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Synthesis and Properties of the Strained Alkene Perfluorobicyclo[2.2.0]hex-1(4)-ene

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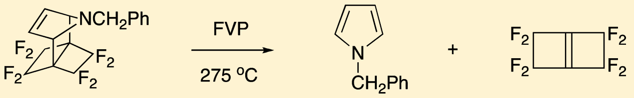
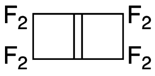
Ⓢ *Supporting Information*

ABSTRACT: The title fluoroalkene has been generated by dehalogenation of dibromide and diiodide precursors and trapped *in situ*. *retro*-Diels–Alder reaction of its adduct with *N*-benzylpyrrole has made the alkene available in high yield and purity. In sharp contrast to its extremely labile hydrocarbon counterpart, the fluoroalkene is very stable yet highly reactive. Its characterization includes its electron affinity, photoelectron spectrum, and the previously reported structure determination by electron diffraction.



INTRODUCTION

Our synthesis and study of the title fluorocarbon (**1**) was inspired in part by the fascinating work of Wiberg's group on the highly strained parent hydrocarbon (**2**).[1] Like its parent, **1** displays striking reactivity, but as a fluorocarbon, its behavior is radically different. Experimental investigations, mostly brief, of the synthesis, nature, and chemistry of **1** have been reported,[2−5] as well as theoretical studies of its structure and behavior.[5−8] Here we flesh out a larger portion of the story of this remarkable compound. Because hydrocarbon **2** dimerizes and polymerizes at temperatures below 0 °C, we were prepared at the outset for **1** to be very labile.



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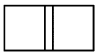

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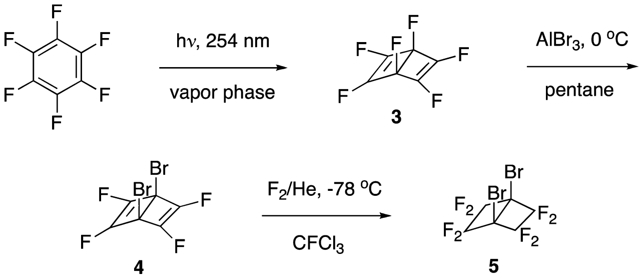
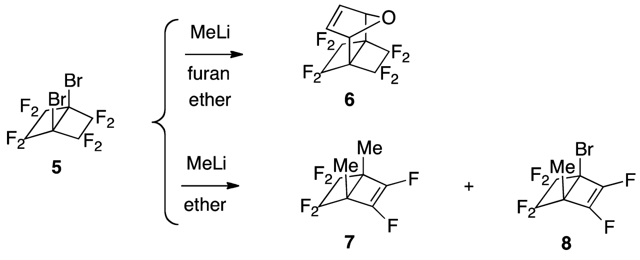
RESULTS AND DISCUSSION

The synthesis of **1** begins with transformation of hexafluorobenzene via its Dewar isomer (**3**)[9] and dibromide **4**[10] into the octafluorodibromide **5** (Scheme 1).[2] Selective replacement of the bridgehead fluorines of **3** presumably occurs by way of pentadienylic cations. In the fluorination of **4**, vigorous mechanical stirring and relatively high dilution are important for minimizing oligomer formation.

Scheme 1



Scheme 2



Initial evidence of the transient existence of alkene **1** appeared when dibromide **5** was treated with methyllithium in the presence of furan, producing the Diels–Alder adduct **6**. Omission of furan did not allow detection of **1**, however, as it reacted with the methyllithium to give alkenes **7** and **8** (Scheme 2). A likely pathway for this over-reduction is shown in Scheme 3, where addition of methyllithium to **1** results in elimination of fluoride ion to give the very strained alkene **9**. Attack on **9** in S_N2' fashion by methyllithium yields **7** and by bromide ion yields **8** with considerable relief of strain. The finding that rapid addition of excess methyllithium gives **7** exclusively is consistent with this interpretation. Assisted by ultrasound, zinc dust also generated alkene **1** from **5**, as shown by the formation of furan adduct **6** (Scheme 4). Again over-reduction

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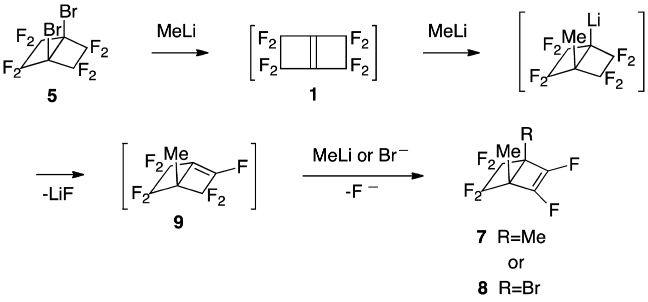
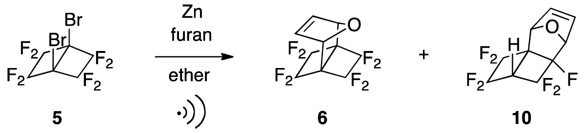
occurred, however, with the formation of an almost equal amount of **10**, a likely mechanism for which appears in Scheme 5.

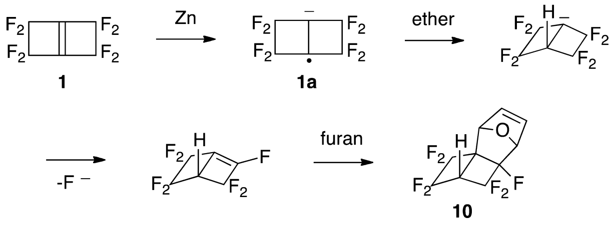
Scheme 3



Scheme 4

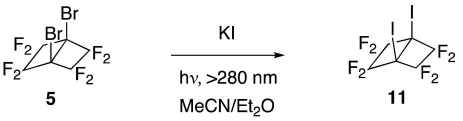


Scheme 5



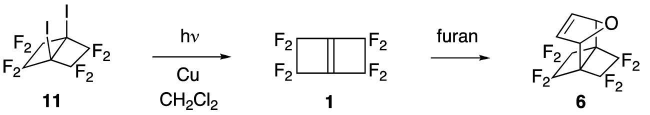
We hoped that diiodide **11**, with its relatively weak C−I bonds, would permit generation of **1** under sufficiently mild conditions that it would survive. Synthesis of **11** could not be accomplished like that of **5**, though, as the fluorination step wreaked havoc with the C−I bonds. Fortunately, the bromines in **5** could be replaced with iodines by UV irradiation of a solution of the dibromide and KI in an acetonitrile/ether mixture (3:1) (Scheme 6).[11] We dubbed this halogen metathesis with iodide ion a "photo-Finkelstein reaction". Unlike its dark S_N2 namesake,[12] the photochemical transformation proceeds via electron transfer. Diiodide **11** was sufficiently reactive that even mercury or silver in acetonitrile reduced it to **1** with assistance from ultrasound, and the alkene was trapped with a variety of reagents.[2]

Scheme 6



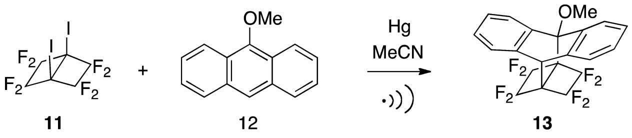
When the diiodide was irradiated with UV light in methylene chloride in the presence of copper powder as an iodine scavenger, the ^{19}F NMR spectrum of the reaction mixture revealed a singlet at δ ca. −100. Addition of furan caused the singlet to disappear with concomitant growth of signals for Diels−Alder adduct **6** (Scheme 7). This was the first successful attempt to observe **1** directly. The reaction required strict exclusion of moisture, because water adds readily to the alkene, and attempts to scale it up were unpromising. Thus, a different approach for isolation of the alkene was sought.

Scheme 7



It seemed possible that a Diels−Alder adduct of **1** could be found that would undergo thermal *retro*-reaction to regenerate the alkene under conditions that would allow its isolation. A suitable diene should possess these characteristics: (1) sufficient nucleophilicity to trap the electron-deficient alkene efficiently, (2) high thermodynamic stability to favor *retro*-Diels−Alder reaction, and (3) low volatility to permit easy separation from **1**. The first candidate to be tried was 9-methoxyanthracene (**12**), prepared from anthrone.[13] This diene reacted with **1** formed by mercury reduction of diiodide **11**, giving adduct **13** (Scheme 8). The ^{19}F NMR spectrum of **13** comprised two overlapping AA′BB′ patterns ("front" and "back") with the same set of coupling constants.

