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Kinetics of the Allylic Amination of Olefins by Nitroarenes Catalyzed by $[CpFe(CO)_2]_2$

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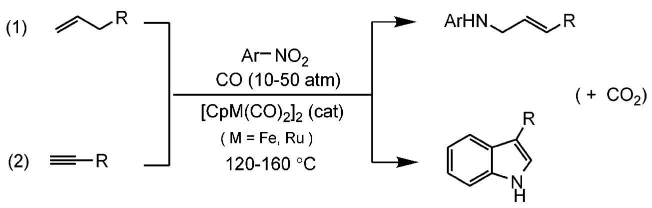
The kinetics of the $[CpFe(CO)_2]_2$-catalyzed allylic amination of α-methylstyrene derivatives by nitroarenes is reported. The reaction is found to be first-order in both alkene and nitroarene, zero-order in CO, and half-order in catalyst. Relative rate studies of *para*-substituted alkenes and nitroarenes show that the rate is increased for electron-deficient nitro compounds and for electron-rich alkenes. On the basis of these results, together with the regioselectivity of the reactions with unsymmetrical alkenes and the outcome of trapping experiments for free nitrosoarenes and nitrenes, a mechanistic scheme is proposed involving C−N bond formation from a CpFe(CO)(RNO)(alkene) intermediate.

Introduction

Transition metal-catalyzed reductions of nitroorganics by carbon monoxide constitute a growing set of useful reactions for the production of various organonitrogen compounds, including isocyanates, ureas, arylamines, and numerous heterocycles.[1] Mechanistic insight into these reductive processes is very limited, especially with respect to the reactive nitrogen species involved. A number of studies[2−4] have demonstrated the involvement of various metallacycles incorporating RNO_2 and CO in the deoxygenation process. Nitrenoid species, free or coordinated, have often been presumed to be intermediates in these reactions,[1] but direct evidence for their involvement or the intervention of other reactive intermediates in the reactions is scarce.

As part of a research program directed toward the development of metal-catalyzed nitrogenation reactions of unsaturated hydrocarbons,[5] we recently reported the allylic amination of olefins[6] and indolization of alkynes[7] by nitroarenes/CO, catalyzed by $[Cp{\wedge}M(CO)_2]_2$ (M = Fe,Ru; Cp∧ = C_5H_5,C_5Me_5) complexes (Scheme 1). These novel transformations feature high regioselectivity with respect to the hydrocarbon component, the ArN unit being introduced at the less substituted carbon of the substrate. A photoassisted, low-pressure variant of the $[Cp^*Fe(CO)_2]_2$-catalyzed allylic amination was also developed which allows the reactions to be conducted in common laboratory glassware.[8] Cenini and Ragaini first reported a $Ru_3(CO)_{12}$-diimine catalytic system for allylic amination using nitroarenes as the aminating agent.[9]

Scheme 1



Our initial studies of the above allylic amination reactions provided some mechanistic clues as to the reactive species that are/are not involved. The distinctive regioselectivity noted above is typical of ene-type reactions,[10] but a catalytic reaction run in the presence of 2,3-dimethyl-1,3-butadiene, an effective Diels−Alder trapping agent for the enophile ArNO,[11] afforded allyl amines exclusively (Scheme 2).[5a] Moreover, the intermediacy of free nitrene, ArN, was excluded by the selective formation of the allyl amine, rather than the nitrene-derived carbazole,[12] from the reaction of 2-nitrobiphenyl with α-methylstyrenerene (Scheme 2).[6a] The apparent noninvolvement of these reactive organic

