.90, −2.25 (4 × br s, Me–Al), 23.41 (s, C(Me)), 47.48, 48.96 (2 × br s, Me$_2$N), 172.00 (s, C(Me)).

2: Yield: 55 %. Elemental analysis calcd for $C_{26}H_{46}N_6Al_4$: C 56.7, H 8.4, N 15.7; found: C 56.4, H 8.4, N 15.2; ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta = -0.66$, −0.41, −0.27, −0.20 (4 × s, 4 × 3 H, Me–Al), 1.38 (2 × s, 2 × 3 H, MeC), 2.57 (2 × s, 2 × 3 H, MeN), 6.48 – 7.27 (3 × m, 8 H, aryl H); the signal for NH$_2$ was not observed; ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 298 K): $\delta = -12.24$, −12.81 (br, Me–Al), −8.91 (br, Me–Al), −5.99(br, Me–Al); IR: $\tilde{\nu}$(N–H) = 3345 cm^{-1}; MS (EI): m/z: 550 [M^+].

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[7] Crystal data for **1** ($C_{32}H_{84}N_{12}Al_8 \cdot 0.5\,MeCN$): $M_r = 873.5$, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.828(1)$, $b = 33.824(1)$, $c = 13.836(1)$ Å, $\beta = 118.69(1)°$, $V = 5677.2(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.02$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 16.2$ cm^{-1}, $F(000) = 1900$. A clear prism of dimensions 0.97 × 0.50 × 0.37 mm was used. Crystal data for **2** ($C_{26}H_{46}N_6Al_4$): $M_r = 550.6$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.931(1)$, $b = 9.276(1)$, $c = 11.924(1)$ Å, $\alpha = 109.30(1)$, $\beta = 99.00(1)$, $\gamma = 104.55(1)°$, $V = 773.3(2)$ Å^3, $Z = 1$ (the molecule has crystallographic C_i symmetry), $\rho_{calcd} = 1.18$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 15.9$ cm^{-1}, $F(000) = 296$. A clear platy needle of dimensions 0.83 × 0.33 × 0.13 mm was used. For **1** (**2**), 8434 (2205) independent reflections were measured on a Siemens P4 rotating anode diffractometer at 203 K with $Cu_{K\alpha}$ radiation (graphite monochromator) using ω scans. The structures were solved by direct methods, and all the non-hydrogen atoms were refined anisotropically with full-matrix least squares based on F^2 to give $R_1 = 0.056$ (0.052) and $wR_2 = 0.136$ (0.140) for 6563 (1935) independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 506 (168) parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-113552 and CCDC-113553.

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] An isostructural gallium analogue of **1** has been synthesized by a similar procedure using Me_3Ga: V. C. Gibson, C. Redshaw, A. J. P. White, D. J. Williams, unpublished results.

Decreased Electron Transfer Rates of Manganese Porphyrins with Conformational Distortion of the Macrocycle**

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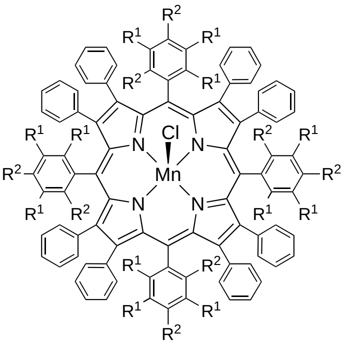
Karl M. Kadish*

Nonplanar conformations of porphyrins have been suggested as being related to their functions in biological systems.[1–4] For example, a deformation of the porphyrin skeleton in heme and photosynthetic proteins is believed to arise from environmental effects.[3, 5, 6] Synthetic dodecaphenylporphyrins which contain a phenyl ring at each β-pyrrole and *meso* position of the porphyrin macrocycle are known to adopt a nonplanar conformation.[3, 7–9] Nonplanarity of the porphyrin ring due to steric repulsion between ring substituents in dodecasubstituted porphyrins affects their optical properties.[7–11] Manganese is an essential metal in several biological systems that are involved in electron transfer reactions,[12] and extensive efforts have therefore been devoted to elucidating electron transfer processes in synthetic manganese porphyrins.[13–16] However, there have been so far no reports on how conformational distortions of the porphyrin ring affect the rates of homogeneous electron transfer reactions in manganese or other transition metal porphyrins.

Here we report the homogeneous electron transfer kinetics for reduction of [(P)MnCl], where P represents the dianion of tetraphenylporphyrin (tpp) or of the dodecaphenylporphyrins (dpp-X, X = H_{20}, $Cl_{12}H_8$, F_{20}). The relationship between the logarithms of the rate constants of electron transfer and the free energy change of electron transfer gives an initial evaluation of reorganization energies λ for reduction of manganese porphyrins with a planar macrocycle, as in [(tpp)MnCl], and a nonplanar macrocycle, as in [(dpp-X)MnCl].



[(P)MnCl]

[(dpp-H_{20})MnCl]: $R^1 = R^2 = H$

[(dpp-$Cl_{12}H_8$)MnCl]: $R^1 = Cl$, $R^2 = H$

[(dpp-F_{20})MnCl]: $R^1 = R^2 = F$

Previous studies of the electrochemistry of [(dpp-X)MnCl] in benzonitrile show that the reduction of Mn^{III} to Mn^{II} is quasireversible[16] and that the potential separation between the cathodic and anodic peak potentials, $\Delta E_p = |E_{pc} - E_{pa}|$, increases in the order [(tpp)MnCl] < [(dpp-H_{20})MnCl] < [(dpp-$Cl_{12}H_8$)MnCl] < [(dpp-F_{20})MnCl] (Table 1).[17] The large ΔE_p value (0.52 V) for the reduction of [(dpp-F_{20})MnCl] may be related to the dissociation of Cl^- after reduction of Mn^{III} to Mn^{II}. However, the fact that the magnitude of ΔE_p remains unchanged after addition of an excess of Cl^- (0.1 M) suggests that the large ΔE_p value is due to slow electron transfer kinetics, as reported for other [(P)MnCl] complexes[15, 18] whose kinetics have been determined by electrochemical methods.[15, 18, 19]

The slow electron transfer in the reduction of [(dpp-X)MnCl] and [(tpp)MnCl] was confirmed in the present study by measuring the kinetics of the homogeneous electron transfer reduction with semiquinone radical anions as chemical reductants whose oxidation potentials[20] are low enough to reduce each Mn^{III} porphyrin to its Mn^{II} form. These reducing agents were prepared by comproportionation of the *p*-benzoquinone derivatives with the corresponding hydroquinone dianions, which were generated by reactions of hydroquinones with tetramethylammonium hydroxide.[21] The kinetics of electron transfer from the semiquinone radical anion to [(tpp)MnCl] or [(dpp-X)MnCl] were then followed by monitoring the increase in absorbance of the Mn^{II} Soret band (e.g., at 488 nm for [(dpp-H_{20})MnCl]).

The electron transfer rate obeys a second-order rate law when the initial concentrations of [(dpp-X)MnCl] and the semiquinone radical anion are equal. The observed second-

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