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Structural and Chemical Properties of a Reactive Metalloporphyrin with Aliphatic Amine *N*-Oxide Axial Ligands. Crystal and Molecular Structure of Bis(*N*-methylmorpholine *N*-oxide)(tetraphenylporphinato)manganese(III) Perchlorate

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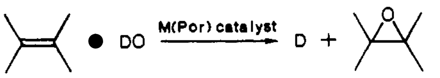
High-spin, $S = 2$, Mn^{III} porphyrin complexes with either strongly or weakly coordinating anionic axial counterions can catalyze the oxygenation of both alkenes and alkanes by aliphatic amine *N*-oxides at temperatures down to 25 °C in nonpolar solvents. One particular aliphatic amine *N*-oxide, *N*-methylmorpholine *N*-oxide (MMNO), not only reacts readily with manganese porphyrins to transfer oxygen to both alkenes and alkanes under mild conditions but also forms a reactive yet isolable 2:1 complex with one manganese porphyrin, (tetraphenylporphinato)manganese(III) perchlorate. Conditions have been found under which isolation of the solvate-free oxygen donor–metalloporphyrin complex bis(*N*-methylmorpholine *N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate, $[(MMNO)_2Mn^{III}TPP]^+ClO_4^-$, $C_{54}H_{50}ClMnN_6O_8$ (**1**), is more rapid than decomposition and hydrocarbon oxidation by this compound. The stoichiometric reactions of **1** with representative alkenes and alkanes are contrasted to catalytic oxygenations of the same substrates using a large excess of the oxygen donor, MMNO, present over the metalloporphyrin. The product distributions for the stoichiometric and catalytic reactions are similar, indicating that the substrate-activating steps and species are similar for both types of processes. Light does not have an effect on the coordination chemistry or oxygen atom transfer chemistry of the ligated *N*-oxide functions. The electronic absorption and ^1H NMR spectra of **1** clearly indicate that the complex is six-coordinate in solution and contains a $S = 2$ Mn^{III} atom. There is no apparent mixing at 25 °C of excited states in **1** that involve electron transfer from metal to MMNO and Mn^{IV} or Mn^{V} character. Green prisms of **1** crystallize in the orthorhombic space group *Pccn* with $a = 12.928$ (10) Å, $b = 17.167$ (23) Å, $c = 21.993$ (31) Å, $V = 4880.9$ (9.9) $Å^3$, and $Z = 4$. The structure was solved by heavy-atom methods and converged to a final R value of 0.0976 ($R_w = 0.0832$). The structure shows bond lengths in accord with the $S = 2$ Mn^{III} atom and a morpholine moiety in the expected chair conformation. The crystal structure indicates that complexation of the oxygen donor does not result in a lengthening of the N–O bond as might be expected for a species lying along the reaction coordinate for oxometalloporphyrin formation by homolytic or heterolytic cleavage of this bond. All available crystallographic data indicates that both O-ligation of the *N*-oxide function and hydrogen bonding to the oxygen atom result in a shortening of the N–O bond by ~0.02 Å.

The investigation of homogeneous hydrocarbon oxygenation processes catalyzed by synthetic metalloporphyrins has resulted in demonstrable progress toward elucidation of a number of the energetic and mechanistic features of hydrocarbon oxidation by cytochrome P-450 and clarification of some features associated with homogeneous liquid-phase catalytic oxygen atom transfer oxidation in general.[1,2] The most thoroughly studied metalloporphyrin-catalyzed homogeneous processes to data are alkene epoxidation (eq 1) and alkane hydroxylation (eq 2) by oxygen



(1)

$$R_3CH + DO \xrightarrow{\text{M(Por) catalyst}} D + R_3COH \qquad (2)$$

DO = oxygen donor = iodosylarene, amine *N*-oxide, peracid, etc.; M(Por) = metalloporphyrin

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donors (DO). Although both the generation of the high-valent oxometalloporphyrin species from various precursors (eq 3) and

$$M(Por)OD \rightarrow M(Por)O + D \qquad (3)$$

the subsequent oxidation of organic substrate by the oxometalloporphyrin species (eq 4) have been extensively examined

$$M(Por)O + S \rightarrow M(Por) + SO \qquad (4)$$

$$S = \text{alkene or alkane substrate}$$

experimentally, some mechanistic questions remain about both types of processes.[2] The "D" atom in eq 3 can be an oxygen atom; that is, oxometal generation can involve the cleavage of a peroxidic bond. This appears to be the case with cytochrome P-450 as well as some of the synthetic metalloporphyrin systems.[1,2] In previous work, both we[17] and others[18,19] have sought to obtain crystalline samples of complexes between activated forms of oxygen or oxygen atom donors and the metalloporphyrins, M(Por)OD, in eq 3. Rigorous characterization of these species could provide direct insight not only into the ground-state electronic and structural features of new metalloporphyrin forms but also structure–reactivity information with respect to oxometalloporphyrin formation (eq 3). Unfortunately the oxygen donor–metalloporphyrin complexes, M(Por)OD, although not as reactive as the oxometalloporphyrins, M(Por)O, are, nevertheless, thermodynamically unstable and of sufficient kinetic lability often that obtaining diffraction quality single crystals is not a simple matter.[17-19] We recently reported the thorough characterization including the single-crystal X-ray structure of a metalloporphyrin complex with aromatic *N*-oxide ligands, bis(2,6-lutidine *N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate.[20] This complex, however, showed little structural or electronic perturbation of the oxygen-donating 2,6-lutidine *N*-oxide moieties and little thermal hydrocarbon oxidation reactivity. The extensive and thorough development by Bruice and co-workers of amine *N*-oxide donors for homogeneous organic oxidation processes catalyzed by iron or manganese porphyrins[3] has spurred us to attempt the isolation of a more reactive complex between an aliphatic amine *N*-oxide and one of these metalloporphyrins. We report here the successful isolation and X-ray crystallographic characterization of one such complex, bis(*N*-methylmorpholine *N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate, $[(MMNO)_2Mn^{III}TPP](ClO_4)$ (**1**). The stoichiometric thermal oxygenation of representative alkenes and alkanes by **1** and the catalytic oxygenation of these substrates by $Mn^{III}TPP(Cl)$ and $Mn^{III}TPP(ClO_4)$ with free *N*-methylmorpholine *N*-oxide (MMNO) are examined.

