On the Mechanism of Allylic Amination Catalyzed by Iron Salts

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Abstract: Iron salts catalyze the allylic amination of alkenes by arylhydroxylamines in moderate to good yields and with high regioselectivity resulting from double-bond transposition. The iron-catalyzed reaction of phenylhydroxylamine with representative alkenes in the presence of 2,3-dimethylbutadiene, an effective PhNO trap, produces allyl amines exclusively, excluding the intermediacy of free PhNO in the amination reaction. The reaction of $FeCl_{2,3}$ with PhNO or PhNHOH produces a novel azo dioxide iron complex, $\{Fe[Ph(O)NN(O)Ph]_3\}[FeCl_4]_2$ (**1a**), whose structure has been established by X-ray diffraction. The structure of **1a** features essentially tetrahedral $Fe(III)Cl_4^-$ anions and a novel six-coordinate dication having iron(II) bound through the oxygens of three azobenzene *N*,*N*-dioxide ligands. Evidence that **1a** is the active aminating agent in the catalytic reactions includes (1) its isolation from the catalytic reaction; (2) its facile reaction with alkenes to produce allyl amine in high yield and regioselectivity; (3) its amination of alkenes without the intervention of free PhNO; and (4) its efficient catalysis of amination by PhNHOH. The reaction of 2-methyl-2-pentene (2-MP) with **1a** (dioxane, 70 °C) was examined kinetically; the appearance of allylamine was found to be first order in **1a** and first order in alkene. Rate constants determined for the reactions of **1a** with a set of *para*-substituted α-methylstyrenes lead to a Hammett ρ value of −3.0. A small kinetic D-isotope effect, 1.4 ± 0.2, is found for the intermolecular amination of α-(trideuteriomethyl)styrene by **1a**. Low-temperature reactions of **1a** with 2-MP, β-methylstyrene, and styrene produce isolable alkene adducts **3a**−**c**. Thermolysis of **3a** in dioxane gives the corresponding allyl amine while treatment of **3a**−**c** with nitrosoarenes regenerates the respective alkenes. IR, NMR, and UV−vis spectroscopic data also support the formulation of **3a**−**c** as alkene complexes. Evidence that azo dioxide complex **1** transfers a PhNO (rather than PhN) unit to alkene, producing an intermediate allylhydroxylamine which is subsequently reduced to the ultimate allyl amine, is provided from model reaction studies and GC/MS monitoring. Various mechanistic pathways are presented and analyzed. The mechanism most consistent with all of the accumulated evidence involves alkene coordination to **1** via dechelation of an azo dioxide ligand, intramolecular RNO transfer to coordinated alkene to produce the allylhydroxylamine, reductive deoxygenation of the allylhydroxylamine to allylamine, and regeneration of azo dioxide complex **1** by oxidation of another PhNHOH molecule by iron(III).

Background

The development of selective methods for direct hydrocarbon functionalization represents one of the great challenges in synthetic chemistry. 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 elusive goal. Among the few commercially important examples are the Mo-Bi-catalyzed ammoxidation of propylene to acrylonitrile[2] and the Ni-catalyzed hydrocyanation of butadiene to adiponitrile.[3] Laboratory methods for the direct N-functionalization of alkenes are few but receiving increasing attention. These include stoichiometric allylic amination by S-[4] and Se-imido[5] derivatives and indirect routes, mostly based on ene reactions of organonitrogen compounds, e.g. with azo-[6], *N*-carboalkoxynitroso-[7], and *N*-sulfinylcarbamate derivatives.[8] The recent development of metal-catalyzed amino hydroxylation,[9] aziridination,[10] and hydroamination[11] reactions of alkenes promises to provide more useful and general access to various classes of organonitrogen compounds.

The paucity of direct nitrogenation reactions and mechanistic questions regarding the few known ones has, in turn, stimulated

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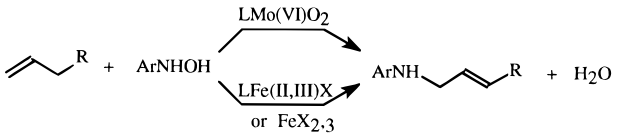
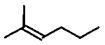
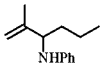
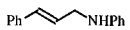
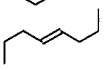
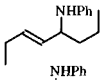
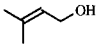
Scheme 1



interest in the chemistry of organonitrogen metal complexes, including those having amido,[12] imido,[13] and C-nitroso[14] ligands. To date, however, examples of N-transfer from such species to hydrocarbons are rare.[15] In early work Sharpless[16] and Mares[17] reported examples of stoichiometric α-amination of alkenes and cyclohexanone by C-nitroso complexes (molybdooxaziridines), $L_nMoO(\eta^2\text{-RNO})$. More recently, on the basis of these early communications, we developed molybdenum(VI)-*catalyzed* allylic aminations using arylhydroxylamines as aminating agents (Scheme 1).[18] Both the stoichiometric and catalytic versions display distinctive ene reaction-like regioselectivity, occurring with transposition of the carbon−carbon double bond. Thereafter, apparently similar iron-catalyzed allylic aminations were reported by Jorgensen's group utilizing iron phthalocyanine complexes[19] and by our group employing simple Fe(II,III) salts.[20]

Mechanistic studies of the reactions catalyzed by $LMo^{VI}O_2$[21] and (phthal)Fe^{II} [22] point to the intermediacy of PhNO, a proven enophile,[23] as the active aminating agent, accounting for the observed regioselectivity and alkene relative reactivity. The role of the catalyst in these reactions thus is to serve as a redox agent, oxidizing the starting hydroxylamine to the reactive nitroso arene and then reducing the derived allylhydroxylamine. In contrast, our initial probe of the aminations catalyzed by iron salts[20] excluded the intermediacy of free ArNO, suggesting that a coordinated organonitrogen species could be the active aminating agent. Recent follow-up studies led to the identification of a novel iron azo dioxide complex {Fe[Ph(O)NN(O)-Ph]$_3$}[$FeCl_4$]$_2$ (**1a**)[24] which appears to be the active aminating agent in the reactions promoted by iron salts. This compound could be isolated from catalytic amination reaction mixtures, is an active amination catalyst with PhNHOH as aminating agent, and reacts readily with alkenes to produce the corresponding allylamines even in the presence of a diene trapping agent for free PhNO. We now report the full details of these preliminary synthetic, structural, and mechanistic studies of allylic amination catalyzed by iron salts. Included as well are new kinetic and reactivity investigations of **1a**, including the isolation of alkene adducts **3** derived from **1** which appear to be on the catalytic amination pathway as well.

Table 1. Allylic Amination Catalyzed by Iron Salts

Run	Substrate	Catalyst	Product	Yield (%)[a]	N-chemoselectivity (%)[b]
1		A + B (9:1)[c]		61(48)	90
2		" + "		72[d]	>90
3		C + D (9:1)[c]		23	67
4		**1a**[c]		88	95
5		A + B (9:1)		50	93
6		A + B (9:1)		43(29)	82
7		A + B (9:1)		34(22)	92
8		A		26	76
9		B		29	90
10		$FeCl_2$		25	71
11		$FeCl_3$		28	62
12		C + D (9:1)		41	80
13		A + B (9:1)		22	40
14		A + B (9:1)		13	42
15		A + B (9:1)		12	48
16		A + B (9:1)		11	40

[a] GC yield, naphthalene standard (isolated yield after chromatography. [b] Allylamine/(allylamine + aniline + azobenzene + azoxybenzene), by GC. [c] A = $FeCl_2 \cdot 4H_2O$, B = $FeCl_3 \cdot 6H_2O$; C = $Fe(ClO_4)_2 \cdot 6H_2O$; D = $Fe(ClO_4)_3 \cdot 6H_2O$; **1a** = {Fe[Ph(O)NN(O)Ph]$_3$}[$FeCl_4$]$_2$. [d] 2.5:1 PhNHOH/alkene ratio.

