Houk's calculations support the experimental results obtained by Kishi, Evans, and Still.[15] Modification of Houk's model to rationalize our results leads to model **8** (X = CH_2, CHR, O). This model provides minimal steric interactions by placing the alkyl groups (R′) on boron in proximity with the small group of the chiral center. However, there is an increased steric repulsion of the R group with the M group in this model. Thus, in reduction of the ketone with a small reducing agent, BH_3, the model leading to the Cram product is apparently favored. In the case of an olefin (X = CH_2, CHR), one can postulate that model **7** is further destabilized by the interaction of the vinyl groups with the medium group. Thus, hydroboration of the olefin is more selective than reduction of the ketone with similar reagents.

In summary, the reduction of acyclic chiral ketones, unlike the cyclic examples, proceeds via different stereochemical pathways when performed by nucleophilic or electrophilic reducing agents. The anti-Cram selectivity observed in the hydroboration of the corresponding olefin is thus an example of this dichotomy. Although the models may not represent the actual transition state, they may be used in a predictive fashion. Finally, it is comforting to note that the experimental facts back up the theoretical predictions.

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Registry No. **1**, 38388-16-8; **2**, 55509-37-0; **3**, 85650-30-2; **4**, 1778-02-5; **5**, 53603-96-6; **6**, 14553-79-8; 3β,20*Z*-cholesta-5,20(22)-diene-3-ol acetate, 60132-90-3; 3β,20*E*-cholesta-5,20(22)-diene-3-ol acetate, 54548-85-5; thexylborane, 3688-24-2; disiamylborane, 6838-83-1; dicyclohexylborane, 1568-65-6; bis(*trans*-2-methylcyclohexyl)borane, 34611-76-2; 3-phenyl-2-butanone, 769-59-5; BMS, 13292-87-0; 9-BBN, 280-64-8; $NaBH_4$, 16940-66-2; $LiAlH_4$, 16853-85-3; $LiEt_3BH$, 22560-16-3; K-*s*-Bu_3BH, 67940-40-3; Li-*s*-Bu_3BH, 63717-73-7; NB-enantride, 81971-15-5.

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[15] Kishi, Y. *Aldrichimica Acta* **1980**, *13*, 23. Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 259. Evans, D. A.; Bartroli, J.; Godel, T. *Tetrahedron Lett.* **1982**, *23*, 4577. Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. The effect of oxygen substituents in these reactions remains to be explored.

[16] **Note Added in Proof**: Hydroboration of 2-methyl-3-phenyl-1-butene with bis(*trans*-2-methylcyclohexyl)borane provides the anti-Cram product as predicted by **8** (R = CH_3; X = CH_2; S = H; M = CH_3; L = C_6H_5) in a 10:1 ratio.

Electrophile-Induced Reduction of Coordinated Nitrogen Monoxide. Sequential Conversion of a μ_3-NO Group to μ_3-NOH and μ_3-NH Ligands by Protonic Acids[1]

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The principal impetus for the investigation of the reactivity of coordinated nitrogen monoxide derives from the widespread occurrence of nitrogen oxides as atmospheric pollutants.[2] Initial studies in this regard were focused primarily on the behavior of nucleophiles or electrophiles toward linear or bent M–NO linkages, respectively.[3] More recent research has begun to examine the analogous reactivity patterns of transition-metal complexes containing doubly bridging NO groups.[4,5] However, maximum reduction of the N–O bond order (and hence optimum activation of the bound NO) should occur in $M_3(\mu_3\text{-NO})$ systems. Accordingly, we have investigated the reactions of one such system with strong protonic acids and now report the unprecedented, sequential transformations shown in eq 1 (where M = $(\eta^5\text{-}C_5H_4Me)Mn(NO)$) which involve an overall formal reduction of the μ_3-NO ligand.

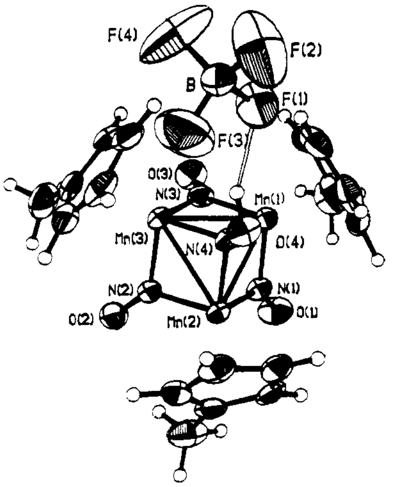

Figure 1. Molecular structure of **2a**. The hydrogen atoms have been assigned arbitrarily lower temperature factors for clarity. Selected bond lengths (Å) and angles (deg) are Mn–Mn (av) = 2.5083 (9), Mn–μ_2-N (av) = 1.856 (4), μ_2-N–O (av) = 1.207 (5), Mn–N(4) (av) = 1.873 (3), N(4)–O(4) = 1.393 (4), O(4)–H(NO) = 0.85 (6), H(NO)–F(1) = 1.91 (6), F(1)–B = 1.395 (6), B–F (av) = 1.321 (8), Mn–N(4)–Mn (av) = 84.1 (2), Mn–N(4)–O(4) (av) = 129.3 (2), N(4)–O(4)–H(NO) = 107 (4), O(4)–H(NO)–F(1) = 156 (6), H(NO)–F(1)–B = 112 (2).

