

# Catalytic Photodefluorination of Perfluoroalkanes to Perfluoroalkenes with a Ferrocene Photosensitizer

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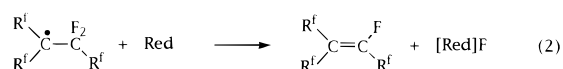
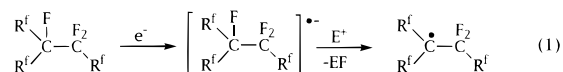
Perfluoroalkenes are obtained from perfluoroalkanes by photoinduced electron transfer from an organometallic photosensitizer, decamethylferrocene, in the polar solvent thf. In the presence of Zn, the reaction becomes catalytic in ferrocene because the decamethylferrocenium product of the photolysis is reduced to the starting decamethylferrocene. Tertiary C–F bonds are the most reactive, and for example, perfluoro-1-methylcyclohexene is obtained from perfluoromethylcyclohexane with up to 110 turnovers and up to 12% conversion.

## Introduction

Fluoroalkanes are attractive targets for functionalization by C–F activation because the value added is far greater than in alkane activation and so more sophisticated approaches, such as might be provided by organometallic chemistry, could be commercially significant. Despite recent advances,<sup>1</sup> few such reactions are currently available. Important prior work, most notably by Richmond<sup>1b,e</sup> and by Pez,<sup>1f</sup> shows the reduction of perfluorodecalin is possible with strongly reducing organometallic species, such as Cp<sub>2</sub>ZrCl<sub>2</sub>/Mg<sup>1e</sup> (where Zr(III) is a plausible intermediate), CoCp<sub>2</sub>,<sup>1b</sup> or Na[Ph<sub>2</sub>CO].<sup>1f</sup> Turro has shown that perfluorodecalin reduction to the 9,10-alkene is possible with an organic photosensitizer.<sup>1h</sup> Other work may also involve electron transfer in the key step.<sup>1</sup> An important review<sup>1k</sup> has summarized all but the most recent work.

The fluoroalkane functionalization strategy we considered in designing the present system incorporates (i) electron transfer from a strong reducing agent to a fluoroalkane C–F σ\* level; (ii) the use of a polar medium,<sup>2</sup> required to stabilize charge separations in the transition state; and (iii) the presence of an electrophile, to remove fluoride ion from the resulting fluorocarbon radical anion. After fluoride loss, this procedure is expected to lead to a reactive fluorocarbon radical that could in principle undergo a number of useful functionalization reactions.<sup>3a</sup> The one seen in this work is

reduction to form the corresponding perfluoroalkenes, valuable intermediates in fluorocarbon chemistry.<sup>3</sup> Equations 1 and 2 (R<sup>f</sup> = fluoroalkyl; E<sup>+</sup> = electrophile; Red



= reductant) show the pathway as applied to a substrate of the type studied here, with a tertiary C–F bond adjacent to a secondary CF<sub>2</sub> group, where selective initial reduction at the tertiary site appears to occur. Prior to our work, on which a communication has appeared,<sup>1i</sup> few methods to obtain fluoroalkenes from the readily available saturated perfluoroalkanes had been found, although an organometallic method has been reported for the special case of perfluorodecalin,<sup>1h</sup> and elemental carbon is also effective at 400 °C.<sup>1j</sup>

Organometallic species seem promising candidates for achieving selective perfluoroalkane reduction, because their reduction potentials can be tuned over a wide range. With the strong reductants required to react with fluoroalkanes, the main problem seems to be avoiding unselective overreduction, ultimately giving carbon and fluoride, a process that is normally favored because the initial reduction products of a fluoroalkane, such as a fluoroalkene, are known<sup>4</sup> to be much more reactive than the starting material. By tuning the reduction potential, however, Marsella, Pez, and co-workers<sup>1f</sup> were able to achieve selective stoichiometric fluoroalkane reduction. As will appear below, a similar situation may apply in the present work.

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(2) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: Cambridge, U.K., 1995; Chapter 1, p 10.

(3) (a) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: 1973. (b) Fokin, A. V.; Kolomiets, A. F.; Vasil'ev, N. V. *Russ. Chem. Rev.* **1984**, *53*, 238. (c) Bryce, M. R.; Chambers, R. D.; Kirk, J. R. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1391. (d) Kolenko, I. P.; Filyakova, T. I.; Zapelov, A. Y.; Lur'e, E. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2509.