Experimental Section

Methods. Elemental analyses were performed by Atlantic Microlabs. Visible spectra were recorded on a Hewlett-Packard 8451A spectrophotometer. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph equipped with flame ionization detectors and a Hewlett-Packard 3390A reporting integrator. A 12-m OV-101 fused silica capillary column with nitrogen as the carrier gas was used. Yields were determined by internal standard methods. The identities of the products were verified by co-injection with authentic samples and by gas chromatographic–mass spectrometric (GC/MS) analysis. ^1H NMR spectra were obtained by using a Nicolet Model 360-NB spectrometer operating at 361.0 MHz with a probe temperature of 25 °C.

Materials. All reagents were the best possible grade commercially available. Solvents were glass-distilled grade from Burdick and Jackson. Prior to use, the hydrocarbon substrates were checked by gas chromatography or NMR spectroscopy to insure that no oxidation products were present. Removal of trace peroxides in all substrates was accomplished by passing them through a column of activity grade I alumina. The higher boiling and solid substrates were dissolved in fresh anhydrous diethyl ether, the ether solution was passed through a column of activity grade I alumina, and then the ether was removed in vacuo. All treated olefins were then stored under argon to preclude the formation of oxidation products. The complexes $Mn^{III}TPP(OAc)$,[17b] $Mn^{III}TPP(Cl)$,[17b] and $Mn^{III}TPP(ClO_4)$[21] were prepared by literature methods. *Caution! Although the $Mn^{III}TPP(ClO_4)$ complexes investigated in this paper have given no indication of sensitivity to shock or grinding, perchlorate salts such as these are potentially dangerous and related materials have been known to detonate.* Anhydrous *N*-methylmorpholine *N*-oxide (MMNO) was used in all reactions. Hydrated MMNO consistently gave lower and less reproducible yields of hydrocarbon oxygenation products. The anhydrous oxygen donor was prepared by dehydrating the MMNO monohydrate (Aldrich) for 2–3 h at 90 °C in vacuo.

Synthesis of Bis(*N*-methylmorpholine *N*-oxide)(tetraphenylporphinato)manganese(III) Perchlorate, $[(MMNO)_2Mn^{III}TPP]^+ClO_4^-$ (1). $Mn^{III}TPP(ClO_4)$ (1.0 g) was dissolved in 600 mL of hot toluene. The solution was allowed to cool to room temperature; then, with stirring, 2.5 equiv of dry MMNO was added, and the solution was stirred for 1 h. After 150 mL of *n*-heptane was gently layered on top of the sill solution, the mixture was allowed to sit undisturbed for 12 h. Under these conditions, the thermal degradation products generated from **1** did not interfere with isolation of the complex. The green crystals of **1** were collected, washed with heptane, and dried in vacuo for 12 h. ^1H NMR (3.6×10^{-6} M in $CDCl_3$; δ): 8.11 (s, broad, ortho and meta Ph*H*, 16 H), 7.50 (s, para Ph*H*, 4 H), 4.36 (s, broad, CH_2O, 8 H), 2.73 (s, broad, CH_2N and CH_3N, no resolvable spin-spin splitting, 14 H), –25.5 (s, broad, β-pyr–*H*, 8 H).

Anal. Calcd for $C_{54}H_{50}ClMnN_6O_8 \cdot 3/4C_6H_4CH_3$ ($\mathbf{1} \cdot {}^3/_4$tol): C, 66.48; H, 5.27; N, 7.85. Found: C, 66.37; H, 4.65; N, 7.83.

Procedures for Catalytic and Stoichiometric Oxidation Reactions. All reactions (see Tables III and IV) were magnetically stirred under an argon atmosphere in Schlenk flasks placed in an oil bath maintained at 90 ± 1 °C. All the catalytic and stoichiometric hydrocarbon oxygenation reactions proceeded slowly at ambient laboratory temperature; however, 90 °C was chosen as the temperature for all reactions not only because

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Table I. Crystallographic Data Parameters for Bis(*N*-methylmorpholine *N*-oxide)(tetraphenylporphinato)manganese(III) Perchlorate, $[(MMNO)_2Mn^{III}TPP]^+(ClO_4^-)$ (**1**)

A. Crystal Data	
formula	$C_{54}H_{50}ClMnN_6O_8$
fw	1001.4
space group[a]	orthorhombic *Pccn* (No. 56)
a, Å	12.928 (10)
b, Å	17.167 (23)
c, Å	21.993 (31)
V, Å^3	4880.9 (9.9)
Z	4
D_{calcd}, g cm^{-3}	1.39
D_{obsd}, g cm^{-3}	1.40 (2)
cryst dimens, mm	0.6 × 0.2 × 0.2
color	lustrous black
habit	prismatic
μ_{calcd}, cm^{-1}	3.74
B. Data Collection	
diffractometer	Syntex (Nicolet) $P2_1$
radiation (monochromatic)	Mo Kα (λ = 0.71069, Å)
R(merge); *R*(σ)	0.0073; 0.0655
tot. no. of reflcns measd	2678
no. of indep reflcns	1685 ($F_o > 2.5\sigma(F_o)$)
scan method	ω(Wyckoff)
2θ range, deg	3–40
scan speed, deg min^{-1}	3.91–14.65
bkgd/scan time	1
reflcns measd	$+h,+k,+l$
temp, °C	20
C. Refinement	
abs cor	none
maximum residual electron density, e Å^{-3}	0.624 (1.79 Å from Cl)
R[b]	0.0976
R_w[c]	0.0832
GOF[d]	2.244