Results and Discussion

Synthetic Survey. Slow addition of phenylhydroxylamine (1.5 mM in dioxane) to a heated (70−100 °C) dioxane solution containing an excess of alkene and 10 mol % $FeCl_{2,3} \cdot nH_2O$ or $Fe(ClO_4)_{2,3} \cdot nH_2O$ produces after 8 h the corresponding *N*-phenyl-*N*-allylamines in fair to good yield following chromatography (Scheme 1, Table 1). Important features of these reactions include (1) trisubstituted and 1,1-disubstituted alkenes give the best yields; (2) unsymmetrical alkenes react with virtually complete (>95%) regioselectivity to produce the corresponding allyl amine derived from double-bond transposition; and (3) generally no other alkene-derived products are observed. Features 1 and 2 are typical of ene-type reactions.[25] The major competing process is the formation of N-containing byproducts derived from phenylhydroxylamine decomposition, i.e. aniline and azo- and azoxybenzene; the selectivity for allyl

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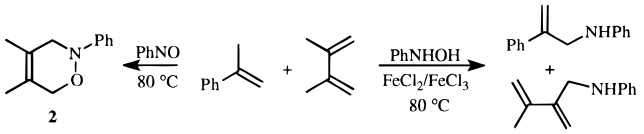
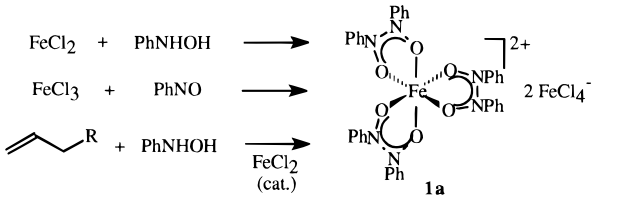
Scheme 2



Scheme 3



amine relative to these byproducts (N-chemoselectivity, Table 1) decreases as the alkene's amination reactivity decreases. Although efforts to optimize the efficiency and to expand the scope of these reactions are continuing and will be reported later, we have found that a significant improvement in yield may be realized by using excess phenylhydroxylamine (run 2, slow addition) with alkene as the limiting reagent or with azo dioxide complex $\{Fe[Ph(O)NN(O)Ph]_3\}[FeCl_4]_2$ (**1a**, *vide infra*) as the catalyst (e.g. run 4) at 50 °C. Although few polyfunctional alkenes have been examined as substrates thus far, ether and hydroxyl functions (e.g. run 16) are tolerated.

Catalyst oxidation and hydration state and counterion have a modest and variable effect on yield and selectivity, e.g. (a) both Fe(II) and Fe(III) salts catalyze the reaction with similar efficiency (cf. runs 8/9, 10/11); (b) anhydrous and hydrated iron chlorides are comparable as catalysts (cf. runs 8/10, 9/11); but (c) in some cases a combination of Fe^{II}/Fe^{III} (9:1) gives slightly improved results (e.g. run 7 vs 8−11); and (d) the relative benefits of $FeCl_{2,3}\cdot nH_2O$ vs $Fe(ClO_4)_{2,3}\cdot nH_2O$ as catalysts are substrate dependent (cf. runs 1/3, 7/12). The similar efficacy of both Fe(II) and Fe(III) salts suggests the intervention of a common catalyst for both reactions and/or a redox shuttling process involving both oxidation states. The ready ability of hydroxylamines to undergo oxidation or reduction is consistent with either of these possibilities.[26]

The present results illustrate that the iron-catalyzed allylic amination of alkenes by phenylhydroxylamine proceeds highly regioselectivity. This selectivity complements and improves upon that generally observed in stoichiometric aminations by $(TolN)_2X$ (X = S, Se),[4,5] which typically favor preservation of the double-bond position but with variable selectivity. Further, the catalysts used in the present system are commercially available and inexpensive.

Trapping Studies of the Catalytic Reaction. The Noninvolvement of PhNO. As we noted earlier, recent studies from Jorgensen's group indicate aminations catalyzed by some iron *complexes* including Fe(phthalocyanine) and Fe(porphyrin)X proceed via free RNO as the active aminating agent.[22] To probe whether this was also the case for the reactions catalyzed by iron *salts* the hetero-Diels−Alder reaction of PhNO with 2,3-dimethylbutadiene (DMB) was employed as a trapping reaction for PhNO.[27] First, the effective Diels−Alder trapping of PhNO by DMB at 80 °C (dioxane) in the presence of α-methylstyrene was established (Scheme 2). When the iron-catalyzed reaction (10 mol % $FeCl_{2,3}$) of phenylhydroxylamine with α-methylstyrene was carried out in the presence of DMB (1:1, 80 °C, dioxane), allylamines derived from the alkene and diene (24% and 20% respectively) were formed exclusively; i.e. the PhNO Diels−Alder adduct **2** was not detected. A control experiment established that **2** is stable under the amination conditions. These results clearly demonstrate that *free* nitrosobenzene is not produced in the iron salt-catalyzed reactions. This finding is also consistent with the involvement of an Fe-coordinated species in the transfer of an RN or RNO group to the alkene.

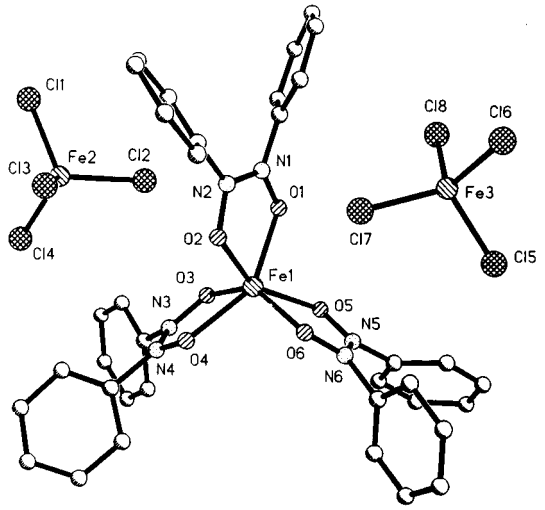


Figure 1. X-ray structure of **1a**·1.5(CH_2Cl_2).

Isolation of a Novel, Catalytically Relevant Complex. Seeking to identify possible 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 **1a** whose IR (1600, 1481, 1462, 1374 cm^{-1}) and FAB mass spectra (214 ($Ph_2N_2O_2^+$), 269 [$Fe(PhNO)_2^+$]) suggested the presence of coordinated PhNO (Scheme 3). An analogous compound **Ib** was produced in the reaction of *o*-nitrosotoluene with $FeCl_2$. Compound **1a** was also formed (along with PhNO and azo- and azoxybenzene) when $FeCl_3$ and PhNHOH (20 °C, $CHCl_3$) were combined and, importantly, **1a** 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 **1a**·1.5(CH_2Cl_2) was established by X-ray diffraction and is shown in Figure 1; selected bond lengths and angles are given in Table 2.[28] Complex **1a** thus has the composition $\{Fe[Ph(O)NN(O)Ph]_3\}[FeCl_4]_2$, consisting of essentially tetrahedral $Fe^{III}Cl_4^-$ anions and a six-coordinate dication having iron(II) bound through the oxygens of three azobenzene *N*,*N*-dioxide ligands. The complex ion is distinctly distorted, being closer to trigonal prismatic than to octahedral (twist angle, θ(av) = 18°).[29] The nearly planar chelate rings exhibit rather varied Fe−O (2.12 Å av) lengths but relatively uniform O−N (av 1.28 Å) and N−N (av 1.29 Å) distances. The N−N and N−O lengths lie between typical sp^2−sp^2 single- and double-bond values, i.e. N−O 1.42 Å, N═O 1.20 Å, N−N 1.36 Å, N═N 1.235 Å,[30] indicating that the chelate rings are

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(28) Crystal data and structure refinement for **1a** are provided in Table 3; tables of atomic coordinates, anisotropic thermal parameters, and a full listing of bond lengths and angles are provided as Supporting Information to ref 24.