(4) (a) Compare for example the electron affinities<sup>3a</sup> of hexafluorobenzene (C<sub>6</sub>F<sub>6</sub>), 0.51 eV, and perfluorocyclohexene (C<sub>6</sub>F<sub>10</sub>), >1.4 eV. (b) Chowdhury, S.; Grimsrud, E. P.; Heinis, T.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 3630. (c) Drzaic, P. S.; Marks, J.; Brauman, J. I. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: Orlando, FL, 1984; Vol 3, p 167.

A second potential problem is that the initial alkene or arene product is normally very sensitive to nucleophilic attack and if the medium is too nucleophilic, as in our previously described<sup>5</sup> Hg-photosensitized chemistry, which uses the strategy outlined above, the initial product can be converted in this way to substituted derivatives of limited general utility. This problem severely limits the choice of photosensitizer and has forced us to add a fourth element to the strategy: (iv) the use of nonnucleophilic conditions. In this paper, we report a photocatalytic ET system for defluorinating saturated perfluorocarbons in thf, using a nonnucleophilic organometallic photosensitizer,  $\text{FeCp}^*_2$ . Some of this work has appeared in a communication.<sup>6</sup>

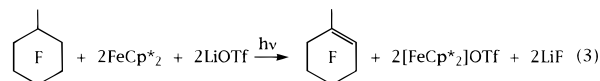
## Results and Discussion

**Choice of Reagents and Conditions.** The nonnucleophilic  $\text{FeCp}^*_2$  was chosen as the electron donor but the ground state is not sufficiently reducing to react with perfluorocarbons at room temperature; hence we need the enhanced reducing power of the excited state.<sup>7</sup> Not only is  $\text{FeCp}^*_2$  strictly nonnucleophilic in the ground state, excited state, and the oxidized form, but in addition, the expected final organometallic product,  $[\text{FeCp}^*_2]^+$ , can easily be reduced by zinc, allowing the reaction to be catalytic in ferrocene. Lithium trifluoromethanesulfonate was chosen as the electrophile because it was previously used successfully by Richmond.<sup>1b</sup> The relatively polar solvent thf was chosen because it can dissolve both the electron donor ( $\text{FeCp}^*_2$ ) and the electrophile ( $\text{Li}[\text{O}_3\text{SCF}_3]$ ). A potential disadvantage of thf is its tendency to act as an H atom donor to reactive radicals, but this problem does not seem to be significant under our low-conversion conditions. The fluoroalkanes were purified before use (see Experimental Section) to guard against the possibility that products arise from some reactive impurity in the starting alkane.

**Stoichiometric System.** In a stoichiometric version of the system, a solution of purified perfluoromethylcyclohexane,  $\text{FeCp}^*_2$ , and  $\text{Li}[\text{O}_3\text{SCF}_3]$  in dry thf was irradiated (medium-pressure 200-W Hg lamp, Pyrex vessel) under nitrogen. After 30 min, the color had already changed from the yellow of  $\text{FeCp}^*_2$  to the green of the dexamethylferricinium ion, suggesting ET had indeed occurred. Irradiation was continued for 17 h to complete the reaction and the mixture analyzed. A green solid product, obtained after removal first of the volatiles from the filtered product solution and second of the remaining  $[\text{FeCp}^*_2]$  with pentane, proved to be  $[\text{FeCp}^*_2][\text{O}_3\text{SCF}_3]$ . IR spectroscopy showed absorption bands consistent with the presence of  $\text{CF}_3$ ,  $\text{SO}_3$ , and  $\text{CH}_3$  groups. MS (70 eV) showed a parent ion peak at  $m/e$  326, consistent with the presence of the  $\text{FeCp}^*_2^+$  fragment. UV spectroscopy showed absorption bands identical in position and intensity with those seen for the  $\text{FeCp}^*_2^+$  ion.<sup>8</sup>

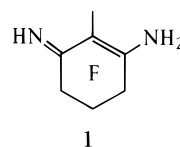
The volatile fraction from the reaction consisted of a thf solution of the perfluoroalkane and 1-perfluoro-

methylcyclohexene, as shown by the appearance of a new UV band at 262 nm ( $\epsilon = 17\,000$ ) in the UV spectrum and of the known characteristic  $^{19}\text{F}$  NMR resonances<sup>9</sup> of the alkene.



Using only a stoichiometric amount of perfluoromethylcyclohexane in order to try to maximize conversions, no perfluoroalkene was formed, presumably because overreduction occurs in this situation. Examination of the volatile product fraction by  $^{19}\text{F}$  NMR showed that the resonances of the perfluoromethylcyclohexane starting material were entirely absent. In addition, this fraction also failed to react with  $\text{NH}_3$ , and no perfluoroaromatic products were detected by GC/MS. Only with a large excess of perfluoroalkane can the desired perfluoroalkene be formed, presumably because the overreduction problem is only successfully avoided at low conversion.

