(n = 3) the low steric demand of the short linking chain permits nickel(II) and its four coordinating nitrogen atoms to adopt the energetically more favorable planar form. As the steric demands of the linker chains increase across the series n = 3 to n = 6, the structure progressively distorts toward the tetrahedral form. This distortion and the accompanying expansion in the Ni–N bond lengths (Table I) are typical for bis-chelate nickel(II) complexes having four nitrogen donor atoms.[17] The present series of complexes provides an interesting demonstration of these structural trends.

The ^{1}H NMR properties of the complexes[12] (Table II) were analogous to those reported for the extensively studied bis(troponeiminato)nickel(II) complexes.[19,20] The molecules formed from ligands **1** (n = 3) and **1** (n = 4) have shifts consistent with their nearly square-planar diamagnetic stereochemistries, whereas the more tetrahedral nickel complexes of **1** (n = 5) and **1** (n = 6) exhibit large isotropic ^{1}H contact shifts owing to the planar (S = 0) $\rightleftharpoons$ tetrahedral (S = 1) equilibrium.

The tropocoronand ligands thus provide a new class of N_4-coordinating macrocycles, the structures of which can be readily modified. The steric constraints at the metal center can be adjusted to achieve the full range of structures from square planar to tetrahedral; this behavior is illustrated for the complete series of nickel(II) complexes.

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters for the nickel(II) complexes of **1** (n = 3–6) and **1** (n = 2)–O–(n = 2) (5 pages). Ordering information is given on any current masthead page.

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Activation and Transfer of Nitrogen from a Nitridomanganese(V) Porphyrin Complex. The Aza Analogue of Epoxidation

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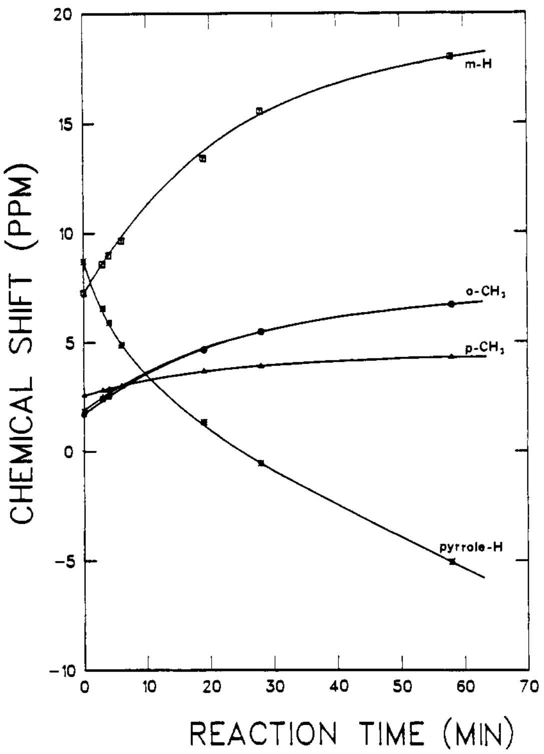

Figure 1. Plots of chemical shifts (δ) vs. reaction time for the reaction of TMPMn(V)N (**1**) with trifluoroacetic anhydride (10 equiv) in methylene chloride at 25 °C.

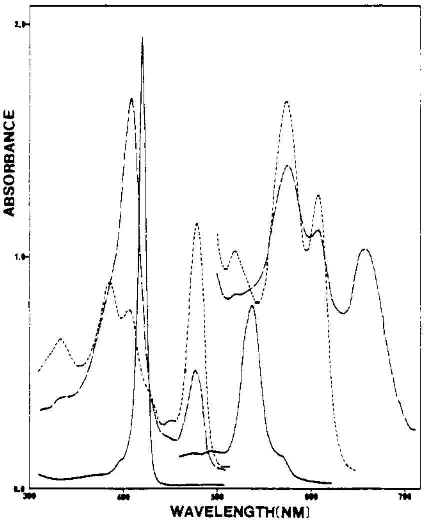

Figure 2. Visible spectra of (a) TMPMn(V)N (3.81×10^{-6} M) in methylene chloride (—) λ_{max} (log ϵ) 420.5 nm (5.71), 5.36 (4.33); (b) TMPMn(V)N (1.52×10^{-5} M) plus 100 equiv of trifluoroacetic anhydride (– –); (c) TMPMnTFA produced after addition of excess cyclooctene to b (- - -).

