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Photoassisted, iron-catalyzed allylic amination of olefins with nitroarenes

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Abstract—Olefins react with nitroarenes and carbon monoxide photochemically in the presence of $[Cp^*Fe(CO)_2]_2$ ($Cp^* = \eta^5$-C_5Me_5) to produce *N*-aryl-*N*-allyl amines in moderate to good yields. Unsymmetrical olefins react highly regioselectively with *N*-functionalization at the less substituted vinylic carbon. Mechanistic probes using 2′-nitrobiphenyl, 2,3-dimethylbutadiene and nitrosobenzene suggest that neither aryl nitrenes nor nitrosoarenes are the active aminating agents in these reactions. © 2002 Elsevier Science Ltd. All rights reserved.

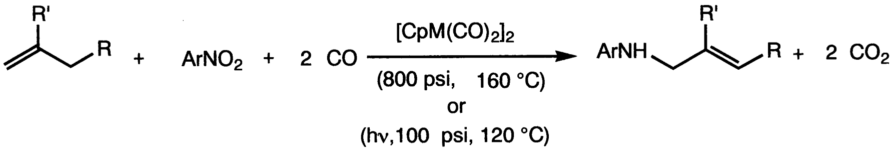
1. Introduction

The direct synthesis of allyl amines from olefins is an attractive goal since these compounds are both versatile synthetic intermediates[1] and valuable end products[2] but their preparation typically involves nucleophilic substitution of allylic electrophiles which can suffer from poor regioselectivity.[3] The alkene to allyl amine transformation has been accomplished stoichiometrically with group 16 imido compounds ($R'N{=}X{=}NR'$; $X =$ S,[4] Se[5]) as aminating agents, which display moderate regioselectively for retention of the position of unsaturation. Ene reactions of azo-,[6] nitroso-[7] and *N*-sulfinylcarbamate[8] derivatives display high regioselectivity with double bond migration but require additional N–N or N–O reduction steps to produce the allyl amines.

We and others have investigated metal-catalyzed allylic nitrogenation reactions which produce amines directly from olefins and with exceptional regioselectivity. Initially, molybdenum[9] and iron[10]-catalyzed reactions of olefins with aryl hydroxylamines were developed which proceed regioselectively with *N*-functionalization at the less substituted olefinic carbon. Recently, metal-promoted allylic aminations using the more readily available nitroarenes as aminating agents, carbon monoxide as reductant, and $Ru_3(CO)_{12}$/diimine[11] or $[Cp(^*)Fe(CO)_2]_2$[12] as catalysts have been discovered (Eq. (1)); the latter catalyst system also displays high ene reaction-type regioselectivity. Although these reactions employ neutral conditions, their high operating temperature and pressure (150–200°C, 25–50 atm) are disadvantages that could their limit widespread utilization. We describe herein *photoassisted* nitroarene-based allylic aminations which proceed efficiently under much milder conditions, allowing the reactions to be carried out conveniently in glass reaction vessels. The results of preliminary mechanistic probes are also presented.

2. Results and discussion

While mechanistic studies of the thermal, iron-catalyzed process are ongoing, we suspected that either CO dissociation or homolysis of the Fe–Fe bond could be important steps in generating the catalytically active



(1)

$[CpFe(CO)_2]_2$ (=Fp_2,**1a**); $[(C_5Me_5)Fe(CO)_2]_2$ (=Fp^*_2,**1b**); $[(C_5Me_5)Ru(CO)_2]$, (=Rp^*_2,**1c**)

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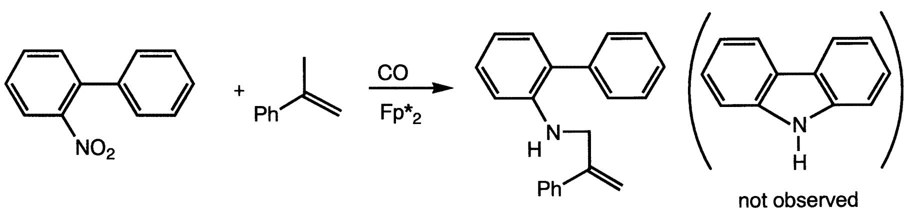
species, either of which should be promoted photochemically.[13] Indeed, experiments revealed that near UV irradiation (>300 nm) of dioxane solutions containing α-methyl styrene, nitrobenzene and dinuclear complexes **1a**–**c** (10 mol%) at 80–120°C under 3–6 atm of CO in a Fisher–Porter bottle[14] produced the corresponding allyl amine (R′ = Ph, R = H) with the Cp*–iron complex **1b**[15] being the most effective (Table 1). Variable quantities of aniline, azo- and azoxybenzene were formed as byproducts. No allyl amine was formed in the absence of CO or catalyst.

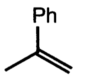
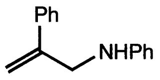
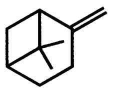
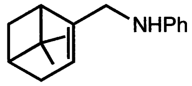
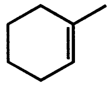
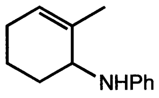
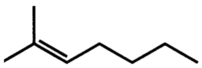
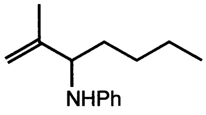
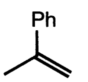
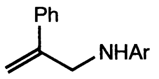
$[Cp^*Fe(CO)_2]_2$ (**1b**) was then employed as the catalyst to survey the scope and selectivity of the photoinduced amination with a representative set of olefins and nitroarenes.[16] The following features of these reactions are illustrated in Table 1: (1) acyclic trisubstituted and 1,1-disubstituted olefins react most efficiently; (2) unsymmetrical olefins react with excellent regioselectivity, with *N*-incorporation occurring at the less substituted olefinic carbon; and (3) nitrobenzene and electron deficient nitroarenes give the highest yields. The yields and the reactivity and selectivity features of these photoassisted reactions are comparable to those observed for the thermal reactions catalyzed by **1b**.

