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Chemistry of the Highly Strained Alkene Perfluorobicyclo[2.2.0]hex-1(4)-ene

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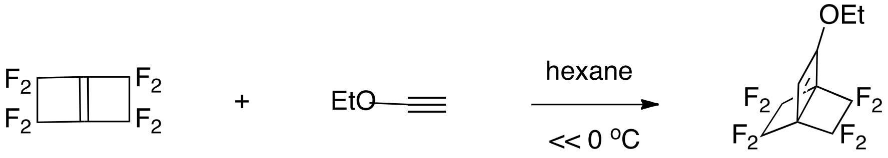

Abstract

Several varieties of cycloaddition as well as nucleophilic and free radical addition to the highly reactive central bond of the title fluorocarbon (**1**) are described. [2 + 2] Cycloaddition to **1** has made available four of the five known representatives of the [2.2.2] propellane ring system, rare because of their extreme strain (in the absence of fluorine substitution) and high reactivity. Two of these, a propellanone and a propellene, are first reported here. Quantum mechanical calculations have shed light on many of these transformations.

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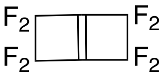
Introduction

Previous reports have presented syntheses, properties, and aspects of the chemistry of the title alkene **1**.[1-6] The compound is a very reactive and versatile electrophile, yet it is also strikingly robust.[7] That stability opened a wide temperature window for exploration of its reactivity, making possible, for example, Diels-Alder addition to benzene.[3] Its behavior is the more remarkable when compared with that of the parent hydrocarbon, which dimerizes and polymerizes at temperatures below zero.[8] The present account describes further transformations of **1**, all of which were carried out near r.t. or below. Reactions were run either with isolated alkene prepared by flash vacuum pyrolysis of its Diels-Alder adduct with N-benzylpyrrole, or *in situ* by reduction of a dihalide adduct.[6]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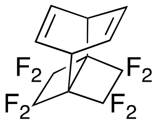
Results and Discussion

Quantum mechanical calculations have been performed to enhance understanding of both newly and previously reported reactions of the alkene. All were carried out initially at the B3LYP/cc-pVDZ+ level of theory,[9] but it became apparent that some of the computed energies were grossly inconsistent with experimental findings. The earlier-described[3] Diels-Alder addition of alkene **1** with benzene to yield adduct **2** was an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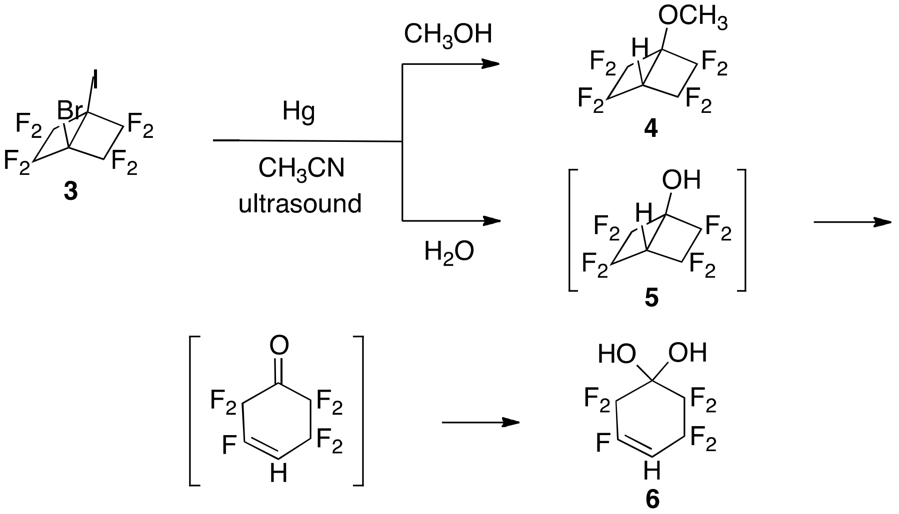
egregious case, as the reaction that afforded adduct in 65% yield (120 °C, 6 h) was predicted to be endoergic by nearly 20 kcal/mol. Additional calculations for this cycloaddition were therefore performed with an array of theoretical methods (Table 1), optimizations starting from the B3LYP/cc-pVDZ+ results. The only reasonable results were obtained with the MO6/DZVP2 and composite correlated molecular orbital theory G3MP2 levels (see Experimental Section for discussion of the computational details). These are the methods used later in this account, and energies obtained with the B3LYP functional are also reported for the sake of comparison.

