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LETTER

The preparation of nitridomanganese and nitridochromium macrocyclic complexes by complete intermetal nitrogen atom transfer from nitridomanganese octaethylporphyrin

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Atom transfer reactions involve the net transfer of an atom and one or more electrons from a donor molecule to an acceptor [1]. Over the past two decades, metal-centered oxygen atom transfer reactions have been intensively studied. Oxygen atom transfer from M=O containing donor complexes to olefins, paraffins and other substrates has been achieved and a consistent mechanistic picture is beginning to emerge [2]. Relatively few examples of non-oxygen heteroatom transfer have been reported. In most instances, such transfer is not complete, i.e. the atom is shared by both the donor metal and the acceptor group. Holm has described complexes of this type as examples of partial atom transfer [1].

Takahashi [3] documented the first example of complete intermetal nitrogen atom transfer with the quantitative preparation of NCr(T-4-Me-PP)** from NMn(T-4-Me-PP) and ClCr(T-4-Me-PP). Woo and Goll [4] reported the reversible transfer of the nitride between NMn(T-4-Me-PP) and Mn(OEP), a second example involving the net transfer of three electrons with the nitrogen atom. We discovered the irreversible transfer of the nitride from nitridomanganese(V) to chlorochromium(III) porphyrins [5] as well as the reversible transfer between nitridochromium(V) and chromium(III) porphyrins [6]. Reversible nitrogen atom transfer between nitridomanganese(V) and chlorochromium(III) porphyrins has also been independently observed by Neely [7] and Woo *et al.* [8]. These reactions involve the net transfer of two electrons with the nitrogen atom. Our present efforts are directed to the exploration of the generality of the nitrogen atom transfer reaction and the exploitation of its synthetic utility. In this communication, we report the first example of nitrogen atom transfer involving non-porphyrinic acceptors and demonstrate the utility of this reaction in preparing nitridometallomacrocyclic compounds.

Experimental

Literature methods have been employed in the preparation of NMn(OEP) [9] as well as the nitrogen atom acceptors ClCr(TPP) [10], ClCr(Sal_2en) [11], ClMn(Sal_2en) [12] and ClMn(TMTAA) [13]. The purity of each complex was verified by electronic, ^{1}H NMR and mass spectral measurements.

Visible spectral measurements were obtained with a diode array rapid scanning spectrometer system composed of a Tracor Northern model 6050 spectrometer containing a crossed Czerny-Turner spectrograph in conjunction with a Tracor Northern model 1710 multichannel analyzer. Spectra were acquired by irradiation of the sample with polychromatic light from a xenon arc lamp and the subsequent spatial dispersion of the transmitted radiation onto a 512 diode array detector by a grating with a 300 grooves/nm rule and a blaze of 500 nm. Wavelength calibration was achieved with either a holmium oxide or NIST standard filter. All measurements reported herein represent the ensemble average of at least 56 spectral acquisitions. For display purposes, a five-point Savitsky-Golay smoothing algorithm was applied to each spectrum depicted. EPR experiments were performed on a Varian E3 spectrometer. All experiments were carried out at ambient temperature (23 ± 1 °C).

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**Abbrevations used: 1,2-dichloroethane = DCE; porphyrin dianion = POR; nitrido[*meso*-tetrakis(4-methylphenyl)porphinato]chromium(V) = NCr(T-4-Me-PP); nitrido[*meso*-tetrakis(4-methylphenyl)porphinato]manganese(V) = NMn(T-4-Me-PP); nitrido[*meso*-tetraphenylporphinato]chromium(V) = NCr(TPP); nitrido[*meso*-tetraphenylporphinato]manganese(V) = NMn(TPP); nitrido[octaethylporphinato]chromium(V) = NCr(OEP); nitrido[octaethylporphinato]manganese(V) = NMn(OEP); chloro[*meso*-tetraphenylporphinato]manganese(III) = ClMn(TPP); nitrido[bis-*N*,*N*′-(salicylaldehyde)ethylenediiminato]chromium(V) = NCr(Sal_2en); nitrido[bis-*N*,*N*′-(salicylaldehyde)ethylenediiminato]manganese(V) = NMn(Sal_2en); chloro[bis-*N*,*N*′-(salicylaldehyde)ethylenediiminato]chromium(III) = ClCr(Sal_2en); chloro[bis-*N*,*N*′-(salicylaldehyde)ethylenediiminato]manganese(III) = ClMn(Sal_2en); nitrido[6,17-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato(2−)]manganese(V) = NMn(TMTAA); chloro[6,17-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato(2)−)]manganese(III) = ClMn(TMTAA).