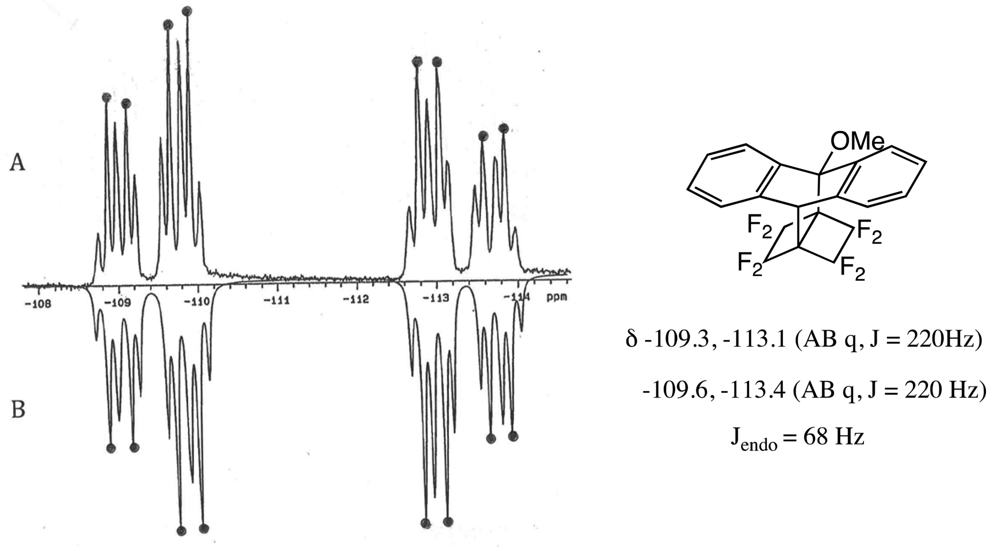
Scheme 8



Computer simulation with gNMR[14] confirmed the structure assignment and revealed the F−F coupling constants (Figure 1). The endo−endo F−F coupling constant could not be measured directly from the spectrum because of the plane of symmetry that makes endo-coupled fluorines chemical-shift equivalent. Each half of each AA′BB′ pattern consists of two pseudotriplets, the splitting of which depends on the value of $J_{FF(endo)}$ (and disappears when that value is small). The X-ray crystal structure of **13** was determined, and it reveals F−F endo distances of 2.50 and 2.52 Å, well within the sum of the atomic radii (2.94 Å). The 68 Hz coupling arises primarily, if not exclusively, from through-space interaction. When **13** was heated, it did undergo the desired *retro*-Diels−Alder reaction, but not until the temperature exceeded 180 °C.

The next diene to be tried as the source of a precursor for alkene **1** was a pyrrole. Pyrroles offer the dual advantages of high nucleophilicity to favor the trapping reaction and robust aromaticity to promote the *retro*-Diels−Alder reaction. *N*-Benzylpyrrole (**14**),[15] chosen for its nonvolatility, trapped alkene **1** efficiently, yielding adduct **15**. The reaction was run using diiodide **11** and mercury in acetonitrile with ultrasound, but it was conducted most conveniently with dibromide **5** and zinc or a zinc/copper couple (Scheme 9).[3] The nicely crystalline adduct **15** (mp 99−100 °C) proved to be an excellent precursor for **1**.

Like adduct **13**, **15** has C_S symmetry, but its plane of symmetry is perpendicular to that of **13**. As a result, its ^{19}F NMR spectrum (Figure 2) offers an interesting contrast with that of the 9-methoxyanthracene adduct. The spectrum comprises two AB quartets, with the lower field half of each split into doublets by the endo−endo coupling, here shown directly. A 7 Hz through-space coupling between the vinyl



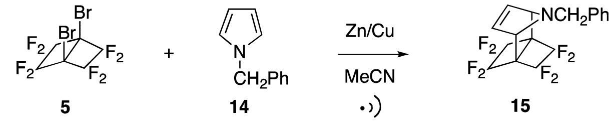
δ -109.3, -113.1 (AB q, J = 220Hz)

-109.6, -113.4 (AB q, J = 220 Hz)

J_{endo} = 68 Hz

Figure 1. Experimental (A) and simulated (B) ^{19}F NMR spectra ($CDCl_3$) of 9-methoxyanthracene adduct **13**.

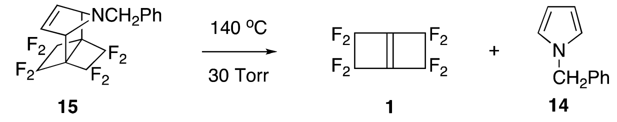
Scheme 9



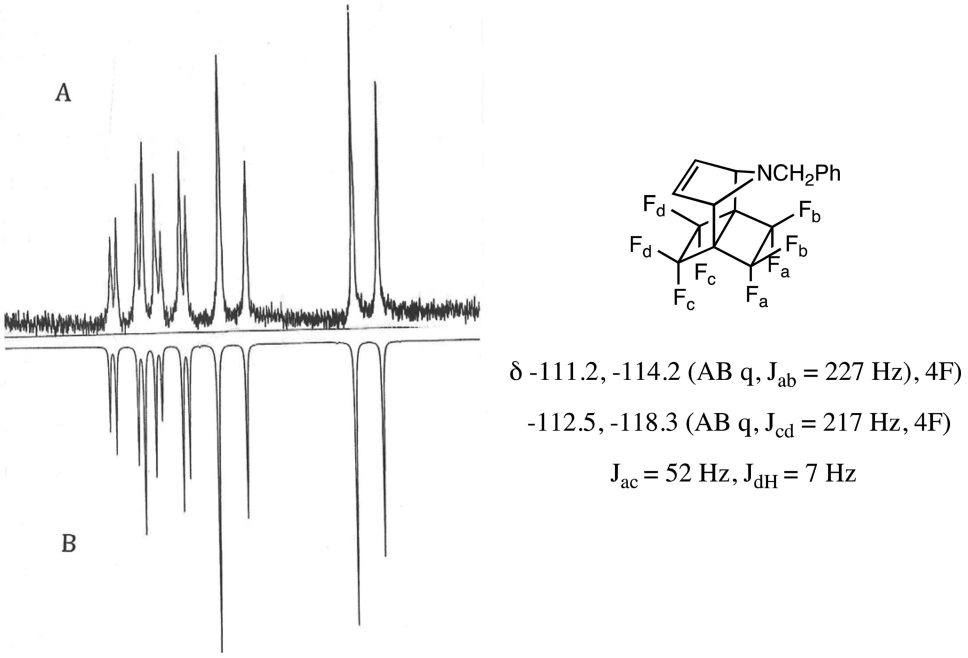
protons and neighboring *exo* fluorines, revealed by the ^1H and HF COSY spectra, facilitated complete assignment of the fluorine spectrum. Simulation of that spectrum is also shown in Figure 2. The smaller $J_{FF(endo)}$ for **15** as compared with that of **13** indicates a somewhat longer endo–endo F–F distance, presumably because the pyrrole "cap" on the fluorocarbon moiety exerts less nonbonded repulsion on it than does the anthracene "cap". Consistent with this finding, the X-ray crystal structure of **15** reveals F–F endo distances of 2.56 Å.

N-Benzylpyrrole adduct **15** underwent *retro*-Diels–Alder reaction at a suitable rate at 140 °C, a temperature considerably lower than that for adduct **13** (Scheme 10). It was heated under

Scheme 10



aspirator pressure in a flask connected to a cold trap (77 K) with furan frozen on its walls. After methylene chloride was added and the trap warmed to RT, the ^{19}F spectrum of the resulting solution showed only signals for furan adduct **6**. Repetition of the experiment with an empty cold trap gave a



δ -111.2, -114.2 (AB q, J_{ab} = 227 Hz), 4F)

-112.5, -118.3 (AB q, J_{cd} = 217 Hz, 4F)

J_{ac} = 52 Hz, J_{dH} = 7 Hz

Figure 2. Experimental (A) and simulated (B) ^{19}F NMR spectra ($CDCl_3$) of *N*-benzylpyrrole adduct **15**.

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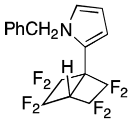
solution that showed a singlet at δ −99.1 in its ^{19}F NMR spectrum (−70 °C), a singlet that persisted at RT. Thus, alkene **1** was shown to be an isolable and stable compound.