**Perfluoroalkene Derivatization.** At the low conversions required to achieve adequate selectivity, isolation of the dilute alkene as a pure material proved impossible because of the large excess of perfluoroalkane present, but we were able to use the thf solution of the product mixture directly for the subsequent synthesis and isolation of perfluoroalkene derivatives since the perfluoroalkane itself does not react under these conditions. The model case of 1-perfluoromethylcyclohexene was taken as an example of perfluoroalkene functionalization; treatment of the reaction mixture from the photochemical step with  $\text{NH}_3$  (1 atm, 10 mL/min, 60 min) led to the formation of  $\text{NH}_4\text{F}$  and the known amine **1** (92% based on alkene). This amine has physical



properties very different from those of the starting alkane and could readily be isolated and purified from the mixed solvent in almost quantitative yield. This amine was previously synthesized<sup>10</sup> from the pure alkene by the same route. The pathway proposed for this transformation, involving  $\text{NH}_3$  addition/HF elimination steps, is consistent with the known chemistry of perfluoroalkenes. Purification of **1** proved possible by either chromatography (TLC on silica gel,  $\text{CH}_2\text{Cl}_2$  eluent,  $R_f = 0.6$ ) or recrystallization from  $\text{CCl}_4$ ; both yielded pure amine, **1**.

Amine **1** was identified by comparison with literature data,<sup>10</sup> in particular the mp (obsd, 99–100 °C; lit., 101 °C) and the UV spectrum (obsd (EtOH), 275 nm; lit., 275 nm) matched those of authentic **1**. More convincing, perhaps, were the other spectral data. The IR spectrum

(5) Burdeniuc, J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 10119.

(6) Burdeniuc, J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2525.

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(8) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

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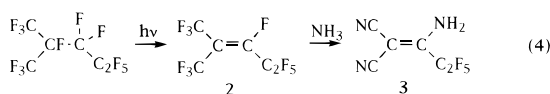
(10) (a) Carter, P. A.; Patrick, C. R.; Tatlow, J. C. *J. Fluorine Chem.* **1982**, *21*, 407. (b) Doyle, A. M.; Pedler, A. E. *J. Chem. Soc. C* **1971**, 282.

showed the presence of a C=C group ( $\nu(\text{C}=\text{C}) = 1676 \text{ cm}^{-1}$ ), an  $-\text{NH}_2$  group ( $\nu(\text{NH}_2) = 3505, 3345 \text{ cm}^{-1}$ ) and C-F bonds ( $\nu(\text{C}-\text{F}) = 1268, 1096 \text{ cm}^{-1}$ ). The resonances at  $-57.8, -117.9, -123.0,$  and  $-136.6 \text{ ppm}$  in the  $^{19}\text{F}$  NMR spectrum were assigned to the  $-\text{CF}_3$  and three  $-\text{CF}_2$  groups of **1**. The MS fragmentation pattern showed a mass peak of  $m/e = 286$  as well as peaks at 267 and 186 indicating the loss of F and  $\text{C}_2\text{F}_4$ , as expected for **1**. The  $-\text{NH}_2$  and  $=\text{NH}$  groups resonated in the  $^1\text{H}$  NMR spectrum at 5.75 and 10.5 ppm, respectively.

**Catalytic System.** We verified that a sample of the ferricinium salt is rapidly and quantitatively reduced by granular Zn in thf to give  $\text{FeCp}^*_2$ . This meant that the use of zinc in the photolytic system allowed us to employ ferrocene as a catalyst in the reduction of the perfluoroalkane, although photons are still required to drive the ET process. Irradiation of a mixture of perfluoromethylcyclohexane,  $\text{FeCp}^*_2$ , and  $\text{Li}[\text{O}_3\text{SCF}_3]$  in dry thf was carried out in the presence of granular Zn. After 40 h of irradiation, the liquid fraction was separated by vacuum distillation and collected in a liquid  $\text{N}_2$  trap. When a gentle flow of  $\text{NH}_3$  was passed through this solution, a white precipitate of  $\text{NH}_4\text{F}$  was immediately formed. The thf solution was removed in vacuo to yield a yellow solid from which amine **1** was purified as described above; assuming a quantitative yield, the amount of pure **1** obtained corresponded to 110 catalytic turnovers (3.9% conversion); 92% yield of **1** was found based on reacted perfluorocarbon, so the mass balance was satisfactory. No change in the reaction selectivity occurred on moving from stoichiometric to catalytic conditions, suggesting that the role of the zinc is limited to recycling the ferrocene.