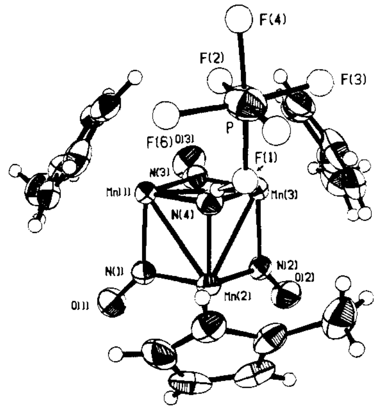

Figure 2. Molecular structure of **3b**. The hydrogen and fluorine atoms have been assigned arbitrarily lower temperature factors for clarity. Selected bond lengths (Å) and angles (deg) are Mn–Mn (av) = 2.5027 (7), Mn–μ_2-N (av) = 1.860 (3), μ_2-N–O (av) = 1.205 (4), Mn–N(4) (av) = 1.872 (3), N(4)–H = 0.81 (3), H–F(1) = 2.24 (4), P–F (av) = 1.528 (4), Mn–N(4)–Mn (av) = 83.95 (12), Mn–N(4)–H (av) = 129 (3), N(4)–H–F(1) = 165 (3).

$$\begin{tikzcd} M_3(\mu_3\text{-NO}) \arrow[r, shift left, "H^+"] \arrow[rr, bend right, "3H^+,\ 2e^-"'] & {[M_3(\mu_3\text{-NOH})]^+} \arrow[l, shift left, "Et_3N"] \arrow[r, "2H^+"', "2e^-"] & {[M_3(\mu_3\text{-NH})]^+} \end{tikzcd} \quad (1)$$

Addition of 1 equiv of acid [$HBF_4\cdot OMe_2$ or $HPF_6(aq)$] to a CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_4$ (**1**)[6] results in the rapid formation of $[(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_3(NOH)]Y$ (Y = BF_4, **2a**; Y = PF_6, **2b**).[7] (The reverse transformation, **2** → **1**, may

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[1] Organometallic Nitrosyl Chemistry. 18. For part 17 see: Legzdins, P.; Nurse, C. R. *Inorg. Chem.* **1982**, *21*, 3110.

[2] Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79 and references therein.

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be cleanly effected with a stoichiometric amount of Et_3N.) Further treatment of **2a** or **2b** with 2 equiv of acid affords low yields of $[(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_3(NH)]Y$ ($Y = BF_4$, **3a**; $Y = PF_6$, **3b**), which may be more conveniently obtained from the reactions of **1** with an excess of the appropriate acid in CH_2Cl_2.[8] The product complexes **2** and **3** are relatively air-stable, black crystalline solids.

Single-crystal X-ray crystallographic analyses of **2a** and **3b**[9] confirmed the identities of the hydroxyimido- and imido-containing cations, respectively, and revealed their molecular structures (Figures 1 and 2). To the best of our knowledge, **2a** and **3b** represent the first structurally characterized examples of $M_3(\mu_3\text{-}NOH)$ and $M_3(\mu_3\text{-}NH)$ linkages.[10] In both complexes, the central $Mn_3(NO)_3$ core is essentially the same as that found for $(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_4$ (**1'**),[12] the cyclopentadienyl analogue of **1**; selected intramolecular dimensions are presented in the captions to Figures 1 and 2. The most chemically interesting features of both structures involve the unique apical ligands. Both ligands are attached closer to the equilateral Mn_3 triangle than the triply bridging nitrosyl ligand in **1'** (i.e., Mn-N(4) (av) = 1.872 (3) or 1.873 (3) Å vs. 1.929 (11) Å). Also, the N-O bond length of the NOH ligand in **2a** (i.e., 1.393 (4) Å) is considerably longer than that of the μ_3-NO ligand in **1'** (i.e., 1.247 (5) Å). These two structural features are indicative of the relatively greater electron-accepting abilities of the μ_3-NOH and μ_3-NH groups. Both the hydroxyimido and the imido ligands in **2a** and **3b**, respectively, are also linked by hydrogen bonds to the counteranions. This hydrogen bonding in **2a** (H···F = 1.91 (6) Å) produces a pronounced distortion of the BF_4^- anion to local C_{3v} symmetry, but in **3b** (H···F = 2.24 (4) Å) it is not sufficiently strong to result in a unique P-F bond length in the PF_6^- anion.