However, the yield of **1** was very low (<10%), and thick, black tar remained behind in the reaction flask. In the hope that dilution would improve yields by minimizing intermolecular reactions, the pyrolysis was repeated in a similar fashion by injecting a solution of **15** into a refluxing solvent. Of the variety of inert, high-boiling point solvents tried, 1,2,4-trichlorobenzene proved to be the best, affording 23−24% yields of furan adduct **6**.

Analysis of the residual black tar revealed the presence of compound **16**, an isomer of the starting material with a lower energy as a consequence of aromaticity and diminished ring strain. Most of the starting adduct was being converted to **16** even in dilute solution. Attempted purification of **16** by preparative GC yielded instead an isomer (**18**) with considerable release of strain. This rearrangement probably occurred via zwitterionic intermediate **17** (Scheme 11).



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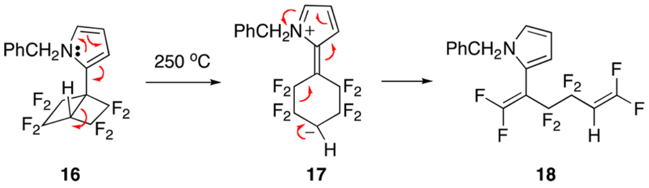
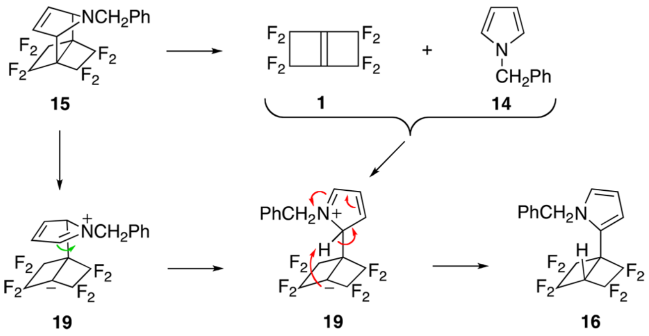
Scheme 11



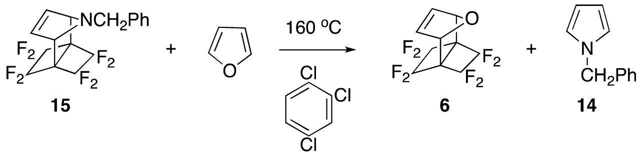
The ^{19}F NMR spectrum of **18** at RT comprised four singlets for vinyl fluorines, one singlet for the CF$_2$ group distal to the pyrrole ring, and an unresolved AB quartet for the proximal CF$_2$. Recognizable as a quartet at 0 °C, this last resonance became a sharp singlet by 60 °C. Thus, VTNMR of **18** revealed that rotation about either single bond or both nearest to the pyrrole ring is sufficiently hindered to occur at an intermediate rate on the NMR time scale at RT.

Formation of **16** might take place in either of two ways, via intramolecular rearrangement of **15** or *retro*-Diels−Alder reaction followed by electrophilic substitution on the pyrrole ring; i.e., zwitterionic intermediate **19** could be formed via either pathway (Scheme 12). To distinguish between the inter- and intramolecular pathways, adduct **15** and excess furan were heated together at 160 °C in a sealed tube. Furan adduct **6** was obtained, but no **16** was present in the product (Scheme 13). Therefore, **16** had been produced in the earlier pyrolysis experiments solely via *retro*-Diels−Alder reaction of **15**.

Scheme 12

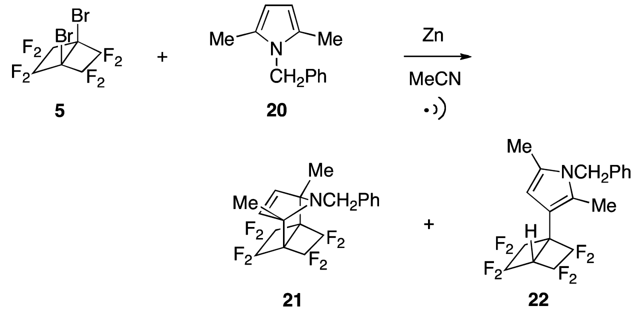


Scheme 13



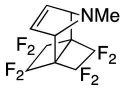
We speculated that the adduct of **1** with a pyrrole substituted at positions 2 and 5 might undergo less isomerization upon being heated than **15**. Accordingly, *N*-benzyl-2,5-dimethylpyrrole (**20**)[16] was tried at RT as a trap for alkene **1** (Scheme 14).

Scheme 14



Early in the reaction, ^{19}F NMR indicated that adduct **21** was the only product, but at higher conversion, peaks grew in for the more stable isomer **22**, in which the pyrrole ring was substituted at position 3. Although it is possible that the **21** to **22** transformation proceeded intramolecularly by way of a [2.2.2]propellane intermediate, *retro*-Diels−Alder reaction/recombination seems more likely. In any event, it is striking that the isomerization occurs at RT. Gas chromatography at 250 °C transformed the mixture of **21** and **22** into an isomer analogous to **18**.

N-Methylpyrrole behaved like **20** under the same gentle conditions, giving at first exclusively adduct **23** but eventually a 1:1 mixture of **23** and **24**. This was a surprising result, because *N*-methylpyrrole is not very different in character from the *N*-benzyl derivative. It is not known whether the intra- or intermolecular pathway shown in Scheme 5 was followed by adduct **23**.



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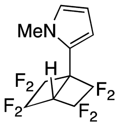

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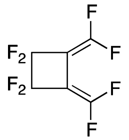
It was now clear that the *N*-benzylpyrrole adduct **15** was the precursor of choice for **1**, but the problem of low yield remained. To forestall the recombination of **1** and pyrrole **14** that was occurring at 140 °C even in rather dilute solution, flash vacuum pyrolysis (FVP) was conducted with adduct **15**. The apparatus consisted of a flask joined to a Pyrex pyrolysis tube connected in turn to a pair of U-traps, the first at 0 °C and the second at 77 K. With the pyrolysis tube at 300 °C, compound

15 was sublimed from the flask at 30 mTorr. *N*-Benzylpyrrole collected uncontaminated with fluorine-containing material in the 0 °C trap, and alkene **1** appeared in the 77 K trap in 85% yield as determined by NMR. Under these conditions, a small amount of **25**,[17] the dimer of tetrafluoroallene, was formed by electrocyclic ring opening of **1**. The optimal temperature for maximizing the yield of **1** and minimizing that of **25** was found to be 275 °C.



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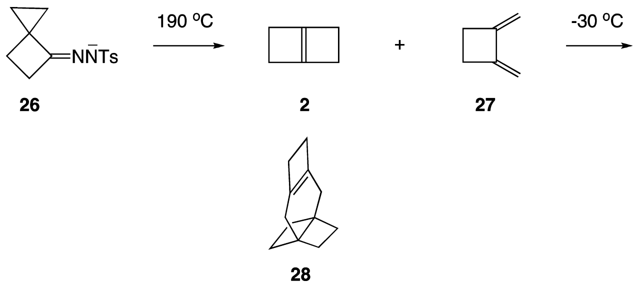
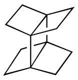
Finally, a source of pure **1** was available, and it was already apparent that the contrasts between the fluorocarbon and its very labile hydrocarbon counterpart **2** would be profound. When **2** was prepared by pyrolysis at 190 °C of tosylhydrazone anion **26**, ring-opened 1,2-dimethylenecyclobutane (**27**) was obtained in yields as high as 75%, and **2** reacted with **27** to give adduct **28** even at −30 °C (Scheme 15).[1a] No reaction took place between **1** and its ring-opened isomer **25** at 80 °C.

Scheme 15



Hydrocarbon **2** dimerizes to give **29** (a transient intermediate that ring opens) with a $\Delta H^{\ddagger}$ of only 11.5 kcal/mol,[1] but its fluorinated counterpart **1** does not form dimer **30** at any temperature. We assumed that nonbonded repulsions between fluorines in **30** were primarily responsible for the contrast, but a thorough analysis by Borden[6] based on density functional theory has revealed a somewhat greater contribution to the calculated difference of 44.6 kcal/mol in ΔH for the two dimerizations: the π bond in **1** was found to be 16 kcal/mol stronger than that in **2**. Approximately 25% of this difference was ascribed to stabilization of the π bond of **1** by donation of its electrons into C−F σ^* orbitals and 75% to destabilization of the broken π bond. The latter effect arises because eclipsing a pyramidalized carbon radical with a C−X bond is unfavorable for X = F relative to X = H.