Table 1. Benzene adduct formation energies in kcal/mol

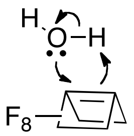
Level of Theory	ΔH_{0K}	ΔH_{298K}	ΔG_{393K}
B3LYP/DZVP2	-6.8	-8.0	14.7
BP86/DZVP2	-8.8	-9.9	12.7
PW91/DZVP2	-14.6	-15.8	6.9
PBE/DZVP2	-13.9	-15.1	7.7
M06/DZVP2	-23.7	-24.8	-2.5
SVWN/DZVP2	-43.0	-44.2	-21.5
G3MP2	-25.8	-27.0	-4.4

Non-cyclic Additions. All additions to alkene **1** occur in syn fashion; anti addition would create a very strained trans 4/4 ring fusion. When the alkene was generated in methanolic acetonitrile by treatment of bromoiodo precursor **3** with mercury in an ultrasonic bath, methanol adduct **4** was formed in high yield (Scheme 1).[1] A similar experiment with aqueous acetonitrile afforded monocyclic *gem*-diol **6**,[1] the consequence of ring opening of the initial water adduct **5** with loss of HF followed by hydration of the resulting ketone.

Scheme 1



Seeking to understand the mechanism by which **5** (and **4**) were formed, we considered the possibility of concerted cycloaddition by a water molecule and by water dimer. Calculations revealed pseudopericyclic transition states represented by **7** and **8** (Figure 1).[10-12] Activation enthalpies and free e□□□□□□□□for these processes are presented in Table 2, where it is clear that concerted addition of a single water molecule at r.t. is out of the question. On the other hand, reaction with water dimer to yield adduct **5** plus a molecule of water is very facile as evaluated at the G3MP2 level of theory, and we propose that this is how the addition occurs.[13]



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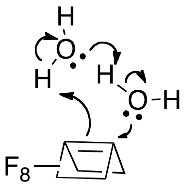

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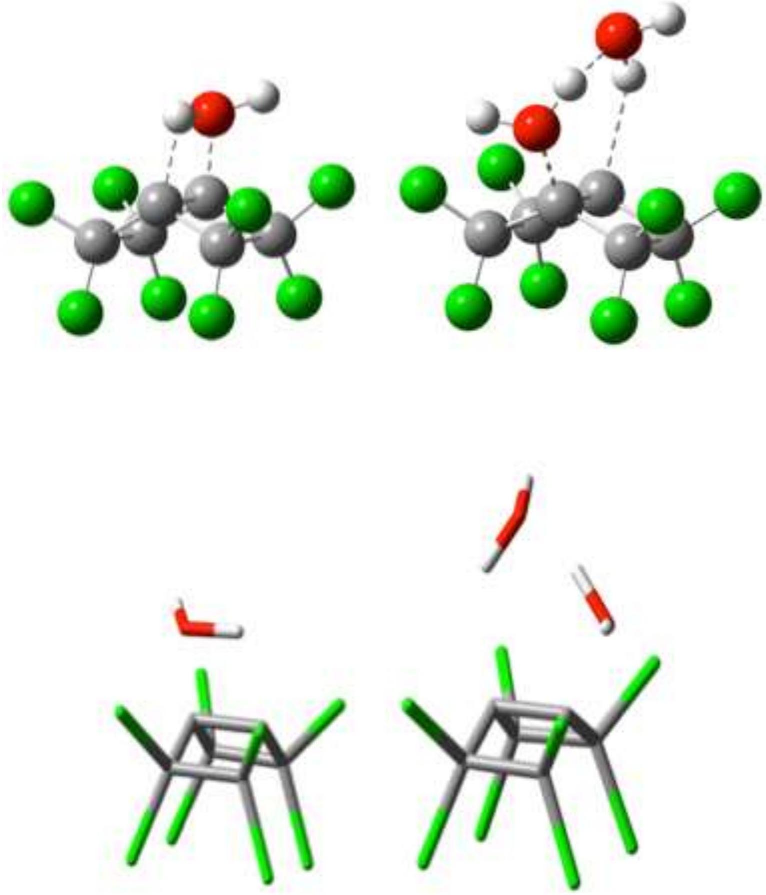


Figure 1. Two depictions of the transition states for addition of water (left) and of water dimer (right) to alkene **1** (B3LYP/DZVP2). A single negative frequency was found for each transition state.