[a] Systematic absences: $0kl$, $l = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$. [d] GOF (goodness of fit) = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$ where n_0 is the number of observations, n_v is the number of parameters, and $w^{-1} = (\sigma^2(F) + |0.0002|F^2)$.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	*x*	*y*	*z*	U_{eq}[a]
Mn	5000	5000	0	42 (1)
O(1a)	5799 (3)	5216 (4)	−898 (5)	70 (3)
N(2a)	6192 (4)	5799 (4)	−1160 (7)	55 (3)
C(3a)	6574 (5)	6022 (7)	−286 (9)	91 (6)
C(4a)	6948 (6)	5338 (8)	54 (11)	123 (7)
O(5a)	7306 (3)	5062 (5)	−796 (7)	125 (4)
C(6a)	6950 (5)	4814 (7)	−1595 (9)	108 (6)
C(7a)	6589 (5)	5483 (7)	−2013 (9)	93 (6)
C(8a)	5853 (5)	6481 (6)	−1536 (9)	82 (5)
N(1)	5020 (4)	4014 (4)	−804 (5)	45 (3)
N(2)	5531 (3)	4501 (4)	1069 (6)	44 (3)
C(1)	4737 (4)	3895 (5)	−1758 (7)	42 (4)
C(2)	4878 (5)	3123 (5)	−2108 (7)	59 (4)
C(3)	5249 (5)	2804 (6)	−1401 (8)	68 (5)
C(4)	5342 (4)	3353 (5)	−587 (7)	42 (4)
C(5)	5712 (4)	3240 (5)	232 (7)	48 (4)
C(6)	5797 (4)	3774 (5)	1024 (7)	47 (4)
C(7)	6146 (5)	3677 (6)	1945 (8)	73 (5)
C(8)	6103 (4)	4320 (6)	2510 (8)	63 (4)
C(9)	5718 (4)	4834 (6)	1983 (7)	51 (4)
C(10)	5592 (4)	5583 (5)	2306 (6)	36 (4)
C(11)	5807 (5)	5842 (6)	3345 (7)	50 (4)
C(12)	6323 (5)	6230 (7)	3504 (8)	82 (6)
C(13)	6507 (5)	6479 (7)	4439 (9)	85 (6)
C(14)	6157 (6)	6352 (7)	5259 (8)	82 (6)
C(15)	5640 (6)	5980 (10)	5156 (9)	156 (9)
C(16)	5474 (6)	5706 (8)	4172 (9)	114 (7)
C(17)	6057 (4)	2492 (6)	316 (7)	54 (4)
C(18)	6566 (5)	2412 (8)	−139 (15)	193 (10)
C(19)	6896 (6)	1706 (8)	−65 (16)	219 (12)
C(20)	6711 (7)	1136 (8)	423 (12)	107 (7)
C(21)	6194 (9)	1192 (10)	813 (17)	228 (13)
C(22)	5877 (7)	1904 (9)	786 (16)	212 (11)
Cl	7500	7500	1893 (4)	84 (2)
O(2)	7116 (8)	7672 (9)	2403 (15)	474 (17)
O(3)	7385 (8)	6853 (9)	1414 (10)	275 (9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

the oxygenations proceeded very rapidly at this temperature but also because subsequent rearrangement, further oxidation, or degradation of the initial kinetic products remained minimal at this temperature. The solvent and substrate were degassed and placed under argon before use. The substrate was always present in at least a 100-fold excess relative to metalloporphyrin. For exact conditions, see table captions or experimental procedures below. Control reactions are discussed below.

In a typical catalytic reaction, 5 mL of degassed Burdick and Jackson chlorobenzene, 0.50 mL of cyclooctene, and 2 × 10^{-5} mol of MnTPP(Cl) were placed in a Schlenk flask containing a magnetic stirring bar. The flask was sealed with a septum stopper, thoroughly degassed with a dual-manifold vacuum line and filled with argon. Dry MMNO (2 × 10^{-4} mol) was then added, the contents of the Schlenk flask were degassed again, and the vessel was placed in an oil bath at 90 ± 1 °C. After 2 h, the flask was removed from the bath and internal standard was added; then the contents were analyzed immediately by GC or GC/MS.

In a typical stoichiometric reaction, 5 mL of degassed Burdick and Jackson chlorobenzene, 0.50 mL of cyclooctene, and 2 × 10^{-5} mol of **1** were placed in a Schlenk flask containing a magnetic stirring bar and sealed. Again, the flask was placed in a 90 ± 1 °C oil bath for 2 h, and then worked up and analyzed in the same manner as described for the catalytic reactions above.

A number of control reactions were run to validate the product distributions in both Tables III and IV (see Results and Discussion). Inasmuch as amine *N*-oxides have a well-documented and rich photochemistry,[22] the effect of light on the reactions in the tables was examined. Identical product distributions were obtained in complete darkness and under maximum room lighting. No products were produced under the reaction conditions in the tables if either the metalloporphyrin catalyst or the MMNO was deleted from the reaction system. However, *cis*-stilbene was shown to undergo a small but detectable amount of isomerization (ca. 3%) to the thermodynamically more stable trans isomer under these conditions. The reactions were run initially at a number of temperatures. As indicated above, the reactions in the tables were run at 90 °C rather than at room temperature for ease of product analysis. In conjunction with this, all products were independently examined for stability under the reaction conditions. Epoxides, alcohols, and ketones all showed some losses but the losses were small and reproducible. It was also established that none of the reactants or products isomerized or reacted in the injector port of the gas chromatograph.

X-ray Crystallography

Collection and Reduction of Intensity Data. A benzonitrile solution of MMNO was initially added to a toluene solution of Mn^{III}TPP(ClO$_4$). Crystals for X-ray diffraction were then grown by layering the resulting solution with heptane. One exemplary crystal was affixed to the end of a glass capillary with epoxy cement. The capillary was then mounted on a goniometer head, which was placed on a Syntex $P2_1$ four-circle diffractometer. Crystal and data collection parameters along with final values for the residuals are summarized in Table I. Cell dimensions were obtained by least squares refinement of 21 centered reflections (4.39 < 2θ < 12.86°). The crystal showed no evidence of deterioration based on intensity measurements of 3 standards every 197 reflections.

Structure Solution and Refinement. The computer hardware and software were described previously.[20] The space group was uniquely determined as indicated in Table I. The Mn atom was assigned the special position $^1/_2$, $^1/_2$, 0 to correspond with the crystal volume and density. Subsequent Fourier syntheses and least-squares refinement provided locations for the remaining non-hydrogen atoms. Hydrogen positions were not readily discernible from electron density difference maps. They were placed in their calculated positions and allowed to "ride" on their parent carbon atoms [C–H = 0.96 Å; U_{iso}(H) = 1.2 U_{eq}(C)]. All non-hydrogen atoms were refined anisotropically. Blocked-cascade least-squares refinement of 318 variables gave the final agreement factors listed in Table I. On the last cycle of the least-squares refinement, the ratio of the maximum shift to the estimated standard deviation was 0.007. Semiempirical (ψ-scan) methods indicated that the data did not require correction for absorption. Scattering factors were

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[22] Review: Albini, A.; Alpegiani, M. *Chem. Rev.* **1984**, *84*, 43.

