Iron-catalyzed allylic amination by nitroorganics

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[CpFe(CO)$_2$]$_2$ catalyzes the reaction of nitroaromatics with olefins under CO to produce allyl amines regioselectively; a coordinated organonitrogen species is implicated as the active aminating agent.
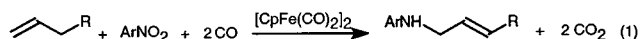
In contrast to oxygenation, synthetically useful methods for the direct introduction of nitrogen into hydrocarbons (nitrogenation) are few. Metal-mediated nitrogenation reactions have been receiving increasing attention, as evidenced by recent reports of metal-catalyzed aziridinations[1] and hydroaminations[2] of olefins, both of which involve addition to the double bond. Processes for the direct *allylic* nitrogenation of hydrocarbons, which could expand the scope of the commercially important ammoxidation of propylene to acrylonitrile,[3] also hold considerable appeal. Recent efforts in this laboratory and others have led to the development of Mo-[4] and Fe-catalyzed[5] reactions of olefins with aryl hydroxylamines, which provide *N*-aryl-*N*-allyl amines in generally moderate yields and with excellent regioselectivity. A novel azodioxide–iron complex has been implicated as the active aminating agent in the allylic aminations catalyzed by iron salts.[5b]

In order to enhance the synthetic utility of metal-catalyzed allylic aminations and to further explore the reactivity of coordinated organonitrogen species, we have been interested in the use of more readily available prospective aminating agents, including amines[6] and, here, nitroorganics. The metal-catalyzed reactions of nitroarenes and CO can produce various useful organonitrogen compounds, including amines, urethanes, ureas and isocyanates.[7] We now report the discovery of a new allylic amination system, which employs nitroarenes as aminating agents and inexpensive [CpFe(CO)$_2$]$_2$ as the catalyst [eqn. (1)].

$$\text{olefin} + \text{ArNO}_2 + 2\,\text{CO} \xrightarrow{\text{[CpFe(CO)}_2]_2} \text{ArNH-allyl-R} + 2\,\text{CO}_2 \quad (1)$$

Initial experiments indicate that this system is distinct, both mechanistically and chemoselectively, from the recently reported Ru$_3$(CO)$_{12}$/(α-diimine)-catalyzed system for allylic amination.[8]

The reactions of olefins with nitroarenes catalyzed by [CpFe(CO)$_2$]$_2$ (5 mol%) were carried out in dioxane at 150–180 °C under 50–75 atm of CO.‡ Representative results for a number of olefins and nitro compounds are summarized in Table 1. The desired allyl amines were the only olefin-derived products detected, generally constituting 75–95% of the volatile N-containing products; *N,N*-diaryl ureas are the principal byproducts.§ The yield of allyl amine depends markedly on the structure of both the olefin and the nitro compound. Among the small set of test olefins 1,1-disubstituted derivatives were aminated most efficiently (entries 1,2) while 1,2-disubstituted, trisubstituted and terminal olefins were aminated less efficiently (entries 3–5). With unsymmetrical alkenes (entries 1–5) single regioisomers were obtained which are derived from introduction of nitrogen at the less-substituted vinylic carbon with double bond transposition, characteristic of ene reactions.[9] Probing the structure/reactivity correlation of the nitroarene component with α-methylstyrene (AMS) as the substrate

(entries 1, 6–9), nitrobenzene gave a nearly quantitative yield, nitroarenes bearing electron-withdrawing groups gave moderate yields, and nitroanisole afforded a poor yield of the corresponding allyl amine.

Initial screening experiments demonstrated that the dinuclear **1** is the most active among several related complexes tested as amination catalysts. In the reaction of nitrobenzene with AMS (dioxane, 160 °C, 70 atm CO) neither bimetallic Cp$_2$Mo$_2$(CO)$_4$ nor other mono-iron complexes, *e.g.* Fe(CO)$_5$, CpFe(CO)$_2$Br or CpFe(CO)$_2$(THF)$^+$, produced appreciable quantities of allyl amine. However, a 52% yield of the allyl amine from AMS was obtained using CpFe(CO)$_2$(η^1-allyl) (**2**, 5 mol%) as (pre)-catalyst. The documented ability of the two active (pre)-catalysts, **1** and **2**, to generate the CpFe(CO)$_2$ radical[10,11] suggests that this species may be involved in the catalytic mechanism.

Given the unprecedented catalytic activity of **1** and the distinctive regioselectivity of the amination reaction several experiments were conducted to probe the nature of the actual aminating species. Firstly, evidence was gathered indicating that two potential reactive free organonitrogen species are not involved. Nitrosobenzene, an established enophile,[12] was excluded as an intermediate since the amination of AMS by nitrobenzene proceeded cleanly in the presence of the PhNO-trapping agent, 2,3-dimethylbutadiene [eqn. (2)],[13] with none of the corresponding hetero-Diels–Alder adduct being produced.¶

Table 1 Allylic amination by nitroarenes catalyzed by [CpFe(CO)$_2$]$_2$

| Entry	Alkene	Nitroarene	Allylamine	Yield^{a,b} (%)
1	Ph-substituted alkene	PhNO$_2$	Ph-allylamine NHPh	92
2	bicyclic alkene	PhNO$_2$	bicyclic NHPh	64
3	cyclohexene	PhNO$_2$	cyclohexenyl NHPh	27
4	methyl-substituted alkene	PhNO$_2$	allylamine NHPh	10
5	Ph-CH=CH-CH$_3$	PhNO$_2$	Ph-allyl NHPh	13
6	Ph-substituted alkene	Cl$_2$C$_6$H$_3$NO$_2$	Ph NHC$_6$H$_3$Cl$_2$	54^c
7	Ph-substituted alkene	C$_6$F$_5$NO$_2$	Ph NHC$_6$F$_5$	57^c
8	Ph-substituted alkene	CF$_3$C$_6$H$_4$NO$_2$	Ph NHC$_6$H$_4$CF$_3$	52^c
9	Ph-substituted alkene	CH$_3$O-C$_6$H$_4$-NO$_2$	Ph NHC$_6$H$_4$OCH$_3$	2^c

^{a} GC yield, naphthalene standard. ^{b} New compounds were isolated and characterized spectroscopically. ^{c} Isolated yield.

