# Perfluoroalkane photodefluorination *via* mercury photosensitization: experimental and theoretical aspects†

**Juan Burdeniuc,**[‡,a] **Per E. M. Siegbahn***[,b] **and Robert H. Crabtree***[,a]

[a] *Department of Chemistry, Yale University, 225 Prospect St., New Haven, CT 06520-8107, USA*
[b] *Department of Physics, University of Stockholm, Box 6730, S-11385, Stockholm, Sweden*

Mercury photosensitization in the presence of $NH_3$ leads to partial defluorination and functionalization of a variety of perfluoroalkanes to give perfluoroalkyl imines, amines and nitriles. Poly(tetrafluoroethylene) (PTFE) can be surface-functionalized to give a robust hydrophilic surface by this method. Theoretical studies with DFT-B3LYP geometries and PCI-80 energies suggest the $[Hg^*(NH_3)_2]$ excited state complex may be involved as a key reactive intermediate. These studies show that while pure F-atom abstraction by the H atom is very slow, the highly reducing exciplex can give a net F-atom abstraction by a concerted electron transfer/fluoride ion back-transfer pathway, which has a very much lower activation barrier. Subsequent formation of perfluoroalkene is thought to be followed by nucleophilic attack by ammonia, which initiates an ammonia addition/HF elimination sequence leading to the final products.

Mercury photosensitization, pioneered by Hill[1] and Steacie[2] and their co-workers in the 1920s and 1930s, was most intensively studied in the 1940–1973 period.[3] This early work did not develop the synthetic aspects of the area and left several mechanistic questions unanswered, for example, exactly how excited state Hg (or Hg*) interacts with the substrate. Since 1985, we have been able to develop conditions[4,5] that are suitable for a wide series of transformations on a synthetically useful scale and involving most common classes of volatile organic compounds, leading to the functionalization of CH bonds, even those of methane.[6] In the last few years, Siegbahn[7a] has applied DFT quantum chemical methods to the mechanistic problem and has obtained details of the structure of the organometallic excited state complexes[7b] (exciplexes) involved when Hg* interacts with alkanes, alkenes and arenes, and in collaboration with us has suggested mechanistic pathways for the common Hg-sensitized reactions.

Under our conditions, a key feature of these reactions is their vapor pressure selectivity. Only volatile species undergo reaction, so when the products of a Hg-photosensitized reaction condense they are protected from further reaction. This prevents overoxidation of the alkane; for example, cyclohexane gives bicyclohexyl and not higher oligomers, even though bicyclohexyl is intrinsically more reactive than cyclohexane, having two tertiary C—H bonds.[4a] This aspect of the reaction has also been used to good effect in the work to be described here.

Fluoroalkane functionalization by C—F activation is a field of current interest,[8] but few general methods are yet known. Prior work has involved thermal electron transfer (ET) from strongly reducing organometallic species[8b,e,f] and photoreduction to an alkene is known with an organic[8h] or an organometallic[9] photosensitizer.

## Experimental Results and Discussion

### Initial strategy

Since HF has a much higher bond energy (136 kcal $mol^{-1}$) than typical aliphatic C—F bonds (*ca.* 120 kcal $mol^{-1}$), the abstraction of HF by H atoms from a fluoroalkane [eqn. (1)] seemed a reasonable target, especially because the analogous reaction of H atoms with alkane C—H bonds [eqn. (2)] is very efficient:

$$R^f{-}F + H\cdot \rightarrow R^{f\cdot} + H{-}F \tag{1}$$

$$R{-}H + H\cdot \rightarrow R\cdot + H_2 \tag{2}$$

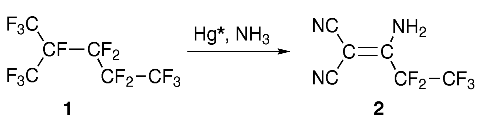
where R is an alkyl and $R^f$ is a perfluoroalkyl.

Hg photosensitization of $H_2$ is a copious source of H atoms,[5] but we find that fluoroalkanes such as perfluoro-2-methylpentane are entirely unaffected under these conditions, so contrary to our original expectations, eqn. (1) is not efficient. To check that H atoms are indeed being generated we showed that in a mixture of perfluoroalkane and cyclohexane, the alkane indeed undergoes the expected H-atom-initiated alkene dimerization to bicyclohexyl, but the pefluoroalkane is unaffected. In the theory section below, we will show that the HF abstraction of eqn. (1) is in fact a very high barrier process and is not expected to occur at a significant rate.

Thinking that the presence of a base might facilitate reaction (1), we added $NH_3$ to the reaction mixture and found that aminated fluorocarbons are now produced. From the mechanistic and quantum chemical studies discussed below it became clear that the true mechanism is probably net F-atom abstraction by concerted electron transfer/fluoride ion back-transfer.

### Photoamination reactions

Purified $(CF_3)_2CFCF_2CF_2CF_3$ (**1**) was irradiated at 40° in a quartz tube for 19 h with 254 nm light from a low pressure Hg lamp, with a drop of Hg and with a flow of $NH_3$ gas (2 mL $min^{-1}$). The major products [eqn. (3)] were $NH_4F$ and the dinitrile **2**,



(3)

formed in good chemical (95%) and acceptable quantum yield (0.02) and isolated by preparative TLC chromatography on silica with $CH_2Cl_2$–THF (95 : 5 v/v) as eluent. Being involatile under the reaction conditions, **2** is protected from over-

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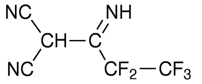
† Non-SI units employed: eV ≈ $1.60 \times 10^{-19}$ J; kcal $mol^{-1} \approx 4.18 \times 10^3$ J $mol^{-1}$; atm ≈ $10^5$ Pa.

‡ Present address: Air Products Corporation, Corporate Science Center, Allentown, PA 18105, USA.

reduction. Dinitrile **2** was identified by comparison with literature data[10] [**2**: mp obsd., 201–202 °C; lit., 201–203 °C; UV (EtOH) obsd., 287 nm ($\varepsilon = 12\,500$ dm$^3$ mol$^{-1}$ cm$^{-1}$); lit., 287 nm ($\varepsilon = 13\,750$ dm$^3$ mol$^{-1}$ cm$^{-1}$)]. In addition, **2** has a mass of 211 as determined by GC-MS and shows a fragmentation pattern consistent with the proposed structure, notably the presence of strong peaks at $m/z = 185$ and 142, corresponding to loss of CN and $CF_3$, respectively. The $C_2F_5$ group resonated in the $^{19}F$ NMR spectrum at $-80.7$ and $-115.3$ ppm.

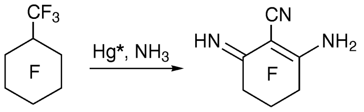
The enamine formulation (**2**) is preferred over the imine tautomer (**3**) because the IR spectrum shows two N—H stretching vibrations corresponding to an $—NH_2$ group [$\nu(NH_2) = 3312$, 3181 cm$^{-1}$], as well as the $—C{\equiv}N$ group [$\nu(CN) = 2207$ cm$^{-1}$].



**3**

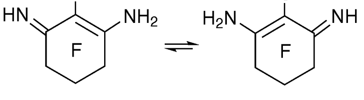
In addition, the $^1H$ NMR spectrum showed a resonance at 1.26 ppm, consistent with the presence of the $—NH_2$ group, and no resonances in the range 8 to 11 ppm, indicating the absence of =NH groups. The preference for **2** may be the result of the additional conjugation present in **2** and not in **3**. The physical data previously reported[11] for **2**, obtained from $NaCH(CN)_2$ and $C_2F_5CN$, was closely comparable with our data, confirming the identification.