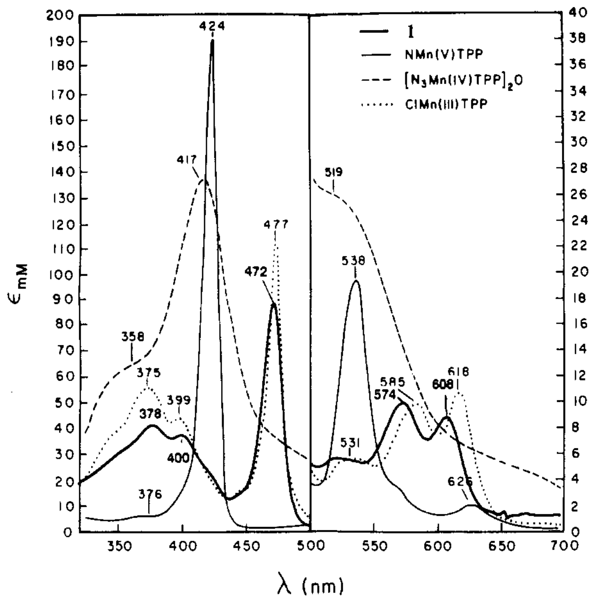


Figure 1. Electronic absorption spectra of **1** and representative manganese(III), manganese(IV), and manganese(V) tetraphenylporphyrin complexes. All solutions are ca. 1 mM in toluene at 25 °C. The spectrum for NMn^VTPP in the 325–500-nm region is half-scale.

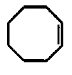
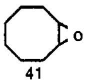
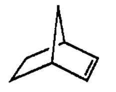
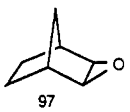
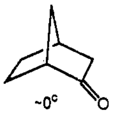
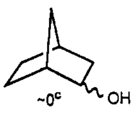
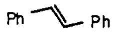
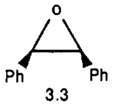
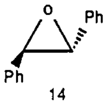
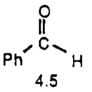
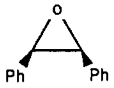
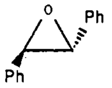
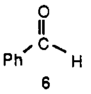
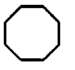
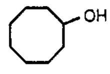
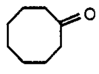
those used for neutral atoms.[23] The final positional and thermal parameters are given in Table II.

Results and Discussion

The aliphatic amine *N*-oxide, *N*-methylmorpholine *N*-oxide (MMNO), reacts thermally in homogeneous solution with $S = 2$ manganese(III) porphyrin complexes containing either weakly coordinating anionic axial counterions, as in $Mn^{III}TPP(ClO_4)$, or strongly coordinating counterions, as in $Mn^{III}TPP(Cl)$, resulting in both the epoxidation of olefins and the hydroxylation of alkanes (eq 1 and 2, respectively) analogous to the *N*,*N*-dimethylanaline *N*-oxide/metalloporphyrin systems investigated in some depth by Bruice and co-workers.[3] Although one amine *N*-oxide complex, bis(2,6-lutidine *N*-oxide)(tetraphenylporphinato)manganese perchlorate, was amenable to both detailed X-ray crystallographic examination in the solid state and NMR characterization in solution, it was not of sufficient reactivity that its stoichiometric and catalytic hydrocarbon oxygenation processes could be compared.[20] This is not the case in the system constituted by manganese tetraarylporphyrins and MMNO. Two-to-one complexes (oxygen donor to porphyrin) form in solution if both weakly coordinating solvents and $S = 2$ manganese(III) porphyrins with weakly coordinating axial ligands are used. The preparation of bis(*N*-methylmorpholine *N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate (**1**) can be effected by this method. If highly purified hydrocarbon solvents are used, crystallization of **1** is more rapid at room temperature than its subsequent decomposition and hydrocarbon oxygenation reactions.

The thermal stability of **1** in highly purified solvents was adequate to allow rapid determination of the electronic absorption and ^1H NMR spectral features of the complex at ambient laboratory temperature. In Figure 1, the absorption spectrum (λ 325–700 nm) of **1** is compared with the spectra for representative Mn^{III}-, Mn^{IV}-, and Mn^VTPP complexes that were thoroughly characterized previously.[17,20] The absorption spectrum of **1** clearly shows the "split Soret" band and other bands typical of d-type hyperporphyrin spectra,[24] including the spectra of most manganese(III) porphyrins. The high-energy spectral features in the 410–430-nm region that characterize all the manganese(IV) and manganese(V) tetraarylporphyrin complexes examined to date are absent in the spectrum of **1**. The isolable adduct between $[MnTPP]^+$ and the oxygen donor iodosylbenzene, $[XMn^{IV}TPP(OIPh)]_2O$, X = Cl^- or Br^-,[17b] is qualitatively distinct from **1**, an isolable adduct between $[MnTPP]^+$ and the oxygen donor MMNO. Complexation of the oxygen donor in the former case results in production of an adduct with a formal oxidation of the manganese to the +4 oxidation state while complexation in the latter case does not. The ^1H NMR spectrum of **1** substantiates the S = 2 Mn^{III} formulation for the ground electronic state of the complex in solution. The isotropically shifted resonances for the MMNO protons together with the single resonances for the ortho and meta phenyl protons indicate that the symmetrical six-coordinate form of the complex predominates in solution at 25 °C.

Table III. Stoichiometric Oxidation of Representative Alkenes and Alkanes by $[(MMNO)_2Mn^{III}TPP](ClO_4)$ (**1**)[a]

substrate	product yields,[b] %		
	 41		
	 97	 ~0[c]	 ~0[c]
	 3.3	 14	 4.5
	 19	 13	 6
	 2.2	 10.4	

[a] Mole ratio of oxidant (**1**) to substrate was 1:50 for the stilbene reactions and 1:100 for the others; all reactions were run under argon at 90 °C in chlorobenzene for 2.0 h and then worked up and the products analyzed as described in the text. [b] Yields were based on two 2-electron oxidizing equivalents contained in each molecule of **1**; yields were reproducible within ±5%. [c] Below limit of detection (≪1%).