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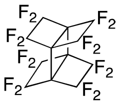

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Fluorocarbon **1** is a liquid at RT with a narrow liquid range: mp 19−20 °C, bp 52.5 °C. Its ^{19}F NMR spectrum ($CDCl_3$) consists of a sharp singlet at δ −99.1, and the ^{13}C spectrum ($CDCl_3$) comprises a signal at δ 121.6 for the four CF_2 carbons and one at δ 175.8 for the bridgehead carbons. Hydrocarbon **2** is a flat molecule with D_{2h} symmetry, but for **1**, a roof-shaped structure (C_{2v}) was a reasonable alternative (Figure 3). The fact that the ^{19}F NMR spectrum of **1** was a narrow singlet even at −70 °C was not inconsistent ith C_{2v} geometry, as pyramidal inversion of this structure should be very rapid. We believed that the combination of ring strain and the effect of eight fluorines might force the bridgehead carbons to pyramidalize. Insofar as fluorine's electronegativity results in enhanced p character in the C−F bonds (Bent's Rule),[18] transmission of that effect to the bridgehead carbons would favor a change from sp^2 to sp^3 hybridization.

Figure 3. Possible geometries for the skeleton of alkene **1**.

Infrared absorption is forbidden for the C=C stretching vibration in D_{2h} but allowed in C_{2v} symmetry. Whereas the Raman spectrum of **1** displayed a band a 1621 cm^{-1} for the C=C stretching mode, there was no band at this position in the infrared spectrum. The conclusion from these observations that the molecule is flat with D_{2h} symmetry was confirmed by an electron diffraction study coupled with hybrid density functional calculations conducted by Kenneth Hedberg at Oregon State University.[5] It is bow-tie-shaped, with $r(C_1{-}C_4)$ = 1.376(14) Å, $r(C_1{-}C_2)$ = 1.530(3) Å, and $r(C_2{-}C_3)$ = 1.627(5) Å.

The electron deficiency of **1** is reflected in its gas phase electron affinity, 1.3 ± 0.2 eV. The electron-accepting LUMO is depicted in Figure 4. For the radical anion **1a**, the proton affinity is <348 ± 2 kcal/mol, as it is less basic than the acetate ion. These results are in accord with M06-2X/maug-cc-pVT(+d)Z//M06-2X/aug-cc-pVDZ predictions of EA(**1**) = 1.67 eV and PA(**1a**) = 329.4 kcal/mol. Together with the ionization potential of the hydrogen atom (313.6 kcal/mol) and the computed electron and proton affinities, these findings suggest that $D[C{-}H]$ = 54 kcal/mol for the new bond in **31** (Scheme 16).

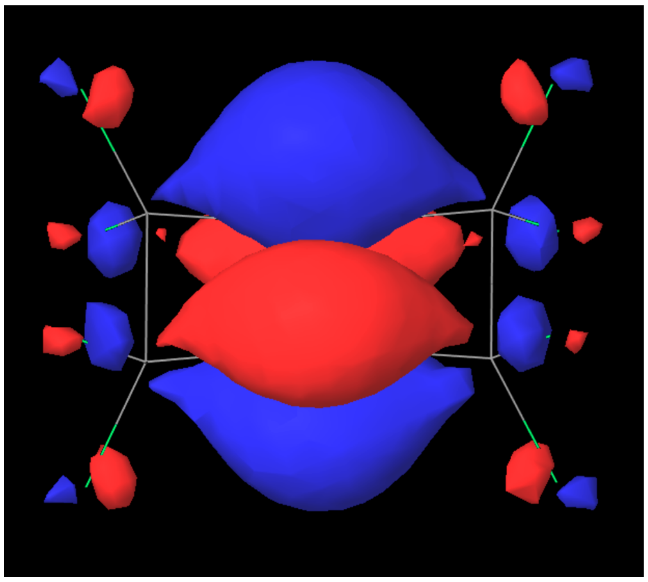
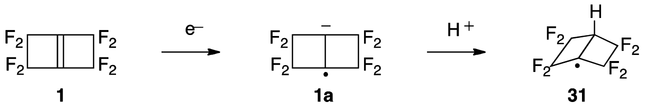
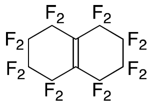


Figure 4. LUMO of alkene **1** (B3LYP/6-311G**+ level of theory).[19]

Scheme 16



The He(I) photoelectron (PE) spectrum of **1** shows two broad features between 12 and 14.5 eV. The first feature is composed of a shoulder at $I_{v,1}$ = 12.2 eV belonging to a broad Gaussian-like band superimposed upon a narrow band at $I_{v,2}$ = 12.7 eV. The second broad feature centered at 13.6 eV originates from at least three ionization processes. With regard to the first feature, the Gaussian-like band is typical for an ionization process from σ orbitals, whereas the second, narrower band is often found in ionization processes from π orbitals. The empirical assignment of the second band to the ionization from the π orbital of **1** is further underlined by the first PE band (π) of perfluoro-Δ^9-octalin (**32**)[20] at I_v = 13.0 eV. The slightly higher value of the π ionization energy found for **32** is due to the stronger inductive effect of two octafluoro bridges of **32** as compared to that of the two tetrafluoro bridges of **1**. The PE spectra of **1** and **32** appear in the Supporting Information.



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To assign the first two ionization processes of **1**, we make use of Koopmans' approximation,[21] which correlates the measured vertical ionization energies with the calculated negative value of the orbital energies of the ground state ($I_{v,j} = -\varepsilon_j$). This supports the empirical assignment of σ above π for **1**. Both MOs are shown in Figure 5, the HOMO encompassing the strained carbon skeleton. Their ionization energies lie far above those of ethylene (10.6 eV) and tetrafluoroethylene (10.52 eV) that are nearly identical as a consequence of the perfluoro effect.[22]

SUMMARY

Strained alkene **1** has been generated at RT by reduction of dibromide (**5**), and under milder conditions diiodide (**11**) precursors, and trapped *in situ*. Photolysis of the diiodide permitted the first direct observation of the alkene. Pyrolysis in solution of the Diels–Alder adduct **15** of **1** with *N*-benzylpyrrole gave an isomeric adduct (**16**) with a low yield of **1**. Rearrangement of the adducts of **1** with other pyrroles occurred even at RT. It was found that isomerization of **15** took place via *retro*-Diels–Alder reaction followed by recombination, and flash vacuum pyrolysis made it possible to preclude the latter process. This technique made alkene **1** available in high yield and purity.

The alkene is very stable toward reaction with itself, in sharp contrast to its extremely labile parent hydrocarbon. Electron diffraction measurements and hybrid density functional calculations[5] confirmed the indication from vibrational spectra that it possesses D_{2h} symmetry. Gas phase studies have revealed its photoelectron spectrum, its electron affinity, and an upper limit for the proton affinity of its radical anion.

EXPERIMENTAL SECTION

The ^{19}F NMR spectra were recorded at 282.2 or 470.3 MHz on a 300 or 500 MHz spectrometer. ^{19}F chemical shifts are reported on the δ scale (parts per million from internal standard trichlorofluoromethane, upfield negative). ^{1}H NMR spectra were recorded at 300 or 500 MHz with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded at 75.4 MHz on the 300 MHz spectrometer. Melting points were measured in open capillary tubes and were not corrected. Ultrasonic irradiation was performed in a Bronsicator Ultrasonic B-22-4 cleaning bath. Preparative gas chromatography was performed with a thermal conductivity detector. The column was 10 ft × $^1/_8$ in., 10% OV 101 on Chromosorb-P acid washed, and the standard program was as follows: detection at 200 °C, injection at 200 °C, column temperature as noted in text. All analytical GC was conducted using a 25 m methyl silicone capillary column and flame ionization detector. The standard program was as follows: carrier pressure, 25 psi; detector, 200 °C; injector, 150 °C; temp$_1$, 50 °C; temp$_2$, 250 °C; time$_1$, 5 min; 50 °C and then increasing at a rate of 15 °C/min to 250 °C. Photochemistry was conducted using a 450 W Canrad-Hanovia medium-pressure mercury lamp, with filters used as noted in the text. **Caution:** *Eye protection is essential when using this intense source of UV radiation.* For photoreaction mixtures that needed to remain at room temperature, cooling was achieved with a stream of tap water directed onto the outside of the reaction vessel. The runoff was collected in a plastic tub beneath the photochemical apparatus.