It was possible to choose conditions to maximize the conversion by using 2.5 times as much  $\text{FeCp}^*_2$ . In this case, a 90% recovery of  $\text{FeCp}^*_2$  was effected from the products by prompt removal of the Zn and pentane extraction of the solid residue obtained after vacuum separation of the volatile fraction. This shows that the zinc does indeed efficiently reduce the ferricinium ion under the conditions of the reaction.

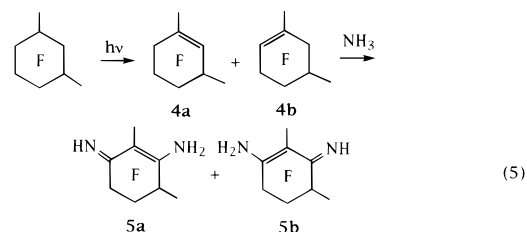
**Other Substrates.** Other substrates were examined under catalytic conditions to maximize the quantities of products formed. A linear perfluoroalkane, perfluoro-2-methylpentane, is also catalytically reduced (turnover (t.o.) 40) to the corresponding trisubstituted perfluoroalkene, as shown in eq 4. Perfluoro-2-methyl-2-pentene



(**2**) was identified in the resulting thf solution from the characteristic UV and  $^{19}\text{F}$  NMR spectra by comparison with a commercial sample of **2** (Aldrich). Isolation of the alkene again proved impossible, but treatment of the product with  $\text{NH}_3$  under conditions similar to those described above gave the isolable aminodinitrile **3**. The same dinitrile was previously made<sup>5</sup> in our laboratory by a Hg-photosensitized reaction with  $\text{NH}_3$  and so an authentic product was available for comparison. A pathway similar to that proposed for the formation of amine **1** is expected to apply. Unlike the case of the reaction of the cyclic alkene that gives the amine **1**,

however, the  $\text{C}(\text{CF}_3)_2$  groups also participate in the linear case, to give a  $\text{C}(\text{CN})_2$  group in the product.

A second cyclic species was also studied. Perfluoro-1,3-dimethylcyclohexane was irradiated in the presence of  $\text{FeCp}^*_2/\text{LiO}_3\text{SCF}_3/\text{Zn}$  to give a mixture (**4**) of alkene products which were again not isolable.  $^{19}\text{F}$  NMR analysis of the thf fraction showed new resonances at  $-195.6, -148.71, -137.9, -125.0, -113.4, -87.15, -56.9$  and  $-57.0 \text{ ppm}$  together with other signals of smaller intensities. These data are consistent with the presence of two major perfluoroalkene isomers of structures **4a** and **4b**, which are reasonable by analogy with



the product of the  $\text{CF}_3\text{C}_6\text{F}_{11}$  case, but authentic materials were not available to confirm these proposals.

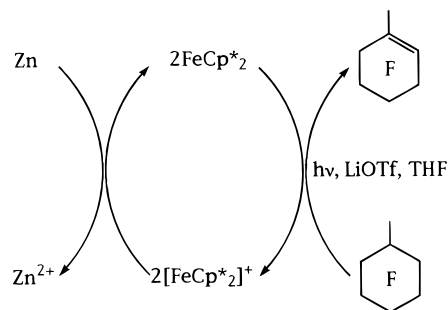
In this case, reaction of the products with ammonia as previously described gives the new isolable enamine **5**, in an amount that corresponds to t.o. = 60 of alkene being formed in the photochemical step. Enamine **5** is present as a mixture of isomers **5a** and **5b**, as indicated by the physical and spectral data. Each isomer showed almost identical retention time by GC and their separation by preparative TLC on silica gel was not possible, even though a wide range of solvent combinations was used. Nevertheless, we isolated **5** as a mixture by preparative TLC on silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent ( $R_f = 0.44$ ) and measured the spectral data. The compounds were identified as the enamines shown in eq 5. In particular, MS data show a parent ion peak at  $m/e = 336$  as well as peaks at  $m/e = 290$  and 186 which are consistent with the loss of  $\text{F}-\text{C}=\text{NH}$  and  $\text{C}_3\text{F}_6$ . IR spectroscopy showed absorption bands assigned to a C=C group ( $\nu(\text{C}=\text{C}) = 1652 \text{ cm}^{-1}$ ) and to  $-\text{NH}_2$  groups ( $\nu(\text{NH}_2) = 3570, 3448, 3350,$  and  $3180 \text{ cm}^{-1}$ ).  $^{19}\text{F}$  NMR resonances corresponding to four different  $-\text{CF}_3$  groups were observed at  $-57.0, -57.5, -70.4,$  and  $-74.2 \text{ ppm}$ . Moreover, resonances corresponding to fluorine bound to two different tertiary carbons were observed at  $-184.6$  and  $-184.9 \text{ ppm}$ . The  $-\text{NH}_2$  and  $=\text{NH}$  groups resonated in the  $^1\text{H}$  NMR spectrum at 5.7 and 10.6 ppm, respectively. These data are most consistent with the structures **5a** and **5b** shown in eq 5 for the enamine, which are in turn consistent with these enamines being formed from the precursor alkenes of structures **4a** and **4b** as suggested above.