Other fluorocarbons behaved similarly. Reaction of **4** under Hg*–$NH_3$ conditions gives $NH_4F$ and the nitrile **5** [eqn. (4), chemical yield: 85%, quantum yield: 0.04].



(4)

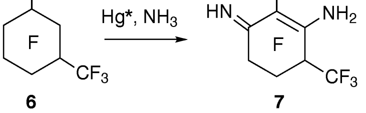
The fluoroorganic products were extracted with $CH_2Cl_2$ and purified by preparative TLC on silica gel, using $CH_2Cl_2$–THF (95 : 5) as eluent and identified independently and by comparison with a literature report[11a] in which **5** was prepared from aq. $NH_3$ and perfluoro-1-nitrile-1-cyclohexene. The GC-MS shows a parent ion peak at 243 Da and peaks at $m/z = 216$ and 197, indicating the loss of HCN and F, respectively, which is consistent with the proposed structure. Three inequivalent $—CF_2—$ groups resonated at $-117.9$, $-121.3$ and $-136.1$ ppm in the $^{19}F$ NMR spectrum. The IR (neat film) spectrum showed the presence of a C≡N group [obsd., $\nu(C{\equiv}N) = 2224$ cm$^{-1}$, lit., 2220 cm$^{-1}$], a C=N group [obsd., $\nu(C{=}N) = 1659$ cm$^{-1}$, lit., 1660 cm$^{-1}$] and an $—NH_2$ group [$\nu(NH_2) = 3431$, 3244 cm$^{-1}$]. When dissolved in $CD_3OD$, the nitrile $^{19}F$ NMR resonances (dry $CH_2Cl_2$) of **5** at $-117.93$ and $-121.3$ ppm were replaced by a single broad resonance at $-122.3$ ppm, while the other $—CF_2—$ resonance at $-136.1$ ppm remained unchanged. This was ascribed to a rapid amino–imino tautomerism [eqn. (5)].



(5)

The GC-MS of the recovered nitrile **5** had a parent ion $M^+$ peak at 246, indicating H/D exchange of three protons.

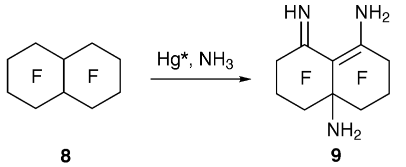
Perfluoro-1,3-dimethylcyclohexane (**6**) also reacts with Hg*–$NH_3$ to give nitrile **7** (chemical yield: 30%, quantum yield: 0.01) as shown in eqn. (6).



(6)

This compound shows a GC-MS parent ion peak of 275 Da and other major peaks at $m/z = 69$ and 100, corresponding to $CF_3$ and $C_2F_4$ groups, respectively. Five resonances were observed in the $^{19}F$ NMR spectrum, one assigned to a $—CF_3$ group at $-78.18$ ppm and the other four at $-111.3$, $-122.12$, $-127.25$ and $-139.0$ ppm correspond to a set of five inequivalent fluorines with one pair overlapped. Tautomer equilibration analogous to eqn. (5) is therefore likely to be fast on the NMR timescale in this case; alternatively, the presence of one rigid tautomer cannot be excluded. The IR spectrum showed the C=NH groups [$\nu(C{=}NH) = 1647$ cm$^{-1}$], the $—NH_2$ group [$\nu(NH_2) = 3410$ cm$^{-1}$] and the C≡N groups [$\nu(C{\equiv}N) = 2215$ cm$^{-1}$]. The UV spectrum in $CH_2Cl_2$ shows absorption bands at 218, 254 and 265 nm ($\varepsilon = 2800$, 1900 and 2500 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively), consistent with the presence of extensive unsaturation in the molecule.

Perfluorodecalin (**8**, 1 : 1 *cis–trans* mixture) gave enamine **9** on reaction with Hg*–$NH_3$ as shown in eqn. (7) (chemical yield: 92%, quantum yield: 0.05–0.06).



(7)

Enamine **9** was identified by comparison of the spectroscopic and mass spectral data with a literature report[11b] [UV (EtOH): obsd., 320 nm ($\varepsilon = 6800$ dm$^3$ mol$^{-1}$ cm$^{-1}$); lit., 318 nm ($\varepsilon = 7900$ dm$^3$ mol$^{-1}$ cm$^{-1}$)] in which **9** was prepared from $NH_3$ and the corresponding 9,10-alkene. Also consistent with the proposed structure, the GC-MS fragmentation pattern shows a mass of 395 Da as well as peaks at $m/z = 378$ and 278, corresponding to loss of $NH_3$ and $C_2F_4$, respectively. Six $^{19}F$ NMR resonances assigned to $—CF_2—$ groups were observed at $-98.0$, $-107.6$, $-107.8$, $-109.0$, $-122.2$ and $-127.2$ ppm, implying fast tautomeric equilibrium. The IR spectrum showed the C=N groups [obsd., $\nu(C{=}N) = 1640$ cm$^{-1}$; lit., 1635 cm$^{-1}$] and the $—NH_2$ group [obsd., $\nu(NH_2) = 3486$, 3316 cm$^{-1}$].

## Surface amination of PTFE

Secondary $—CF_2—$ groups also react under $NH_3$–Hg* conditions and tertiary C—F bonds are therefore not required. Purified, distilled $n$-$C_9F_{20}$ reacted with $NH_3$–Hg* to give $NH_4F$ (IR) and a fluororganic material that was a mixture of isomers and could not be purified. The $^1H$ and $^{19}F$ NMR spectra were consistent with reaction in the interior part of the perfluoroalkane chain to give imine and enamine functionalities of the type $HN{=}C{—}C{=}C{—}NH_2$. Two main resonances of equal intensity at $-63.14$ and $-77.94$ ppm indicate[12] the presence of intact terminal $—CF_3$ groups. The $^1H$ NMR spectrum showed resonances at 1.3–6.7 ppm, consistent with the presence of =NH and $—NH_2$ groups. IR spectroscopy showed a broad N—H band at $\nu(N{—}H) = 3388$ cm$^{-1}$, but no $\nu(C{\equiv}N)$ band from cyanide groups, which would have resulted from attack at the terminal $—CF_3$ groups. The presence of C=C groups is suggested by the IR $\nu(C{=}C)$ band at 1675 cm$^{-1}$ and the broad UV band at 254 nm.