Solvents used in this work were reagent grade. Acetonitrile was distilled from calcium hydride and tetrahydrofuran from potassium/benzophenone. Zinc dust was purified using the method of Shriner and Neumann.[23] The zinc/copper couple was generated by first grinding together a mixture of finely powdered $CuSO_4{\cdot}5H_2O$ (2 g) and zinc dust (2 g) in a 10 mL vial. The vial was then covered with a rubber septum that was pierced by a needle, and 0.5 mL of DMF was added while the contents were being stirred to catalyze the reduction

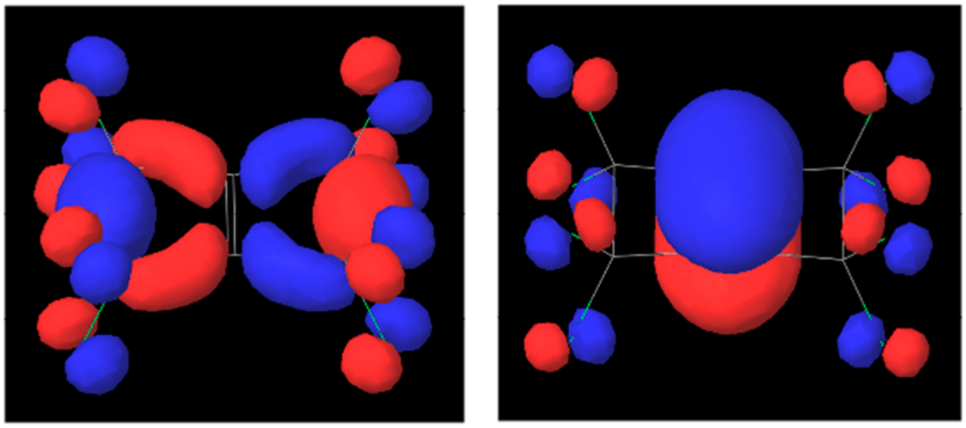

Figure 5. HOMO (left) and NHOMO (right) orbitals of alkene **1** (B3LYP/6-311G**+ level of theory).[19]

of copper. An exothermic reaction ensued, and once the vial returned to room temperature, the resulting black Zn/Cu couple was ground to a fine wet powder. The Zn/Cu couple was then heated under vacuum (150 °C, 30 mTorr) to remove the DMF and stored under nitrogen.

The X-ray crystal structure data for **15** were collected by J.P.J.. Using the Olex2 software package,[24] the structure was determined with SUPERFLIP[25] using charge flipping and refined with the ShelXL[26] refinement package using least-squares minimization. R.G. obtained the He(I) photoelectron spectra of **1** and **32**, which were recorded at room temperature. The calibration was done with Ar and Xe. A resolution of ~30 meV was achieved with the $^2P_{3/2}$ Ar line. Other gas phase experiments were conducted by S.R.K. with a dual cell Fourier transform mass spectrometer that was described previously.[27] Low-energy electron ionization (1.6 eV) or the reduction of **1** by NO^- (which was generated from nitrous oxide) was used to produce **1a**. This ion was isolated and then transferred to the second reaction region in the instrument where it was cooled with a pulse of argon, reisolated, and allowed to react with selected reference reagents.[28] In some cases, reverse processes were also examined by allowing an anion of interest generated by electron ionization to react with **1**. The proton and electron affinity data given in the Results and Discussion were obtained in this way (see the Supporting Information for further details). Computations on **1**, **1a**, and **31** were conducted by S.R.K. using Gaussian 09.[29] M06-2X geometry optimizations and vibrational frequencies were calculated with the aug-cc-pVDZ basis set,[30,31] and M06-2X/maug-cc-pVT(+d)Z[32] single-point energy determinations were subsequently conducted. The resulting proton and electron affinities and bond energies are given at 298 K.

Hexafluoro Dewar Benzene (3). **Caution:** *Hexafluoro Dewar benzene is explosive and has been known to detonate capriciously. Protective clothing (heavy jacket, leather gloves, and face shield) are recommended for handling it.* A cylindrical quartz vessel (5 L) fitted with a PTFE valve was evacuated (30 mTorr). The vessel was then sealed and removed from the vacuum line, and the bottom of the vessel was placed in an ice bath. A rubber septum was attached to the inlet valve extension, the valve opened, and hexafluorobenzene (6.0 mL, 9.6 g, 52 mmol) injected. The valve was closed and the vessel then irradiated at 254 nm for 4−6 days in a cylindrical photoreactor lined with ten 25 W germicidal lamps. The resulting Dewar benzene was vacuum transferred into a 100 mL U-trap containing 10 mL of *n*-pentane at 77 K. This trap was then surrounded by a wire cage and allowed to warm slowly to room temperature. The resulting pentane solution was checked by ^{19}F NMR to determine yield by integration. Yields varied from 5.8 to 7.6 g (from 60 to 80%). The product's ^{19}F NMR spectrum matched the literature values.[9]

1,4-Dibromotetrafluorobicyclo[2.2.0]hexa-2,5-diene (4).[2] **Caution:** *Compound 4 has been known to detonate, so this reaction was conducted behind a blast shield. Protective clothing (heavy jacket, leather gloves, and face shield) are recommended when handling it.* Hexafluoro Dewar benzene (23.4 g, 0.126 mol) in 150 mL of *n*-pentane was added dropwise to a stirred suspension of aluminum bromide (50.5 g, 0.189 mol) in 150 mL of *n*-pentane at 0 °C over a period of 1 h, and stirring was continued for an additional 1 h at 0 °C. The mixture was poured over 200 mL of crushed ice in a separatory funnel, and the pentane layer was gently washed with three 100 mL portions of cold water until the orange color faded. After the mixture had dried over magnesium sulfate, most of the pentane was removed with a rotary evaporator behind a blast shield in an ice bath; the residue was moved into a hood and evaporated using a water aspirator (20 Torr) at 0 °C until bubbling ceased. Trichlorofluoromethane (500 mL) was then added as the solvent for the next step. ^{19}F NMR ($CDCl_3$): δ −131.4 (s, 4F).

1,4-Dibromooctafluorobicyclo[2.2.0]hexane (5).[2] **Caution:** *Elemental fluorine, 30% in helium, is an extremely aggressive reagent that must be handled with care in a well-ventilated hood.* The trichlorofluoromethane solution described above was placed in a 1 L three-neck flask. The middle neck was fit with a mechanical stirrer shaft mounted in a PTFE bearing. In another neck, a Pyrex tube that reached almost to the bottom of the flask was used to admit fluorine-containing gas. A takeoff adapter in the remaining neck was connected to an aqueous KOH trap to remove any fluorine from the effluent gas before being vented into the hood. (Rapid mechanical stirring was essential to ensure an optimal yield for this reaction. The PTFE bearing does not require any grease for lubrication, thus ensuring that proper stirring can be maintained for the duration of the reaction.) The solution was cooled to −78 °C and flushed with N_2 for 15 min. A mixture of 30% fluorine in helium was then bubbled (5−6 bubbles per second) through the solution until ^{19}F NMR indicated that reaction was complete, ~4 h. This reaction proceeded via the partially fluorinated intermediate 1,4-dibromohexafluorobicyclo[2.2.0]hex-2-ene, which could also be seen by ^{19}F NMR. A distinct pale yellow color appeared upon completion of the fluorination. Nitrogen was then bubbled through the stirred solution for 20 min to purge it of any remaining fluorine gas. The trichlorofluoromethane was removed by distillation for reuse (it was washed with saturated $Na_2S_2O_3/H_2O$ to remove bromine, dried, and recycled), and the residual thick maroon liquid was vacuum transferred at 60 mTorr to give a waxy colorless solid (25.0 g, 51.7% yield for two steps). ^{19}F NMR ($CDCl_3$): δ −103.8, −113.4 (AX q, J = 261 Hz, 8F). The chemical shifts match those in the literature, but the reported J value is incorrect.[2]