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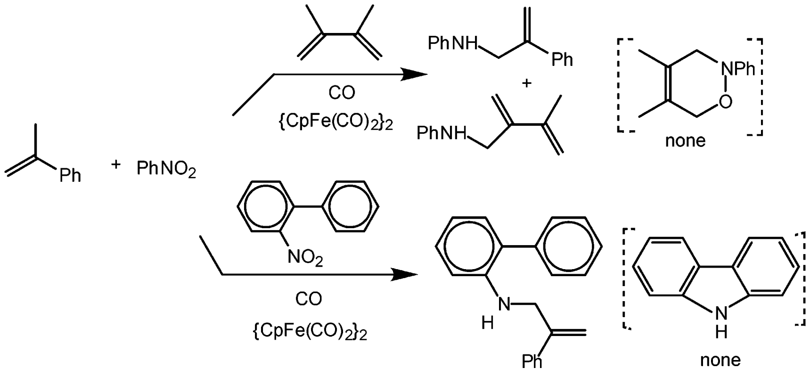
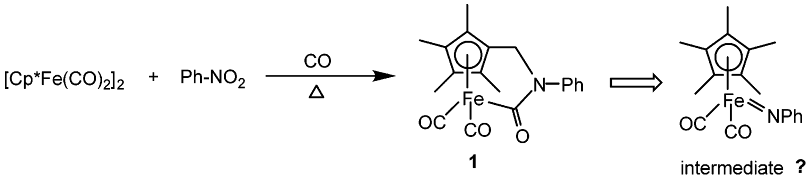
Scheme 2



Scheme 3

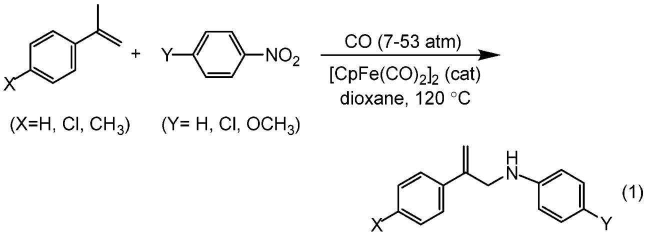


intermediates suggested that coordinated organonitrogen species could play a role in the reactions. This possibility was further supported by the isolation of the novel cyclometalated carbamato complex **1** from amination reactions promoted by $[Cp^*Fe(CO)_2]_2$ (Scheme 3).[5b]

Here we present the results of kinetic studies of the $[CpFe(CO)_2]$-catalyzed amination of α-methylstyrenerene derivatives by nitroarenes, which provide additional insight into the reaction pathway, including the likely involvement of a monometallic organonitrogen complex as the nitrogen transfer agent.

Results

Kinetic data were collected by GC monitoring of the allyl amine formation over time (initial rate method, 0–10% conversion) in the $[CpFe(CO)_2]_2$-catalyzed reaction between nitrobenzene (NB) and excess α-methylstyrenerene (AMS) under CO (eq 1) at 120 °C. The concentration of each reacting component was systematically varied, while holding the others constant. The rate versus concentration data were then plotted to obtain the rate dependence for each reaction component. The results for NB and AMS shown in Figures 1 and 2 indicate that the reaction is cleanly first-order in each of these reactants over the concentration range of 0.0–1.0 M and 0.0–4.5 M, respectively. Over the pressure range of 100–800 psi CO,[13] however, the rate of allyl amine formation was essentially unchanged (±15%; not shown), indicative of a zero-order process in CO.



The rate/concentration dependence on the $[CpFe(CO)_2]_2$ (Fp_2) catalyst, shown in Figure 3a, is especially interesting, as it is clearly nonlinear. However, a good linear correlation ($R^2 = 0.99$) is obtained when the initial rate is plotted versus $[Fp_2]^{0.5}$ (Figure 3b), indicating that the reaction is half-order in the added dimer concentration. Overall, the apparent rate law for the amination reaction is thus, rate $= k[AMS][NB][Fp_2]^{0.5}$.