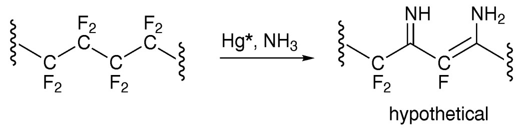
Our success with $n$-$C_9F_{20}$ prompted us to look at the reaction of PTFE with Hg*–$NH_3$, where we find surface modification indeed occurs. Prior work by Allmer and Feiring[13a] showed surface modification of PTFE by photostimulated electron transfer from a number of nucleophiles but we were able to show by control reactions in the presence and absence of mercury that under our conditions all the chemistry described here arises from a Hg-photosensitized route. We

**Table 1** Measured water contact angles of PTFE upon photomodification

| Irradiation time/h | Contact angle/°[a] |
|---|---|
| 0 | 108 |
| 12 | 75 |
| 24 | 63 |
| 48 | 50 |
| 72 | 50 |

[a] Surface contact angle of a 10 μl drop of water, measured after washing ($H_2O$, THF and $CH_2Cl_2$) and drying of the surface.

exposed a film of PTFE to $NH_3$ in a quartz tube containing a drop of Hg and irradiated (at 254 nm) for 72 h. Measuring the surface water contact angle in the product (Table 1 and *Experimental*) showed a progressive decrease in the hydrophobicity. The initial angle[13b] of 108° indicated the usual very hydrophobic surface, but after treatment the contact angle decreased to 50°, indicating greatly decreased hydrophobicity. IR spectroscopy of the treated strip showed bands at 3210, 3069 and 2816 $cm^{-1}$, as well as a group in the region of 1630–1700 $cm^{-1}$. The first three bands are assigned to $NH_4F$ by comparison with an authentic sample deposited on PTFE and the group at lower energy to NH bending in surface-bound amino or imino functionalities by comparison with the IR data from the $n$-$C_9F_{20}$ case. Washing the surface with water removed the $NH_4F$ (IR) and the groups responsible for the bands at 1630–1700 $cm^{-1}$, presumably by imine hydrolysis, but the surface maintained its hydrophilic character for which the measured contact angles were obtained. Eqn. (8) shows a hypothetical possibility for the PTFE functionalization reaction, based on the spectral data and by analogy with the chemistry described above for the small molecule cases.

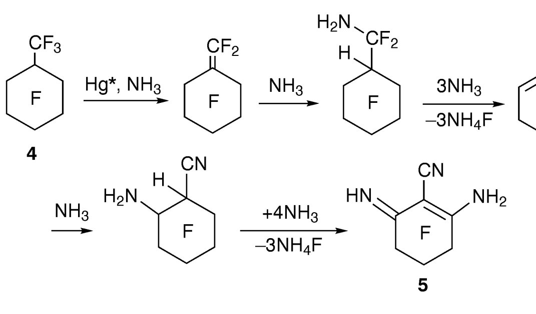


(8)

As a qualitative indicator of the nature of the surface-functionalization, adhesive tape failed to adhere well to the starting PTFE strip, but adhered very strongly to the treated strip. The surface modification is robust and the properties are retained in moist air.

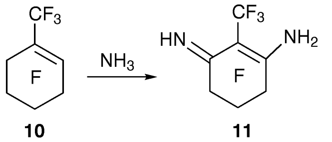
## Mechanism

The very complex structure of the enamine and nitrile products is at first sight rather surprising, but they can all be explained as the result of a multistep dark reaction of $NH_3$ with the corresponding alkenes, as indicated in eqn. (9) for the case of the exocyclic perfluoromethylenecyclohexane.



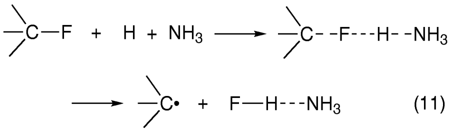
(9)

Analogous alkenes are therefore assumed to be intermediates formed during the photochemical steps for all the cases studied. The particular alkenes involved are, unfortunately, unavailable to verify the pathway given in eqn. (9) experimentally, but very similar alkenes give analogous products, as we have reported in a parallel study of a related photochemical system with $FeCp^*_2$ as sensitizer.[9] For example, the endocyclic alkene **10** gives the enamine **11** on reaction with $NH_3$ [eqn. (10)] by a pathway analogous to that of eqn. (9). Only the exocyclic alkene of eqn. (9) is expected to give the nitrile **5** however, rather than the imine **11** of eqn. (10), on reaction with $NH_3$.



(10)

We now turn to the initial steps of the Hg*–$NH_3$ reaction. Normally Hg photosensitization of $NH_3$ goes *via* NH bond homolysis to give H atoms and $NH_2$ radicals.[6] Since the HF bond strength is higher while the NF bond strength is lower than the CF bond strength, only H atoms could possibly abstract F from perfluoroalkanes, but the Hg-photosensitized reaction of $H_2$, which gives abundant H atoms,[14] fails to give products from perfluorodecalin. H atoms are still formed in the presence of perfluorodecalin because cyclohexane is converted to bicyclohexyl[4a] (yield 72%) in the presence of perfluorodecalin. Hg* alone also failed to react with perfluorodecalin, as did direct photolysis in the absence of photosensitizer. We are therefore forced to reject a pathway involving H-atom abstraction from a CF bond as the key step.



(11)

Base promotion of F-atom abstraction [eqn. (11)] by $NH_3$ was tested by comparison of the results obtained from perfluorodecalin for $H_2$–$NH_3$ mixtures (Table 2); pure $NH_3$ was 6.3 times more efficient than $H_2$–$NH_3$ (50 : 50 v/v), contrary to the expectation of the base promotion idea. In ammonia–argon mixtures (Table 3), faster rates were observed than for $NH_3$–$H_2$ at the same partial pressures of ammonia, so the presence of $H_2$ inhibits the reaction, probably by efficient competitive quenching of Hg* to give unreactive H atoms. A plot of the ammonia–argon data in the usual form of ln(rate) against ln[$p(NH_3)$] (Table 3) gives a slope of 1.97(±0.1), corresponding to a second-order dependence on ammonia partial pressure, again inconsistent with simple base assistance.

Many prior perfluorocarbon reactions[1] were thought to go *via* initial electron transfer (ET) and we therefore considered possible ET routes. The Rydberg radical $NH_4$, formed when Hg is photosensitized in the presence of $NH_3$ and experimentally detected in the $ND_4$ case, is a candidate[15] electron donor. $NH_4$ can best be thought of in this context as a gas phase $NH_4^+$ ion with an electron in an outer ($n > 3$) orbital. The electron makes radiative transitions to lower and lower

**Table 2** Reaction of **8** to give **9** using $H_2$–$NH_3$ mixtures with Hg photosensitization

| $p(NH_3)$/atm[a] | **9** obtained/mmol[b] |
|---|---|
| 1 | 126 |
| 0.75 | 34 |
| 0.50 | 20 |
| 0.25 | 7 |
| 0 | 0 |

[a] With $H_2$ present to make up 1 atm total pressure. [b] After 19 h.

**Table 3** Moles of **9** obtained from **8** with $NH_3$–Ar mixtures under Hg photosensitization

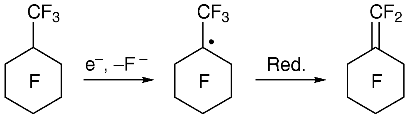
| $p(NH_3)$ /atm[a] | **9** obtained /mmol[b] | ln(rate) /mmol $h^{-1}$ | $\ln[p(NH_3)$ /atm] |
|---|---|---|---|
| 1.0 | 126 | 1.89 | 0 |
| 0.75 | 81 | 1.45 | −0.288 |
| 0.50 | 23 | 0.191 | −0.693 |
| 0.25 | 9 | −0.74 | −1.386 |
| 0 | 0 | — | — |

[a] With argon present to make up 1 atm total pressure. [b] After 19 h.