11-Oxa-7,7,8,8,9,9,10,10-octafluorotetracyclo[4.2.2.1^{2,5}.0^{1,6}]undec-3-ene (6).[2] A mixture of 1,4-dibromooctafluorobicyclo[2.2.0]hexane (**5**, 0.398 g, 1.04 mmol), ether (3 mL), and furan (3 mL) was contained in a nitrogen-flushed 25 mL round-bottom flask. The flask was capped with a septum, and connection to a nitrogen bubbler was maintained via a syringe. After the mixture was cooled to −84 °C in an ethyl acetate/liquid N_2 bath, a solution of methyllithium (2.25 mmol) in 4 mL of ether, also cooled to −84 °C, was added dropwise with stirring via a gastight syringe. The bath was allowed to warm slowly to RT. Product was washed with water, and the aqueous phase was extracted with ether. The combined ether phase was dried over $MgSO_4$, filtered, and distilled at atmospheric pressure, leaving a pale yellow oil. This oil was dissolved in a small amount of ethyl acetate and flushed through a 6 in. column of silica gel. Slow removal of the solvent deposited white crystals of **6**. Alternatively, the product could be purified by sublimation (10 mTorr, 75 °C bath, 0 °C coldfinger). Mp: 124.5−126 °C. Yield: 0.234 g (77%). ^{19}F NMR ($CDCl_3$): δ −113.2, −114.8 (AB q, J = 224 Hz, 4F), −115.3, −121.7 (AB q, J = 228 Hz, 4F), J_{endo} = 48 Hz. ^1H NMR ($CDCl_3$): δ 6.4 (d, J_{HF} = 7.5 Hz, vinyl, 2H), 5.3 (s, bridgehead, 2H). IR: 1336, 1315, 1290, 1262, 1228, 1211, 1186, 1170, 1115, 1096, 1014 cm^{-1}. MS: m/z 292 (M^+), 68 (base, $C_4H_4O^+$). HRMS calcd for $C_{10}H_4F_8O$, 292.0134; found, 292.0124.

1,4-Dimethylhexafluorobicyclo[2.2.0]hex-2-ene (7) and 1-Bromo-4-methylhexafluorobicyclo[2.2.0]hex-2-ene (8). A solution of 1,4-dibromooctafluorobicyclo[2.2.0]hexane (**5**, 0.398 g, 1.04 mmol) in ether (6 mL) contained in a nitrogen-flushed, septum-capped 25 mL round-bottom flask was cooled to −84 °C with an ethyl acetate/liquid N_2 bath. A solution of methyllithium (2.25 mmol) in 4 mL of ether, similarly cooled, was injected dropwise with stirring. The mixture was allowed to warm slowly to RT and then washed with water. The aqueous phase was extracted with ether, and the combined ether phase was dried over $MgSO_4$, filtered, and evaporated to leave a mixture of **7** and **8**. ^{19}F NMR ($CDCl_3$) of **7**: δ −112.0, −125.8 (AB q, J = 220 Hz, 4F), −123.6 (s, vinyl, 2F). ^1H NMR ($CDCl_3$): δ 1.30 (s, 6H). MS: m/z 216 (M^+), 201 ($C_6F_6Me^+$), 117 (base, $C_5F_3^+$). HRMS calcd for $C_8H_6F_6$, 216.0374; found, 216.0370. ^{19}F NMR ($CDCl_3$) of **8**: δ −110.5, −114.8 (AB q, J = 208 Hz, 4F), −114.0, −122.2 (AX q, J = 205 Hz, 4F), −119.7 (s, vinyl, 1F), −123.5 (s, vinyl, 1F). ^1H NMR ($CDCl_3$): δ 1.42 (s, 3H). MS: m/z 280/282 (M^+), 201 (base, $C_6F_6Me^+$). HRMS calcd for $C_7H_3F_6Br$, 279.9322; found, 279.9330. Product composition was dependent upon the rate of addition of methyllithium, as quick injection gave only **7** and polymeric products. Gas chromatographic separation of **7** and **8** was not successful.

Debromination of 1,4-Dibromooctafluorobicyclo[2.2.0]hexane (5) with Zinc. Ether (3 mL), furan (3 mL), **5** (0.190 g, 0.493 mmol), and activated zinc (0.2 g, 3 mmol) were placed in a 25 mL round-bottom flask. Connected to a nitrogen bubbler, the flask was rocked for 2 h with a modified Kugelrohr motor in an ultrasound bath. After filtration, the product solution was washed with water, and the aqueous phase was extracted with ether. The combined ether solution was dried with $MgSO_4$, filtered, and distilled to give a colorless oil containing 11-oxa-7,7,8,8,9,9,10,10-octafluorotetracyclo-[4.2.2.$1^{2,5}$.$0^{1,6}$]undec-3-ene (**6**, 82 mg, 57%) and 11-oxa-3,3,4,4,6,6,7-heptafluorotetracyclo[6.2.1.0.^{2,5}.$0^{2,7}$]undec-3-ene (**10**). ^{19}F NMR ($CDCl_3$) of **10**: δ −106.7, −119.4 (AX q, *J* = 222 Hz, 2F), −110.5, −116.9 (AB q, *J* = 219 Hz, 2F), −113.7, −114.5 (AB q, *J* = 228 Hz, 2F), −182.7 (bridgehead). MS: *m*/*z* 274 (M^+, $C_{10}H_5F_7O^+$), 223 (base, $C_9H_4F_5O^+$), 68 ($C_4H_4O^+$).

1,4-Diiodooctafluorobicyclo[2.2.0]hexane (11).[2] Compound **5** (4.0 g, 8.4 mmol) was placed in a cylindrical 50 mL Pyrex tube along with 45 mL of an acetonitrile/ether mixture [3:1 (v/v)]. Potassium iodide (3.0 g, 18 mmol) was also added to this solution, producing a light yellow suspension. The mixture was stirred magnetically and cooled with a stream of water (18 °C) under nitrogen while being irradiated by the 450 W Canrad-Hanovia lamp until reaction was complete as determined by ^{19}F NMR (10−15 h). At this point, the mixture contained mostly the desired diiodo compound and was dark brown in color. Workup involved washing with 3 × 50 mL portions of water to remove the acetonitrile, and back-washing the aqueous phase with 2 × 20 mL portions of ether. The combined ether layers were washed with a saturated $Na_2S_2O_3$ solution, then dried over $MgSO_4$, and distilled to ∼25% of the original volume. The remaining solution was vacuum transferred at 30 mTorr and then blown down to an oil using a stream of nitrogen. The oil was purified by preparative GC (column temperature of 160 °C) to give pure **11** (2.2 g, 4.6 mmol, 45% yield). The product's ^{19}F NMR spectrum and melting point (112.5−113.5 °C) matched the literature values.[23] The UV−vis spectrum of this compound showed a λ_{max} at 276 nm ($\varepsilon \sim 602$). ^{19}F NMR ($CDCl_3$): δ −90.8, −112.1 (AB q, *J* = 220 Hz, 8F). Analytical GC retention time: 5.7 min.

Photochemical Generation of Alkene 1. To a flame-dried 10 mL quartz tube were added diiodide **11** (19 mg, 4.0 × 10^{-5} mol), 28 μL of furan (26 mg, 3.9 × 10^{-4} mol, 9.7 equiv), 100 mg of copper powder (1.6 × 10^{-3} mol, 40 equiv, to intercept iodine), and 5 mL of dry acetonitrile. This suspension was externally cooled with water, magnetically stirred under nitrogen, and irradiated for 6 h using a Vycor-filtered 450 W Canrad-Hanovia lamp. The only signals present in the ^{19}F NMR spectrum were those of furan adduct **6**.

To a flame-dried 10 mL quartz tube were added diiodide **11** (20 mg, 4.2 × 10^{-5} mol), 2 mL of dry methylene chloride, and copper powder (900 mg, 1.4 × 10^{-2} mol, 330 equiv). This suspension was irradiated as described above using a Corex-filtered 450 W Canrad-Hanovia lamp. After 2 h, a singlet appeared at −100 ppm (not referenced) representing alkene **1**. Further irradiation continued to yield more alkene, and then addition of furan to this reaction mixture produced ^{19}F NMR peaks corresponding to furan adduct **6**.