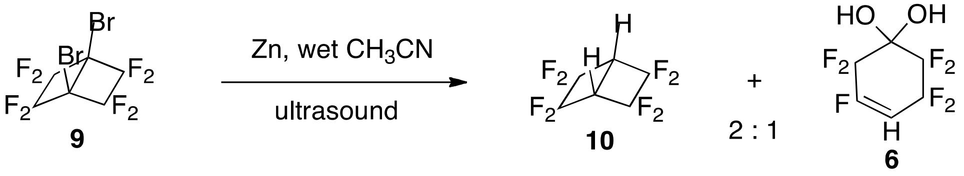
Table 2. Energetics of water and water dimer addition to alkene **1** in kcal/mol.

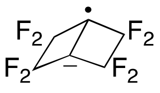
Transition State	B3LYP/DZVP2		M06/DZVP2		G3MP2	
	$\Delta H^{\ddagger}_{298K}$	$\Delta G^{\ddagger}_{298K}$	$\Delta H^{\ddagger}_{298K}$	$\Delta G^{\ddagger}_{298K}$	$\Delta H^{\ddagger}_{298K}$	$\Delta G^{\ddagger}_{298K}$

Water **TS 7**	35.2	47.4	30.2	42.9	36.6	48.7
Water dimer **TS 8**	11.6	27.4	7.5	22.5	-5.0	10.5

When dibromide **9** was treated in an ultrasonic bath with zinc dust in acetonitrile containing a little water, adduct **6** was formed again via **1**, but the dominant product with this more electropositive metal was dihydro compound **10** (Scheme 2).[14,15] Probably generation of **1** was followed by reduction to radical anion **11** and/or organozinc anion **12**, then protonation by water.

Scheme 2





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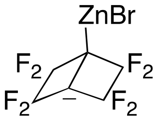

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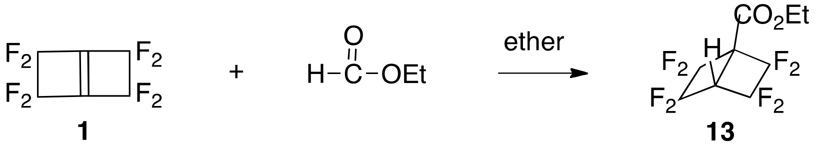
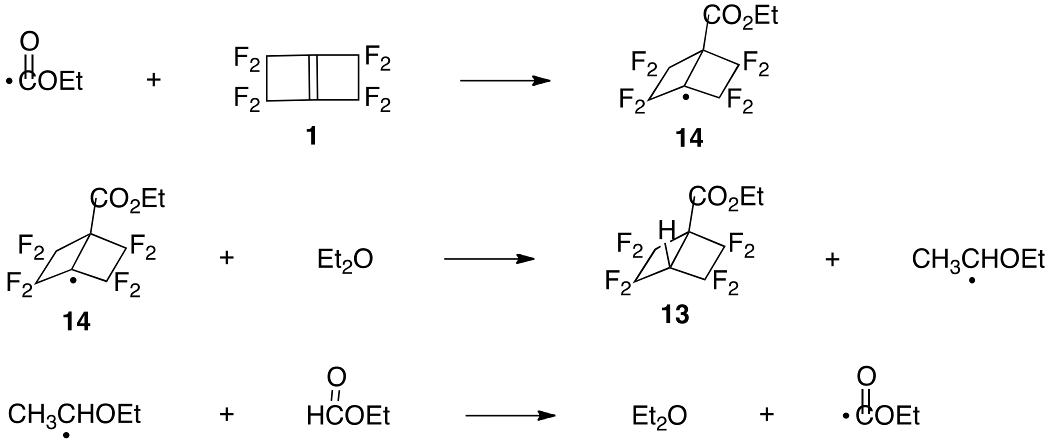
As described below, 1,3-cyclohexadiene reacts readily with alkene **1**, but the reaction fails completely when **1** is generated *in situ* from dibromide **9** and zinc in acetonitrile. If the solvent is wet, **10** and **6** are formed again,[16] and if anhydrous no product is obtained because the alkene is destroyed by zinc. Much of the chemistry of **1** explored using this method was carried out before the alkene was isolated, and the method was only effective when the desired reaction competed successfully with attack on the alkene by zinc.