energy levels (Rydberg levels) until it finally decays to the ground electronic state, at which point the molecule dissociates[16] to H atoms and $NH_3$. $NH_4$ is isoelectronic with Na (IP = 5.15 eV, 121.5 kcal $mol^{-1}$) and K (IP = 4.34 eV, 100.1 kcal $mol^{-1}$) and like them, is highly reducing (IP = 4.65 eV, 107.2 kcal $mol^{-1}$).[17] The low IP makes $NH_4$ an excellent one-electron reducing agent. In addition, the hydrogen-bonding character of the system in principle allows it to accept back-transfer of the incipient $F^-$ ion expelled from the reduced fluorocarbon, leading to net F-atom abstraction from the fluorocarbon. The lifetime of a Rydberg radical[18] is known to be very strongly dependent on isotopic substitution (as a result of tunneling), going from $10^{-10}$ s ($NH_4$) to $2.3 \times 10^{-6}$ s ($ND_4$), and so if $NH_4$ ($ND_4$) were involved in the reaction, we would expect a very strong isotopic effect. Identical amounts of product were obtained with $ND_3$ *vs.* $NH_3$ however, so this proposal was abandoned. $NH_4$ forms ammonia adducts $NH_4(NH_3)_n$ however, having even lower IPs and longer lifetimes. For the $n = 2$ case, the IP is 3.29 eV and the lifetime between 6 and 160 ms.[17b]

After theoretical studies to be described below, the exciplexes $[Hg^*(NH_3)_n]$ ($n = 1$, 2) were identified as the most probable candidates for the electron donor, having even lower IPs than $NH_4$. Excited state Hg*, which can be thought of in this context as a $Hg^+$ ion with an electron in a higher orbital, shares with the $Hg^+$ ion the property of binding ligands to give complexes. The intermediacy of $[Hg^*(NH_3)_2]$ would help explain the observed second-order behavior on $p(NH_3)$, but we cannot be certain that it is the only reactive intermediate. Since ammonia seems to participate in the defluorination (see below) it is somewhat surprising that we see no isotope effect.

After electron transfer from $[Hg^*(NH_3)_n]$, followed by or concerted with fluoride ion back-transfer from the fluorocarbon, we expect the tertiary carbon-centered radical to form. This was seen in prior reactions of fluoroalkanes and is shown in the case of perfluoromethylcyclohexane in eqn. (12).



(12)

The radical can be reduced to the alkene but, as mentioned above, to explain the products we need to invoke formation of the exocyclic alkene, presumably *via* reaction with a reductant such as $NH_3$ or its dimer. At present we are unable to explain why this reaction apparently gives the exocyclic alkene.

While the exciplex is proposed as the reactive species in the gas phase experiments, we are less certain that the same holds in the experiments with PTFE, where adsorption or other surface phenomena might play a role.

## Theoretical Studies

### Fluorine abstraction by H atoms

To test the ideas discussed above, we have carried out DFT-B3LYP theoretical studies.[7] The first point of interest was the failure of perfluoroalkanes to give F-atom abstraction with H atoms. This we have modeled by reaction (13), for which an exothermicity of 10.3 kcal $mol^{-1}$ was found.

$$H\cdot + CF_4 \rightarrow HF + \cdot CF_3 \qquad (13)$$

The transition state was located and found to be very high at 36 kcal $mol^{-1}$ above the reagents, the H···F and F···C distances being 1.34 and 1.64 A, respectively. Inclusion of polarization functions in the geometry optimization had only a minor effect on the results. This high barrier is consistent with the absence of reaction as seen experimentally, but is very surprising considering that the barriers for H-atom abstraction from alkanes are normally much lower. F-atom abstraction by H can therefore by safely ruled out.

### Formation and reaction of $NH_4$

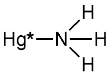
The formation of the Rydberg radical $NH_4$ from $^3P_1$ Hg (= Hg*) and the ammonia dimer proved to be energetically possible, Hg* having an excitation energy[3] of 112.2 kcal $mol^{-1}$ (exptal) or 109.0 kcal $mol^{-1}$ (calcd), which is greater than the ammonia dimer triplet excitation energy of 102.3 kcal $mol^{-1}$ (calcd). The energy cost for triplet ammonia conversion to $NH_2$ and $NH_4$ is a reasonable 3.4 kcal $mol^{-1}$ (calcd). A minor problem is that basis set superposition error (BSSE) makes $NH_4$ *ca.* 4 kcal $mol^{-1}$ more stable than it should be, but its formation should still be possible under the reaction conditions. The IP of $NH_4$ is found to be 107.6 kcal $mol^{-1}$, in excellent agreement with the experimental value (107.2 kcal $mol^{-1}$). The transition state for F abstraction from $CF_4$ by $NH_4$ *via* eqn. (14)

$$CF_4 + \cdot NH_4 \rightarrow H_3N\cdots HF + \cdot CF_3 \qquad (14)$$

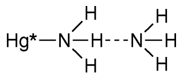
was located and found to be 27.6 kcal $mol^{-1}$ above the reagents, again far too high to make a significant contribution. Of course, the true substrates have weaker secondary and tertiary CF groups, but a study of the reaction of $CH_3F$, having a much weaker CF bond, with $NH_4$ shows that the barrier height is 17.8 kcal $mol^{-1}$, only 7.8 kcal $mol^{-1}$ lower than for $CF_4$. The computed CF bondstrength is 107.4 kcal $mol^{-1}$, as much as 18.8 kcal $mol^{-1}$ lower than the 126.2 kcal $mol^{-1}$ calculated for $CF_4$, so only about one-half of the bond weakening appears in the transition state. The free triplet ammonia dimer might also abstract an F atom, but the barrier for this step is also 17.8 kcal $mol^{-1}$, so this dimer is no better than $NH_4$. Both experiment and theory tend to eliminate $NH_4$ as a kinetically important intermediate, and so we moved on to the Hg–$NH_3$ exciplexes as alternatives.

### Formation and abstraction by $[Hg^*(NH_3)_2]$

For $[Hg^*(NH_3)_n]$ exciplexes, the $n = 1$ species proved to have the structure shown in **12**, with an energy of −17 kcal $mol^{-1}$ relative to the separated reagents, in good agreement with the experimental[7b] value of −18.2 kcal $mol^{-1}$; the $n = 2$ exciplex on the other hand had structure **13**, with the second $NH_3$ hydrogen-bonded to the first and with an energy of −26 kcal $mol^{-1}$ relative to Hg* and two $NH_3$.



**12**



**13**

Since the reaction is carried out at 1 atm of $NH_3$, the $n = 2$ adduct should certainly be present. The IPs (including estimates of spin-orbit effects, see *Computational Details* section) of both species are very low, 101.0 and 95.0 kcal $mol^{-1}$ ($n = 1$ and 2, respectively), so they are comparable with (for $n = 1$) or more reducing than (for $n = 2$) the potassium atom. To simplify the calculations, $CH_3F$ was taken as the model CF bond

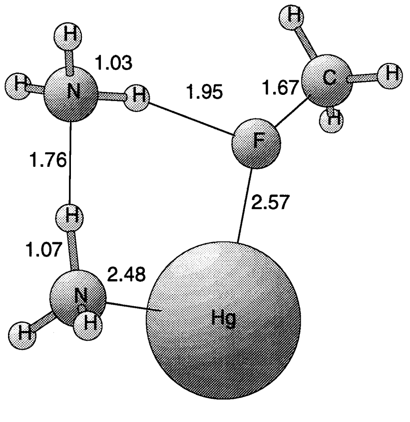


**Fig. 1** The transition state found in quantum chemical studies for the reaction of $[Hg^*(NH_3)_2]$ with $CH_3F$, showing what is interpreted as a net F-atom transfer *via* a concerted electron transfer/fluoride back-transfer step

for studies with the bis-ammonia exciplex, $[Hg^*(NH_3)_2]$, in the model transformation of eqn. (15).

$$[Hg^*(NH_3)_2] + CH_3F \rightarrow [Hg^*{-}NH_2{-}NH_3{-}HF] + \cdot CH_3 \quad (15)$$

The reaction barrier is 9.4 kcal $mol^{-1}$ and the exothermicity is 35.5 kcal $mol^{-1}$, making this a plausible pathway for the chemistry observed. The corresponding values for the analogous reaction with the $n = 1$ exciplex, 8.9 and 33.0 kcal $mol^{-1}$, respectively, are comparable.