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Results and discussion

We have discovered that NCr(Sal$_2$en) is produced when equimolar amounts of ClCr(Sal$_2$en) and NMn(OEP) are mixed in DCE. The progress of this reaction was monitored spectrally and a typical data set is shown in Fig. 1. Over a period of an hour, the spectrum of NMn(OEP), with its characteristic Soret band at 405 nm, is replaced by the spectrum of ClMn(OEP). The final spectrum is composed of two low intensity bands at 476 and 366 nm. These bands are characteristic of ClMn(OEP) and NCr(Sal$_2$en), respectively. Isosbestic points are observed at 391, 432, 495, 520, 545 and 576 nm and indicate the absence of long-lived intermediates. The conversion of ClCr(Sal$_2$en) into NCr(Sal$_2$en) was also monitored by EPR spectroscopy. At ambient temperature, the spectrum of ClCr(Sal$_2$en) in benzene exhibits a very broad singlet centered at $g=1.996$. Addition of the diamagnetic NMn(OEP) results in the appearance of a sharp seven line pattern centered at $g=1.992$ whose intensity increases with time. The final spectrum is identical to that obtained on NCr(Sal$_2$en) prepared by photolysis of N_3Cr(Sal$_2$en) [14]. The seven line pattern arises from the interaction of the d^1 metal center with the three nitrogen atoms of nuclear spin 1. The contribution of the ^{54}Cr isotope (relative abundance of 15%) with spin 3/2 results in a low intensity quartet analogous to NCr(TPP).

When the reaction was carried out on a preparative scale, the NCr(Sal$_2$en) product was recovered by chromatography over deactivated alumina ($CHCl_3$ eluant) in 40% yield based on ClCr(Sal$_2$en). Interestingly, significant quantities of NMn(OEP) were recovered even though an electronic spectrum acquired prior to chromatographic separation indicated that no NMn(OEP) remained. An IR spectrum obtained on the isolated NCr(Sal$_2$en) contained the ν(Cr=N) stretch at 1012 cm^{-1} as well as the other ligand based vibrations previously reported for this compound.

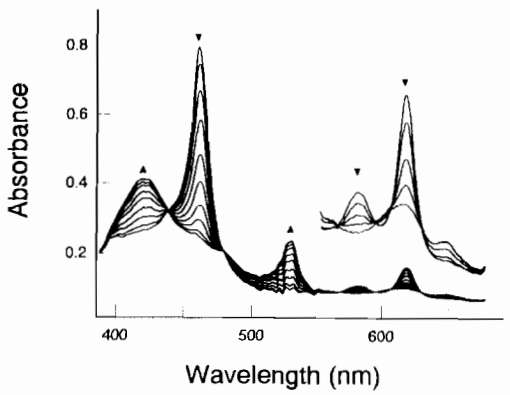

Fig. 1. Electronic spectra acquired as a function of time of the reaction between 65 μM NMn(OEP) and 150 μM ClCr(Sal$_2$en) in DCE.

Previously reported methods for preparing nitridochromium porphyrins involve the photochemical decomposition [15] of N_3Cr(POR) or the treatment of (OH)Cr(POR) with NH_4OH and NaClO [16]. We have found that NCr(POR) can be prepared in quantitative yield by stirring ClCr(POR) with an equivalent of NMn(OEP) in DCE at ambient temperature. After 4 h, the mixture is concentrated and the product isolated by elution with benzene from an alumina column.