Since the amination reaction rate was found to be dependent on both the AMS and NB concentrations (vide supra), we sought to probe the electronic characteristics of the steps up to and including the turnover-limiting step through a substituent effect study on the reaction rate. A small representative set of *para*-substituted styrene and nitroarene derivatives was employed (X = Cl, CH_3; Y = Cl, OCH_3, eq 1) in kinetic

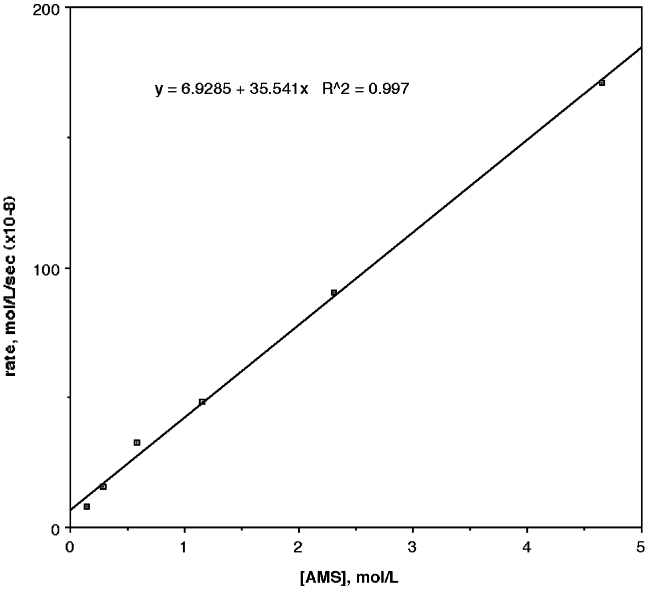


Figure 1. Rate dependence on $PhNO_2$ concentration. [AMS] = 0.29 M, $[Fp_2]$ = 19 mM, P(CO) = 46 atm, dioxane, 120 °C. Each data point (•) is the result of a linear least-squares fit to the [allyl amine] vs time plot for at least six different times at ≤10% conversion; the line drawn is the theoretical least-squares fit to the experimental data points with the indicated correlation coefficient (R^2) and equation.

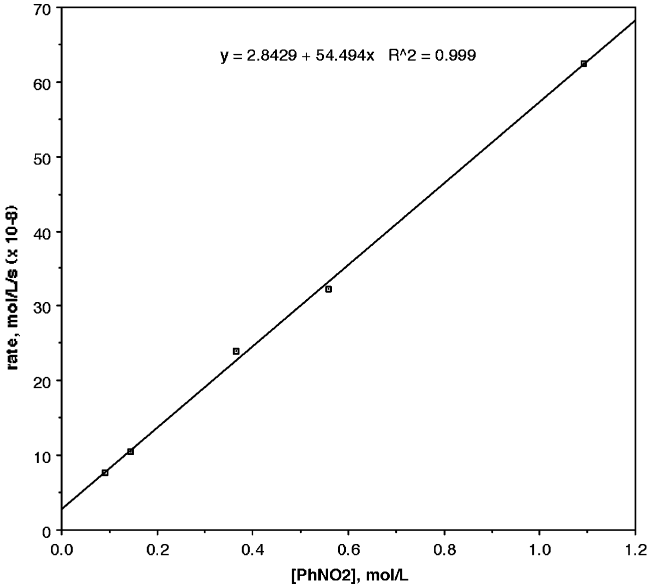


Figure 2. Rate dependence on AMS concentration. [$PhNO_2$] = 0.30 M, [Fp_2] = 19 mM, P(CO) = 46 atm, dioxane, 120 °C.