The structure of the transition state that was located (Fig. 1) shows the F atom being transferred from the $CH_3$ group to the NH group of the exciplex, assisted by the proximity of the Hg atom, to which the fluoride ion is weakly bound. This is perhaps best considered as an electron transfer coupled to $F^-$ ion back-transfer for a net F-atom abstraction by the exciplex.

## Conclusions

Partial reduction of perfluoroalkanes occurs by reaction with $NH_3$ with Hg photosensitization and leads to a variety of perfluoroalkyl derivatives containing imino, amino and nitrile groups. The reaction gives not only functionalized perfluoroalkyl derivatives, but also a method to obtain photomodified PTFE surfaces that has potential applications in polymer technology.

Pure F-atom abstraction from perfluoroalkanes by an intermediate such as the H atom has a high barrier and was not observed in our experiments. Reaction becomes possible when the reactive intermediate, believed to be the exciplex $[Hg^*(NH_3)_2]$ in our case, is an efficient electron donor and fluoride ion acceptor; the resulting electron transfer/$F^-$ ion back-transfer is equivalent to F-atom abstraction. This is reminiscent of certain H-atom transfers that have been shown to go by coupled electron/proton transfer. Although other pathways cannot yet be excluded, the absence of isotopic effect, the higher stability and lower IPs of the exciplexes *vs.* the Rydberg radical and the second-order dependence of the rate on $p(NH_3)$ suggest that the most likely mechanism involves the exciplex $[Hg^*(NH_3)_2]$. Two important mechanistic aspects emerge from our study. The low IP of $[Hg^*(NH_3)_2]$ makes it a very powerful electron donor and the presence of an acidic proton is expected to assist the departure of the incipient $F^-$ ion formed during the reaction, leading to net F-atom abstraction from the substrate.

The results of this work have led us to design better systems for C—F activation, by avoiding the nucleophilic conditions required here. By substituting the non-nucleophilic sensitizer, $FeCp^*_2$, we were able to form perfluoroalkene products related to the postulated intermediates described here, directly from perfluoroalkanes.[9]

## Experimental

### General

$^1H$ NMR spectra were determined on Bruker 250 MHz and Y-490 MHz instruments using TMS as internal standard. $^{19}F$ NMR spectra were determined on a Y-490 MHz NMR instrument using a solution of $CCl_3F$ in $CH_2Cl_2$-$d_2$ as external standard. Full spectral data (in ppm) are given where not previously available. We used the following units and notation: s, singlet; d, doublet ..., $J$ in Hz; $J_{FF}{}^g$ and $J_{FF}{}^v$ are geminal and vicinal coupling constants, respectively. GC-MS data were obtained on a HP 5890 Gas chromatograph [29 m; 0.25 i.d.; cap. SE 30 column (0.25 mm film), HP 5972A MS detector]. IR spectra were measured on a Midac Gram/386 instrument with NaCl windows and UV spectra on a Cary 3E spectrophotometer. The photoreactor consisted of a vacuum tight 18 ml quartz tube with a condenser to allow degassing by freeze-thaw cycling. Irradiation was carried out using a Rayonet photochemical reactor model RMR-600 with 4–8, 8 W low pressure Hg lamps (254 nm).

**Quantum yields.** To determine the quantum yield ($\Phi$), we placed two identical quartz tubes in the photochemical reactor, one containing the perfluorocarbon (2.0 ml) and the other containing $Et_3SiH$ (2.0 ml). The perfluorocarbon reacted with $Hg^*$–$NH_3$, while $Et_3SiH$ reacted with Hg* under argon. The quantum yield for the dehydrodimerization reaction of $Et_3SiH$ to give hexaethyldisilane (HEDS) has previously been determined ($\Phi = 0.8$).[19] Hexaethyldisilane was determined by GC and the fluorocarbon product **A** was isolated and purified as described below. The quantum yield was then calculated using the equation: $\Phi = 0.8$ [moles of **A**]/[moles of HEDS].

**Fluoroalkane purification.** In some cases, we have found that commercial perfluorocarbons contain impurities (unsaturated perfluorocarbons) that interfere with our studies. The samples were therefore purified by reaction with an excess of *n*-butylamine at room temperature. This provides an easy spot test to detect the presence of small amounts of perfluoroalkanes by the immediate formation of a yellow precipitate. The precipitate of fluoroimines and $NH_4F$ formed was filtered and the perfluorocarbon liquid was washed with an excess of 0.1 M HCl and then with water. Samples were dried over $MgSO_4$ and distilled.

**Control experiments.** No reaction was observed when perfluorocarbons were irradiated under $NH_3$ in the absence of Hg. The quartz tubes were previously heated in a furnace at 400 °C to eliminate any traces of Hg. Furthermore, no reaction was observed when perfluorodecalin was irradiated in the presence of Hg with no $NH_3$ present.

### Reactions

**Synthesis of 9 from perfluorodecalin.** Perfluorodecalin (PCR Inc.) was a 1 : 1 mixture of *cis–trans* isomers (95%, GC). No C—H or C=C bonds were detected in the starting material ($^1H$ NMR, IR, UV) so the impurities are probably other saturated perfluoro compounds. Perfluorodecalin (3.0 g, 6.5 mmol, 1.6 ml) was placed in a quartz tube together with a drop of Hg (0.1 g) and irradiated for 19 h under ammonia flow (10 ml $min^{-1}$) at 45 °C. The residue was then extracted with dry $CH_2Cl_2$ (5 × 3 ml) and the suspension thus obtained gave a residue after evaporation containing $NH_4F$ (16 mg), as determined by $^{19}F$ NMR ($NaCF_3CO_2$ int. std.). GC-MS showed a single major product (**9**, 74 mg, 3.1% conversion, 92% based on reacted perfluorodecalin, $\Phi = 0.05–0.06$) with MW = 395. The yellow oil initially obtained was purified by preparative TLC on silica gel with a mixture (95 : 5) of $CH_2Cl_2$–THF as eluent to give pure material (68 mg, 2.7% conversion; $R_f = 0.73$). Spectroscopic data for **9**: $^1H$ NMR ($CD_2Cl_2$): 1.25 (s, 1H); 1.96 (s, 2H); 9.06 (br, 2H). $^{19}F$ NMR ($CD_2Cl_2$): −98.07 (dd, $J_{FF}{}^g = 280.07$, $J_{FF}{}^v = 12.2$, 2F); −107.59 (d, $J_{FF}{}^g = 270$, 2F); −107.8 (dm, $J_{FF}{}^g = 270$, 2F); −109.0 (d, $J_{FF}{}^g = 262.5$, 2F); −122.2 (d, $J_{FF}{}^g = 270$, 2F); −127.2 (d, $J_{FF}{}^g = 262.5$, 2F). IR (NaCl, film): 3486 (NH), 3316 (NH), 1640 (C=N), 1540 (NH), 1320 (CF), 1170 (CF), 1064 $cm^{-1}$ (CF). MS (70 eV): 395 ($M^+$), 378 ($M^+ - NH_3$), 278 ($M^+ - NH_3 - C_2F_4$), 244 ($M^+ - NH_3 - NHF - C_2F_4$). UV (EtOH): 320 nm ($\varepsilon = 6800$ $dm^3$ $mol^{-1}$ $cm^{-1}$).