**Mechanism.** No perfluoroalkane conversion at all was observed in attempted reactions of  $\text{CF}_3\text{C}_6\text{F}_{11}$  with the other ferrocenes,  $\text{FeCp}_2$ ,  $(\text{MeCp})_2\text{Fe}$ , and  $(\text{MeCO-Cp})_2\text{Fe}$ . The factor that differs in this series may be the reduction potential of the excited state. Table 1 shows that  $\text{FeCp}^*_2$  has a very low ground-state oxidation potential<sup>11</sup> and is the most strongly reducing of the ferrocenes studied, so the excited state may also show

(11) Togni, A. In *Ferrocenes: homogeneous catalysis, organic synthesis, materials science*; Togni, A., Hayashi, T., Eds.; VCH: New York, 1995; p 436.

**Table 1. Redox Potentials of Some Ferrocene Complexes**

compound	oxidation potential (V) <sup>a</sup>
Cp <sub>2</sub> Fe	+0.44
(MeCp) <sub>2</sub> Fe	+0.24
Cp* <sub>2</sub> Fe	+0.12
(C <sub>5</sub> Et <sub>5</sub> ) <sub>2</sub> Fe	-0.11
Cp* <sub>2</sub> Fe	-0.12

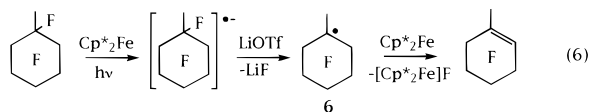
<sup>a</sup> Relative to SCE.**Scheme 1. Catalytic Cycle Proposed for the Title Reaction**

the same order of reducing power. These observations are consistent with ET being the key step. The data also suggest that in FeCp\*<sub>2</sub> we may have fortuitously tuned the excited-state reduction potential to that which just allows the reduction, where selectivity might be expected to be maximal, as previously found by Pez<sup>1f</sup>.

No reaction was observed in the absence of irradiation or of Li[O<sub>3</sub>SCF<sub>3</sub>], suggesting that the defluorination step requires electrophilic assistance. Use of a less polar medium, Et<sub>2</sub>O instead of thf, also fails, implying that solvation of the charge-separated intermediates and transition states may be important. Also consistent with an ET/fluoride abstraction mechanism is the fact that the tertiary CF bond is always found to be most reactive. Only one such bond is required for successful reaction, however, consistent with removal of the second fluoride by the route shown in Scheme 1.

We have previously reported that isolable 1:1 (or 2:2) molecular complexes are formed between ferrocenes and perfluoroarenes, as shown by X-ray crystallographic studies of [FeCp<sub>2</sub>]<sub>2</sub>{perfluorophenanthrene}<sub>2</sub> and [FeCp\*<sub>2</sub>]<sub>2</sub>{perfluorophenanthrene}.<sup>12</sup> In an attempt to detect a CT band of a possible weak complex between the ferrocene and the perfluoroalkane substrates, we have also measured the UV spectra of solutions of FeCp\*<sub>2</sub> and the perfluorocarbons in various solvents but without success. This makes it more likely that reaction occurred not via irradiation of a CT band but by direct excitation of the FeCp\*<sub>2</sub>, relying on the enhanced reducing power of photoexcited FeCp\*<sub>2</sub>.