7,7,8,8,9,9,10,10-Octafluoro-2-methoxydibenzo[*c*,*m*]quadricyclo[4.2.2.$2^{2,5}$.$0^{1,6}$]dodeca-3,11-diene (13). To a flame-dried 20 mL flask were added diiodide **11** (230 mg, 4.8 × 10^{-4} mol), 9-methoxyanthracene **12** (500 mg, 1.44 × 10^{-3} mol, 3.0 equiv), 4 mL of dry acetonitrile, and 2 mL of mercury. This mixture was placed under nitrogen in the ultrasonic bath, which was cooled with water passing through a U-tube immersed in the bath. After 8 h, the ^{19}F NMR spectrum of the resulting yellow solution contained only peaks corresponding to adduct **13**. The reaction mixture was extracted with 5 × 10 mL portions of benzene. The combined benzene layers were then dried over $MgSO_4$, reduced in volume to 2 mL under reduced pressure, and placed on a silica gel column. Elution with pentane gave a yellow solid. At this point, adduct **13** was still contaminated with 9-methoxyanthracene. Recrystallization from a 1:1 pentane/ether mixture over the course of a week gave the desired product as a colorless crystalline solid. An X-ray crystal structure was obtained from these crystals, confirming the proposed structure. ^{19}F NMR ($CDCl_3$): δ −109.3, −113.1 (AB q, *J* = 220 Hz, 4F), −109.6, −113.4 (AB q, *J* = 220 Hz, 4F), J_{endo} = 68 Hz. ^1H NMR ($CDCl_3$): δ 7.5−7.1 (m, 8H), 4.72 (s, 1H), 3.99 (s, 3H). MS: *m*/*z* 253, 208 ($C_{15}H_{12}O^+$), 193 (base, $C_{14}H_9O^+$), 165, 82. Mp: 166.0−167.0 °C.

11-Aza-11-benzyl-7,7,8,8,9,9,10,10-octafluoroquadricyclo-[4.2.2.$1^{2,5}$.$0^{1,6}$]undec-3-ene (15) from Diiodo Compound 11. To a flame-dried 10 mL flask were added diiodo compound **11** (30 mg, 6.3 × 10^{-5} mol), *N*-benzylpyrrole **14** (30 mg, 1.9 × 10^{-4} mol, 3 equiv), 4 mL of dry acetonitrile, and 1 mL of mercury. This mixture was placed in a water-cooled ultrasonic bath for 5 h. The resulting yellow solution contained only the desired adduct as determined by ^{19}F NMR. Workup involved adding 10 mL of water and extracting with 3 × 3 mL portions of pentane. The combined pentane layers were dried over $MgSO_4$ and evaporated to 1 mL under reduced pressure. A white solid (15 mg, 62%) precipitated upon standing at 0 °C overnight. ^{19}F NMR ($CDCl_3$): δ −111.2, −114.2 (AB q, *J* = 227 Hz, 4F), −112.5, −118.3 (AB q, *J* = 217 Hz, 4F), J_{endo} = 52 Hz, $J_{F(exo)H}$ = 7 Hz. ^1H NMR ($CDCl_3$): δ 7.26 (m, 5H), 6.35 (d, *J* = 7 Hz, vinyl, 2H), 4.31 (s, bridgehead, 2H), 3.49 (s, benzylic, 2H). (Proton/fluorine assignments were verified by an HMQC experiment.) ^{13}C NMR ($CDCl_3$): δ 137.5, 134.7, 129.4, 128.5, 127.8, 66.0, 49.5. ^{13}C NMR ($CDCl_3$, ^{19}F-decoupled): δ 115.4, 114.1, 59.9. MS: *m*/*e* 381 (M^+), 91 ($C_7H_7^+$). Mp: 99.0−100.0 °C dec at 135−140 °C. Anal. Calcd for $C_{17}H_{11}NF_8$: C, 53.55; H, 2.91; N, 3.67. Found: C, 53.51; H, 2.90; N, 3.53. IR (KBr): 2860, 1499, 1459, 1331, 1313, 1218, 1166, 1093, 998, 914, 892, 864, 827, 791, 768, 734, 702 cm^{-1}.

11-Aza-11-benzyl-7,7,8,8,9,9,10,10-octafluoroquadricyclo-[4.2.2.$1^{2,5}$.$0^{1,6}$]undec-3-ene (15) from Dibromo Compound 5. To a flame-dried 25 mL flask were added dibromo compound **5** (0.83 g, 2.2 × 10^{-3} mol), 15 mL of dry acetonitrile, *N*-benzylpyrrole (0.35 g, 2.2 × 10^{-3} mol, 1.0 equiv), and 1.0 g of zinc/copper couple. This mixture was placed in a water-cooled ultrasonic bath and rocked using a modified Kugelrohr motor for 4 h. The ^{19}F NMR spectrum of the resulting yellow solution showed complete conversion to desired adduct **15**. The acetonitrile layer was combined with 25 mL of water, and this solution was then extracted with 3 × 10 mL portions of ether. The combined ether layers were dried over $MgSO_4$, and the ether was removed under reduced pressure, leaving a brown sticky solid. Recrystallization from ether at 0 °C gave large colorless crystals (0.60 g, 73% yield). An X-ray crystal structure was obtained from this crop of crystals that confirmed the proposed structure. Crystallographic data for $C_{17}H_{11}NF_8$: M_r = 381.27, monoclinic, $P2_1/c$, a = 12.154(3) Å, b = 9.965(3) Å, c = 12.740(3) Å, β = 101.872(19)°, V = 1510.1(7) Å^3, Z = 4, T = 298 K, μ(Mo Kα) = 0.168 mm^{-1}, D_{calc} = 1.677 g/cm^3, 3622 reflections measured (5.332° ≤ 2θ ≤ 54.992°), 3465 unique (R_{int} = 0.0481, R_{sigma} = 0.0938), which were used in all calculations. The final R_1 was 0.0444 [$I > 2\sigma(I)$], and wR_2 was 0.1583 (all data). CCDC = 1016151. The remaining brown ether layer was reduced in volume and chilled to produce an additional 100 mg of a brown solid; its purity was lower than that of the original product. When a very high purity is desired, this compound can be sublimed at 75 °C under vacuum (30 mTorr) to give a white powder.

GC/MS analysis of this compound also showed a peak that eluted before adduct **15** corresponding to olefin **1**, formed via *retro*-Diels−Alder reaction while in the injection port. MS: *m*/*z* 205 ($C_6F_7^+$), 174 ($C_5F_6^+$), 155 ($C_5F_5^+$, base), 124 ($C_4F_4^+$), 93 ($C_3F_3^+$), 69 (CF_3^+).

Generation of Alkene 1 via *retro*-Diels−Alder Reaction of *N*-Benzylpyrrole Adduct 15. To a flame-dried 10 mL round-bottom flask equipped with a reflux condenser and a septum-covered side arm was added 5 mL of 1,2,4-trichlorobenzene. The condenser was connected to a U-trap, which was connected in turn to a water aspirator. The trap was cooled to −196 °C, and 1 mL of furan was added. With water running through the condenser, the pressure in the system was reduced (30 Torr), and an oil bath was used to heat the solvent to 150 °C. A solution of *N*-benzylpyrrole adduct **15** (0.10 g, 2.6 × 10^{-4} mol) in 3 mL of 1,2,4-trichlorobenzene was then injected into the side arm in 0.5 mL portions over 10 min. The heating was continued for an additional 30 min, at which time the cold trap was disconnected from the apparatus and allowed to warm to room temperature. Hexafluorobenzene (20 μL, 1.7 × 10^{-4} mol) was then added as an internal standard. Integration of the ^{19}F NMR spectrum of this solution determined the ratio of furan adduct **6** to hexafluorobenzene, thus revealing that the amount of alkene **1** generated was 13 mg (23% yield).

Sealed Tube Reaction of *N*-Benzylpyrrole Adduct 15 with Furan. To a flame-dried Pyrex tube (15 cm × 1 cm, 4 mm inside diameter) were added *N*-benzylpyrrole adduct **15** (70 mg, 1.8 × 10^{-4} mol), 3 mL of 1,2,4-trichlorobenzene, and 0.5 mL of furan. The tube was cooled to −196 °C and sealed with a flame under reduced pressure (30 mTorr). It was then placed in a 160 °C oil bath for 30 min. After it was cooled again to −196 °C, the top was broken off and the solid was allowed to thaw. Hexafluorobenzene (30 μL, 2.6 × 10^{-4} mol) was added as an internal standard. ^{19}F NMR of the solution showed only furan adduct **6** and hexafluorobenzene. Integration revealed that 45 mg of **6** had been formed (85% yield).

1-Benzyl-2-(2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.0]hex-1-yl)-1*H*-pyrrole (16). This compound was generated as a thick black oil during the pyrolysis of **15** and was very difficult to purify. ^{19}F NMR ($CDCl_3$): δ −109.7, −112.8 (AB q, J = 226 Hz, 4F), −112.0 (s, 4F).