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(2)

(3)
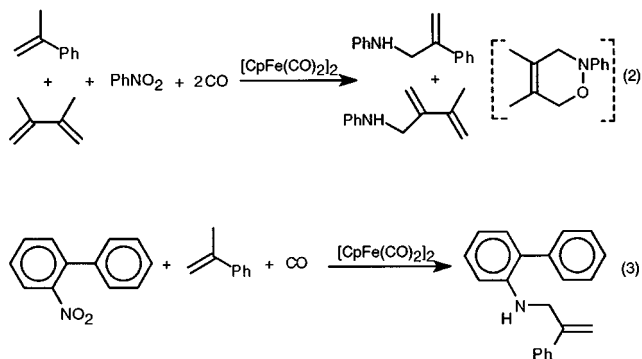
Similarly, amination of AMS by 2-nitrobiphenyl afforded the corresponding *N*-biphenyl-*N*-allyl amine exclusively [eqn. (3)], but no detectable carbazole, the established product of intra-molecular nitrene trapping.[14] Together these results suggest that a coordinated organonitrogen species serves as the active aminating agent in the reactions catalyzed by **1**.

More direct information on the iron species involved in the catalytic reaction was obtained by examining a dark red paramagnetic compound **3** which can be isolated from the stoichiometric reaction of **1** with nitrobenzene in the absence of olefin (dioxane, 100 °C, 75 atm CO, Scheme 1). Although we have not yet established the structure of **3**,‖ this compound appears to be catalytically relevant since it both stoichiometrically (in the absence of nitrobenzene) and catalytically (in the presence of nitrobenzene) efficiently aminates AMS (dioxane, 160 °C, 60 atm CO, TON *ca.* 8). Moreover, **3** aminates AMS in the presence of the nitrosobenzene trap, 2,3-dimethylbutadiene, again suggesting that the nitrogen fragment is transferred in the coordination sphere of the metal.
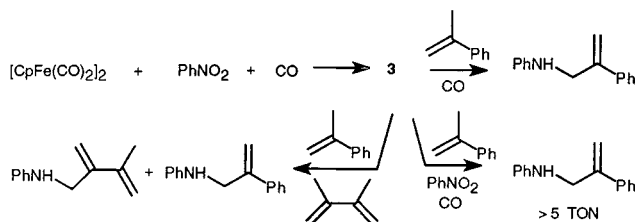
Scheme 1

In summary, $[CpFe(CO)_2]_2$ has been found to be an effective catalyst for the regioselective allylic amination of olefins by nitroarenes. It is significant that iron-catalyzed reactions involving nitroorganics and CO are rare.[15] Moreover, the differing chemoselectivity and trapping results between the present system and the $Ru_3(CO)_{12}/\alpha$-diimine-catalyzed amina-tions[8]** suggests the involvement of distinctly different active aminating agents. Further insight into the mechanism of this new catalytic amination process, including the nature of the active iron species involved, awaits the results of studies in progress.

Notes and references

‡ *General procedure*: $[CpFe(CO)_2]_2$ (0.15 mmol), nitrobenzene (2.9 mmol), olefin (3.8 mmol) and dioxane (10 ml) were placed in the glass liner of a stainless steel autoclave under nitrogen. The autoclave was charged with CO (900–1000 psi) and then heated at 160–180 °C for 22–24 h, during which time aliquots were withdrawn *via* dip tube for GC analysis. The autoclave was cooled, the solution was transferred to a Schlenk tube, and the volatiles were removed *in vacuo*. The residue was triturated with light petroleum–Et$_2$O. The insoluble residue contained the *N,N*-diaryl ureas. The

extracts were chromatographed on silica gel using light petroleum–Et$_2$O as eluent to afford the allyl amine. New compounds were characterized by NMR and MS analysis.

§ Small amounts of aryl amine (1–20%), azoarene (1–5%), and azoxyarene (1–5%) were also detected by GC–MS analysis. Non-volatile *N,N*-diaryl urea by-products were isolated by crystallization/chromatography.

¶ The hetero-Diels–Alder adduct was shown to be stable under the conditions of the catalytic reaction.

‖ *Selected data* for **3**: ν_{max}(KBr)/cm^{-1} 2033 and 1965; EPR (CH$_2$Cl$_2$)/G 3525 (bs); *m/z* (FAB) 628, 471, 396, 342, 288, 195; the elemental analysis of **3**, while indicating the presence of C, H, N and Fe, suggests contamination by an organic impurity.

** In the $Ru_3(CO)_{12}$/diimine-catalyzed reactions, aryl amines are the major byproducts (ref. 8) and amination in the presence of dimethylbutadiene affords substantial quantities of the hetero-Diels–Alder adduct. F. Ragaini and S. Cenini, personal communication, 1998.

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