Manganese macrocyclic compounds also act as nitrogen atom acceptors. ClMn(TMTAA) and ClMn(Sal$_2$en) undergo reversible reaction with NMn(OEP) to an equilibrium distribution of reactants and products even when the nitride acceptor is present in upto a two-fold excess. The progress of the reaction between NMn(OEP) and ClMn(TMTAA) was monitored spectrophotometrically. The Soret band of NMn(OEP) at 405 nm decreased in intensity with the concomitant increase in bands at 372 and 476 nm. Isosbestic points were observed at 375, 421, 506 and 572 nm. The concentrations of reactants and products were calculated by solving four simultaneous equations at the absorbance maximum for the intense bands of each reactant and product in solution. Analysis of the concentration data as a function of time indicated that the data was best fit by a second order rate law. The value of the forward rate constant for the bimolecular reaction was calculated using King's equations [17]. The values of K_{eq} and k_f were found to be 0.69 ± 0.05 and 22 ± 3 M^{-1} s^{-1}, respectively. Similarly, spectral monitoring of the reaction of NMn(OEP) with ClMn(Sal$_2$en) and subsequent analysis of the absorbance data as a function of time yields K_{eq} and k_f values of 0.050 ± 0.009 and 12 m^{-1} s^{-1}, respectively. For comparison, the K_{eq} and k_f values reported [9] for the reaction between NMn(OEP) and ClMn(T-4-Me-PP) at ambient temperature are 23.5 ± 3.6 and 0.010 ± 0.007 M^{-1} s^{-1}, respectively. The substantial differences in K_{eq} reflect the differences in substrate macrocycle basicity.

The substantial increase in forward rate constants measured for formation of NMn(TMTAA) and NMn(Sal$_2$en) compared to NMn(T-4-CH_3-PP) suggests that these materials hold promise as aziridination synthons. It has been previously shown that NMn(TPP) can be readily converted into an acylimido complex by reaction with substituted acetic anhydrides [18]. Subsequent treatment of the acylimido complex with olefin results in the transfer of the acylimido group to the olefin in analogous fashion to metalloporphyrin-catalyzed epoxidations [19]. The smaller pocket of the TMTAA macrocycle compared to that found in porphyrins elevates the nitridomanganese moiety from the

macrocyclic plane. Transformation of NMn(TMTAA) into an acylimido complex and the subsequent functionalized nitrogen atom transfer to olefins may proceed at rates which will render NMn(TMTAA) and other nitrido metallomacrocyclic complexes as useful aziridination synthons because of the increased accessibility of the nitridomangenase moiety. This hypothesis is currently under investigation.

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References

1 R. H. Holm, *Chem. Rev., 87* (1987) 1401.
2 (a) F. P. Guengerich, *Crit. Rev. Biochem. Mol. Biol., 25* (1990) 97; (b) T. G. Traylor and F. Xu, *J. Am. Chem. Soc., 112* (1990) 178.
3 T. Takahashi, *Ph.D. Dissertation,* University of Michigan, 1985.
4 L. K. Woo and J. G. Goll, *J. Am. Chem. Soc., 111* (1989) 3755.
5 L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc., 111* (1989) 5955.
6 L. A. Bottomley and F. L. Neely, *Inorg. Chem.,* accepted for publication.
7 F. L. Neely, *Ph.D. Dissertation,* Georgia Institute of Technology, 1989.
8 L. K. Woo, D. J. Czapla and J. G. Goll, *Inorg. Chem., 29* (1990) 3915.
9 J. W. Buchler, C. Dreher, K.-L. Lay, A. Raap and K. Gersonde, *Inorg. Chem., 22* (1983) 879.
10 D. A. Summerville, R. D. Jones, B. M. Hoffman and F. Basolo, *J. Am. Chem. Soc., 99* (1977) 8195.
11 S. Yamada and K. Iwasaki, *J. Chem. Soc., Chem. Commun.,* (1969) 1463.
12 T. Matsushita, L. Spencer and D. T. Sawyer, *Inorg. Chem., 27* (1988) 1167.
13 (a) V. L. Goedken, J. Molin-Case and Y. A. Whang, *J. Chem. Soc., Chem. Commun.,* (1973) 37; (b) D. R. Neves and J. C. Dabrowiak, *Inorg. Chem., 15* (1976) 129.
14 S. I. Arshankow and A. L. Poznjal, *Z. Anorg. Allg. Chem., 481* (1981) 201.
15 J. T. Groves, T. Takahashi and W. M. Butler, *Inorg. Chem., 22* (1983) 884.
16 (a) C. L. Hill and F. J. Hollander, *J. Am. Chem. Soc., 104* (1982) 7318; (b) J. W. Buchler, C. Dreher, K.-L. Lay, A. Raap and K. Gersonde, *Inorg. Chem., 22* (1983) 879.
17 E. L. King, *Int. J. Chem. Kinetics, 14* (1982) 1285.
18 L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc., 110* (1988) 6748.
19 J. T. Groves and T. Takahashi, *J. Am. Chem. Soc., 105* (1983) 2073.