Ethyl formate added spontaneously to isolated **1** in ether at r.t. Ester 13 was the sole product by ^{19}F NMR and was isolated by preparative GC (Scheme 3). When the reaction was carried out in $CDCl_3$, it stopped after low conversion and deuterium replaced the bridgehead hydrogen in **13**. The same thing happened in THF-d_8, but now the reaction was much faster and stopped after about 60% conversion. Apparently there was a trace of a reactive initiator present that set off a radical chain process involving the solvent. Presumed chain propagation steps are shown in Scheme 4.[17]

Scheme 3

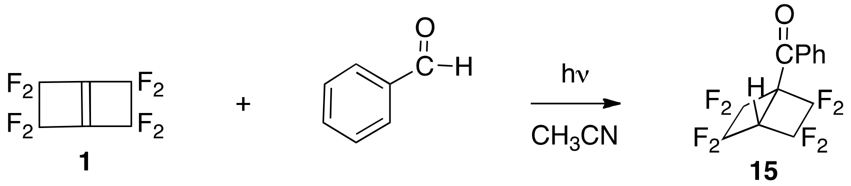


Scheme 4



In the Paterno-Büchi reaction, ultraviolet irradiation of an aldehyde or ketone results in [2 + 2] cycloaddition to an alkene, yielding an oxetane.[18] Attempts to carry out such an addition to isolated **1** with hexafluoroacetone and with benzophenone resulted in no reaction, but benzaldehyde did react, albeit to give an unexpected product. Addition of the aldehyde C-H bond occurred across the alkene double bond to afford ketone **15**, presumably the result of a light-initiated radical chain process (Scheme 5). No reaction took place in the absence of UV irradiation.

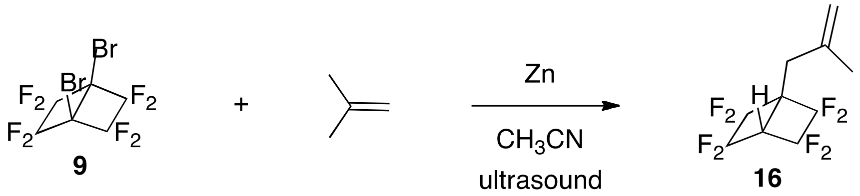
Scheme 5



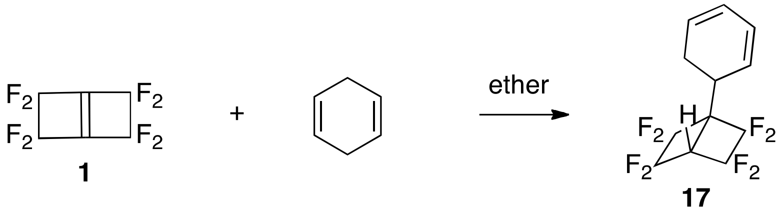
Addition of methyllithium to **1** and its consequences have been described elsewhere.[6]

[4 + 2] Cycloadditions. When dibromide **9**, zinc dust, isobutene, and acetonitrile were combined in a sealed tube and subjected to ultrasonic irradiation in a water-cooled bath, ene product **16** was formed in high yield by NMR (Scheme 6). Similarly, isolated **1** combined with 1,4-cyclohexadiene in ether at r.t. in another ene reaction to afford **17** (Scheme 7). Because this adduct has a chiral center, all eight fluorines are inequivalent,