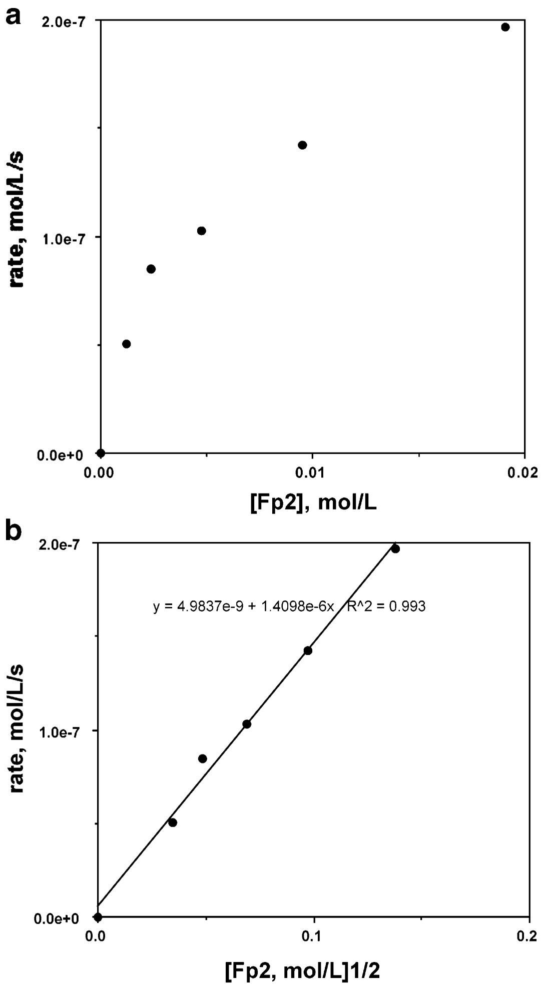


Figure 3. (a) Rate dependence on Fp_2 concentration. [$PhNO_2$] = 0.30 M, [AMS] = 0.29 M, P(CO) = 46 atm, dioxane, 120 °C. (b) Rate dependence on square root of Fp_2 concentration. [$PhNO_2$] = 0.30 M, [AMS] = 0.29 M, P(CO) = 46 atm, dioxane, 120 °C.

competition experiments versus the parent compounds (X, Y = H) under typical reaction conditions. The resulting product mixtures were analyzed by GC and GC/MS to obtain the ratio of allyl amine products, which is approximately equal to k_{rel}.[14] Although the data set is limited and only semiquantitative, it is clear from Hammett plots (SI)[15] that the reaction rate is increased for electron-rich alkenes (ρ ca. −2) and for electron-deficient nitroarenes (ρ ca. +2).

Finally, evidence for the intervention of radical intermediates in the catalytic reactions was provided by the following experiment. When AMS, NB, and Fp_2 were heated with CO under standard reaction conditions in the presence of excess CCl_4, an established Cl atom source for metalloradicals,[16] little conversion occurred and no allyl amine was produced.

Discusssion

We review first the prior mechanistically relevant observations on the $[CpM(CO)_2]_2$-catalyzed allylic aminations: (1) allyl amines are produced with high regioselectivity, the result of ArN addition to the less-substituted vinylic carbon with double-bond transposition; (2) trapping tests for known organonitrogen reactive intermediates, i.e., nitrosoarenes and aryl nitrenes, were negative; and (3) a monometallic iron carbamato derivative **1** was isolated from the $[Cp^*Fe(CO)_2]_2$-catalyzed reaction.

In the present study the kinetic determination of the substrate dependence for the Fp_2-catalyzed reaction of nitrobenzene with α-methylstyrene revealed first-order behavior for each of these reactants and zero-order in carbon monoxide (over the concentration range studied). Together these features indicate that the operative reaction pathway involves both the nitroarene and the olefin in reversible steps before or in the turnover-limiting (TL) step. The observed CO rate independence could indicate that its role comes after the TL step or may reflect kinetic saturation behavior in CO over the pressure range investigated. Practically speaking, the CO dependence also showed that these reactions can proceed effectively at lower pressures than previously employed.

The half-order dependence on the Fp_2 catalyst is strongly suggestive of a dimer−monomer equilibrium in which the 17-electron monomeric species ($CpFe(CO)_2^\bullet$ = Fp) is catalytically active.[17] This equilibrium (K_{eq} at 23 °C = 2 × 10^{-17}), in fact, has been well established through thermal and photochemical trapping studies.[18] Additional support for the involvement of the Fp radical in the present reaction is provided by (1) the complete reaction inhibition in the presence of CCl_4[19] and (2) our earlier isolation of the mononuclear iron-carbamato complex **1** in the reactions catalyzed by Fp^*_2.[5b]

A mechanistic proposal that is consistent with the kinetic and mechanistic data now available is presented in Scheme 4. The thermally generated 17-electron $Fp^\bullet$ species is suggested to first react reversibly with the