**Synthesis of 5 from perfluoromethylcyclohexane.** Perfluoromethylcyclohexane (90%, Aldrich; impurities with C—H and C=C bonds absent by $^{19}F$ NMR, $^1H$ NMR, IR, UV and GC analysis; 3.0 g, 8.6 mmol, 1.6 ml) was placed in a quartz tube together with a drop of Hg (0.1 g) and irradiated for 19 h. Twenty-six milligrams of light yellow solid were obtained upon working up the mixture as before, which contained a product (90%) with MW = 243 (GC-MS). Preparative TLC with a mixture (95 : 5) of $CH_2Cl_2$–THF as eluent gave **5** (22 mg, 1% conversion, 85% based on reacted fluorocarbon, $\Phi = 0.04$). ($R_f$: 0.29, mp obsd., 155–156 °C; lit.,[11] 160 °C). Spectroscopic data for **5**: $^1H$ NMR ($CD_2Cl_2$): 1.59 (s, 2H); 6.20 (br, 1H). $^{19}F$ NMR ($CD_2Cl_2$): −117.93 (s, br, 2F); −121.31 (s, br, 2F); −136.1 (s, 2F). $^{19}F$ NMR (THF): −117.93 (br); −121.3 (br). IR (NaCl, film): 3431 (NH), 3244 (NH), 2224 (nitrile), 1659 (C=N), 1615 (NH), 1577 (NH), 1154 $cm^{-1}$ (CF). MS (70 eV): 243 ($M^+$), 216 ($M^+ - HCN$), 197 ($M^+ - HCN - F$), 143 ($M^+ - HCN - F - C_2F_4$). UV (THF): 285 nm ($\varepsilon = 17\,600$ $dm^3$ $mol^{-1}$ $cm^{-1}$).

**Synthesis of 7 from perfluoro-1,3-dimethylcyclohexane.** Perfluoro-1,3-dimethylcyclohexane (PCR Inc., no impurities with C—H or C=C bonds detected) as a mixture of *cis* and *trans* isomers (3.0 g, 7.5 mmol, 1.6 ml) was reacted as described previously. The residue was extracted with dry THF (5 × 3 ml) and filtered through a silica gel column. The extract (26 mg) was vacuum-dried and analyzed by GC-MS. Three main products were obtained, two having MW = 293 (46.4% and 22.3%) and the other with MW = 275. **7** (MW = 275 by GC-MS) was separated from the mixture by preparative TLC with a mixture of $CH_2Cl_2$–THF (95 : 5) as eluent (7.86 mg, 3.4% conversion, 30% based on reacted perfluorocarbon, $\Phi = 0.01$; $R_f$: 0.37). Spectroscopic data for **7**: $^1H$ NMR ($CD_2Cl_2$): 1.56 (s, 2H); 2.12 (s, 1H); 7.6 (br, 1H). $^{19}F$ NMR ($CD_2Cl_2$): −78.18 (m, $J_{FF}{}^v = 18.0$, 3F); −111.3 (dt, $J_{FF}{}^g = 290.0$, $J_{FF}{}^v = 15.20$, 1F); −122.12 (dm, $J_{FF}{}^g = 290$, $J_{FF}{}^v = 12.2$, 1F); −127.25 (dt, $J_{FF}{}^g = 272$, $J_{FF}{}^v = 17.7$, 1F); −139.0 (dm, $J_{FF}{}^g = 272$, $J_{FF}{}^v = 12.2$, 1F). MS (70 eV): 275 ($M^+$), 274 ($M^+ - H$), 247 ($M^+ - H - CN$), 244 ($M^+ - H - 2HN$), 254 ($M^+ - H - HF$), 177 ($M^+ - H - HF - CF_2CNH$), 69 ($CF_3$), 100 ($C_2F_4$). IR (NaCl, film): 3410 (NH), 2919 (CH), 2215 (nitrile), 1647 (C=N), 1604 (NH), 1190 (CF), 1327 $cm^{-1}$ (CF). UV ($CH_2Cl_2$): 218 nm ($\varepsilon = 2800$ $dm^3$ $mol^{-1}$ $cm^{-1}$), 254 ($\varepsilon = 1900$), 265 ($\varepsilon = 2500$).

**Synthesis of 2 from perfluoro-2-methylpentane.** Commercial **1** (TCI) contained traces of unsaturated fluorocarbons that were eliminated by the purification process discussed previously. In the distillation step, the fraction collected had a bp 59–61 °C; C=C bonds were absent (UV). Purified perfluoro-2-methylpentane (3.0 g, 5.7 mmol) was reacted as described previously. However, in this case a cold finger containing acetone–dry ice at −20 °C as coolant was used instead of a water condenser. After 19 h, the yellow residue (10 mg) was extracted from the cold finger with THF (4 × 5 ml) and analyzed. GC-MS showed only a single product (**2**) with $M^+ = 211$. Preparative TLC on silica gel using a mixture (95 : 5) of $CH_2Cl_2$–THF as eluent yielded the pure compound (8.0 mg, $\Phi = 0.02$; $R_f = 0.4$, mp = 201–202 °C). Spectroscopic data for **2**: $^1H$ NMR ($CD_2Cl_2$): (1.26, s, 2H). $^{19}F$ NMR ($CD_2Cl_2$): −80.7 (3F); −115.3 (2F). MS (70 eV): 211 ($M^+$); 192 ($M^+ - F$); 185 ($M^+ - CN$); 142 ($M^+ - CF_3$), 119 ($M^+ - 2CN - C - CNH_2$); 92 [$(CN)_2CCNH_2$]; 69 ($CF_3$). IR (NaCl, film): 3312 (N—H); 3181 (N—H); 2207 (nitrile); 1286 (C—F); 1129 $cm^{-1}$ (C—F). UV ($CH_2Cl_2$): 278 nm ($\varepsilon = 17\,300$ $dm^3$ $mol^{-1}$ $cm^{-1}$).

**Reaction of perfluorononane.** *n*-Perfluorononane (Aldrich, 5 g) contained no detectable impurities with C—H or C=C bonds, but when irradiated in the presence of $NH_3$–Hg for 1 h, a light yellow oil was formed that showed no fluorine resonances in $^{19}F$ NMR. This oil, assumed to be derived from a reaction between $NH_3$ and an impurity in the sample, was therefore separated by passage through silica gel and the remaining perfluorononane distilled. The pure fraction that distilled at 129 °C was used for the $NH_3$–Hg reaction. Distilled purified perfluorononane (3.0 g, 1.6 ml, 6.1 mmol) was irradiated for 72 h as previously described. The unreacted perfluorononane was removed and a yellow precipitate was extracted with dry THF (4 × 3 ml) and the extracts passed through silica gel. A yellow mixture (10 mg) was obtained and analyzed. A THF-insoluble residue (10 mg) corresponding to $NH_4F$ was determined by $^{19}F$ NMR spectroscopy. Spectroscopic data: $^1H$ NMR ($CD_3CN$): 1.30 (s); 4.83 (s, br); 6.7 (s, br). $^{19}F$ NMR (THF–$C_6D_6$): −63.14 (s, $CF_3$); −77.94 (s, $CF_3$); minor peaks observed at −85.28 ($CF_3$) and −122.52 ($CF_2$). IR (NaCl, film): 3388 (vs, br), 1675 (s, C=N), 1386 (m, CF), 1180 $cm^{-1}$ (m, CF). UV (THF): 254, 258 nm.

