A Novel Intermediate in Allylic Amination Catalyzed by Iron Salts

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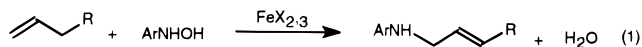
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Received January 11, 1996

In contrast to hydrocarbon oxidation which provides several important industrial and laboratory processes for the production of oxygenated compounds,[1] the direct synthesis of organonitrogen compounds from hydrocarbons remains an attractive but largely exclusive goal.[2−6] The paucity of direct nitrogenation reactions and mechanistic questions regarding the few known ones has, in turn, stimulated interest in the chemistry of organonitrogen metal complexes, including those having amido,[7] imido,[8] and C-nitroso[9] ligands. To date, however, examples of *N*-transfer from such complexes to hydrocarbons are rare.[10]

Following early reports by Sharpless and Mares of stoichiometric allylic amination of olefins and acetylenes by L_nMoO-(η^2-RNO)[9b,c] and X(=NTs)$_2$ (X = S,Se),[11] we and others recently have found that $L_nMo(VI)O_2$[12] and Fe(II,III) com-

plexes[13] and salts[14] *catalyze* the allylic amination of olefins by arylhydroxylamines (eq 1). These catalytic reactions display

$$\text{\raisebox{0pt}{$\diagdown\!\!\diagup\!\!\diagdown$}R} + \text{ArNHOH} \xrightarrow{\text{FeX}_{2\cdot3}} \text{ArNH}\diagup\!\!\diagdown\!\!\diagup\text{R} + \text{H}_2\text{O} \quad (1)$$

unusual and synthetically attractive ene-reaction-type regioselectivity (resulting in double-bond transposition). Mechanistic studies of the reactions catalyzed by $LMo(VI)O_2$[15] and (phthal)-Fe(II)[16] point to the intervention of PhNO, a proven enophile,[17] as the active aminating agent, accounting for the observed regioselectivity. However, our initial probe of the aminations catalyzed by iron salts[14] excluded the intermediacy of free ArNO, suggesting that a coordinated organonitrogen species could be the active aminating agent. To elucidate the mechanism of these latter reactions we report herein (1) the isolation and first structural elucidation of a metal complex of a C-nitroso dimer and (2) evidence that this novel compound is the key aminating agent in allylic aminations catalyzed by iron salts.

Scheme 1
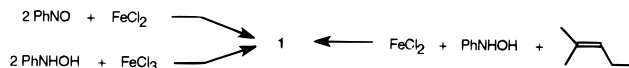
To identify the intermediate iron complex(es) in the FeCl$_{2,3}$-catalyzed aminations, preparative reactions of the iron chlorides with PhNHOH and PhNO were conducted. The reaction of FeCl$_2$ with PhNO (1:2) in CHCl$_3$ (20 °C) or dioxane (80 °C) produced azoxybenzene and a dark red brown product **1** (ca. 50% yield following CH$_2$Cl$_2$/hexane recrystallization) whose IR spectrum[18] suggested the presence of coordinated PhNO (Scheme 1). Compound **1** was also formed (along with PhNO and azo- and azoxybenzene) when FeCl$_3$ and PhNHOH (20 °C, CHCl$_3$) were combined, and most importantly, **1** also could be isolated from the FeCl$_2$-promoted amination reaction of 2-methyl-2-pentene (2-MP) by PhNHOH (80 °C, dioxane, 2 h). The structure of **1**·1.5(CH$_2$Cl$_2$) was established by X-ray diffraction[19] and is shown in Figure 1 along with key bond lengths and angles. Complex **1**, {Fe[Ph(O)NN(O)Ph]$_3$}[FeCl$_4$]$_2$, is thus found to consist of tetrahedral Fe(III)Cl$_4^-$ anions and a six-coordinate dication having iron(II) bound through the oxygens of three azobenzene dioxide ligands. Remarkably, while C-nitroso compounds are well known to exist as azo dioxide dimers in the solid state,[20] *1 provides the first crystallographically established metal complex having a C-nitroso dimer (azo dioxide) ligand.*[21] The distinctly distorted, nonoctahedral cation

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(2) Among the few useful hydrocarbon nitrogenation reactions are propylene ammoxidation (ref 3), butadiene hydrocyanation (ref 4), and olefin aziridination (ref 5) and hydroamination (ref 6).