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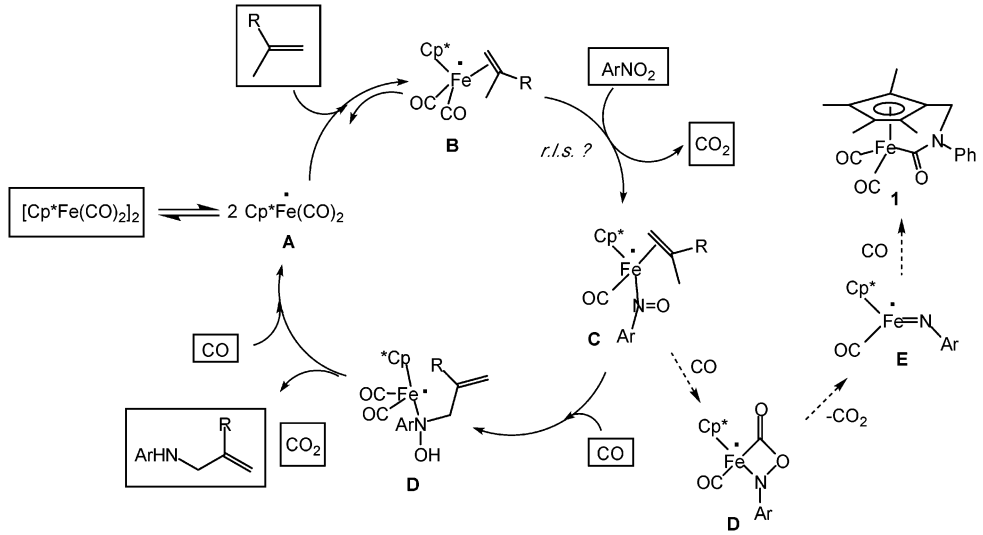
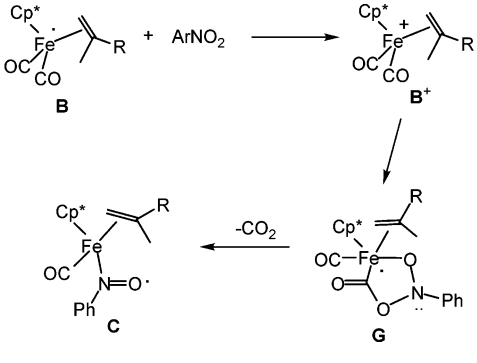
Scheme 4



olefin to produce the 19-electron complex **B**. Reaction between **B** and the nitroarene with O-transfer (vide infra) could lead to nitrosoarene complex **C** (and CO_2). An intramolecular, metal-assisted ene reaction of **C** and CO association would afford the allyl hydroxylamine complex **D**. Deoxygenation of **D** via O-transfer to coordinated CO would produce the product allyl amine and CO_2 and regenerate $Fp^{\bullet}$.[20] A competing (and irreversible) process in which coordinated ArNO (as in **C**) undergoes deoxygenation (to coordinated CO), rather than the ene-reaction, could produce a reactive imido complex, e.g., **F**, which would account for the formation of the observed metallocarbamate **1** via C−H activation and migratory insertion of CO.