Scheme 6



Scheme 7



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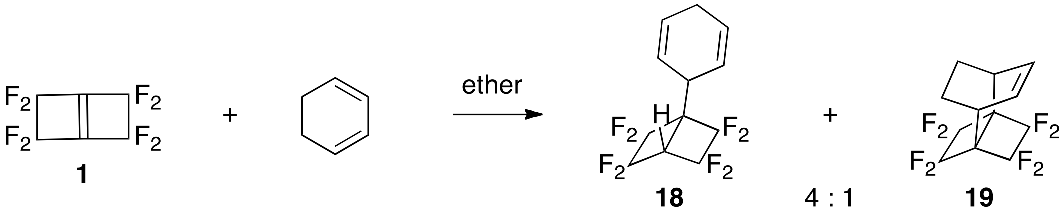
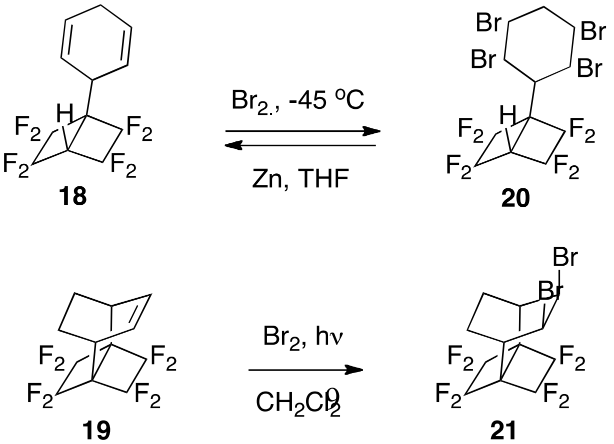
with the result that the ^{19}F NMR spectrum is a very complicated combination of two narrow AB quartets and two AX patterns. While alkene **1** failed to react with 1,3-cyclohexadiene when generated from dibromide **9** with zinc, as noted earlier, isolated **1** added to the diene in ether at rt, quantitatively by NMR (Scheme 8). Both ene reaction to give **18** and Diels-Alder addition to afford **19** occurred, with the former predominant. Steric hindrance by the flanking fluorines in the Diels-Alder transition state may explain the preference for the ene reaction. In contrast to its isomer **17**, the ^{19}F NMR spectrum of achiral **18** comprised a single AA'BB' quartet and AA'XX' pattern. Derivatives of **1** with a bridgehead hydrogen such as **16-18** characteristically fragment in the mass spectrometer by splitting down the middle to produce a prominent peak at m/z 113. This allylic cation, $C_3HF_4^+$, is usually the base peak.

Scheme 8



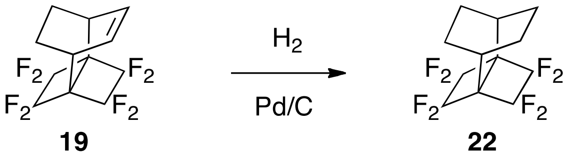
Bromine reacted readily with **18** at -45 °C in the dark to give **20** (Scheme 9).

Scheme 9



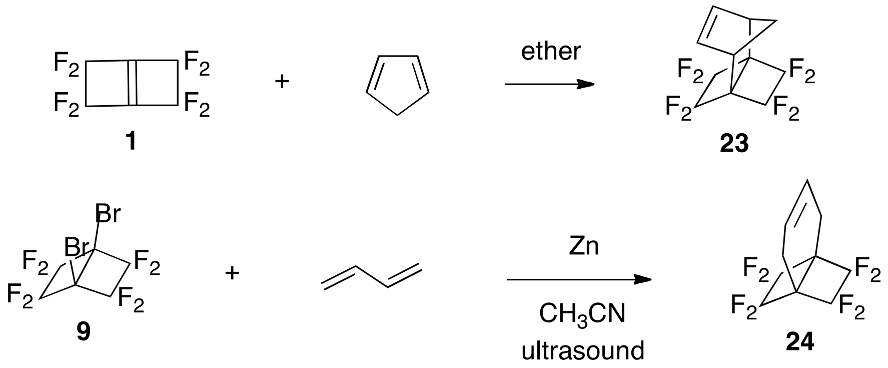
Adduct **19** was inert under these conditions, presumably because the backside of the double bond was shielded from attack. Vacuum transfer at rt separated the Diels-Alder adduct from the nonvolatile tetrabromide, from which **18** could be regenerated with zinc. In the presence of light, bromination of **19** did occur at rt, affording **21** (Scheme 9). This was a radical chain reaction, as it failed in the dark. Catalytic hydrogenation of **19** yielded symmetrical (C_{2v}) molecule **22**, the crystal structure of which is presented in the Supporting Information (Scheme 10).