The products derived from the stoichiometric reactions of **1** with representative alkenes and alkanes and the products derived from the catalytic reactions of $Mn^{III}TPP(Cl)$ with an excess of MMNO for the same hydrocarbon substrates are given in Tables III and IV, respectively. All these reactions proceed at room temperature, although some are quite slow. When $Mn^{III}TPP(ClO_4)$ is used in place of $Mn^{III}TPP(Cl)$ as the catalyst, the product distributions are very similar but greater degradation of MMNO with the former catalyst results in lower yields for the intermolecular hydrocarbon oxygenation products. For this reason, the data in Table IV were collected with $Mn^{III}TPP(Cl)$ as the catalyst. A reaction temperature of 90 ± 1 °C was used in all studies to speed up some reactions and to aid the analysis of products. Other reaction conditions are given in the tables. A substantial number of control experiments, discussed in the Experimental Section, were conducted to establish that neither the reaction conditions nor the product analyses had a demonstrable effect on the observed product distributions. Likewise, light was shown to have a negligible effect on the chemistry. Subsequent oxidation and/or rearrangement of the initially produced kinetic products was not of major importance for the product yields reported in Tables III and IV. The oxidizing equivalents represented in MMNO or **1** not accounted for by the products given in the tables are consumed primarily by degradation of the MMNO moieties. Substantial quantities of morpholine are produced in all reactions. Unfortunately the irreproducible peak shapes and other factors usually encountered in the gas chromatographic analysis of amines are

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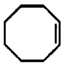
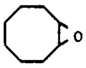
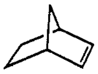
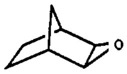
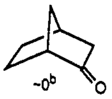
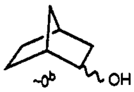
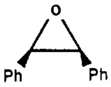
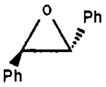
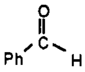
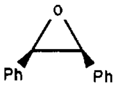
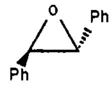
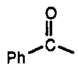
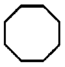
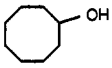
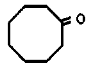
(23) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1074; Vol. IV, Table 2.2B.

(24) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol III, Part A, Chapter 1.

Table IV. Oxidation of Representative Alkenes and Alkanes by *N*-Methylmorpholine *N*-Oxide Catalyzed by $Mn^{III}TPP(Cl)^a$

substrate	product yields based on oxidant (based on catalyst), %		
	 46 (455)		
	 86 (860)	 ~0^b	 ~0^b
	 ~1 (7)	 3.6 (35.5)	 1 (10)
	 33 (325)	 22 (220)	 5 (50)
	 ~1 (8)	 2.2 (22)	

^{a}Catalyst:oxidant (MMNO):substrate molar ratios were 1:10:100 for the stilbene reactions and 1:10:200 for all others; reactions were run under argon at 90 °C in chlorobenzene solvent for 2 h and then worked up and the products analyzed as described in the text. Yields outside parentheses were based on oxidant; those inside parentheses were based on MnTPP(Cl). Yields were reproducible to within ±5%. ^{b}Below limit of detection (≪1%).

Table V. Selected Bond Lengths (Å)

Mn-O(1a)	2.139 (7)	Mn-N(1)	1.987 (7)
Mn-N(2)	2.002 (8)	O(1a)-N(2a)	1.366 (10)
N(2a)-C(3a)	1.458 (15)	N(2a)-C(7a)	1.508 (15)
N(2a)-C(8a)	1.471 (13)	N(1)-C(1)	1.397 (11)
N(1)-C(4)	1.367 (12)	N(2)-C(6)	1.380 (12)
N(2)-C(9)	1.377 (12)	C(1)-C(2)	1.434 (13)
C(2)-C(3)	1.342 (14)	C(3)-C(4)	1.427 (14)
C(4)-C(5)	1.348 (13)	C(5)-C(6)	1.387 (13)
C(6)-C(7)	1.426 (14)	C(7)-C(8)	1.327 (14)
C(8)-C(9)	1.400 (14)	C(9)-C(10)	1.379 (13)
C(10)-C(1a)	1.353 (12)	Cl-O(2)	1.111 (18)
Cl-O(3)	1.297 (15)		

Table VI. Selected Bond Angles (deg)

O(1a)-Mn-N(1)	81.1 (3)	O(1a)-Mn-N(2)	88.3 (3)
N(1)-Mn-N(2)	89.1 (3)	N(1)-Mn-O(1a)	98.9 (3)
O(1a)-Mn-N(1a)	98.9 (3)	N(2)-Mn-N(1a)	90.9 (3)
O(1a)-Mn-N(2a)	91.7 (3)	N(1)-Mn-N(2a)	90.9 (3)
N(1a)-Mn-N(2a)	89.1 (3)	Mn-O(1a)-N(2a)	141.4 (6)
O(1a)-N(2a)-C(3a)	111.4 (8)	O(1a)-N(2a)-C(7a)	106.4 (7)
C(3a)-N(2a)-C(7a)	109.2 (8)	O(1a)-N(2a)-C(8a)	110.1 (7)
C(3a)-N(2a)-C(8a)	109.8 (8)	C(7a)-N(2a)-C(8a)	109.8 (8)
Mn-N(1)-C(1)	125.2 (5)	Mn-N(1)-C(4)	127.7 (6)
C(1)-N(1)-C(4)	106.9 (7)	Mn-N(2)-C(6)	127.3 (6)
Mn-N(2)-C(9)	126.1 (6)	C(6)-N(2)-C(9)	106.6 (7)
N(1)-C(1)-C(2)	108.5 (7)	N(1)-C(1)-C(10a)	127.2 (8)
C(2)-C(1)-C(10a)	124.2 (8)	C(1)-C(2)-C(3)	107.1 (8)
C(2)-C(3)-C(4)	108.7 (9)	N(1)-C(4)-C(3)	108.8 (8)
N(1)-C(4)-C(5)	126.3 (8)	C(3)-C(4)-C(5)	124.8 (9)
C(4)-C(5)-C(6)	124.5 (9)	C(4)-C(5)-C(17)	119.1 (8)
C(6)-C(5)-C(17)	116.4 (8)	N(2)-C(6)-C(5)	124.8 (8)
N(2)-C(6)-C(7)	107.4 (8)	C(5)-C(6)-C(7)	127.8 (9)
C(6)-C(7)-C(8)	108.9 (9)	C(7)-C(8)-C(9)	107.5 (9)
N(2)-C(9)-C(8)	109.6 (8)	N(2)-C(9)-C(10)	126.0 (8)
C(8)-C(9)-C(10)	124.2 (9)	C(9)-C(10)-C(11)	119.1 (8)
C(9)-C(10)-C(1a)	124.5 (8)	C(11)-C(10)-C(1a)	116.3 (8)