The discovery that iodosylarenes would transfer oxygen atoms to transition metalloporphyrin complexes to give reactive metal–oxo species[1] and the application of this reaction to the catalytic oxygenation of hydrocarbons[2-4] have suggested that a similar approach could lead to reactive imido or nitrido complexes capable of direct oxidative amination of hydrocarbons. The oxyamination and bis-amination of olefins by imido–osmium complexes has been reported.[5] However, while nitrido complexes of osmium,[6] molybdenum,[7] chromium[8] and manganese[9] and an imido–iron complex[10] are now known, these compounds have not been reported

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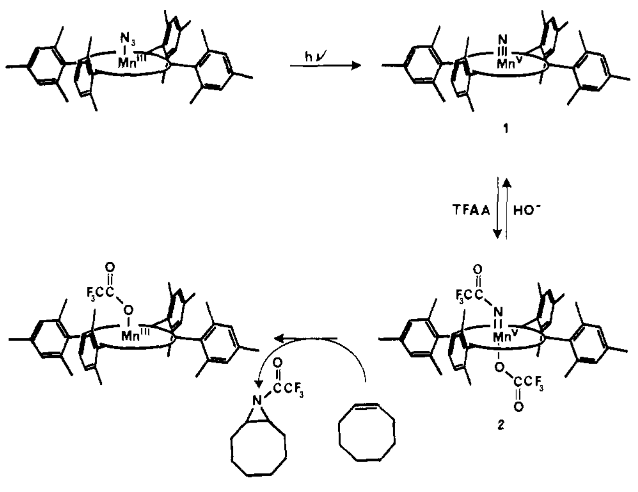
Scheme I



to undergo nitrogen-transfer reactions with organic compounds.[11] We report here the first example of metal nitride activation to give aziridines in the presence of double bonds; the aza analogue of epoxidation.

Irradiation of azido(5,10,15,20-tetramesitylporphyrinato)-manganese(III) in benzene[8] for 4 h followed by column chromatography on basic alumina afforded red-purple crystals of nitrido(5,10,15,20-tetramesitylporphyrinato)manganese(V) (**1**),[12] TMPMn(V)N) in 80% yield. This manganese(V) nitride was found to be diamagnetic, consistent with a low-spin d^2 electronic configuration. Accordingly, the ^1H NMR spectrum of **1** showed sharp resonances in the normal range of chemical shifts (Figure 1). The visible spectrum of **1** showed a strong and sharp Soret maximum at 420 nm (Figure 2a). TMPMn(V)N (**1**) is an extraordinarily stable complex and was unaffected by iodide ion, olefins, or triphenylphosphine. Compound **1** was also found to be resistant to acid, base, and oxygen.

TMPMn(V)N did react in methylene chloride with trifluoroacetic anhydride at room temperature to give a new, green, paramagnetic complex **2**. Thus, reaction of **1** with a 20-fold excess of trifluoroacetic anhydride for 40 min afforded a soln. that showed ^1H NMR resonances at δ −23.02 (β-pyrrole H), 5.67 (*p*-Me), 10.84 (*o*-Me), and 26.13 (*m*-H). Weaker resonances due to TMPMn(III) trifluoroacetate could also be discerned. The visible spectrum of the intermediate **2** showed a Soret band at 409 nm (Figure 2b).