### Surface modification of poly(tetrafluoroethylene)

PTFE powder (Aldrich) was pressed into translucent films (1 cm diameter) that showed the usual strong IR C—F absorption bands at 1257 $cm^{-1}$. The films were irradiated in an $NH_3$ atmosphere (1 atm) in the presence of one drop of Hg (0.1 g). The changes in the surface properties were monitored by measuring the change in the contact angle (by goniometer after washing with $H_2O$, THF, $CH_2Cl_2$ and then vacuum drying) with a 10 µl drop of water. The data obtained are reported in Table 1. Spectroscopic data on the treated film: IR spectroscopy showed bands at 3210, 3069 and 2816 $cm^{-1}$ and in the region 1630–1700 $cm^{-1}$. $NH_4F$ was deposited on a PTFE film by immersion in a dilute solution (0.1 M) of $NH_4F$ in water and then dried. The IR of this film showed absorption bands at 3210, 3069 and 2816 $cm^{-1}$, however, there was no significant absorption in the region 1630–1700 $cm^{-1}$. This absorption band was therefore assigned to ν(C=N). Upon washing the surface with water, not only did the bands assigned to $NH_4F$ disappear but the band at 1630–1700 $cm^{-1}$ also vanished. The resulting surface had hydrophilic character (contact angle = 50°).

### Mechanistic studies

**Radical abstraction.** No reaction was detected by GC-MS and $^{19}F$ NMR when perfluorodecalin was irradiated at 254 nm in the presence of $H_2$–Hg.

**Pressure dependence and $H_2$–$NH_3$ mixtures.** By using mixtures of $NH_3$–Ar and $NH_3$–$H_2$, the partial pressure of $NH_3$ was varied, keeping 1 atm total pressure in the system. The data obtained are shown in Tables 2 and 3.

**Reaction of perfluoroalkene with $NH_3$.** Perfluoro-2-methyl-2-pentene (0.82 g, 2.7 mmol) was added to 60 ml of dry THF cooled at $-10$ °C. A gentle flow of $NH_3$ was bubbled through the solution and a white precipitate was formed immediately. After 90 min flow, the mixture was allowed to warm to room temperature and the flow was continued for another 30 min. A white precipitate formed (0.57 g, 81%), which was separated by filtration. The precipitate gave identical IR and $^{19}F$ NMR spectra to that of $NH_4F$. The THF solution was vacuum dried and 0.47 g of a yellow solid were obtained, which contained, based on GC-MS, 93% of a compound with $M^+ = 211$. The compound was further purified by preparative TLC with a mixture (95 : 5) of $CH_2Cl_2$–THF as eluent ($R_f = 0.4$) to give 0.40 g of product. The analytical data found for the product of this reaction and **2** were identical.

**Isotopic effect.** Isotopically substituted $ND_3$ was passed through a trap ($-5$ °C) and into the reaction vessel containing **8** (3.0 g, 6.5 mmol, 1.6 ml). In this and in an identical control experiment at 1 atm with $NH_3$, identical amounts of **9** (40.0 mg, 0.1 mmol) were obtained after purification by preparative TLC as described above.

**Gas phase reaction.** A flow of $NH_3$ (20 ml min$^{-1}$, 3 h, 1 atm) was saturated with perfluoromethylcyclohexane by passing the ammonia gas through the perfluorocarbon liquid. The $NH_3$ flow carrying the perfluorocarbon was passed through a quartz tube (dimensions: 40 cm × 1 cm) containing a small drop of Hg (0.1 g) and irradiated with a low pressure Hg lamp. After 3 h, a yellow precipitate deposited on the walls of the reactor. Using the same procedure described above for perfluoromethylcyclohexane, we obtained **5** (21 mg, 0.08 mmol) in a 90% chemical yield based on reacted perfluorocarbon.

## Computational Details

DFT-B3LYP-PCI-80 theoretical studies were carried out in two stages. First, a geometry optimization was performed *via* a DFT-B3LYP calculation based on hybrid functionals. Second, an *ab initio* PCI-80 calculation was made at the optimized geometry. Both types of methods use semi-empirical corrections with only one or a few parameters, a procedure that has been shown markedly to improve the reliability of the results. Basis sets of double zeta plus polarization quality were used for the final energy evaluation, while polarization was not included for the geometry optimization.

The *ab initio* calculations were carried out *via* a recently developed parametrized scheme, PCI-80,[20a,b] based on calculations with the modified coupled pair functional (MCPF), a standard quantum chemical, size-consistent, single reference state method.[20c] The zeroth-order wavefunctions were determined at the SCF level. All valence electrons were correlated including the 5d and 6s, 6p electrons on Hg. If standard double zeta plus polarization (DZP) basis sets are used, it has been shown that about 80% of the correlation effects on bond strengths are observed independent of the system studied, so a good estimate can be obtained by adding 20%, as is done in the PCI-80 scheme.[20a] The empirical parameter 80 was chosen in a benchmark test with 32 first-row molecules.[20d] For several first-row molecules it has been shown[20a] that a Hartree–Fock limit correction is also needed in the PCI-80 scheme, but it is usually small for heavy metal systems and it has been included in the parametrization, together with basis set superposition errors and core correlation effects. The PCI-80 calculations were implemented with the STOCKHOLM set of programs.[20e]

The DFT calculations were carried out with the empirically parametrized B3LYP method *via* the GAUSSIAN92/DFT package, as has been fully described in prior papers.[7] Zero-point vibrational effects were accounted for at the B3LYP level.

The *ab initio* calculations used Wahlgren's[20f] relativistic effective core potential (RECP) for Hg in which the 4s, 4p, 5s, 5p, 5d and 6s electrons are treated explicitly and a (14s, 11p, 8d, 3f) primitive basis is used. The 4s, 4p, 5s, 5p electrons are described by a single zeta contraction, the 6s, 6p by a double zeta contraction and the 5d by a triple zeta contraction. The f function was contracted to one function giving a [4s, 4p, 3d, 1f] contracted basis for Hg. For C, N (see further below) and F, the primitive (9s, 5p) basis of Huzinaga[21] was used and contracted according to the generalized contraction scheme to [3s, 2p] and one d function was added. For H, the primitive (5s) basis set from Huzinaga, augmented with one p function, was contracted to [3s, 1p].

For the Rydberg molecule, $NH_4$, diffuse basis functions representing the Rydberg character were added for N. This was a single set of s and p functions optimized for $NH_4$ at the B3LYP level with optimal s, p exponents of 0.03.