seen with morpholine in these studies, rendering the quantification of this product very difficult.

The product selectivities and stereoselectivities for the stoichiometric and catalytic conditions, although not identical, are quite similar. Furthermore these product distributions are similar to those encountered in other manganese porphyrin-oxygen donor catalytic hydrocarbon oxidation systems.[2] These facts strongly suggest that similar species, i.e. oxomanganese(V) porphyrins, $O{=}Mn^{V}TPP(L)$ (L = sixth ligand), are likely responsible for the substrate activation processes in all these systems. The small differences in the product distributions in Table III and IV could result from the fact that different distributions of five- and six-coordinate manganese porphyrins with MMNO axial ligands, all capable of producing oxomanganese(V) complexes by cleavage of the N-O bond of the ligand MMNO moiety, could be present at equilibrium. The ratio of MMNO to metalloporphyrin is, after all, one factor that is different between the reactions in Table III and those in Table IV. Not only is the kinetic competence of oxomanganese(V) porphyrins with respect to attack on alkenes and alkanes well established but also there is now much experimental evidence that several different forms of these species, varying only in the degree and type of axial ligation, all capable of hydrocarbon oxidation, can be present under similar conditions in solution.[25]

The MMNO/Mn^{III}TPP system also looks like a good candidate for documenting a well-defined example of the reverse of reaction 3, that is, the trapping of an oxometalloporphyrin, M(Por)O, by the donor molecule, D to re-form the complex between the oxygen donor and the metalloporphyrin, M(Por)OD. A clean example of reversible coordination of a donor ligand, D, to the oxygen atom of a oxometalloporphyrin would greatly aid investigation of the energetic and mechanistic features of oxometalloporphyrin formation. The specific experiment and the most logical one we sought to pursue entailed thermolysis of **1** in the presence of 2,6-lutidine (D′). The product complex, $M(Por)(OD')_2$ in eq 8, is thoroughly documented to be of greater thermal stability than **1** and should be isolable under conditions where **1** is unstable (eq 5-8).[20] Thermolysis of **1** in the presence of up to a 1000-fold

$$\underset{\mathbf{1}}{Mn^{III}TPP(OD)_2} \rightarrow O{=}Mn^{V}TPP(OD) + D \qquad (5)$$

$$O{=}Mn^{V}TPP(OD) + D' \rightarrow Mn^{III}TPP(OD)(OD') \qquad (6)$$

$$Mn^{III}TPP(OD)(OD') \rightarrow O{=}Mn^{V}TPP(OD') + D \qquad (7)$$

$$O{=}Mn^{V}TPP(OD') + D' \rightarrow Mn^{III}TPP(OD')_2 \qquad (8)$$

molar excess of 2,6-lutidine under conditions where bis(2,6-lutidine *N*-oxide)(tetraphenylporphinato)manganese perchlorate, $Mn^{III}TPP(OD')_2$, is known to be stable, failed to produce any evidence for the formation of the latter. Certainly reaction of the oxomanganese(V) intermediates with the 2,6-lutidine at sites other than at the nitrogen atom is quite possible.

Diffraction quality crystals of an orthorhombic modification of **1** could be grown from highly purified benzonitrile and hydrocarbon solvents. A combined atom-numbering and ORTEP diagram for this complex is shown in Figure 2. Selected bond lengths and angles are given in Tables V and VI, respectively. The manganese-porphyrin nitrogen distances, d_{Mn-N}, of 1.987 (7) and 2.002 (8) Å, respectively, are effectively the same as those not only in the previously characterized bis(2,6-lutidine *N*-oxide)-(tetraphenylporphinato)manganese(III) perchlorate complex [1.991 (4)-2.004 (4) Å, values)][20] but also in all other $S = 2$ manganese(III) porphyrins. Both six-coordinate and five coordinate neutral as well cationic $S = 2$ manganese(III) porphyrin complexes have now been structurally characterized.[21,26,27] The

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(25) See studies in footnotes 3, 5, 7, 8, 10, 11, 13, and 15.

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Table VII. Comparison of Structural Data for **1** and Other Aliphatic Tertiary Amine *N*-Oxides

compd	d_{N-O}, Å	angles, deg M-O-N	O-N-CH$_3$	comments	ref
1	1.366 (10)	141.4 (6)	110.1 (7)	see text	this work
N-methylmorpholine *N*-oxide, anhydrous	1.391 (3)	NA	109.5 (2)	no H bonds	30
N-methylmorpholine *N*-oxide hydrate	1.384 (3)	NA	109.8 (2)	single H bond	30
	1.383 (3)	NA	110.2 (2)		
N-methylmorpholine *N*-oxide–2.5H$_2$O	1.392 (3)	NA	109.3 (3)	N–O oxygen atom saturated with H bonds	31
	1.399 (3)		109.9 (3)		
N-methylmorpholine *N*-oxide–*trans*-1,2-cyclohexanediol	1.383 (3)	NA	109.1 (3)	H bonds to diol	32
trimethylamine *N*-oxide (TMANO)	1.388 (5)	NA	110.0 (6) (av of 3)		33
N,*N*-dimethylethanolamine *N*-oxide (DMEAO)	1.41 (1)	NA	108 (1)	only the third listed N–O is H bonded	34
	1.41 (2)		108 (1)		
	1.38 (2)		110 (1)		
(μ-H)Re$_2$(CO)$_7$(μ-NC$_5$H$_4$)(Me$_3$NO)	1.41 (1)	128.1 (5)	...	N–O bonded to low-valent metal	35
aqua(*N*,*N*-dimethylethylenediamine *N*-oxide)(oxalato)copper(II) dihydrate	1.410 (6)	123.7 (3)	NA	N–O in chelate ring (6-membered)	36