Several lines of evidence support an acylimidomanganese(V) trifluoroacetate[13] for **2**: (i) The IR spectrum of solutions of **2** showed new bands at 1697 and 1745 cm^{-1} for the trifluoroacetate and imidotrifluoroacetate groups, respectively. The lack of any band near 1270 cm^{-1} argues against a porphyrin π-cation radical.[14] (ii) The ^1H NMR spectrum of a reaction mixture of **1** and 10 equiv of trifluoroacetic anhydride exhibited unusual dynamic behavior. The sharp proton resonances due to **1** were observed to broaden and shift *gradually* with time toward the resonance positions for **2** (Figure 1), while the visible spectrum showed only the appearance of **2** at the expense of **1**. Thus, the NMR spectra of **1** and **2** are averaged by a rapid self-exchange process. N-acylation of **1** and facile, reversible acyl transfer from **2** to **1** would explain this observation. (iii) The reaction of **2** with tetrabutylammonium hydroxide in methylene chloride regenerated the starting nitride (**1**). (iv) The N-trifluoroacetyl group in **2** would be expected to decrease the π-donor properties of the axial nitrogen ligand. The conversion from a diamagnetic configuration for **1** to a paramagnetic state for **2** is consistent with the resultant lowering of the d_{xz} and d_{yz} orbitals of manganese. Such a lowering is evident in the $(d_{xz},d_{yz})^4(d_{xy})^1$ configuration for the closely related TPPMn(III) nitrosyls.[15] (v) The addition of cyclooctene to solutions of **2** gave TMPMn(III)TFA and the (trifluoroacetyl)-aziridine of cyclooctene.[16]

In a typical reaction, 30 mg of TMPMn(V)N (**1**) was dissolved in dry, redistilled dichloromethane that contained an 11-fold excess of cyclooctene. The addition of 1.2 equiv of trifluoroacetic anhydride caused the reaction mixture to turn from red to green after 30 min at room temperature. Analysis of the reaction mixture by GLPC showed that 9-(trifluoroacetyl)-9-azabicyclo[6.1.0]-nonane was produced in 82–94% yield by comparison of the isolated product to an authentic sample.[17] Treatment of the reaction mixture with aqueous base and extraction with dilute HCl afforded the parent aziridine in similar yield.

A mechanism consistent with the nitrogen activation and transfer described here is presented in Scheme I.[18]

Acknowledgment. Financial support of this research by the National Science Foundation (CHE-81-06064) is gratefully acknowledged. The National Science Foundation provided funds for the purchase of a 360-MHz NMR spectrometer.

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Ring Methyl to Phosphorus Hydrogen Shifts in Pentamethylcyclopentadienyl-Substituted Phosphorus Cations: Parallel between Main-Group and Transition-Metal Chemistry

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The activation of C–H bonds by d- and f-block elements is a topic of considerable current importance.[1] We now report (i) C–H bond activation by a main-group element and (ii) evidence for the first polyhedral phosphorus cations with only P–C bonds.[2]

The η^1 attachment of the Me_5C_5 ring in $(Me_5C_5)(t\text{-Bu})PCl$ (**1**)[3] is apparent from the $^{13}C\{^1H\}$ NMR (50.31 MHz) spectrum in the methyl and ring carbon regions: Me_a (d, δ 20.8, J_{PCC} = 16.5 Hz), Me_b or $Me_{b'}$ (s, δ 13.6 or s, δ 12.2), Me_c and $Me_{c'}$ (s, δ 11.3), C_a (d, δ 61.4, J_{PC} = 49.4 Hz), C_b or $C_{b'}$ (d, δ 136.7, J_{PCC} = 39.0 Hz or d, δ 136.8, J_{PCC} = 19.2 Hz), C_c and $C_{c'}$ (s, δ 135.5).

Treatment of **1** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution at 0 °C results in Cl^- abstraction as demonstrated by the detection of $AlCl_4^-$ as the sole aluminum-containing product in ^{27}Al NMR experiments.[4] Production of the cation,

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