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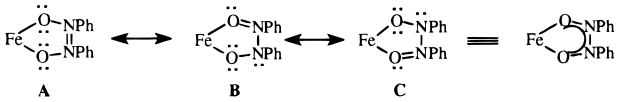
Table 2. Selected Bond Lengths and Angles for $\{Fe[Ph(O)NN(O)Ph]_3\}[FeCl_4]_2$ (**1a**)

Bond Lengths (Å)			
Fe(1)−O(1)	2.107(7)	N(1)−N(2)	1.300(11)
Fe(1)−O(2)	2.083(7)	N(2)−O(2)	1.299(10)
Fe(1)−O(3)	2.105(7)	Fe(2)−C(1)	2.173(4)
Fe(1)−O(4)	2.158(8)	Fe(2)−Cl(2)	2.213(4)
Fe(1)−O(5)	2.150(7)	Fe(2)−Cl(3)	2.189(4)
Fe(1)−O(6)	2.097(7)	Fe(2)−Cl(4)	2.177(4)
O(1)−N(1)	1.270(10)		

Bond Angles (deg)			
O(1)−Fe(1)−O(4)	147.7(3)	N(2)−O(2)−Fe(1)	116.4(6)
O(1)−Fe(1)−O(2)	72.6(3)	O(2)−Fe(1)−O(4)	83.5(3)
Fe(1)−O(1)−N(1)	115.9(6)	O(1)−Fe(1)−O(4)	147.7(3)
O(1)−N(1)−N(2)	118.1(8)	Cl(1)−Fe(1)−Cl(2)	109.9(2)
N(1)−N(2)−O(2)	116.4(7)	Cl(1)−Fe(1)−Cl(3)	108.4(2)

electronically delocalized. Resonance forms **A**−**C** may thus contribute to the hybrid electronic structure. The constraints

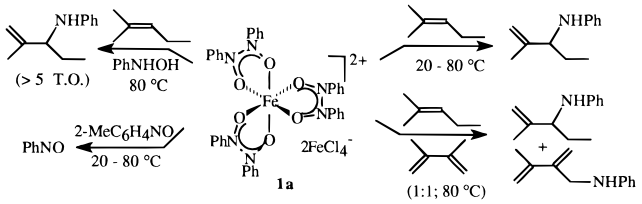


imposed by the planar chelate rings may account for the strong distortion toward trigonal prismatic since angular overlap considerations predict for Fe(II) that the octahedral geometry should be strongly favored for the low spin case and weakly favored with high spin Fe(II).[29] Interestingly, comparison of the N−N and N−O bond lengths of **1a** with those of azobenzene dioxide itself[31] (N−O 1.268 (4) Å and N−N 1.321(5) Å) reveals surprisingly little difference between the free and complexed species.

Remarkably, while C-nitroso compounds are well known to exist as azo dioxide dimers in the solid state,[32] **1a** provides the first crystallographically established example of an azo dioxide serving as a ligand. The formation of Pb, Sn, and Ti azo dioxide complexes has been proposed based on IR or ^{13}C NMR data.[33] Absorptions in the 1000−1100 cm^{-1} region for these compounds have been assigned to N−O stretching vibrations, a decrease of ca. 300 cm^{-1} relative to the free azodioxide. Although complexes **1a,b** also display moderate intensity absorptions in this range (1076 and 1020 for **1a** and 1040 for **1b**), the multiple N−O bond character suggested by the N−O bond lengths of **1a** would more likely give rise to higher energy absorptions. In fact both the *tris*-azo dioxide complexes **1a,b** and the derived alkene adducts **3** (*vide infra*) display a moderate to intense band in the 1320−1330 cm^{-1} region, which we tentatively assign to N−O stretching.

An important, but as yet unanswered, question is the spin state of iron(II) in the complex cation of **1a**. This has consequences both in terms of the nature of the bonding between iron and the azo dioxide ligands and ligand lability/reactivity. The issue is clouded by the presence of the necessarily paramagnetic d^5 $Fe^{III}Cl_4^-$ ions and the strong absorptions bands in the visible region (presumably charge transfer in nature) which obscure potentially informative d−d transitions. It is noteworthy that the ^1H NMR spectra of **1a** and the derived alkene adducts (*vide infra*), while broadened, are not contact-shifted, more consistent with a low spin, diamagnetic Fe(II) center. Unfortunately, initial attempts to metathetically substitute the $FeCl_4^-$ ions of **1a** with diamagnetic anions (e.g. BF_4^-, BPh_4^-) have failed to produce pure products. Efforts toward this end are continuing as are magnetic susceptibility, Mossbauer, EPR, and electrochemical studies in order to identify the electronic state of iron(II) in **1**.

Scheme 4



The formation of **1a** from either PhNHOH/$FeCl_{2,3}$ or PhNO/$FeCl_2$ probably accounts for the similar efficacy of Fe(II) and Fe(III) salts as catalysts in the amination reactions. The mechanism and stoichiometry by which **1a** is produced in the preparative reactions, however, is unclear at present. Obviously, complex redox processes are involved as indicated by the mixed iron oxidation states of **1a** and the various N-byproducts produced.

Reactivity Studies of 1a: Role in the Catalytic Amination of Alkenes. Having identified novel azodioxide derivative **1a**, we sought to determine its relevance to the iron-catalyzed aminations, i.e. is an azo dioxide complex on the product-forming catalytic pathway or is it a dead end? A series of reactions were examined to address this question. First, treatment of **1a** with 2-methyl-2-pentene (2-MP, 1:25) in dioxane resulted in smooth conversion, slowly at room temperature, 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 4). Moreover, as found in the $FeCl_{2,3}$-catalyzed reactions, **1a** aminates alkenes without the intervention of free PhNO since heating **1a** with an equimolar mixture of 2-MP and 2,3-dimethylbutadiene (DMB) produced allylic amination products exclusively (70:30), i.e. no Diels−Alder adduct from DMB and PhNO was detected. Finally, **1a** also was found to catalyze the allylic amination of 2-MP by PhNHOH (80 °C, 8 h, 81%) at an initial rate comparable to (or somewhat faster than) that of the $FeCl_2$-catalyzed reaction. The improved yield and N-selectivity in the reaction catalyzed by **1a** *vis a vis* the corresponding $FeCl_{2,3}$-catalyzed reaction (cf. Table 1) probably reflects in part elimination of the inefficient (and byproduct-forming) catalyst genesis phase. These observations, combined with the isolation of **1a** in the $FeCl_{2,3}$-catalyzed reactions, provide strong evidence that this complex is on the catalytic pathway, and is possibly the actual aminating agent.

