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Iron Lewis Acid Catalyzed Reactions of Phenyldiazomethane and Olefins: Formation of Cyclopropanes with Very High *Cis* Selectivity

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Abstract: The iron Lewis acid, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+$ (1) catalyzes the cyclopropanation reaction of phenyldiazomethane with olefins to provide *cis* cyclopropanes in high selectivity.

The tungsten benzylidene complex, $(CO)_5W{=}CHPh$[1] and the iron benzylidene complexes, $Cp(CO)(L)Fe^+{=}CHPh$ (L= CO, PR_3),[2] have been found to be effective in transferring their carbene ligands to alkenes to form a wide variety of phenyl-substituted cyclopropanes. Transfer frequently occurs with nearly exclusive formation of the sterically more crowded, thermodynamically less stable, *cis* isomer of cyclopropane. But all of the reactions involving metal benzylidene complex reported to date have been stoichiometric reactions.[3] Herein, we would like to report the first catalytic cyclopropanation reaction of phenyldiazomethane with olefins by iron Lewis acid **1** to provide cyclopropanes with extremely high *cis* selectivity.[4]

The iron Lewis acid $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+BF_4^-$ (1) was synthesized in high yield by protonation of the known methyl complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$.[5] Normally, less than one equivalent of $HBF_4{:}OEt_2$ was used for the protonation reaction, and the acid 1 was recrystallized many times from CH_2Cl_2/THF to insure that no HBF_4 was left as an impurity to contaminate the reaction. The results of the Lewis acid catalyzed cyclopropanation of phenyldiazomethane with olefins are summarized in Table 1. With 10 mol% catalyst, styrene gave an excellent yield of cyclopropanation (80%) with phenyldiazomethane. The most important aspect of this reaction was the stereoselectivity; the reaction gave 96% *cis* cyclopropanation. With *p*-methylstyrene, phenyldiazomethane gave 51% of all *cis* cyclopropane **4b**. The use of cyclopentene gave 97% endo cyclopropanation in 25% yield. The trisubstituted olefin, 2-methyl-2-butene, also reacted with phenyldiazomethane to provide all *cis* cyclopropanation. Vinyl acetate also yielded

51% of all *cis* cyclopropanation. To our knowledge, these are first examples of overwhelming *cis* preference in these cyclopropanation reactions under catalytic conditions. The unoptimized isolated yields of cyclopropanes are much better than earlier reported GC yields from catalytic reactions of the same olefins with phenyldiazomethane.[6]

Table 1: Isolated yields of cyclopropanes from reactions of phenyldiazomethane with olefins catalyzed by Iron Lewis acid, $(\eta^5\text{-}C_5H_5)Fe^+(CO)_2(THF)BF_4^-$, **1**.[a]

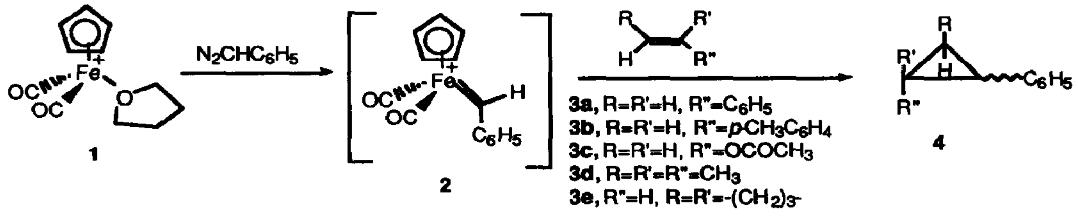
Olefin[b]	Temp	Time (hr)	Yield[c,d] (%)	*Cis/Trans*[e]	*Cis/Trans* From Stoichiometric Reactions[f]
styrene	RT	12	80	96/4	>100/1
p-methylstyrene	RT	12	51	all cis	------
vinylacetate	RT	12	51	all cis	-----
cyclopentene[g]	RT	12	25	97/3[h]	>200/1[h]
2-methyl-2-butene[g]	RT	12	20	all cis	>50/1

[a] 10 mole % catalyst was used. [b] 5 equivalents of olefin were used unless otherwise stated. [c] Yields were based upon phenyldiazomethane. [d] 7-25% of *cis/trans* stilbenes were isolated from the reaction. In addition, 3-16% of azine along with an unidentified product were also isolated. [e] Ratios were determined by GC and/or ^{1}H-NMR. [f] Reactions were performed at -78°C (ref. 2a). [g] 10 equivalents were used. [h] endo/exo

In a typical reaction, the catalyst was dissolved in methylene chloride under nitrogen. To the stirred solution, the appropriate amounts of olefin were added, and phenyldiazomethane was added slowly over a period of 2-4 hrs at room temperature. After stirring overnight, the solution was filtered through a plug of silica with ethyl ether as the eluent. The solvent was removed and the products were isolated by column chromatography. The ratio of isomers were determined by GC and/or by ^{1}H-NMR.[6]

The reaction of phenyldiazomethane with Lewis acid **1** was studied by variable temperature ^{1}H-NMR spectroscopy in order to observe any characteristic absorptions of the iron carbene complex **2** (Scheme I).[7] No characteristic absorption for the iron carbene complex **2**[8] was observed. However, formation of the carbene dimers, *cis/trans* stilbenes[9] and observation of *cis* selectivity in the cylopropane products[10] led us to suggest that the iron carbene complex **2** is an intermediate in our cyclopropanation reactions.

***Scheme I**: Iron Lewis acid **1** catalyzed cyclopropanation reactions*



In summary, the discovery of the iron Lewis acid catalyzed cyclopropanation is important in many regards. The iron Lewis acid is relatively inexpensive, readily synthesized, and provides the first example of catalytic cyclopropanation involving an iron benzylidene carbene complex with very high *cis* selectivity. The mechanistic details of this catalytic reaction are currently under investigation.

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(4) Recently, we reported the iron Lewis acid catalyzed cyclopropanation of ethyl diazoacetate with olefins: Seitz, W. J.; Saha, A. K.; Casper, D.; Hossain, M. M. *Tetrahedron Lett.* **1992,** *33,* 7755 and Seitz, W. J.; Saha, A. K.; Hossain, M. M. *Organometallics* **1993,** *12,* 2604.

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(7) The α-hydrogen of the iron carbene, $Cp(CO)_2Fe^+{=}CHPh$ (**2**) exhibited absorption at 16.86 ppm: see ref. 2b.

(8) It is possible that the concentration of the carbene complex **2** was too low to be observed by ^{1}H-NMR or it could be that the carbene complex **2**, as it forms, reacts with additional diazo compound to yield *cis/trans* stilbenes.

(9) The formation of *cis/trans* stilbenes is strong indirect proof of a metal carbene intermediate: (a) Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1972**, *23*, 2277. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

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