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(18) For **1**: IR (KBr, cm^{-1}) 3099 (w), 3077 (w), 1681 (m), 1651 (m), 1600 (m), 1481 (s), 1462 (s), 1374 (s), 1161 (s), 1076 (s), 1020 (m) 962 (s), 922 (m), 762 (s), 686 (s); UV−vis (nm) 215, 280, 300; MS (FAB) 214 (Ph$_2$N$_2$O$_2^+$), 269 [Fe(PhNO)$_2^+$].

(19) Crystals of **1** (CH$_2$Cl$_2$/hexane) are triclinic P1, a = 15.572(9) Å, b = 16.308(5) Å, c = 19.841(7) Å, α = 88.87(3)°, β = 86.80(4)°, γ = 86.60-(4)°, V = 5021(4) Å^3. Data were collected at 198 K with Mo Kα (λ = 0.71073 Å) radiation and corrected for Lorentz, polarization, and empirical absorption effects. The structure was solved by the heavy atom method and refined by full-matrix least squares on F^2 using all reflections (SHELXTL 5.0); final conventional $R1$ = 0.088 (WR^2 = 0.0206, GOF = 1.0) for 7928 "observed" reflections with $I \geq 2\sigma(I)$. The asymmetric unit contains two dications, four anions, and three CH$_2$Cl$_2$ molecules.

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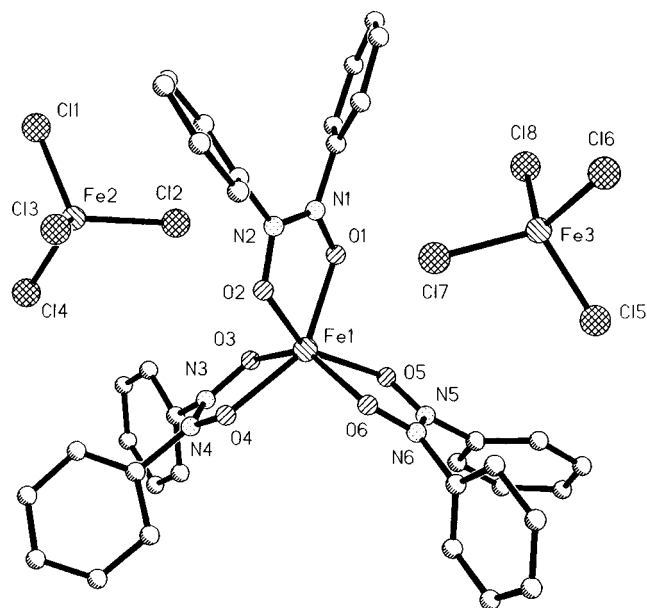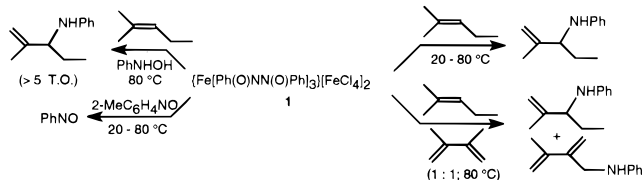
Figure 1. X-ray structure of **1**·1.5(CH$_2$Cl$_2$). Selected bond lengths (Å) and angles (deg): Fe(1)−O(1) 2.107(7), Fe(1)−O(2) 2.083(7), Fe-(1)−O(3) 2.105(7), Fe(1)−O(4) 2.158(8), Fe(1)−O(5) 2.150(7), Fe-(1)−O(6) 2.097(7), O(1)−N(1) 1.270(10), N(1)−N(2) 1.300(11), N(2)−O(2) 1.299(10); O(1)−Fe(1)−O(4) 147.7(3), O(1)−Fe(1)−O(5) 86.1(3), Fe(1)−O(1)−N(1) 115.9(6), O(1)−N(1)−N(2) 118.1(8), N(1)−N(2)−O(2) 116.4(7), N(2)−O(2)−Fe(1) 116.4(6); Fe(2)−Cl(1) 2.173(4), Fe-(2)−Cl(2) 2.213(4), Fe(2)−Cl(3) 2.189(4), Fe(2)−Cl(4) 2.177(4).

Scheme 2

of **1** features planar chelate rings and rather varied Fe−O (2.12 Å av) lengths, but relatively uniform O−N (1.28 Å av) and N−N (1.29 Å av) bond lengths. Comparison of the N−N and N−O lengths of **1** to typical sp^2−sp^2 single- and double-bond values (N−O 1.42 Å, N=O 1.20 Å, N−N 1.36 Å, N=N 1.235 Å)[22] and to those of azobenzene dioxide[23] (N−O 1.268(4) Å, N−N 1.321(5) Å) indicates electronically delocalized chelate rings in **1** but rather modest differences in the structure of the free and coordinated ligand.