In the B3LYP geometry optimization, an RECP of Hay and Wadt[22] was used for Hg, in which the valence 5d, 6s and 6p orbitals are described by double zeta contractions and no f function is used. For the other atoms, standard double basis sets without polarization were used except for N, where the diffuse s, p set described above was added. The only exception was the use of a d polarization function on N needed to get the right umbrella angle in $NH_3$. The geometries of the transition states were obtained using Hessians at the B3LYP level. Only one imaginary frequency was found at the optimized geometries, thus verifying their identity as transition states.

Because Hg is one of the heaviest atoms in the periodic table it is absolutely essential to treat the relativistic effects reasonably well and the present RECP has been shown[20f] to perform well. This is also verified for the spin-orbit-averaged excitation energy, which at the PCI-80 level becomes 116.3 kcal mol$^{-1}$ compared to the experimental average value of 119.5 kcal mol$^{-1}$. The RECP should account for all relativistic effects except for spin-orbit effects. In the previous work[7] on Hg* reactions, it was shown that spin-orbit effects can usefully be considered as quenched for Hg*–ligand systems. On this basis, spin-orbit effects will lead to a lowering of the energy of free Hg* by 6.8 kcal mol$^{-1}$, the difference between the calculated value and the Hg* $^3P_1$ component, but will not affect the other systems at all. For the Hg*$(NH_3)_n$ systems the spin-orbit effects were estimated to lower the energy by 8.3 kcal mol$^{-1}$, using an s-quenching model.[23]

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## References

1 H. S. Taylor and D. G. Hill, *J. Am. Chem. Soc.*, 1929, **51**, 2922.

2 E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, 1938, **6**, 179.

3 (*a*) R. J. Cvetanovic, *Prog. React. Kinet.*, 1963, **2**, 39. (*b*) J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966, pp. 60–166. (*c*) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, 1963, **2**, 209.

4 (*a*) S. H. Brown and R. H. Crabtree, *J. Am. Chem. Soc.*, 1989, **111**, 2935. (*b*) S. H. Brown and R. H. Crabtree, *J. Am. Chem. Soc*,, 1989, **111**, 2946. (*c*) S. H. Brown and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1987, 970. (*d*) S. H. Brown and R. H. Crabtree, *Tetrahedron Lett.*, 1987, **28**, 5599. (*e*) R. H. Crabtree, *J. Chem.*

*Educ*., 1988, **65**, 290. (*f*) S. H. Brown and R. H. Crabtree, US Pat. No 4,725,342, Feb. 16, 1988.

5 C. A. Muedas, R. R. Ferguson, S. H. Brown and R. H. Crabtree, *J. Am. Chem. Soc*., 1991, **113**, 2233.

6 (*a*) D. Michos, D. A. Sassano, P. Krajnik and R. H. Crabtree, *Angew. Chem*., *Int. Ed. Engl*., 1993, **32**, 1491. (*b*) P. Krajnik, D. Michos and R. H. Crabtree, *New J. Chem*., 1993, **17**, 805. (*c*) P. Krajnik and R. H. Crabtree, *Inorg. Chem*., 1993, **32**, 1028. (*d*) P. Krajnik and R. H. Crabtree, *New J. Chem*., 1993, **17**, 559.

7 (*a*) P. Siegbahn, M. Svensson and R. H. Crabtree, *J. Am. Chem. Soc*., 1995, **117**, 6458. (*b*) A. B. Callear, *Chem. Rev*., 1987, **87**, 335.

8 (*a*) J. Burdeniuc, B. Jedlicka and R. H. Crabtree, *Chem. Ber*., 1997, **130**, 145. (*b*) B. K. Bennett, R. G. Harrison and T. G. Richmond, *J. Am. Chem. Soc*., 1994, **116**, 11165. (*c*) R. P. Hughes, R. T. Carl, S. J. Doig, R. C. Hemond, D. E. Sankoff, W. L. Smith, L. C. Stewart, R. E. Davis, K. D. Holland, P. Dickens and R. P. Kashyap, *Organometallics*, 1990, **9**, 2732 and refs. cited. (*d*) M. K. Whittlesey, R. N. Perutz and M. H. Moore, *Chem. Commun*., 1996, 787. (*e*) J. L. Kiplinger and T. G. Richmond, *J. Am. Chem. Soc*., 1996, **118**, 1805. (*f*) J. A. Marsella, A. G. Gilicinski, A. M. Coughlin and G. P. Pez, *J. Org. Chem*., 1992, **57**, 2856. (*g*) B. L. Edelbach and W. D. Jones, *J. Am. Chem. Soc*., 1997, **119**, 7734. (*h*) N. A. Kaprinidis and N. J. Turro, *Tetrahedron Lett*., 1996, 2373.

9 J. Burdeniuc and R. H. Crabtree, *J. Am. Chem. Soc*., 1996, **118**, 2525; unpublished work.

10 A. D. Josey, *J. Org. Chem*., 1964, **29**, 707.

11 (*a*) G. S. Phull, R. G. Plevey and J. C. Tatlow, *J. Chem. Soc*., *Perkin 1*, 1984, 455. (*b*) J. A. Olivier, R. Stephens, J. C. Tatlow and J. R. Taylor, *J. Fluorine Chem*., 1976, **7**, 555.

12 C. H. Dungan and J. R. Van Wazer, *Compilation of Reported $F^{19}$ NMR Chemical Shifts*, Wiley-Interscience, New York, 1970.

13 (*a*) K. Allmer and A. E. Feiring, *Macromolecules*, 1991, **24**, 5487. (*b*) *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 1966, vol. 9, p. 827.

14 M. C. Duval, B. Soep and W. R. Breckenridge, *J. Phys. Chem*., 1991, **95**, 7145.

15 E. A. Whittaker, B. J. Sullivan, G. C. Bjorklund, H. R. Wendt and H. E. Hunziker, *J. Chem. Phys*., 1984, **80**, 961.

16 I. Dabrowski and G. Herzberg, *Can. J. Phys*., 1980, **58**, 1238.

17 (*a*) G. I. Gellene, E. A. Cleary and R. F. Porter, *J. Chem. Phys*., 1982, **77**, 3471. (*b*) R. Signorelli, H. Palm and F. Merst, *J. Chem. Phys*., 1997, **106**, 6523.

18 G. I. Gellene and R. F. Porter, *J. Phys. Chem*., 1984, **88**, 6680.

19 A. W. Nay, G. Woodall, H. E. Gunning and O. P. Strausz, *J. Am. Chem. Soc*., 1965, **87**, 179.

20 (*a*) P. E. M. Siegbahn, M. R. A. Blomberg and M. Svensson, *Chem. Phys. Lett*., 1994, **223**, 35. (*b*) P. E. M. Siegbahn, M. Svensson and P. J. E. Boussard, *J. Chem. Phys*., 1995, **102**, 5377. (*c*) D. P. Chong and S. R. Langhoff, *J. Chem. Phys*., 1986, **84**, 5606. (*d*) J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari and L. A. Curtiss, *Chem. Phys*., 1989, **90**, 5622. (*e*) P. E. M. Siegbahn, M. R. A. Blomberg, L. G. M. Petersson, B. O. Roos and J. Almlöf, *STOCKHOLM*, University of Stockholm, Sweden, 1994. (*f*) U. Wahlgren, private communication.

21 S. Huzinaga, *Approximate Atomic Functions II*, Department of Chemistry Report, University of Alberta, Edmonton, 1971.

22 P. J. Hay and W. R. Wadt, *J. Chem. Phys*., 1985, **82**, 299.

23 U. Wahlgren and P. E. M. Siegbahn, unpublished data.

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