The spectroscopic properties of the trimetallic cationic complexes[9] can be readily understood in terms of their solid-state molecular structures, thus confirming that the basic structural units also persist in solutions. The IR absorptions attributable to the μ_2-NO groups in both **2** and **3** occur some 40 cm^{-1} higher in energy than those in **1**, thereby indicating the diminished electron density of the $Mn_3(\mu_2\text{-}NO)_3$ framework in the former species. The distortion of the BF_4^- anion in **2a** is also detectable by IR spectroscopy both in the solid state (Nujol) and in weakly coordinating solvents such as CH_2Cl_2. Analogous effects of hydrogen bonding are not observable in the IR spectra of the other cations. The ^1H NMR spectra of **3a** and **3b** in CD_2Cl_2 verify that the imido hydrogen atom remains bonded to the μ_3-N atom (e.g., for **3a**, δ 21.95 (1 H, t, $J_{^1H-^{14}N}$ = 61 Hz)). However, similar spectra of **2a** and **2b** in $(CD_3)_2CO$ do not display detectable signals due to μ_3-NOH in the range δ +30 to -35, a probable consequence of H bonding (vide supra).

The proton-induced transformations $\mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{3}$ represent two steps of a possible process for the reduction of NO to NH_3. (The two electrons required in the second step are most likely provided intermolecularly by the manganese atoms of the cluster.) In this sense, the process is analogous to that described by Shriver and co-workers for the conversion of bound CO to CH_4 by strong protonic acids.[13] Unlike the related carbonyl clusters, however, the cations **3** are unaffected by $HBF_4{\cdot}OMe_2$ or HPF_6(aq). Investigations concerning other aspects of the characteristic chemistry of complexes **1**-**3** are currently in progress.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this research (Grant A5885) and to the University of British Columbia for the award of a University Graduate Fellowship to C.R.N. We also thank the U.B.C. Computing Centre and the Xerox Corp. of Canada for financial assistance.

Registry No. 1, 66795-25-3; **2a**, 85649-56-5; **2b**, 85661-38-7; **3a**, 85649-58-7; **3b**, 85649-59-8.

Supplementary Material Available: Listings of all spectroscopic and X-ray diffraction data and tables of fractional coordinates and isotropic and anisotropic thermal parameters for **2a** and **3b** (8 pages). Ordering information is given on any current masthead page.

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[7] Yields: **2a**, 66%; **2b**, 43%. Anal. Calcd for $C_{18}H_{22}Mn_3N_4O_4PF_6$ (**2b**): C, 32.35; H, 3.32; N, 8.39. Found: C, 32.38; H, 3.36; N, 8.24.

[8] Yields: **3a**, 13%; **3b**, 14%. Anal. Calcd for $C_{18}H_{22}Mn_3N_4O_3BF_4$ (**3a**): C, 36.39; H, 3.73; N, 9.43. Found: C, 36.19; H, 3.74; N, 9.18.

[9] Supplementary material.

[10] $Ru_3(CO)_{10}(\mu_3\text{-}NOH)^5$ and $Fe_3(CO)_{10}(\mu_3\text{-}NH)^{11}$ have been characterized spectroscopically.

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Atomic Fits to Electron Densities in Polyatomic Molecules. Correlation of Atom Size and Charge

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The size and shape of a molecule may be defined by a surface of constant electron density. Size comparisons among different molecules may be made either by defining a single value of the electron density function, ψ^2, as the surface value for all systems or by allowing this value to vary from one molecule to another as to enclose a fixed (high) percentage of the total electron density.[2] Representation of molecular size and shape is also the function of space-filling (CPK) models.[3] While these provide highly portable representations, i.e., molecules are built up from atoms, they cannot be expected to yield as accurate a picture of three-dimensional size and shape as do total electron density distributions.

In order to combine the accuracy and detail available from total electron densities with the convenience and portability of space-filling models, we have examined fitting total electron density surfaces, calculated from a uniform level of nonempirical molecular orbital theory, to spheres centered on the individual atomic positions. In this initial report we describe briefly the numerical procedures involved in the fitting and, by way of example, illustrate expected correlations between atom sizes in molecules and atomic charges.

The left-hand side of Figure 1 shows the calculated total electron density surface of dimethyl sulfide, obtained by using the 3-21G$^{(*)}$ supplemented split-valence basis set,[4,5] based on a surface contour level of 0.002[6] (corresponding to enclosure of approximately 98% of the total electron density), and produced by using the PHOTOMO computer program.[7] Detailed numerical procedures involved in the construction and display of images such as these are described

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[2] This second approach suffers in that a surface incorporating a fixed percentage of the total density of a molecule containing a large number of electrons is not directly comparable to the surface of equal percentage enclosure for a molecule with a small number of electrons.

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[5] All molecular orbital calculations have been carried out by using the GAUSSIAN 83 program (R. F. Hout, Jr., M. M. Francl, E. S. Blurock, W. J. Pietro, D. J. DeFrees, S. K. Pollack, B. A. Levi, R. Steckler, and W. J. Hehre, to be submitted for publication in *QCPE*) with a Harris H100 digital computer.

[6] This contour level leads to average "sizes" of atoms in molecules that are comparable to van der Waals radii. For a discussion, see: M. M. Francl, R. F. Hout, Jr., and W. J. Hehre, submitted for publication in *J. Am. Chem. Soc.*

[7] R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre, to be submitted for publication in *QCPE*.