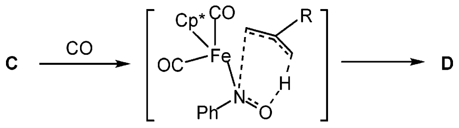
The formation of 19-electron intermediates such as the putative olefin complex **B** in reactions of dinuclear metal complexes with donor ligands is well precedented[21] and, under the high CO pressure (concentration) operating conditions, appears more likely than an alternative 17-electron CpFe(CO)(alkene) species. The limited equilibrium dissociation of Fp_2 to $Fp^{\bullet}$ (**A**),[18] together with reversible olefin coordination expected for a labile 17/19-electron system,[22] is consistent with the observed first-order olefin dependence and half-order dependence for Fp_2. The conversion of **B** to the nitrosoarene-olefin complex **C** would likely be a multistep process. As indicated in mechanistic studies of Ru-[2] and Ni-promoted[23] deoxygenation of nitroarenes, this sequence could proceed via initial electron transfer from complex **B** to $ArNO_2$ (Scheme 5), followed by attack of the resulting $ArNO_2$ radical anion on B^+ (both known species[24,25]) to form a metallacycle **G**; decarboxylation of **G** would give the nitroarene-olefin complex **C**. This electron transfer step could very well be turnover-limiting since CpFe(CO)(PhNO)(AMS) (**B**) is anticipated to be a weaker reductant than needed to transfer an electron to the nitroarene.[26] The overall conversion of **B** to **C**, with net transfer of an oxygen atom from $ArNO_2$ to CO and formation of stable, gaseous CO_2, however, is likely strongly exoergic and thus essentially irreversible. This would be consistent with both the observed rate law (rate = $k[PhNO_2][AMS]$) and the substrate substituent effects, i.e., that the reactions are faster with electron-deficient nitroarenes (more easily reduced) and electron-rich (more reducing) olefins.

Scheme 5



The most important step with respect to the substrate transformation is the suggested conversion of **C** to the allylhydroxylamine complex **D**, a metal-mediated ene reaction (Scheme 6). This could be facilitated if odd-electron complex **C** had appreciable oxygen-centered electron spin density, as is the case for the related,

Scheme 6



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[20] We acknowledge and appreciate the insightful comments of a reviewer for the suggestion that the likely irreversible nature of the O-transfer process and the first-order dependence on both olefin and nitroarene make it likely that the olefin is coordinated during the O-transfer from RNO_2 to CO.

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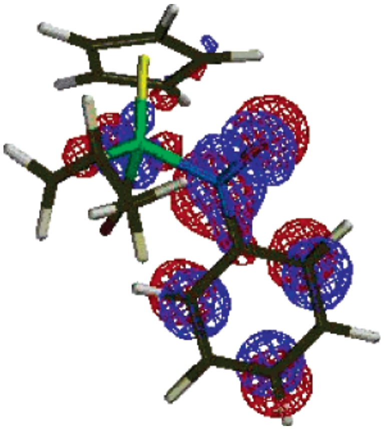

Figure 4. Calculated structure and SOMO of CpFe(CO)(PhNO)(propene).

spectroscopically characterized radicals $CpFe(CO)_2(ArNO)$.[27] The viability, structure, and potential reactivity of the putative olefin-nitrosoarene complex **C** was probed by PM3 semiempirical MO calculations.[28] The calculated structure and singly occupied molecular orbital (SOMO) of **C** are shown in Figure 4. The piano stool geometry is typical of $CpML_3$ complexes, while the SOMO is indeed primarily located on the ArNO ligand. A preponderance of electron spin density is found on the N−O unit (ca. 0.5 electron spin density on N, ca. 0.3 on O). These features of **C** could enable it to engage in a radicaloid ene-type reaction with the coordinated olefin, involving C−N and O−H bond formation with the characteristic double-bond transposition of the catalytic allylic aminations.[10] Alternatively, the **C** → **D** conversion could occur stepwise via a metallacylic intermediate of the type observed in some reactions of C-nitroso complexes with olefins or by way of π-allyl intermediates.[9b,29] Finally, the demonstrated ability of the $[CpM(CO)_2]_2$ complexes to catalyze the deoxygenation of *N*-hydroxyindoles[6] supports the viability of the suggested catalytic pathway for the conversion of the *N*-hydroxy allyl amine **2** to the allyl amine product.

Precedent for the potential intermediacy of an imido complex intermediate such as **E** is more limited since low oxidation state iron-imido complexes are very rare.[30] Allyl amines have been observed among the products of reactions suggested to involve metal-imido complexes,[31] and the carbamato complex **1** isolated from the Fp^*_2-catalyzed reactions could be accounted for by the intermediacy of **E** with subsequent C−H activation and CO insertion.

In summary the kinetics studies of allylic amination presented herein provide evidence for the involvement of reactive monoiron complexes of reduced organonitrogen species that effect ArN transfer to olefins by an ene-type process. Further studies are underway to unequivocally establish the role of the potential intermediates **C** and **E** in the catalysis and to develop more active catalysts for allylic amination with nitroorganics.