A fundamental issue relevant to both the mechanism of group transfer reactions by **1** and the spin state of the complex cation is the lability of the azo dioxide ligands. This issue was addressed qualitatively by determining the dissociability of nitrosobenzene from **1a** in the presence of external RNO. Thus, when **1a** was treated with 3.5 equiv of *o*-nitrosotoluene (80 °C, dioxane, 1−8 h), GC analysis indicated that a 2:3 PhNO/2-MeC_6H_4NO mixture was present (Scheme 4). The presumed resulting mixed azo dioxide complexes $\{Fe[Ar(O)NN(O)Tol]_3\}[FeCl_4]_2$ were not characterized. Why would PhNO dissociate under these conditions but not in the corresponding reaction of **1a** with alkene (*op cit*)? A possible explanation is put forward after we present the results of kinetic and synthetic experiments which probe more deeply the interaction of azo dioxide complex **1a** with alkenes.

Kinetics of the Reaction of Azo Dioxide Complex 1a with Alkenes. To further probe the mechanism by which complex

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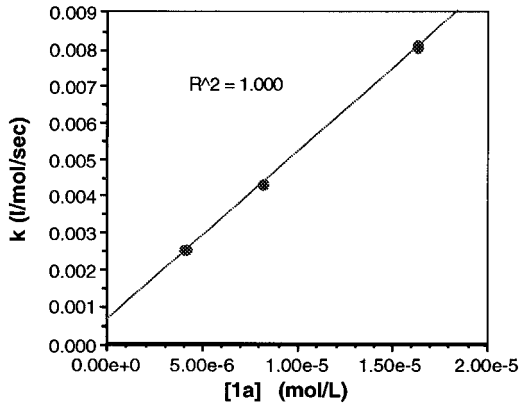


Figure 2. Effect of [**1a**] on k_{obs} for reaction of **1a** with 2-methyl-2-pentene at 70 °C.

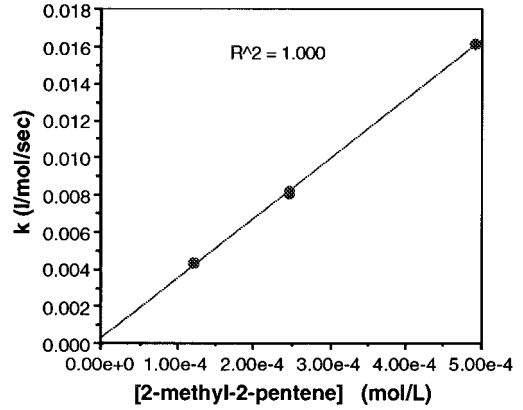


Figure 3. Effect of [2-methyl-2-pentene] on k_{obs} for reaction of **1a** with 2-methyl-2-pentene at 70 °C.

1a aminates alkenes, the reaction of 2-MP (excess) with **1a** (dioxane, 70 °C) was examined kinetically by monitoring (GC) the initial rate of allyl amine formation at low conversion (0−10%). By varying the concentration of **1a** between 0.005 and 0.02 mM at constant alkene concentration, the appearance of allyl amine is cleanly first order in the iron complex (Figure 2). At constant concentration of **1a** (0.02 mM) the rate of reaction also is first order in alkene over the concentration range of 0.1−0.5 mM (Figure 3). β-Methylstyrene, an unreactive substrate in the $FeCl_2$-catalyzed reaction, was found to inhibit the amination of 2-MP by **1a**. Thus, the rate of amination was halved in the presence of equimolar β-methylstyrene. Taken together, these results indicate the involvement of alkene before or in the rate determining step and suggest that alkene coordination may be involved.

Temperature-dependent rate studies of the reaction of **1a** with 2-MP between 50 and 90 °C afforded rate constants which were subjected to Eyring analysis (Figure 4), yielding the activation parameters $\Delta H^{\ddagger} = 19 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -0.2 \pm 2$ eu. These results, especially the negligible entropy of activation, point to a rate-determining step which is neither highly associative nor dissociative.

To assess the electronic character of the transition state, rate constants were determined for the reactions of **1a** with a small set of *para*-substituted α-methylstyrenes at 70 °C (Figure 5). Electron-withdrawing groups (X = F, Cl) were found to depress the rate, while the more electron rich X = Me reacted faster relative to the parent α-methylstyrene, resulting in a substantially negative Hammett ρ value of −3.0. This is indicative of a transition state with considerable positive charge development at the benzylic carbon.[34] This value may be compared to somewhat larger ones found in related polar reactions, e.g. those

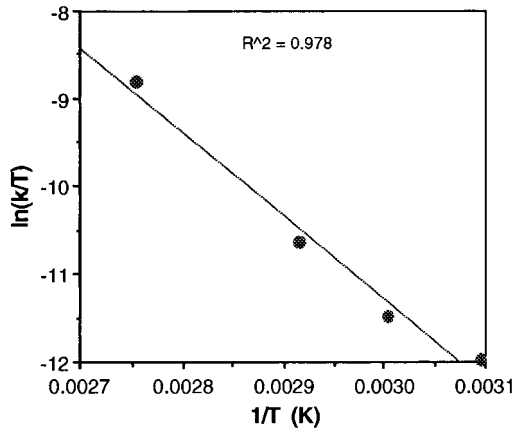


Figure 4. Temperature dependence of k_{obs} for reaction of **1a** with 2-methyl-2-pentene.

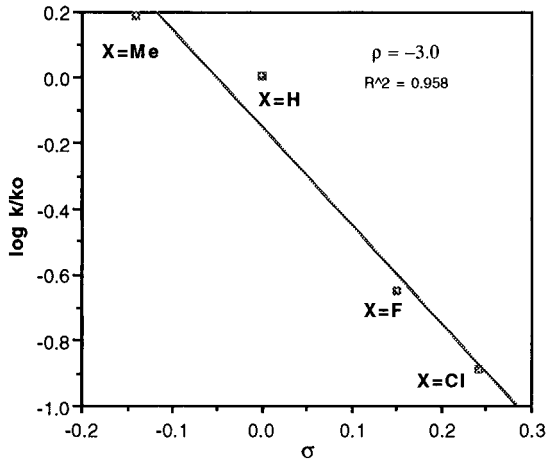
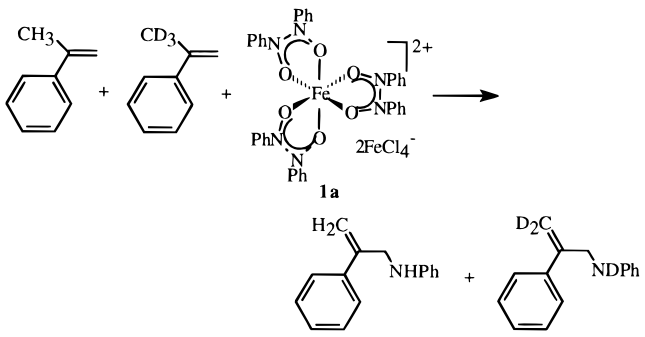


Figure 5. Hammett plot for reactions of **1a** with *para*-substituted α-methylstyrenes.