Scheme 10



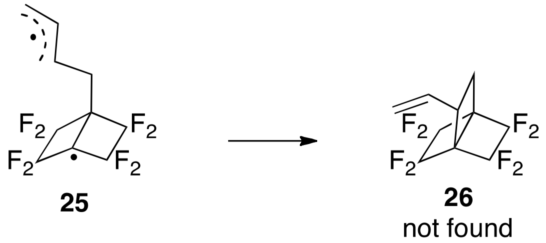
Diels-Alder reactions of **1** with furan, pyrroles, and aromatic hydrocarbons have been reported elsewhere.[1,3,6] Analogous addition to cyclopentadiene at rt to give **23** was rapid and quantitative by NMR (Scheme 11). Butadiene reacted at r.t. with **1** generated

Scheme 11



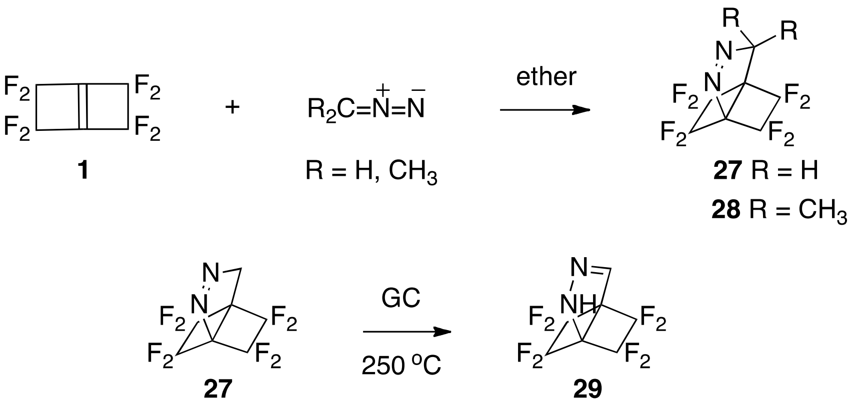
in situ from dibromide **9** and zinc, affording Diels-Alder adduct **24** (Scheme 11). Because butadiene exists ~97% in the s-trans form at rt,[19] if reaction had occurred stepwise, the principal diradical that arose would have been **25** (Scheme 12). Bond rotation in the allylic moiety of **25** required to form **24** would have faced a barrier of ~14 kcal/mol,[20] too high to compete with ring closure to the [2.2.2]propellane **26**.[21] Thus, formation of **24** instead of **26** constitutes strong evidence that the Diels-Alder reaction occurred concertedly.

Scheme 12



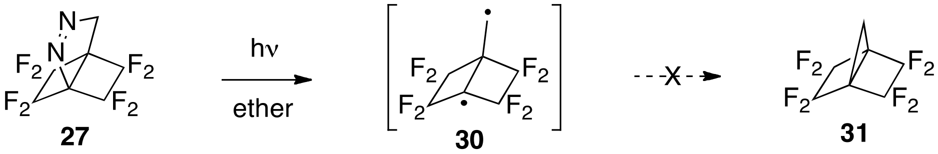
Diazomethane added instantaneously to **1** to give 1-pyrazoline **27**, and 2-diazopropane reacted similarly, affording adduct **28** (Scheme 13). Attempted purification of **27** by gas chromatography resulted in isomerization to 2-pyrazoline **29**. Both **27** and **28** were labile compounds that decomposed upon standing at rt.