In addition to its detection in catalytic reaction mixtures, several other *experiments strongly implicate nitrosobenzene dimer complex 1 as the active aminating agent in allylic aminations catalyzed by iron salts*. Firstly, treatment of **1** with 2-MP (1:25) in dioxane results in smooth conversion, even at room temperature (8 h) (rapidly at 80 °C), to the corresponding allyl amine (83% yield) with the same distinctive regioselectivity found in the FeCl$_{2,3}$-catalyzed reactions (Scheme 2). Moreover, as found in the FeCl$_{2,3}$-catalyzed reactions,[14] **1** aminates olefins without the intervention of free PhNO since heating **1** with an equimolar mixture of 2-MP and 2,3-dimethylbutadiene (DMB) produced allylic amination products exclusively, i.e. no Diels−Alder adduct from DMB and PhNO was detected.[24] Finally, **1**

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Scheme 3
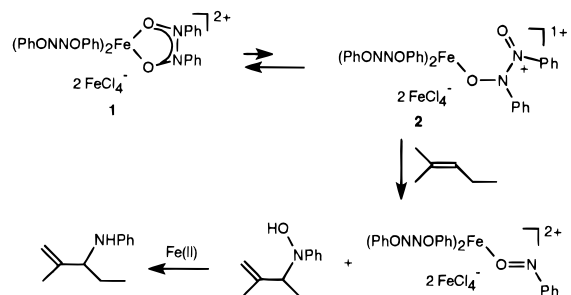
was found to catalyze the allylic amination of 2-MP by PhNHOH (80 °C, 8 h, 81% yield) at an initial rate comparable to (or somewhat faster than) that of the FeCl$_2$-catalyzed reaction.

The following initial observations and features provide some clues to possible mechanistic pathways: (1) the ene-reaction-type regioselectivity; (2) the noninvolvement of free PhNO; (3) the coordinative saturation of the complex ion {Fe(II)[Ph(O)-NN(O)Ph]$_3$}$^{2+}$; and (4) the facile, induced exchange of coordinated and free nitrosoarene with **1**. The latter was demonstrated by treatment of **1** with 3.5 equiv of 2-MeC$_6$H$_4$NO (20 °C, dioxane, 2 h) after which a 2:3 PhNO/2-MeC$_6$H$_4$NO mixture was detected by GC. Taking these features into consideration, we suggest (Scheme 3) that amination by **1** may proceed via initial dechelation of an azo dioxide ligand, generating an electrophilic nitrosating species (e.g. **2**) which transfers the activated ArNO unit to an olefin (free or coordinated) by an ene-reaction-type process; reduction of the resulting allyl hydroxylamine by Fe(II) would generate the allyl amine.[25] Interception of five-coordinate **2** by nitrosotoluene (in the exchange experiments) could cause release of PhNO from the dangling chelate arm and subsequent rechelation to form a mixed nitroso dimer complex.

In summary we have established with **1** the first structurally verified metal complex of a C-nitroso dimer and its unprecedented reactivity and selectivity for the allylic N-functionalization of olefins. Its involvement as the aminating agent in FeX$_{2,3}$-catalyzed allylic amination also has been strongly implicated. Studies are underway to establish the mechanism by which **1** is formed and how it transfers the imido (or PhNO) unit to the substrate and to develop enantioselective catalysts based on **1**.

Supporting Information Available: Experimental details for the preparation of **1** and X-ray crystal structure determination and refinement; X-ray structural drawings, tables of crystal data, atomic coordinates, anisotropic thermal parameters, hydrogen coordinates, and bond distances and angles (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

(24) Separate control experiments have established that (1) 2,3-dimethylbutadiene efficiently traps PhNO as a hetero-Diels−Alder adduct even in the presence of 2-MP (60 °C, dioxane) and (2) this adduct is stable at 80 °C in the presence of FeCl$_2$ and 2-MP.

(25) The feasibility of this step is indicated by the facile reduction of PhNHOH to PhNH$_2$ by FeCl$_2$ (20 °C, dioxane). Other metal-based reductants also convert RNHOH to RNH$_2$ by an undetermined mechanism; see for example ref 15 and refs in the following: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 1218.