Scheme 5



proceeding through benzylic carbocations, typically ca. −4 to −5,[35] and in a Lewis acid-promoted ene reaction of carbonyl compounds, −3.9.[36]

The characteristic double-bond transposition observed in the iron-promoted aminations requires cleavage of an allylic C−H bond. In an effort to assess whether this occurs in the rate-determining step the kinetic D-isotope effect was determined for the competitive amination of a 1:1 mixture of α-methylstyrene and α-(trideuteriomethyl)styrene (90 %) by **1a** at 60 °C (Scheme 5). NMR and MS analysis of the isolated allyl amine revealed a ratio of H_3-amine/D_3-amine (k_H/k_D) of 1.7 ±

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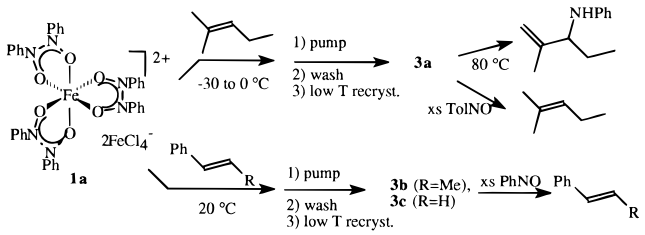
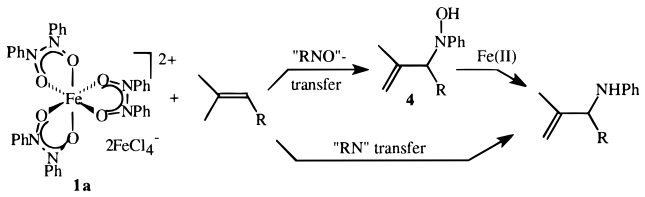
Scheme 6



0.1 which, when corrected for the isotopic purity of α-(trideuteriomethyl)styrene, affords a k_H/k_D of 1.4 ± 0.1. The magnitude of this effect may be interpreted either in terms of a small, primary isotope effect or a large secondary one. If primary, the result would be consistent with an early (or late) transition state with modest or unsymmetrical C−H bond breaking. Alternatively, given the evidence for positive charge development in the transition state (*op cit*), a composite secondary isotope effect resulting from hyperconjugative interactions of the β-H(D)'s or α-rehybridization ($sp^3 \rightarrow sp^2$) could also account for such a moderate k_H/k_D. By comparison, intermolecular isotope effects in ene reactions of carbonyl compounds have been reported over the range of 1.1−2.8, with smaller values more typical for the Lewis acid-promoted reactions.[37] A more reliable distinction between a concerted, asynchronous process with modest C−H bond breaking and a stepwise mechanism involving C−H bond breaking in a rapid second step could possibly be made on the basis of planned comparisons of inter- and intramolecular isotope effects.[38]

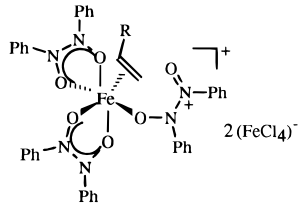
Formation of Alkene Adducts from 1a. In considering the key question of how an RN group is transferred from **1** to alkene we wondered whether the latter is coordinated during group transfer. To address this question the low-temperature interaction of **1a** with three alkenes was examined: with 2-methyl-2-pentene (2-MP), efficiently aminated by **1a** or $FeCl_{2,3}$/PhNHOH, and with β-methylstyrene and styrene, poor (or non) amination substrates (Scheme 6). Complex **1a** was stirred with an excess of alkene in dioxane at ≤0 °C for 2-MP or at 20 °C for α-methylstyrene or styrene; removal of solvent and free alkene *in vacuo*, trituration with hexane, and recrystallization afforded dark red compounds **3a**−**c**. Evidence that these species are alkene adducts is as follows. Thermolysis of **3a** (80 °C) in dioxane produced the corresponding allylamine in good yield (65% by GC). Treatment of **3a** with *o*-nitrosotoluene at 15 °C produced 2-MP (53% assuming a 1:1 complex) and the derived allylamine (34%). Similarly, reaction of the styrene and α-methylstyrene derived compounds, **3b,c** with nitrosotoluene at 20 °C regenerated the respective alkenes (44 and 45%). The ^{1}H NMR spectra of **3a**−**c**, paramagnetic by virtue of the $Fe^{III}Cl_4^-$ and, possibly high spin $Fe^{II}L_6^{+2}$ ions, exhibited not only broad aromatic resonances, but also showed broadened resonances derived from the alkene, somewhat displaced (0.2−0.5 ppm) from those of the free ligand. A shoulder in the UV−vis spectrum of **3a** at 380 nm, not present in the azo dioxide complex precursor, was also noted. The IR spectra of **3a**−**c** each exhibited a medium-intensity absorption band at ca. 1500 cm^{-1}, not present in either the alkene or the precursor azo dioxide complex **1a**, which tentatively is assigned to the coordinated C═C. The resulting coordination shift, ca. 100−150 cm^{-1}, suggests a strong Fe−alkene bonding interaction,[39] comparable to that observed for $CpFe(CO)_2(alkene)^+$ com-

Scheme 7



plexes.[40] Unfortunately, attempts to obtain crystals of **3a**−**c** suitable for X-ray diffraction thus far have failed.

Taken together, the spectroscopic features of **3**, the percent recovery of displaced alkene, and the failure of GC analyses of the reaction mixtures to detect free PhNO suggest the formation of 1:1 adducts between **1a** and alkenes, without dissociation of PhNO. On the basis of these considerations general structure **3** is tentatively assigned to these complexes. We note that



3

outside of the well-known $CpFe(CO)_2(alkene)^+$ derivatives,[40] examples of isolable Fe^{II}−alkene complexes are rare.[41] Structural questions notwithstanding, the isolation and reactivity of these alkene complexes supports their intermediacy in the catalytic amination reactions. Additionally, the unreactivity toward RN group transfer of β-methylstyrene complex **3b** may explain the inhibitory effect of β-methyl styrene on the amination of 2-MP by **1a**.

RN or RNO Group Transfer? Another issue of fundamental mechanistic importance is whether allylamine is formed via transfer of an arylimido (RN) group directly from **1a** to alkene or whether an arylnitroso (RNO) unit is initially transferred, giving an intermediate allylhydroxylamine which is subsequently reduced to the amine (Scheme 4). The latter possibility should be considered since (1) it was found to be operative in allylic aminations effected by Mo−nitrosoarene complexes, $L_nMo(\eta^2$-RNO);[21] (2) the azo dioxide ligand of **1a** appears better set up to transfer an RNO fragment (leaving another RNO behind on iron) than an imido fragment (leaving RNO_2); and (3) the regioselectivity and electrophilic nature of the aminations by **1a** are typical of organic ene reactions, including those involving RNO as an enophile.[7,23] Some additional evidence supporting the RNO-transfer scheme was gathered from the following experiments (Scheme 7): First, $Fe^{II}Cl_2$ was found to be effective for reducing PhNHOH to $PhNH_2$ (20 °C, by GC), suggesting that Fe(II) complexes present in the catalytic reactions would be capable of reducing an intermediate allylhydroxylamine. More directly, during the kinetic studies of the reaction of **1a** with 2-MP GC monitoring revealed the presence of a transient compound which formed before the allylamine (with similar retention time), reached a low steady-state concentration while the amine concentration increased, and then disappeared after

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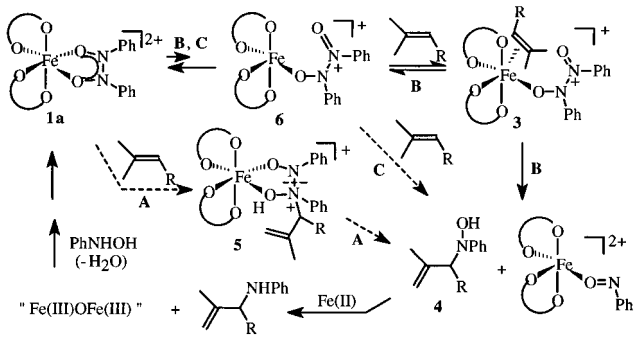
Scheme 8



the reaction was complete. We believe this transient species is the allylhydroxylamine **4** (R = Et). However, the thermal lability of this intermediate and of a crude sample presumed to contain authentic **4** (prepared by reaction of 2-MP with PhNO) has prevented unambiguous structural assignment by GC/MS. Components in the two mixtures suspected to be **4** had comparable retention times and similar (but not identical) mass spectra with appropriate fragment ions but no molecular ion corresponding to the hydroxylamine. Nonetheless, the circumstantial evidence provided above supports the proposal that complex **1a** transfers a PhNO unit to alkene producing an allylhydroxylamine intermediate which is subsequently reduced to the product allyl amine.