Scheme 13

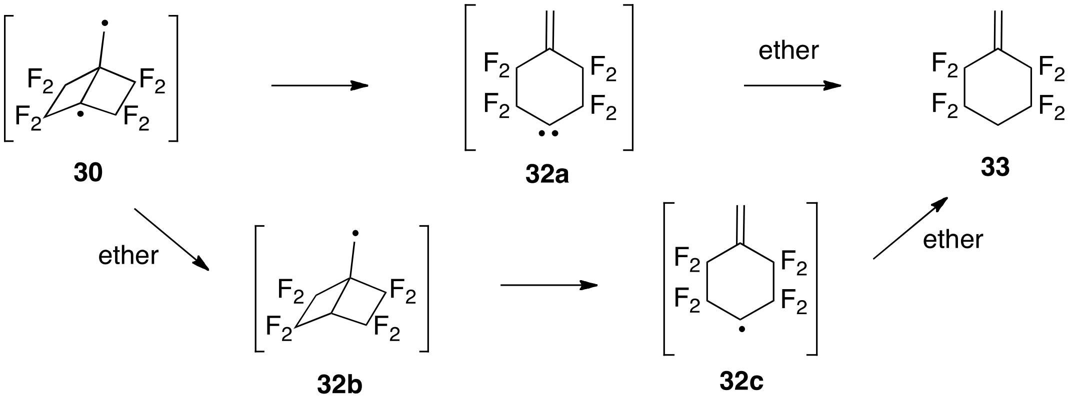


We hoped that photolysis of pyrazoline **27** would produce the extremely strained [2.2.1]propellane **31** via 1,3-diradical **30** (Scheme 14).[22] Though **31** might not be observed directly under our reaction conditions, low temperature photolysis or trapping experiments should reveal it if formed. Nature decided otherwise, as strain-releasing ring scission instead of ring closure occurred to give methylenecyclohexane **33**, and **28** reacted analogously (Scheme 15). This might have proceeded via ring opening of diradical **30** to carbene **32a**, which underwent sequential abstraction of hydrogen atoms from the ether solvent. Reviewers have proposed that the electrophilic tertiary radical center in diradical **30** abstracted a hydrogen atom from ether to give **32b**; ring opening to **32c** and a second hydrogen transfer followed. Though perfluoroalkylcarbenes are capable of both C-H insertion and hydrogen abstraction,[23] the absence of insertion product here argues for the pathway that bypasses the carbene.

Scheme 14



Scheme 15



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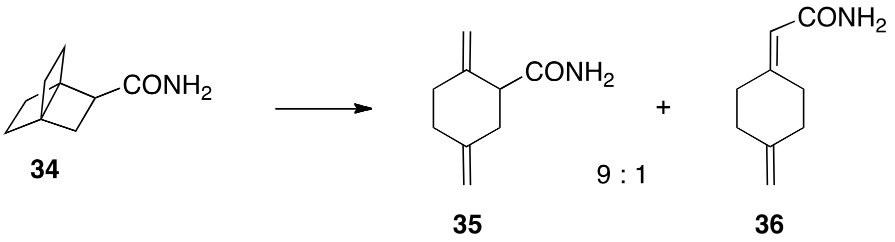
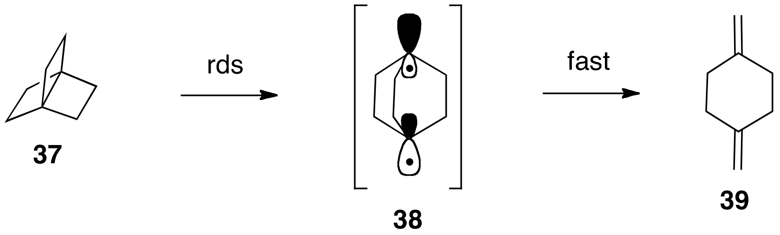
[2 + 2] Cycloadditions. Arguably, the most interesting transformations of alkene **1** are [2 + 2] cycloadditions because they create the highly strained [2.2.2]propellane ring system. The literature offers only a single well authenticated example of a [2.2.2]propellane other than those derived from **1**. In 1973, Eaton and Temme synthesized **34**, a very labile compound with a half-life for ring-opening to **35** and **36** of 28 min at 25 °C (Scheme 16).[24]

