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Communication

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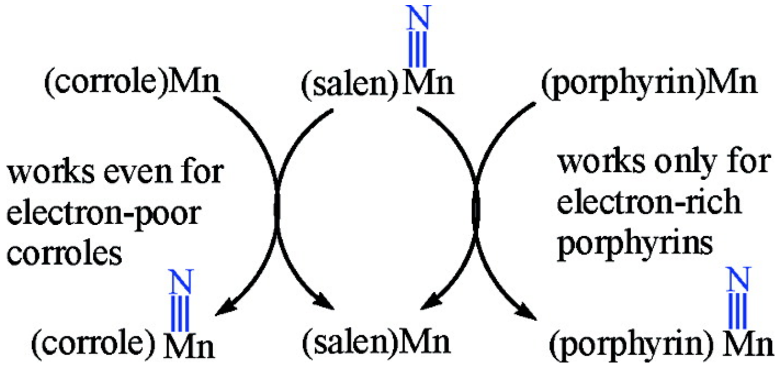

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COMMUNICATIONS

Nitrogen Atom Transfer between Manganese Complexes of Salen, Porphyrin, and Corrole and Characterization of a (Nitrido)manganese(VI) Corrole

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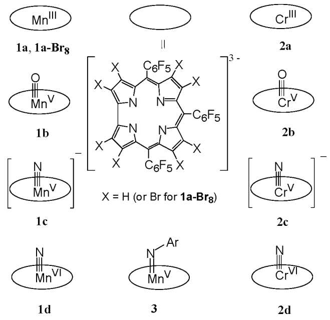
Nitrogen atom transfer reactions and (nitrido)metal complexes remain at the front of scientific interest due to their relevance to the processes and complexes involved in nitrogen fixation.[1,2] Recent work on corroles suggests that the corresponding metal complexes might be relevant for such purposes, as they are surprisingly stable in high oxidation states.[3,4] This may be appreciated by the isolation of the following pentavalent metal complexes: (tpfc)Mn^{V}(O) (**1b**),[5] [(tpfc)Mn^{V}(N)]$^{-}$ (**1c**),[6] (tpfc)Mn^{V}(NAr) (**3**),[7] (tpfc)Cr^{V}(O) (**2b**),[8] and [(tpfc)Cr^{V}(N)]$^{-}$ (**2c**),[9] where tpfc stands for the trianion of 5,10,15-tris(pentafluorophenyl)corrole (Chart 1).[10,11] Even the highly oxidizing Cr^{VI} ion was reported to be supported by the same ligand, as exemplified by bleach oxidation of **2a** to [(tpfc)Cr^{VI}(N)] (**2d**).[9] Another aspect of significance to nitrogen fixation is the unique reactivity of trivalent metallocorroles, manifested in activation of molecular oxygen by chromium(III) and iron(III) corroles and the nitrogen atom transfer from (nitrido) manganese(V) salophen to chromium(III) corrole **2a**.[9,12] In the current work we show that nitrogen atom transfer can be used for preparation of (nitrido)-manganese(V) corroles and that their oxidation yields quite novel manganese(VI) complexes.[13] We also report the first kinetic investigation of the nitrogen atom transfer step between tri- and pentavalent metal complexes.[14,15]

The treatment of various manganese(III) complexes with the known (nitrido)manganese(V) complex **4**[16] revealed nitrogen atom transfer as a suitable route for preparation of complexes **1c** and **5**,[17] but not of **6** (Scheme 1).[18] The similar structures of **1c** and **6** rule out steric effects as responsible for these results, while the different electron-richness of the porphyrin ligand in **5** and **6** highlights the importance of that factor as the main driving force for complete nitrogen atom transfer. There was also no reaction between (nitrido)manganese(V) and manganese(III) complexes of porphyrins and corroles in both plausible directions, i.e., **1c** and **5** did not react with (oep)Mn(Cl) and **1a**, respectively. Apparently, the larger stability of **1c** relative to that of **5**, reflected in the 0.31 V less positive oxidation potential of the former (Scheme 1, inset), is not a strong enough driving force.

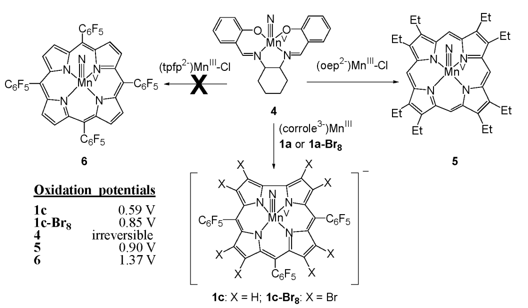
The superiority of corroles in stabilizing the [Mn$^{V}\equiv$N] moiety may further be appreciated by successful synthesis of **1c-Br$_8$**, the even more electron-poor analogue of complex **1c**. Interestingly, the oxidation potential of **1c-Br$_8$** is similar to that of **5**. These observations lead to a qualitative order for stabilization of the (nitrido)manganese(V) moiety: corrole > porphyrin ≫ salen.