Experimental Section

Kinetics: Determination of Reaction Order. In a typical kinetics run $[CpFe(CO)_2]_2$ (catalyst), $PhNO_2$ (limiting reagent), α-methylstyrene (in excess), naphthalene (internal GC standard), and enough dry dioxane to produce a total volume of 8.0 mL were measured and transferred to the glass liner of a Parr SS minireactor containing a magnetic spin bar. The reactor was flushed three times with CO and then pressurized. The reactor was then lowered into a thermostated aluminum block heater (120 °C) and stirred. After 20−30 min for thermal equilibration, samples were withdrawn periodically via the dip tube, diluted with pentane, filtered through a plug of silica, and then analyzed by gas chromatography. The product was quantified from its integration and response factor (determined from authentic samples) relative to the internal naphthalene. The initial rate was determined from the slope of the product concentration versus time plot over the 1−10% conversion range. The concentration of each component (AMS, NB, CO, and catalyst) was varied in separate runs while holding the concentrations of the others constant. The product concentration/time (initial rate) plots for the various AMS, NB, and CO concentrations are provided in the Supporting Information. The initial rates showed no significant correlation with CO pressures: 100 psi (5.7×10^{-8} M/s), 200 psi (6.7×10^{-8} M/s), 400 psi (6.1×10^{-8} M/s), and 800 psi (6.9×10^{-8} M/s). The plots of initial rate versus the concentrations of the varied components are given in Figure 1−3.

Kinetics: Substituent Effects. The *para*-substituted alkenes and nitroarenes were obtained commercially. For the substituted olefins reacting with nitrobenzene, 2.3 mmol each of AMS and the substituted olefin, 2.9 mmol of NB, 0.15 mmol of $[CpFe(CO)_2]_2$, 0.15 mmol of naphthalene, and dioxane (to a total volume of 8.0 mL) were transferred to the glass liner of a Parr SS minireactor containing a magnetic spin bar. The reactions were conducted, and the resulting mixtures of allyl amines were analyzed as above after 24 h using the GC response factors of the individual allyl amines. Competition reactions of the substituted nitrobenzenes with AMS were conducted analogously with 2.9 mmol of each nitroarene and 2.9 mmol of AMS. Allyl amine product yields (in parentheses) were as follows: reaction of $PhNO_2$ with AMS/*p*-Cl-AMS (10%/2%); $PhNO_2$ with AMS/*p*-Me-AMS (14%/19%); AMS with $PhNO_2$/*p*-Cl-$PhNO_2$ (9%/20%); AMS with $PhNO_2$/*p*-MeO-$PhNO_2$ (12%; 2%). The ratio of the consumed substituted nitroarene to the unsubstituted one is essentially equal to k_{rel}

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at low conversions (1−10%) but only approximates k_{rel} at higher conversions and when comparing the product amine ratios.[14] The ρ values derived from the Hammett plots (in SI) should thus be considered approximate (est. ±20%). Nonetheless, the observed substituent effects, that electron-rich olefins and electron-deficient nitroarenes react faster, remain valid.

CCl_4 Inhibition. The minireactor was charged with $[CpFe(CO)_2]_2$ (40 mg), naphthalene (20 mg), NB (0.12 mL), AMS (0.5 mL), dioxane (5 mL), and CCl_4 (5 mL). After pressurization with CO (45 atm) and heating at 160 °C for 16 h, GC analysis of an aliquot indicated that no allyl amine had formed and that most of the AMS and NB was still present.

MO Computations. PM3(TM)-level computations were carried out with the MacSpartan Plus program (Wavefunction, Inc.) using the unrestricted Hartree−Fock (UHF) model. The computational output listing of frontier molecular orbitals, energies, and spin/charge densities is provided in the Supporting Information.

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Supporting Information Available: Concentration/time kinetic data and the PM3-MO output tables are available free of charge via the Internet at http://pubs.acs.org.

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