Putative Catalytic Mechanism. The following observations and features must be taken into account in formulating a possible mechanistic scheme for the aminations catalyzed by iron salts and by azo dioxide complex **1a**: (1) the ene reaction-type chemo- and regioselectivity; (2) the noninvolvement of free PhNO; (3) the role of **1a** as a competent and relevant aminating agent; (4) the coordinative saturation of the complex ion $\{Fe^{II}[Ph(O)NN(O)Ph]_3\}^{2+}$ of **1a**; (5) the amination rate's first-order dependency of **1a** and on alkene; (6) a nearly zero entropy of activation; (7) the significantly negative ρ value for the reaction of **1a** with substituted styrenes; (8) the formation of alkene adducts **3**; (9) the facile induced exchange of coordinated and free nitrosoarene with **1a**; (10) inhibition of amination by β-methylstyrene; and (11) the likely intermediacy of allylhydroxylamines.

Taking all of these into consideration we envision at least three basic pathways for allylic amination via RNO transfer (Scheme 8). Pathway **A** begins with direct N-attack of alkene on the coordinated azo dioxide ligand in an ene reaction to form an allylhydroxylamine complex **5**; dissociation of the latter and subsequent deoxygenation by Fe(II) would afford allylamine and an oxidized iron species; this in turn can react with PhNHOH to regenerate **1**. Alternatively, in pathways **B** and **C** dechelation (arm opening) of an azo dioxide ligand produces a five-coordinate intermediate **6** which could (via **B**) coordinate alkene giving the adduct **3**; transfer of the PhNO unit of **3** to the alkene (stepwise or concerted) could produce allylhydroxylamine which is subsequently reduced. Alternatively, intermediate **6** could transfer an RNO unit directly to alkene in an ene reaction without alkene coordination (pathway **C**).

We now consider the relative merits of processes **A**−**C** *vis a vis* the accumulated evidence. In pathway **A** the azo dioxide ligand is activated by Lewis acidic iron(II) toward an ene-type reaction. The regioselectivity, rate dependency on alkene, and effect of alkene substituents on rate can all be accommodated for by pathway **A** if the first step is rate-determining. A feature which is not accounted for in pathway **A** is the experimentally determined negligible entropy of activation; associative, rate-determining conversion of **1** → **5** would be expected to have a substantial negative entropy of activation. Additionally, the formation of alkene adducts **3** and the inhibition by β-methylstyrene would have to be assigned a "dead-end" role, i.e. **3** forms reversibly and does not proceed on to allylhydroxylamine (and allylamine).

In pathway **B** the first-order dependency on alkene would require that alkene coordination to coordinatively unsaturated **6** or subsequent RNO-group transfer to coordinated alkene be rate-determining. Consideration of the activation entropy and the isolability of **3** in would appear to rule in favor of the latter option. Whether conversion of **3** to allylhydroxylamine is concerted or stepwise is unclear (*vide infra*) but its unimolecular nature is consistent with the observed activation entropy. Competitive coordination of β-methylstyrene with 2-MP in **3** but ineffective RNO transfer for the former would account for the observed inhibitory effect of the former. The initial arm-opening step common to pathways **B** and **C** also can account for the fact that PhNO group transfer to the alkene occurs without PhNO dissociation yet reaction of **1a** with TolNO induces PhNO dissociation. For the latter, association of TolNO with unsaturated **6** could be followed by dissociation of PhNO for the dangling arm with reformation of a mixed azo dioxide ligand complex.

In pathway **C** bimolecular reaction of **6** with alkene would have to be rate-determining but, if this were the case, again, a substantial negative entropy of activation should result. Hence, pathway **B** best accommodates all of the experimental data presently available.

Although pathway **B**, via the novel alkene complexes **3** has thus been implicated in iron-catalyzed allylic amination, the details of how **3** could be converted to the allylhydroxylamine are far from obvious. The distinctive regioselectivity of the aminations (with double-bond transposition), the effects of alkene structure on reactivity, the minimal entropy of activation, and the small isotope effect are suggestive of an asynchronous (or stepwise) ene-like reaction. Indeed, it is difficult to envision a concerted process which would proceed directly from **3** to allylhydroxylamine. Mechanistic details notwithstanding alkene coordination to the cationic iron(II) center is expected to increase the acidity of the allylic protons (facilitating the requisite H-transfer), while coordination of the azo dioxide ligand could enhance its electrophilicity and reactivity as an enophile. Related Lewis acid promotion of ene reactions of carbonyl enophiles is well established.[26] Further mechanistic discussions are deferred until additional structural and reactivity data are available on the alkene complexes **3**. We note finally that the present catalysis by iron of an ene-like reaction is reminiscent of the lipoxygenase-catalyzed allylic oxygenations, which may proceed either by radical[42] or organoiron[43] pathways.

Conclusions

The amination of alkenes by arylhydroxylamines catalyzed by iron salts constitutes a useful and regioselective method for the direct preparation of allylamines. We have established with **1a** the first structurally verified metal complex of a C-nitroso

(42) *Lipoxygenases and Their Products*; Crooke, S. T.; Wong, A., Eds.; Academic: New York, 1991. Kuhn, H.; Schewe, T.; Rapoport, S. M. The Stereochemistry of the Reactions of Lipoxygenases and Their Metabolites. Proposed Nomenclature of Lipoxygenases and Related Enzymes In *Advances in Enzymology*; Meister, A., Ed.; Wiley: New York, 1986; Vol. 58, pp 274−311.

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(47) Yield of **1a** estimated assuming $3FeCl_2 + 6PhNHOH \rightarrow 1$(**1a**).

dimer (azo dioxide) and its unprecedented reactivity and selectivity for the allylic N-functionalization of alkenes. The involvement of **1** as the aminating agent in $FeX_{2,3}$-catalyzed allylic amination also has been strongly implicated on the basis of kinetic and isolation studies on its reactions with alkenes. Studies are continuing to further elucidate the mechanism by which the azo dioxide complexes are formed and how they transfer the PhNO unit to the substrate. Although some details of the nitrogen group transfer from iron to alkene remain to be established, the azo dioxide complex **1a** provides the first of a new and useful class of aminating agents. Efforts are underway to expand the synthetic scope and generality of this reaction and to develop enantioselective catalysts based on **1**.