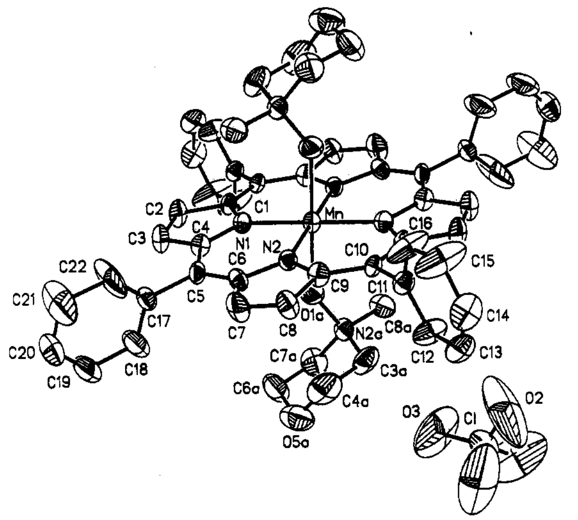

Figure 2. Atom-numbering and ORTEP diagram for **1**. Thermal ellipsoids are at the 30% probability level.

manganese–axial oxygen distance, d_{Mn-O}, of 2.139 (7) Å compares with the values 2.263 (4) and 2.264 (4) Å in the bis(2,6-lutidine *N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate complex,[20] 2.217 (4) Å in the bis(*N*,*N*-dimethylformamide)(tetraphenylporphinato)manganese(III) perchlorate complex,[21] and 2.105 (4) Å in the five-coordinate cationic (aquo)(tetraphenylporphinato)manganese(III) triflate complex.[27] All these distances are long for a single bond from a first-row transition-metal metalloporphyrin to an axial oxygen atom[28] and confirm the tetragonally elongated high-spin d^4 electronic configuration for the Mn atom in **1**. Not surprisingly, the six-membered ring of the MMNO ligand in **1** is in the chair conformation as it is in all other MMNO crystal structures in the literature (vide infra).

Although there are a substantial number of X-ray crystallographic structure determinations on aromatic amine *N*-oxides and complexes containing these ligands,[29] there are very few for aliphatic amine *N*-oxides or complexes containing these ligands. Table VII includes some structural data for all the MMNO crystal structures in the literature. There are four such structure determinations containing collectively five MMNO molecules in the asymmetric units of these structures. Also in Table VII are presented selected structural data for other free and complexed aliphatic amine *N*-oxide molecules. An examination of all the data in Table VII indicates clearly that if the oxygen atom of the aliphatic amine *N*-oxide is either coordinated to a transition-metal atom or hydrogen bonded, then the length of the N–O bond is decreased, not increased. Both coordination "bonds" and hydrogen bonds have a substantial electrostatic component. The shortening of the N–O bond upon complexation to a transition metal appears to result in a shortening of the bond distance by ~0.02 Å. The shortening of the N–O bond of an aliphatic amine *N*-oxide resulting from hydrogen bonding is perhaps most accurately addressed in the recent X-ray crysatallographic investigation by Maia et. al. of *N*,*N*-dimethylethanolamine, which contains three molecules in the asymmetric unit.[34] Two of the molecules do not contain hydrogen-bonded oxygen atoms, d_{N-O} = 1.41 (1) and 1.41 (2) Å, while the third molecule contains an oxygen atom involved in a strong intramolecular hydrogen bond, d_{N-O} = 1.382 (2) Å. The short N–O bond distance in the MMNO moieties of **1**, 1.366 (10) Å, and the other structurally characterized ligated aliphatic amine *N*-oxide molecules, probably results from donation of π-bonding electron density in the *N*-oxide moiety into the d$_{xz}$ or d$_{yz}$ orbitals of the transition metal. An examination of the N–O bond length in the one crystallographically characterized organometallic complex with an aliphatic amine *N*-oxide ligand, trimethylamine *N*-oxide (TMANO), the work of Brown and co-workers, is also of interest. In this case the aliphatic amine *N*-oxide is complexed to a low-valent electron-rich rhenium atom in the complex (μ-H)Re$_2$(CO)$_7$(μ-NC$_5$H$_4$)(Me$_3$NO).[35] The N–O bond is also shortened upon complexation in this compound by ~0.02 Å. The dominant electronic interaction affecting the N–O bond distance in this case may or may not be the same as in the case of **1**.

Interestingly, the structure of the thermally reactive title complex, **1**, involves a small perturbation of the N–O unit that does not appear to lie along the reaction coordinate for either the heterolytic or homolytic cleavage of this bond to generate the oxometalloporphyrin (cf. eq 3). The structural work in this paper indicates that further attempts to obtain definitive structural evidence for the activation of O–D functions of all kinds in metalloporphyrins may not necessarily lead to further elucidation of the mechanistic features involved in peroxide and other O–D

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bond cleavage processes by metalloporphyrins.