1-Benzyl-2-(1-difluoromethylene-2,2,3,3,5,5-hexafluoropent-4-enyl)-1*H*-pyrrole (18). A chloroform solution of impure compound **16** was injected into a preparative gas chromatograph (250 °C), and the peak corresponding to compound **18** was collected as a colorless liquid. ^{19}F NMR ($CDCl_3$): δ −68.4, −70.5, −72.2, −73.4 (vinyl Fs), −108.5 (CF_2, 2F), −111.8 (unresolved AB q, CF_2, 2F, $J \sim$ 265 Hz). By 60 °C, this resonance became a sharp singlet. ^{1}H NMR ($CDCl_3$): δ 7.33 (m, 3H), 7.10 (m, 2H), 6.72 (s, 1H), 6.23 (bs, 2H), 5.00 (s, 2H), 4.70 (dt, J = 22, 13 Hz, 1H). MS: m/e 381 (M^+), 113 ($C_3F_4H^+$, base), 91 ($C_7H_7^+$), 65 ($C_5H_5^+$). IR (neat): 1752 (C=C), 1720 (C=C), 1474, 1364, 1333, 1301, 1207, 1128, 1094, 1039, 977, 944, 893, 865, 803, 720 cm^{-1}. Anal. Calcd for $C_{17}H_{11}F_8N$: C, 53.55; H, 2.91. Found: C, 53.34; H, 2.92.

11-Aza-11-benzyl-7,7,8,8,9,9,10,10-octafluoro-2,5-dimethylquadricyclo[4.2.2.1^{2,5}.0^{1,6}]undec-3-ene (21), 1-Benzyl-2,5-dimethyl-3-(2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.0]hex-1-yl)-1*H*-pyrrole (22), and 1-Benzyl-3-(1-difluoromethylene-2,2,3,3,5,5-hexafluoropent-4-enyl)-2,5-dimethyl-1*H*-pyrrole. To a flame-dried 10 mL flask were added dibromo compound **5** (200 mg, 5.2 × 10^{-4} mol), 2,5-dimethyl-*N*-benzylpyrrole (**20**, 0.40 g, 2.2 × 10^{-3} mol, 4 equiv), 4 mL of dry acetonitrile, and 0.5 g of activated zinc. This mixture was placed in a water-cooled ultrasonic bath and rocked using a modified Kugelrohr motor. A ^{19}F NMR spectrum taken within the first 2 h showed only starting material and compound **21**. The ^{19}F NMR spectrum of the resulting bright yellow solution after 15 h showed an approximately 50:50 mixture of the desired Diels−Alder adduct (**21**) and the rearranged 3-substituted pyrrole (**22**), but the spectral resolution was poor because of the number of overlapping peaks. This solution was added to 15 mL of water, and the aqueous layer was extracted with 3 × 10 mL of pentane. The combined pentane portions were dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a brown oil. Upon attempted purification by preparative gas chromatography at 250 °C, these compounds isomerized to a 3-substituted pyrrole analogous to **18** as the only isolable product. Compound **21**. ^{19}F NMR ($CDCl_3$): δ −110.0, −113.6 (AB q, J = 226 Hz, 4F), −110.6, −115.4 (AB q, J = 226 Hz, 4F), J_{endo} = 61 Hz. ^{1}H NMR ($CDCl_3$): δ 7.31 (m, 5H), 6.15 [d, vinyl, 2H, $J_{\text{F(exo)H}}$ = 7.4 Hz], 3.47 (s, benzyl, 2H), 1.56 (s, CH_3, 6H). Compound **22**. ^{19}F NMR ($CDCl_3$): δ −110.9, −113.0 (AB q, J = 220 Hz, 4F), −112.4 (s, 4F). Pyrolysis product: ^{19}F NMR ($CDCl_3$): δ −72.9 (bs, 1F), −74.2 (s, 1F), −76.2 (s, 1F), −77.2 (bs, 1F), −109.1 (s, 2F), −110.5 (s, 2F). ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 3H), 6.83 (d, 2H, J = 7.2 Hz), 5.88 (s, 1H), 5.02 (s, 2H), 4.64 (dt, J = 23, 14 Hz, 1H), 2.12 (s, 3H), 2.02 (s, 3H). MS: m/z 409 (M^+), 91 (base, $C_7H_7^+$).

11-Aza-7,7,8,8,9,9,10,10-octafluoro-11-methylquadricyclo[4.2.2.1^{2,5}.0^{1,6}]undec-3-ene (23) and 1-Methyl-2-(2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.0]hex-1-yl)-1*H*-pyrrole (24). To a flame-dried 25 mL flask were added dibromo compound **5** (518 mg, 1.3 × 10^{-3} mol), *N*-methylpyrrole (147 mg, 1.8 × 10^{-3} mol, 1.4 equiv), 8 mL of dry acetonitrile, and 0.4 g of activated zinc. This mixture was placed in a water-cooled ultrasonic bath and rocked using a modified Kugelrohr motor. A ^{19}F NMR spectrum after 2 h showed only starting material and compound **23**. The spectrum after 15 h, just as in the 2,5-dimethyl-*N*-benzylpyrrole case, showed a 50:50 mixture of the desired Diels−Alder adduct **23** and its aromatized isomer **24**. This solution was added to 15 mL of water, and the aqueous layer was extracted with 3 × 10 mL of pentane. The combined pentane portions were dried over $MgSO_4$, and the pentane was removed under reduced pressure. In a sublimer at 2.0 Torr and 55−60 °C, the remaining yellow oil gave 157 mg of a white solid (38%). This solid was still a mixture of the two isomers **23** and **24** as determined by ^{19}F NMR, and careful recrystallization from ether did nothing to enrich the mixture. Compound **23**. ^{19}F NMR ($CDCl_3$): δ −111.3, −114.4 (AB q, J = 226 Hz, 4F), −112.7, −119.9 (AB q, J = 226 Hz, 4F), J_{endo} = 53 Hz. ^{1}H NMR ($CDCl_3$): δ 6.27 (d, $J_{\text{F(exo)H}}$ = 6.0 Hz, vinyl, 2H), 4.26 (s, bridgehead, 2H), 2.10 (s, methyl, 3H). Compound **24**. ^{19}F NMR ($CDCl_3$): δ −109.7, −112.8 (AB q, J = 220 Hz, 4F), −112.3 (s, 4F). Elemental analysis was performed on the mixture of isomers. Anal. Calcd for $C_{11}H_7F_8N$: C, 43.28; H, 2.30. Found: C, 43.60; H, 2.24.

Octafluorobicyclo[2.2.0]hex-1(4)-ene (1). Adduct **15** (0.32 g, 0.83 mmol) was placed in a flame-dried 5 mL round-bottom flask, which was connected to a pyrolysis apparatus consisting of a 15 mm outside diameter Pyrex tube enclosed in a 55 cm-long tube furnace. The outlet of the tube was connected to an ice-cold U-trap followed by a liquid N_2-cooled U-trap. The furnace was heated to 275 °C, and then **15** was allowed to sublime slowly into the hot zone under reduced pressure (60 mTorr). *N*-Benzylpyrrole (**14**) was intercepted in the ice−water trap, and alkene **1** was collected in the liquid N_2 trap. The system was filled with N_2, and the liquid N_2 trap was allowed to warm to RT. Alkene **1** was obtained as a colorless liquid (0.154 g, 82%). Mp: 19−20 °C. Bp: 52.5 °C. ^{19}F NMR ($CDCl_3$): δ −99.1 (s). ^{13}C NMR ($CDCl_3$): δ 175.8 (C=C), 121.6 (CF_2). IR (vapor) 1312, 1234, 1184, 886, 827 cm^{-1}. MS: m/z 205 ($C_6F_7^+$), 174 ($C_5F_6^+$), 155 (base, $C_5F_5^+$), 124 ($C_4F_4^+$), 93 ($C_3F_3^+$), 69 (CF_3^+). HRMS calcd for C_6F_8, 223.9880; found, 223.9872. It can be stored in a refrigerator for long periods of time without decomposing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR and PE spectra, X-ray crystallographic information, computational data, and gas phase experimental data. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 1016151 contains the supplementary crystallographic data for $C_{17}H_{12}N_3Cl$ (**15**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K., fax (+44) 1223-336-033, or e-mail deposit@ccdc.cam.ac.uk.

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Notes

The authors declare no competing financial interest.

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