During the preparation of **1c** from **4**, we noted quite a large solvent effect on the time required for completion of the reaction. We also realized that the rate of the actual nitrogen atom transfer step between other metal(III)/metal(V) complexes was not previously determined because of a proceeding and rate-limiting ligand dissociation step.[14] Since manganese(III) complexes of trianionic corroles (as opposed to dianionic porphyrins) do not associate strongly with axial ligands, the reaction between **4** and **1a** provided a unique opportunity for filling this missing gap. The large differences between the electronic spectra of **1a** and **1c** and the excellent isosbestic points (Figure 1) that were obtained during the reaction progress allowed for quite straightforward kinetic monitoring.

Chart 1. Formulas of Reported Metal(III), Oxo-, Amido- and Nitrido Corroles and of the New Manganese(VI) Complexes



Scheme 1. Nitrogen Atom Transfer from **4** to Manganese(III) Complexes as a Synthetic Route for Preparation of (Nitrido)manganese(V) Complexes; Inset: Oxidation Potentials of the Latter



The results revealed a significant solvent effect on the reaction, in the order of CH$_3$CN > MeOH > THF. The reaction in CH$_3$CN was too fast to be measured by conventional methods. Nevertheless, the full kinetic investigation for the two other solvents revealed that the activation enthalpy decreased by about one-half on moving from THF to MeOH ($\Delta H^{\ddagger}_{\mathrm{THF}} = 11.5 \pm 1.3$ and $\Delta H^{\ddagger}_{\mathrm{MeOH}} = 5.9 \pm 0.2$ kcal/mol), which was partially compensated by a more negative activation entropy ($\Delta S^{\ddagger}_{\mathrm{THF}} = -22.3 \pm 3.9$ and $\Delta S^{\ddagger}_{\mathrm{MeOH}} = -33.4 \pm 0.5$ cal/mol·K). This is reasonably explained by realizing that the reaction between the neutral complexes **4** and **1c** leads two oppositely charged products, hence the decrease in $\Delta H^{\ddagger}$ by a polar solvent and the increase in $\Delta S^{\ddagger}$ because of specific interactions with MeOH upon moving to the polar transition state. It might be further assumed that the latter effect is less pronounced for CH$_3$CN and hence the faster reaction in that solvent.

The cyclic voltammetry of **1c** and **1c-Br$_8$** exposed half wave redox potentials that are as low as 0.59 and 0.85 V, respectively,

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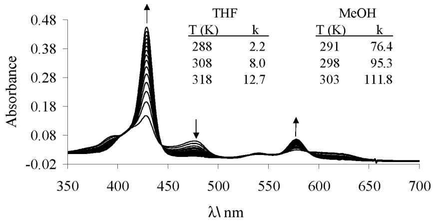

Figure 1. Spectral changes (MeOH, 25 °C) upon transformation of **1a** to **1c**, via the addition of **4**. (Inset) Second-order rate constants of the process, in $M^{-1}\ s^{-1}$.

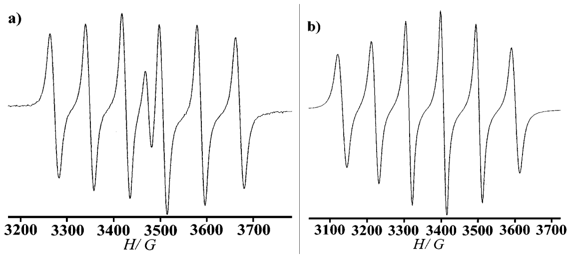

Figure 2. EPR spectra of (a) **1d**, obtained via electrolysis of **1c** at 0.2 V above the Mn^V/Mn^{VI} redox couple (the small central peak is from the probe) and (b) of **1d-Br$_8$** obtained by adding Br_2 to a CH_3CN solution of **1c-Br$_8$**.

suggesting that bromine ($E_{1/2} = 1.09$) could serve as convenient oxidant for these complexes (but not of **6**, ($E_{1/2} = 1.37$). Preparation of the oxidized complexes **1d** and **1d-Br$_8$** by both electrochemical and chemical means revealed that, while the electronic spectra were not sensitive to the oxidation process (hence ruling out oxidation of the corrole), the EPR spectra (Figure 2) displayed characteristic six line hyperfine coupling from ^{55}Mn ($I = {}^5/_2$) that clearly support their assignment as authentic (nitrido)manganese(VI) complexes.[19] The $A^{55}{}_{Mn}$ of values of 8.0 and 9.1 mT for **1d** and **1d-Br$_8$**, respectively, are more than 3 times larger than the $A^{53}{}_{Cr}$ of 2.67 mT obtained for the isoelectronic (nitrido)chromium(V) complex **2c**.[9] However, the 5-times larger isotropic hyperfine coupling constant of Mn relative to Cr (3063 vs −630 MHz, respectively) actually suggest less unpaired spin density on the metal in (nitrido)manganese(VI) than in (nitrido)chromium(V) corroles.