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Supplementary Material Available: Tables of anisotropic temperature factors (Table SI), hydrogen coordinates and temperature factors (Table SII), bond lengths (Table SIII), bond angles (Table SIV), nonbonded distances (Table SV), and torsion angles (Table SVI) (9 pages); a table of observed and calculated structure factors (Table SVII) (10 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Icosahedral Rhodacarboranes Bearing η^3-Allyl, Alkyl, and Acyl Moieties at the Metal Vertex[1]

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The rhodacarboranes [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (H(**1a**)) and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (H(**1b**)) are easily converted to the corresponding anionic **1a**$^-$ and **1b**$^-$ by abstraction of the hydrido ligand at Rh as a proton. The formal Rh(I) species **1a**$^-$ and **1b**$^-$ serve as apparent nucleophiles in reactions with allyl and methallyl chlorides or allyl acetate to afford the corresponding η^3-allyl derivatives. The crystal and molecular structure of [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) has been determined by X-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 12.678 (3) Å, b = 15.391 (4) Å, c = 15.454 (2) Å, β = 121.26 (1)°, and Z = 4. Diffraction data to $2\theta(\max)$ = 50° (Mo Kα radiation) were collected on a Syntex P$\bar{1}$ diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares techniques to a final discrepancy index of R = 0.041 for 3851 independent observed reflections. All atoms, including hydrogen atoms, were located. The molecule has the closo 12-vertex icosahedral geometry, and the rhodium atom exhibits pseudo-octahedral coordination with the dicarbollide ligand occupying three facial coordination sites, the triphenylphosphine occupying a fourth site, and the η^3-allyl ligand filling the remaining two sites. The molecule is monomeric, and there are no intermolecular distances shorter than van der Waals distances. Reactions of **1a**$^-$ and **1b**$^-$ with $(CH_3)_3OBF_4$ produced solvent-stabilized methyl derivatives **4a** and **4b**, [*closo*-3-PPh_3-3-CH_3-3-CH_3COCH_3-3,1,2-$RhC_2B_9H_{11}$] and [*closo*-2-PPh_3-2-CH_3-2-CH_3COCH_3-2,1,7-$RhC_2B_9H_{11}$], respectively. Both **4a** and **4b** were converted to $(PPh_3)_2$ derivatives by $(CH_3)_2CO$ displacement with PPh_3. Benzyl bromide and **1a**$^-$ produced [*closo*-3-PPh_3-3-$PhCH_2$-3-Br-3,1,2-$RhC_2B_9H_{11}$] (**6a**). The corresponding 2,1,7 derivative, **6b**, was similarly prepared. Dihydrogen reacts with complexes **2a**, **2b**, **4a**, and **4b** to produce unstable hydridic species **7a** and **7b** formulated as [*closo*-(PPh_3)(H)(solvent)$RhC_2B_9H_{11}$] isomers with solvent being $(CH_3)_2CO$ or CH_3CN. Complexes **4a** and **4b** react with CO (1 atm, 25 °C) to produce the corresponding isomers of [*closo*-$(PPh_3)(CO)(COCH_3)RhC_2B_9H_{11}$] (**8a** and **8b**, respectively). Similar benzoyl derivatives were obtained through alternative routes.

Introduction

In earlier publications[3,4] we have described the syntheses and structural characterization of the *closo*-rhodacarborane anions [*closo*-3-PPh_3-3-L-3,1,2-$RhC_2B_9H_{11}$]$^-$ (**1a**$^-$, L = PPh_3) and [*closo*-2-PPh_3-2-L-2,1,7-$RhC_2B_9H_{11}$]$^-$ (**1b**$^-$, L = PPh_3), which may be considered to contain formal d^8-$LRh(PPh_3)^+$ vertices combined with the corresponding [*nido*-$C_2B_9H_{11}$]$^{2-}$ ions. The ligand L may be comprised of any one of a number of uncharged electron-pair-donor species, such as η^2-C_2H_4 and CO. In this paper we describe reactions of **1a**$^-$ and **1b**$^-$ that produce novel icosahedral rhodacarborane derivatives bearing an η^3-allyl, alkyl, or acyl group attached to a formal d^6-Rh^{3+} vertex. The structure of [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) was elucidated by an X-ray diffraction study. Furthermore, the interconversions of certain of these conventional organometallic species are described along with the reactions of the η^3-allyl- and alkylrhodacarborane derivatives with H_2. The latter study proved the existence of H_2 activation pathways that appear to involve formal Rh^{5+} intermediates or cyclic concerted processes that require the simultaneous formation of C–H and Rh–H bonds in a cyclic transition state.

Results and Discussion

Syntheses and Characterization of η^3-Allylrhodacarboranes. The reaction of Li^+[*closo*-3,3-$(PPh_3)_2$-3,1,2-$RhC_2B_9H_{11}$]$^-$ (Li(**1a**)) or Li^+[*closo*-2,2-$(PPh_3)_2$-2,1,7-$RhC_2B_9H_{11}$]$^-$ (Li(**1b**)) with allyl chloride produced the respective yellow and pale yellow crystalline 18-electron η^3-allyl complexes [*closo*-3-PPh_3-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**2a**) and [*closo*-2-PPh_3-2-(η^3-C_3H_5)-2,1,7-$RhC_2B_9H_{11}$] (**2b**). Similarly, Li(**1a**) and Li(**1b**) reacted with methallyl chloride to produce the corresponding η^3-methallyl complexes **3a** and **3b**, respectively; however, the latter reactions were complicated by the formation of additional chlororhodium complexes, and pure samples were difficult to obtain. However, a superior synthesis[5] of **2a** was developed by using the reaction of Li(**1a**) with allyl acetate in THF. Similar reactions of Li(**1b**) were more complex and offered no advantage in the preparation of **2b**. As seen in Figure 1, the 25 °C 200-MHz ^{1}H NMR spectrum of **2a** in CD_2Cl_2 displays the resonances expected to arise from the coordinated triphenylphosphine ligand and the two equivalent carboranyl C–H protons in addition to three resonances due to the η^3-allyl ligand. Following the assignments made in other (η^3-allyl)rhodium(III) complexes,[6] we assigned the complex multiplet of relative area equivalent to 1 H that appears at 4.97 ppm to the methine proton (H_1) of the allyl ligand. The two syn protons (H_2) appear as a doublet ($J_{H_1-H_2}$ = 8 Hz) at 4.10 ppm, while the triplet pattern at 2.53 ppm arises from the two anti protons (H_3). Decoupling experiments showed that the two H_3 protons were coupled to H_1 as well as to the phosphorus and rhodium nuclei. Inasmuch as the syn and anti protons have the same bond connectivity, this additional coupling is probably due to stronger "through-space" interactions of the anti protons with the phosphorus and rhodium nuclei compared to those of the syn protons. Indeed, X-ray structural analysis of **2a** (vide infra) supports this view. The ^{1}H NMR spectra of **2b**, **3a**, and **3b** exhibit comparable spectral features.

The formation of the η^3-allyl complex **2a** can be considered to arise from a nucleophilic displacement reaction of allyl chloride

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