A mechanism consistent with current data is shown in Scheme 1. The formation of the carbon radical **6** from the perfluoroalkane seems uncontroversial, but attempts to trap **6** with SO<sub>2</sub>, toluene, or dihydroanthracene were unsuccessful. This confirms our expectation that it would have a very short lifetime in solution under our conditions. Instead, it may react with a reductant in solution to give the product (eq 6). The



alternative possibility that it reacts with a second molecule of photoexcited ferrocene is unlikely because two species with short lifetimes would not be expected to survive long enough to find each other in solution. To distinguish which of the two possible reductants is in fact involved, ferrocene or thf, we carefully examined the stoichiometry of CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> reduction by Cp\*<sub>2</sub>Fe in the absence of Zn. A total of 2 (±0.1) mol of ferricinium ion were formed per mole of **1** recovered after amination, indicating that the ferrocene (eq 6) and not the thf was the reductant.

## Conclusions

In this paper, we illustrate a strategy for fluoroalkane functionalization that involves the following: (i) electron transfer from a strong reducing agent to the fluoroalkane; (ii) use of a polar medium, required to stabilize charge separations in the transition state; (iii) operating in the presence of a lithium salt as electrophile, to remove fluoride ion from the resulting fluorocarbon radical anion; and (iv) the use of nonnucleophilic conditions to prevent the product alkenes from being converted to other less desirable products. Perfluoroalkenes were obtained from perfluoroalkanes by photo-induced electron transfer from FeCp\*<sub>2</sub> in a polar solvent and in the presence of a fluoride acceptor such as Li[O<sub>3</sub>SCF<sub>3</sub>]. In the presence of Zn, the reaction becomes catalytic because the ferricinium product of the photolysis is reduced to the starting ferrocene. Tertiary C–F bonds are the most reactive, and trisubstituted perfluoroalkenes are therefore obtained from branched perfluoroalkanes, but only one such CF bond is needed, in contrast with another recently reported photoreaction involving an organic sensitizer,<sup>1h</sup> where two vicinal tertiary CF bonds are required.

## Experimental Section

Starting materials were used as received (Aldrich), except fluoroalkanes (TCI) which were purified as described below. The thf was distilled from Na[Ph<sub>2</sub>CO] solution.

**Purification of Perfluoroalkanes.** The perfluoroalkanes (5 mL) were treated with *n*-BuNH<sub>2</sub> (1 mL). After the insoluble perfluoroimines and ammonium salts were filtered, the material was washed with HCl (1M 10 mL) and water (3 × 20 mL), dried over anhydrous MgSO<sub>4</sub>, and distilled. The UV spectra of the resulting materials showed that unsaturated alkanes were completely absent.

**Formation and Amination of Perfluoromethyl-1-cyclohexene. (1) Stoichiometric Procedure.** FeCp\*<sub>2</sub> (0.1 g, 0.3 mmol) and LiO<sub>3</sub>SCF<sub>3</sub> (1.3 g, 8.3 mmol) were dissolved in dry thf (10 mL). Perfluoromethylcyclohexane (4.0 g, 11.4 mmol) was added and the mixture was photolyzed (17 h, Rayonet reactor, 1 medium-pressure Hanovia 200-W Hg lamp) under N<sub>2</sub> at room temperature in a Pyrex tube. The volatile fraction, removed under vacuum, was collected in a liquid N<sub>2</sub> cold trap. UV spectroscopy showed a strong absorption at λ = 262 (ε = 17 000) consistent with the presence of a fluoroalkene. The <sup>19</sup>F NMR spectrum was essentially

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identical to that reported<sup>9</sup> for perfluoro-1-methyl-1-cyclohexene: <sup>19</sup>F NMR  $\delta$  obsd -136.3 (CF<sub>2</sub>, 2F), -136.2 (CF<sub>2</sub>, 2F), -122.1 (CF<sub>2</sub>, 2F), -112.3 (CF, 1F), -112.0 (CF<sub>2</sub>, 2F), -61.1 (CF<sub>3</sub>, 3F); (lit.<sup>9</sup> -136.4 (CF<sub>2</sub>), -135.9 (CF<sub>2</sub>), -121.3 (CF<sub>2</sub>), -115.4 (C-F), -110.9 (CF<sub>2</sub>), -61.3 (CF<sub>3</sub>)).

A green residue, obtained on removal of the volatile fraction, was washed with dry pentane to remove FeCp\*<sub>2</sub> (40 mg, 0.12 mmol), with dry ether to remove LiO<sub>3</sub>SCF<sub>3</sub>, and recrystallized from EtOH to give [FeCp\*<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>] (0.088 g, 0.18 mmol). The characterization data were essentially identical to those for an authentic sample of [FeCp\*<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]: IR (NaCl film) 2919 (C-H), 2973 (C-H), 1479 (CH<sub>3</sub>), 1386 (CH<sub>3</sub>), 1138 (CF<sub>3</sub>), 1270 cm<sup>-1</sup> (CF<sub>3</sub>); MS (70 eV) 326; UV (EtOH) 208 (9083), 277 (13 800), 314 nm (8900). Two equivalents of FeCp\*<sub>2</sub> (0.18 mmol) were found by gravimetry to be consumed per equivalent of **1** (0.09 mmol) formed after reaction with NH<sub>3</sub>.