We report nitrogen atom transfer between metal complexes of different macrocycles and demonstrate that stabilization of the $[Mn(N)]^{2+}$ moiety is in the order of corrole > porphyrin ≫ salen. Two (nitrido)manganese(V) corroles were prepared by complete nitrogen atom transfer from (nitrido)manganese(V) salen to manganese(III) corroles and the first kinetic investigation of this fundamental reaction revealed quite a large solvent effect. Intriguingly, the reaction rates of this manganese(V)/manganese(III) system are comparable to those obtained for nitrogen atom transfer from (nitrido)manganese(V) to manganese(II) within a porphyrin system ($k_{THF,20°C} = 2.3\ M^{-1}\ s^{-1}$).[15b] Oxidation of the (nitrido)manganese(V) corroles leads to the first (nitrido)manganese(VI) complexes that are coordinated by tetrapyrrolic ligands. These results highlight the two main features of corroles, the activation and stabilization of low- and high-valent metal ions, respectively.

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(18) **Nitrogen atom transfer reactions:** solid **4** (15 mg, 40 μmol) was added to a solution of 19.5 mg of (oep)$Mn^{III}Cl$/28 mg of **1a**/49 of mg **1a-Br$_8$** (33.3 μmol) in methanol (10 mL). After about 1 min, reaction mixtures were treated by flash column chromatography (silica gel, CH_3CN), upon which the salen complex remained on the top of the column and the desired complexes were eluted to afford **5** (16.2 mg, 27 μmol, 81.8% yield), **1c** (27 mg), **1c-Br$_8$** (45.5 mg). Assuming that the counterion in **1c** and **1c-Br$_8$** is a solvated proton, the yields are about 90%. **1c**: UV−vis (CH_3OH) λ_{max} (relative ϵ): nm 414 (100), 535 (8), 567 (5).^1H NMR (200 MHz, CD_3OD): δ 9.23 (d, $J = 4.13$ Hz, 2H), 8.85 (d, $J = 4.60$ Hz, 2H), 8.77 (d, $J = 3.98$ Hz, 2H), 8.67 (d, $J = 4.69$ Hz, 2H). ^{19}F NMR (188 MHz, CD_3OD): δ −135.10 (dd, $^3J = 23.31$ Hz, $^4J = 8.55$ Hz, 2F), −135.18 (dd, $^3J = 23.50$ Hz, $^4J = 8.65$ Hz, 1F), −135.22 (dd, $^3J = 24.25$ Hz, $^4J = 7.80$ Hz, 2F), −135.87(dd, $^3J = 21.34$ Hz, $^4J = 8.08$ Hz, 1F), −153.11 (dt, $^3J = 20.3$ Hz, $^4J = 8.46$ Hz, 4F), −153.24 (dt, $^3J = 20.12$ Hz, $^4J = 8.46$ Hz 2F), −160.52 (m, 6F). CV (CH_3CN/Bu_4NOH): $E_{1/2} =$ 0.05 and 0.59 V. **1c-Br$_8$**: UV−vis (CH_3OH) λ_{max} (relative ϵ): nm 444 (100), 555 (7), 595 (15). ^{19}F NMR (188 MHz, CD_3CN): $\delta = -133.59$ (s, 3F), −135.13 (d, 3F), −149.74 (s, 3F), −160.15 (d, 6F). CV: (CH_3CN/Bu_4NOH) $E_{1/2} = -0.9$ and 0.85 V. Complex **6** was independently prepared in analogy to the procedure described in ref 15b: NH_4OH (14 μL, 0.36 mmol) and sodium hypochlorite (7.5 mL, 0.14 mmol) were added to a solution of (tpfp)Mn^{III}(Cl) (26.5 mg, 24.9 μmol) in acetonitrile (10 mL). Sodium sulfate was added after 1 min, and the solution was filtered and evaporated to dryness to afford **6** (22 mg, 21.2 μmol, 85% yield). UV−vis (CH_3OH) λ_{max}(relative ϵ): nm 414 (100), 535 (8), 567 (5). ^1H NMR (200 MHz, CD_3OD): δ 9.02 (s, 8H). ^{19}F NMR (188 MHz, CD_3OD): δ −136.25 (dd, $^3J = 23.31$ Hz, $^4J = 7.14$ Hz, 4F), −137.13 (dd, $^3J = 23.59$ Hz, $^4J = 6.76$ Hz, 4F), −151.47 (t, $J = 20.96$ Hz, 4F), −161.356 (dt, $^3J = 22.69$ Hz, $^4J = 8.46$ Hz, 4F), −161.643 (dt, $^3J = 22.31$ Hz, $^4J = 8.46$ Hz, 4F). CV: (CH_3CN/Bu_4NOH) $E_{1/2} = -0.61$ and 1.37 V.

(19) Bulk electrolysis at 0.2 V above the $E_{1/2}$ of a solution of **1c** (10^{-3} M in 0.1 M TBAP/CH_3CN, Pt electrodes) provided **1d**. Alternatively, oxidation of either **1c** or **1c-Br$_8$** with 0.5 equiv of Br_2 provided the corresponding **1d** and **1d-Br$_8$** complexes.

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