The similar reactivity/selectivity features of the thermal[12] and photoassisted reactions catalyzed by **1b** suggest the intermediacy of a common aminating species. To address this issue trapping experiments were conducted to assess the role of reactive organonitrogen and organoiron species in the reactions. First, irradiation of 2-nitrobiphenyl with α-methyl styrene under catalytic conditions produced the corresponding *N*-biphenyl-*N*-allyl amine and 2-biphenylamine but no carbazole, which rules against the intervention of a free aryl nitrene intermediate (Eq. (2)).[17] To test for the intermediacy of nitrosobenzene, a proven enophile,[7c–e] the amination of α-methyl styrene was conducted in the presence of 2,3-dimethylbutadiene, which can trap nitrosobenzene in a facile Diels–Alder reaction.[18] The allyl amines derived from the olefin and diene were produced along with a substantial amount of *N*-phenyl-3,4-dimethylpyrrole, but none of the Diels–Alder adduct (Eq. (3)). While this pyrrole could derive from photoinduced dehydration of the adduct from the diene and free nitrosobenzene,[19]



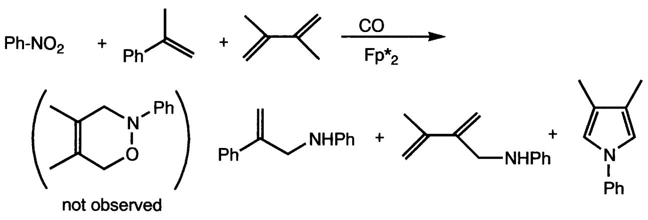
(2)

Table 1. Photoassisted, catalytic allylic amination by nitroarenes

Alkene	Nitroarene	Catalyst[a]	Allyl Amine	Yield, %[b]
	$PhNO_2$	Fp^*_2		63 (42)
		Fp_2		12
		Rp^*_2		34
	$PhNO_2$	Fp^*_2		35
	$PhNO_2$	Fp^*_2		11
	$PhNO_2$	Fp^*_2		73
	$4\text{-}ClC_6H_5NO_2$	Fp^*_2		30
	$4\text{-}CF_3C_6H_4NO_2$	Fp^*_2		52
	$C_6F_5NO_2$	Fp^*_2		100(83)

[a] $Fp^*_2 = [(C_5Me_5)Fe(CO)_2]_2$; $Fp_2 = [CpFe(CO)_2]_2$; $Rp^*_2 = [(C_5Me_5)Ru(CO)_2]_2$

[b] G.C. yield using sensitivity factor vs. naphthalene internal standard; (isolated yield)



(3)

when a dioxane solution of PhNO, α-methylstyrene and complex **1b** were irradiated under the usual conditions little of the allyl amine (<5%) was detected. This finding argues against the intermediacy of free nitrosoarenes in the reactions catalyzed by **1b** and suggests that the pyrrole byproduct above does not arise from free PhNO.

3. Conclusions

The photoassisted allylic amination of olefins by nitroarenes catalyzed by $[Cp^*Fe(CO)_2]_2$ (**1b**) thus provides a direct, regioselective and convenient route to *N*-aryl-*N*-allyl amines. Further studies of the synthetic utilization and mechanism of these reactions are in progress.

Acknowledgements

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14. Fisher–Porter (thick-walled glass) bottles can be obtained from Andrews Glass Co. A convenient head for introduction of gaseous reactants has been described by L. Messerle in *A.C.S. Symp. Ser.* **1987**, *357* (Experimental Organometallic Chemistry), pp. 198–203.

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16. *Experimental*. A 125 mL Pyrex Fisher–Porter bottle (Ref. 14) was charged with 6.15 mmol of olefin, 1.17 mmol of nitroarene, 0.11 mmol of $[Cp^*Fe(CO)_2]_2$ and 10 mL of dry dioxane; runs analyzed by GC contained 0.15 mmol of naphthalene as an internal standard. After addition of a magnetic stirring bar, the head (with attached gauge, inlet valve and pressure relief valve) was attached and the vessel was purged three times with carbon monoxide (*toxic*) in an efficient fume hood. The vessel was pressurized with 100 psi of CO, immersed in a preheated oil bath at 120°C, and then irradiated while stirring in a Rayonett photoreactor with 300 or 350 nm lamps (12×20 W) or with a 400 W Hg vapor lamp for 9–10 h. The vessel was allowed to cool and then was vented (*toxic CO*) in the fume hood. Most of the iron-containing material was precipitated by addition of hexane. Filtration through a plug of silica provided solution samples for GC and GC/MS analysis. Products were isolated by concentrating the hexane/dioxane solution and then chromatographing over neutral alumina, the allyl amines being eluted with 1:10 hexane/ether. The products were identified by comparison of their NMR and mass spectra and GC retention times with those of authentic samples prepared previously (Refs. 9, 10 and 12).
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