**(2) Regeneration of FeCp\*<sub>2</sub> Photosensitizer.** A suspension of [FeCp\*<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>] (0.064, 0.13 mmol) in dry thf (10 mL) was reduced with granular Zn (0.5 g, 7.6 mmol) under nitrogen. After 1 h, the green suspension gave a yellow solution and a white precipitate. The mixture was dried under vacuum and FeCp\*<sub>2</sub> (quant 0.043 g, 0.13 mmol) was then extracted with pentane and identified by comparison with authentic material (IR, NMR, anal.).

**(3) Catalytic Procedure.** The reaction described above with CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> (6 g, 17.14 mmol), FeCp\*<sub>2</sub> (2.0 mg, 6.1  $\mu$ mol), and LiO<sub>3</sub>SCF<sub>3</sub> (1.3 g, 8.3 mmol) in thf (30 mL) was repeated in the presence of granular zinc (0.5 g, 7.6 mmol). After a 17-h irradiation, a brown solution was obtained. The volatile fraction, removed in vacuo and collected in a liquid N<sub>2</sub> trap, gave a solution with the same characteristics described above. FeCp\*<sub>2</sub> (0.083 g, 0.27 mmol, 90%) was recovered and compared with authentic material. A trace of an unidentified soluble purple material (0.01 g) was also found. The alkene reacts with NH<sub>3</sub> as above to give amine **1** (190 mg, 0.67 mmol, 96%, t.o. 110, conversion 3.9%).

Conditions maximizing conversion are as follows: CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> (4 g, 11.43 mmol), FeCp\*<sub>2</sub> (100 mg, 0.30 mmol), and LiO<sub>3</sub>SCF<sub>3</sub> (1.3 g, 8.3 mmol) in thf (30 mL), Zn (0.5 g, 7.6 mmol), and 19 h irradiation. Amine **1** was isolated as before (390 mg, 1.36 mmol, 96%, conversion 11.9%).

Ammonia (20 mL/min, 30 min, 1 atm) was passed through the solution of 1-perfluoromethyl-1-cyclohexene obtained as described above to give a precipitate of NH<sub>4</sub>F (0.14 g, 10.8 mmol), separated by filtration, and a yellow solution, evaporated in vacuo to give **1** (0.39 g, 92% based on reacted fluorocarbon). Compound **1** can be further purified by preparative TLC on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as eluent (*R*<sub>f</sub> = 0.6) or by recrystallization from CCl<sub>4</sub>. The characterization data were essentially identical with the available literature<sup>13</sup> data: MS (70 eV) obsd 286 (M<sup>+</sup>), 267 (M<sup>+</sup> - F), 186 (M<sup>+</sup> - C<sub>2</sub>F<sub>4</sub>), no literature data; <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  obsd 5.75 (2H), 10.5 (1H), no literature data; <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -57.8 (3F), -117.9 (2F), -123.0 (2F), -136.6 (2F), lit. (solvent not

reported), -56.9 (CF<sub>3</sub>), -117.3 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -136.8 (CF<sub>2</sub>); IR (NaCl neat film) obsd 3505 (N-H), 3345 (N-H), 1676 (C=C), 1611 (N-H), 1268 (C-F), 1096 cm<sup>-1</sup> (C-F); lit. (medium not reported), 3450 (N-H), 3270 (N-H), 1665 cm<sup>-1</sup> (C=C); UV(EtOH) obsd 275 ( $\epsilon$  = 21 800), lit.<sup>13</sup> 275 ( $\epsilon$  = 5500); mp, obsd 99–100 °C, lit.<sup>13</sup> 101 °C.