Experimental Section

General Methods and Materials. All reactions were performed in an atmosphere of nitrogen using standard Schlenk tube or drybox techniques. Reagent-grade solvents were dried, distilled, and stored over 4 Å molecular sieves under nitrogen and used in all manipulations. Phenylhydroxylamine,[44] *N*-phenyl-3,6-dihydro-1,2-oxazine,[26] 4-methyl-, 4-methoxy-, 4-chloro-, and 4-fluoro-α-methylstyrenes,[45] and α-methylstyrene-d_3[46] were prepared following literature procedures. IR spectra (FT) were obtained as KBr pellets; ^{1}H NMR spectra (FT) were acquired in $CDCl_3$ solution at 300 or 400 MHz; mass spectra were obtained by direct insertion (70 eV) or FAB; UV−vis spectra were recorded on a diode array spectrophotometer. GC analysis was performed using a h ft glass column packed with OV 101 with naphthalene as internal standard and FI detection; GC/MS (70 eV) analyses were obtained using a SE-54 (30 m) capillary column.

Amination of Alkenes Catalyzed by Iron Salts or 1a. In a typical experiment, a solution of phenylhydroxylamine (0.16 g, 1.5 mmol) in dioxane (10 mL) was added by syringe pump over a period of 5−7 h to a heated solution of the alkene (3.2 mmol) and iron(II,III) chloride (10 mol %) at 70−100 °C in dioxane (5 mL). After cooling the volatiles were removed in vacuo and the residue was dissolved in diethyl ether and chromatographed on silica gel using petroleum ether/diethyl ether as eluant to afford the allylamine (Table 1). These were characterized by IR, NMR, and MS analysis. Spectral data are included in the Supporting Information.

Synthesis of [Fe{Ph(O)NN(O)Ph}$_3$][(FeCl$_4$)$_2$] (1a). To a suspension of $FeCl_2$ (0.60 g, 4.7 mmol) in chlorform was slowly added a chloroform solution of nitrosobenzene (1.02 g, 10 mmol) over a period of 30 min with stirring at ambient temperature. After 5−6 h, the dark reddish-brown mixture was filtered followed by removal of the solvent *in vacuo*. The product was recrystallized from CH_2Cl_2/hexane at −20 °C to give 0.96 g (0.88 mmol, 56%)[47] of dark red-brown crystalline **1a**. GC analysis of the supernatant liquid showed the presence of nitrosobenzene, azobenzene, and azoxybenzene (1:0.12:11): IR (KBr, cm^{-1}) 3099 (w), 3077 (w), 1681 (m), 1600 (m), 1481 (s), 1462 (s), 1374 (s), 1161 (s), 1076 (m), 1020 (m), 962 (s), 922 (m), 762 (s), 686 (s); UV−vis (nm, dioxane) 215 (ϵ 665), 285 (ϵ 1030), 305 (ϵ 1270); MS (FAB) 214 ($Ph_2N_2O_2^+$), 269 [$Fe(PhNO)_2^+$].

Alternatively **1a** could be prepared from $FeCl_3$/PhNHOH as follows. To a solution of iron(III) chloride (0.60 g, 3.7 mmol) in chloroform (25 mL) was added phenylhydroxylamine (0.214 g, 1.96 mmol) at room temperature and the mixture was stirred for 5 h. The solvent was removed in vacuo. The crude material was recrystallized from CH_2Cl_2/hexane at −20 °C to give 0.80 g of dark red-brown solid **1a** (0.73 mmol, 59%).

X-ray Structure Determination of 1a. Crystals of **1a** were obtained from CH_2Cl_2/hexane at 0 °C. Crystal diffraction data were collected at 198 K 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 of F^2 using all relections (SHELXTL 5.0). The asymmetric unit contains two dications, four anions, and three CH_2Cl_2 molecules. Crystal data and structure refinement information for **1a** are summarized in Table 3. Tables of atomic coordinates, anisotropic thermal parameters, hydrogen coordinates, and a full listing of bond lengths and angles are provided as Supporting Information to *J. Am. Chem. Soc.* **1996**, *118*, 3311.

Table 3. Crystal Data and Structure Refinement for **1a**

identification code	kn04f
empirical formula	$C_{75}H_{66}Cl_{22}Fe_6N_{12}O_{12}$
formula weight	2442.40
temperature	198(2) K
wavelength	0.71073 Å
crystal system	triclinic
space group	*P*-1
unit cell dimensions	$a = 15.572(9)$ Å $\alpha = 88.87(3)°$ $b = 16.308(5)$ Å $\beta = 86.80(4)°$ $c = 19.841(7)$ Å $\gamma = 86.60(4)°$
vol, *Z*	5021(4) Å^3, 2
density (calculated)	1.615 Mg/m^3
absorption coefficient	1.489 mm^{-1}
F(000)	2452
crystal size	0.46 × 0.36 × 0.24 mm
θ range for data collection	1.61 to 23.00°
limiting indices	$0 < h < 17$, $-17 < k < 17$, $-21 < l < 21$
reflections collected	14 405
independent reflections	13799 [R(int) = 0.0611]
absorption correction	semiempirical from ψ scans
max and min transmission	0.3142 and 0.2120
refinement method	full-matrix-block least-squares on F^2
data/restraints/parameters	13782/0/1162
goodness-of-fit on F^2	1.025
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0878$, w$R_2 = 0.2060$
R indices (all data)	$R_1 = 0.1557$, w$R_2 = 0.2620$
largest diff peak and hole	1.161 and −0.832 eA^{-3}

Synthesis of [Fe{Tol(O)NN(O)Tol}$_3$][(FeCl$_4$)$_2$] (1b). Iron(II) chloride (0.87 g, 6.8 mmol) was suspended in $CHCl_3$ (20 mL). To this heterogeneous mixture was added 2-nitrosotoluene (1.60 g, 13.7 mmol) in $CHCl_3$ (10 mL) with stirring over a period of 30 min. After the mixture was stirred for an additional 20 h the resulting dark reddish-brown solid was filtered, washed with chloroform, then ether, and dried in vacuo. Recrystallization in THF/hexane produced 1.52 g of dark reddish-brown solid **1b** (1.3 mmol, 55%): IR (KBr, cm^{-1}) 1650 (sh, w), 1633 (s), 1614, 1564, 1537, 1504 (w), 1380 (m), 1040 (s), 891, 769 (w), 556 (br, m).

Reaction of 1a with 2-Methyl-2-pentene. To a dioxane solution (5.0 mL) of **1a** (0.027 g, 0.23 mmol) was added 2-methyl-2-pentene (50 μL, 0.41 mmol), and the reaction mixture was heated at 80 °C for 8 h. The product allylamine (81%) was detected by GC. Reaction of **1a** with 2-methyl-2-pentene at room temperature produced the allylamine in 83% yield (GC) after 24 h.

Reaction of 1a with 2,3-Dimethylbutadiene/2-Methyl-2-pentene. Complex **1a** (0.02 g, 0.009 mmol), 2-methyl-2-pentene (25 μL, 0.02 mmol), and 2,3-dimethylbutadiene (23 μL, 0.02 mmol) were dissolved in 5 mL of dioxane, and the mixture was heated at 70 °C for 8 h. The allylamines derived from 2-MP (70%) and 2,3-DMB (30%) were the only products detected by GC and GC-MS.

Stability of PhNO/2,3-Dimethyl-1,3-butadiene Adduct 2 under Amination Conditions. A mixture containing 0.10 g (0.53 mmol) of **2**, 70 μL (0.57 mmol) of 2-methyl-2-pentene, and 0.011 g (0.55 mmol) of $FeCl_2 \cdot 4\ H_2O$ in 5 mL of dioxane was heated at 80 °C for 5 h. GC analysis detected only the starting adduct **2**; no allylamine derived from 2-MP was detected.