**Formation and Amination of Perfluoro-2-methyl-2-pentene. (1) Catalytic Procedure.** FeCp\*<sub>2</sub> (0.10 g, 0.30 mmol) was dissolved in 10 mL of dry thf together with lithium LiO<sub>3</sub>SCF<sub>3</sub> (1.30 g, 8.33 mmol) and zinc (5 g). An excess of perfluoro-2-methylpentane (4.0 g, 11.8 mmol) was added, and the mixture was photolyzed for 17 h. FeCp\*<sub>2</sub> was quantitatively recovered (0.10 g), and the liquid fraction containing the perfluoroolefin was separated as explained above. <sup>19</sup>F NMR spectroscopy of the thf solution showed new resonances at  $\delta$  -59.41 (s, br, 3F), -61.9 (m, 3F), -85.1 (s, 3F), -118.5 (dd, *J* = 17.1, 1F), and -98.8 (m, 2F) identical with those of an authentic (Aldrich Chemical Co.) sample of **2**. The thf solution of **2** reacted with NH<sub>3</sub> to yield NH<sub>4</sub>F (0.097 g, 2.62 mmol) and **3**. Compound **3** (54 mg, 0.26 mmol, 54% based on reacted fluorocarbon) was obtained pure by preparative TLC on silica gel using a mixture (95:5) CH<sub>2</sub>Cl<sub>2</sub>/thf as eluent (*R*<sub>f</sub> = 0.4, mp 201–202 °C) Its properties were identical with those of the authentic material available from a Hg photosensitized reaction.<sup>5</sup>

**(2) Defluorination and Amination of Perfluoro-1,3-dimethylcyclohexane.** FeCp\*<sub>2</sub> (0.10 g, 0.30 mmol) was dissolved in 10 mL of dry thf together with LiO<sub>3</sub>SCF<sub>3</sub> (1.3 g, 8.3 mmol) and Zn (0.5 g, 7.6 mmol). An excess of perfluoro-1,3-dimethylcyclohexane (4.0 g, 10.0 mmol) was added, the mixture photolyzed for 17 h, and a volatile fraction containing **4** was isolated as above; it showed <sup>19</sup>F NMR resonances at -195.6, -148.71, -137.9, -125.0, -113.4, -87.15, -56.9, and -57.0 ppm together with other signals of smaller intensities. Reaction of this mixture with ammonia at 0 °C gave NH<sub>4</sub>F (0.144 g, 3.89 mmol) and 0.52 g of a yellow oil containing two inseparable isomers with almost identical GC/MS retention times and identical mass peaks, *m/e* 336. The mixture **5** was therefore purified by preparative TLC on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent to give a yellow solid (*R*<sub>f</sub> = 0.44, 0.32 g, 0.95 mmol, 61% based on reacted fluorocarbon): MS (70 eV) 336 (M<sup>+</sup>), 317 (M<sup>+</sup> - F), 290 (M<sup>+</sup> - F - CNH), 186 (M<sup>+</sup> - C<sub>3</sub>F<sub>6</sub>), 166 (M<sup>+</sup> - C<sub>3</sub>F<sub>6</sub> - HF); IR (NaCl film) 3570 (N-H), 3448 (N-H), 3350 (N-H), 3180 (N-H), 1652 (C=C), 1614 (N-H), 1310 (C-F), 1266 (C-F), 1218 (C-F), 1133 cm<sup>-1</sup> (C-F); <sup>19</sup>F NMR (CCl<sub>2</sub>D<sub>2</sub>)  $\delta$  -57.0 (CF<sub>3</sub>, 3F), -57.5 (CF<sub>3</sub>, 3F), -70.4 (CF<sub>3</sub>, 3F), -74.2 (CF<sub>3</sub>, 3F), -106.1 (d, *J*<sub>FF</sub><sup>g</sup> = 290 Hz, 1F, CF<sub>2</sub>), -107.8 (d, *J*<sub>FF</sub><sup>g</sup> = 290 Hz, 1F, CF<sub>2</sub>), -115.6 (dCF bon, *J*<sub>FF</sub><sup>g</sup> = 297 Hz, 1F, CF<sub>2</sub>), -115.8 (d, *J*<sub>FF</sub><sup>g</sup> = 293 Hz, 1F, CF<sub>2</sub>), -119.8 (d, *J*<sub>FF</sub><sup>g</sup> = 290 Hz, 1F, CF<sub>2</sub>), -122.6 (d, *J*<sub>FF</sub><sup>g</sup> = 270 Hz, 1F, CF<sub>2</sub>), -123.0 (d, *J*<sub>FF</sub><sup>g</sup> = 290 Hz, 1F, CF<sub>2</sub>), -130.7 (d, *J*<sub>FF</sub><sup>g</sup> = 290 Hz, 1F, CF<sub>2</sub>), -184.6 (m, br, CF, 1F), -184.9 (m, br, CF, 1F); <sup>1</sup>H NMR (CCl<sub>2</sub>D<sub>2</sub>)  $\delta$  5.7 (br, 2H), 10.6 (br, 1H).

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