Catalytic Amination of 2-Methyl-2-pentene by Phenylhydroxylamine and 1a. To a dioxane solution (5 mL) of **1a** (0.06 g, 0.027 mmol) and 2-methyl-2-pentene (1 mL, 8.2 mmol) at 80 °C was added dropwise phenylhydroxylamine (0.045 g, 0.41 mmol) in dioxane (7 mL) over a period of 5 h. Aniline (4%), azobenzene (3%), azoxybenzene (3%), and the allylamine (76%) were detected by GC and GC-MS after 8 h.

Displacement of PhNO from 1a. 2-Nitrosotoluene (0.012 g, 0.99 mmol) was added to a solution of **1a** (0.04 g 0.33 mmol) in dioxane (5.0 mL). The mixture was stirred at room temperature for 5 min and an aliquot was withdrawn. Thereafter the flask was placed in a thermostated oil bath at 80 °C and aliquots were taken after 1, 2, and 8 h. After the aliquots were passed through a plug of silica gel, the eluates were analyzed by GC and the relative ratios of free nitrosobenzene and 2-nitrosotoluene were calculated.

Synthesis of [{Fe{Ph(O)NN(O)Ph}$_3$}][(FeCl$_4$)$_2$]·[2-methyl-2-pentene] (3a). To a solution of **1a** (0.10 g, 0.80 mmol) in dichloromethane (10 mL) at −30 °C was added 2-methyl-2-pentene (1.0 mL, 8.2 mmol) and the solution stirred for 6 h below 0 °C. The solvent was removed in vacuo below 0 °C and the residue washed with hexane and then vacuum dried overnight. Recrystallization from dichloromethane/pentane at −20 °C gave 0.42 g of **3a** as a dark red solid (0.032 mmol, 40%): IR (KBr, cm^{-1}) 1594, 1516, 1484, 1400 (s), 1379 (w), 1320, 1160 (s), 827 (m), 756, 688 (s); ^{1}H NMR ($CDCl_3$, δ) 0.9 (br, 3H), 1.3 (br, 6H), 1.4−1.9 (br, 2H), 5.3 (br, 1H), 7.24−8.33 (br, 20H); UV−vis (dioxane) 285, 305, and 380 nm.

Synthesis of [{Fe{Ph(O)NN(O)Ph}$_3$}][(FeCl$_4$)$_2$][β-methylstyrene] (3b). As above β-methylstyrene (3.0 mL) and **1a** (0.27 g, 0.2 mmol) were combined in dichloromethane. The mixture was stirred for 1.5 h at 0 °C and then for 20 h at room temperature. Solvent was removed in vacuo; the residue washed with hexane and vacuum dried. Brown solid **3b** (0.12 g, 0.09 mmol) was thus obtained in 41% yield: IR (KBr, cm^{-1}) 1643 (sh, w), 1633 (sh, m), 1602 (s), 1556 (w), 1495 (m), 1454, 1384, 1310, 1253, 1155, 1019, 840 (m), 672, 693 (s); ^{1}H NMR ($CDCl_3$, δ) 1.3 (br, 3H), 6.2−9.0 (br, 37H).

Synthesis of [Fe{Ph(O)NN(O)Ph}$_3$][(FeCl$_4$)$_2$][styrene] (3c). As for the preparation of **3b** a solution of styrene (3.0 mL) and **1a** (0.55 g, 0.45 mmol) in CH_2Cl_2 was stirred at room temperature for 10 h. Dark reddish-black solid **3c** (0.28 g, 0.21 mmol) was obtained in 47% yield following solvent evaporation, washing of the residue with hexane, and vacuum drying: IR (KBr, cm^{-1}) 1690 (w), 1632, 1622 (sh, w), 1597 (s), 1495, 1454 (m), 1409, 1360, 1316, 1260, 1157 (w), 1028 (m), 760, 700 (s).

Thermolysis of 3a. Compound **3a** (0.05 g, 0.38 mmol) was dissolved in dioxane (5 mL) and then heated at 80 °C for 8 h. GC analysis after precipitation of iron-containing compounds with pentane indicated a 65% yield of the allylamine.

Displacement of 2-Methyl-2-pentene/Allylamine from 3a. Compound **3a** (0.05 g, 0.38 mmol) was dissolved in dioxane (5 mL), and the solution was thermostated at 15−16 °C. To this solution 2-nitrosotoluene (0.01 g, 0.08 mmol) was added. The reaction mixture was stirred for 6 h and then analyzed by GC. 2-Methyl-2-pentene (53%) and the corresponding *N*-phenylallylamine (34%) were detected by GC.

Displacement of β-Methylstyrene from 3b,c. Nitrosobenzene (0.037 g, 0.35 mmol) was added to a solution of **3b** (0.07 g, 0.05 mmol) in dichloromethane (10.0 mL), and the mixture stirred at room temperature for 23 h. A sample was withdrawn and analyzed by GC; β-methylstyrene (44%) and traces of azobenzene and azoxybenzene were detected.

Displacement of styrene from **3c** was performed analogously; GC analysis detected 45% of styrene after 24 h.

Deoxygenation of PhNHOH by FeCl$_2$. A suspension of 0.05 g (0.25 mmol) of $FeCl_2 \cdot 4H_2O$ in 3 mL of dioxane was treated with 0.109 g of PhNHOH. After stirring for 24 h at rt, a light green solution containing a brown precipitate formed. GC analysis revealed the presence of aniline (major) and small quantities of azobenzene, azoxybenzene, and nitrosobenzene.

Kinetic D-Isotope Effect. Compound **1a** (0.25 g, 0.20 mmol) was dissolved in dioxane (15 mL). To this solution α-methylstyrene (150 μL, 0.115 mmol) and α-(trideuteriomethyl)styrene (150 μL, 0.115 mmol, 90% D_3) were added. The solution was heated at 60 °C for 20 h. After vacuum removal of the volatiles, the allyl amine was isolated by chromatography on silica gel using petroleum ether and ethyl acetate (95:5). The ratio of protio to deuterio products was determined by ^{1}H NMR integration of the allylic CH_2 and $=CH_2$ groups. Correcting for the % D in the α-(trideuteriomethyl)styrene a 1.4:1.0 ratio of protio/deuterio allylamines (= k_H/k_D) was calculated.

Kinetic Studies. In a three-necked round-bottom flask fitted with a condenser, nitrogen inlet, and a silicone septum stopper, complex **1a** (0.02 g, 0.0164 mmol) was dissolved in dioxane (4 mL). The flask was placed in a thermostated oil bath at 70 °C. After 2 min for thermal equilibration, 2-methyl-2-pentene (30 μL, 0.24 mmol) was added and aliquots were withdrawn and cooled in ice every 2.5 min. The samples were analyzed for allylamine by GC. Initial rates were determined by a plot of the concentration of allylamine vs time during the first 10% conversion.

Activation parameters were calculated by determining rate constants for the reaction of **1a** with 2-methyl-2-pentene as above at 50, 60, 70, 90 °C and then plotting ln k vs $1/T$ according to the Eyring equation.

Determination of the rates of reaction of **1a** with the *para*-substituted α-methylstyrenes was carried out analogously at 70 °C.

Inhibition of the Amination of 2-Methyl-2-pentene by α-Methylstyrene. Following the above general procedure a 1:1 molar mixture of 2-methyl-2-pentene and β-methylstyrene was employed and the reaction conducted at 70 °C. The product mixture was analyzed by GC.

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Supporting Information Available: NMR and MS data for new allyl amines produced (1 page). See current masthead page for ordering and Internet access instructions.

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