Scheme 16



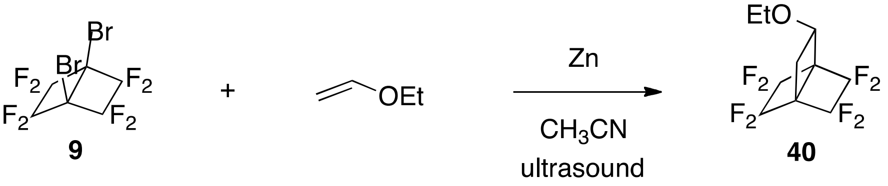
Such ring-opening is orbital topology-forbidden to occur concertedly.[10] Hoffmann[25] and Newton[26] showed that the process begins with rate-determining stretching of the very strained central C-C bond, illustrated with the unknown parent [2.2.2]propellane **37**, which results in an electronic state crossing to antisymmetric singlet **38** (Scheme 17). As the bond lengthens, through-space interaction between the bridgehead carbons loses out to through-bond interaction with the three bridges that both stabilizes the antisymmetric and destabilizes the symmetric state of the developing diradical. Subsequent scission of an external C-C bond in **38** to give **39** is orbital topology-allowed and highly exothermic.

Scheme 17



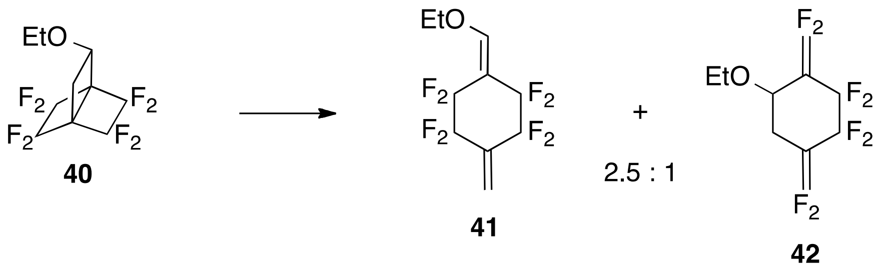
Ethyl vinyl ether reacted with alkene **1** to give [2.2.2] propellane **40**.[1] The reaction was first performed with alkene generated *in situ* from a diiodo precursor and mercury in acetonitrile in an ultrasonic bath. A much better yield of **40**, 77% after purification, was obtained using dibromide **9** and zinc under similar conditions to produce the alkene (Scheme 18). In light of the fact that formation of propellane **40** is an orbital topology-forbidden reaction, it is striking that it takes place so readily.

Scheme 18



The propellane suffered ring opening at r.t. to give dimethylenecyclohexanes **41** and **42** in the ratio 2.5 :1 (Scheme 19). The first order decomposition had a half-life of 40.1 h at 21 °C, signifying a considerable increase in thermal stability relative to Eaton's propellane **34**. Since the enthalpy of **42** is 13.2 kcal/mol more positive than that of **41** (G3MP2), the fact that they were formed in comparable amounts indicates that, in accord with the Hammond postulate, the second transition state comes very early with a low barrier. Formation of **41** from **40** was exothermic by 46.1 kcal/mol (G3MP2).

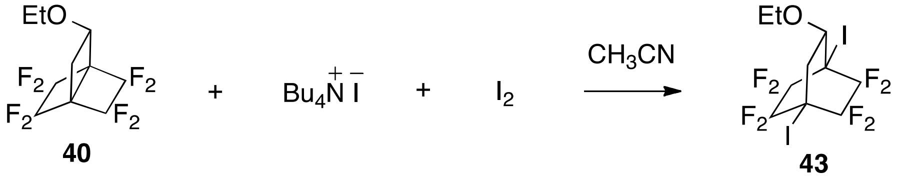
Scheme19



Whereas Eaton's propellane **34** added bromine across the central bond instantaneously at -78 °C,[24] propellane **40** resisted attack by bromine in CH_2Cl_2 at rt, even with irradiation. The same was true with iodine in CCl_4. An attempt to attack **40** with electrophilic iodine using iodine and silver acetate in acetonitrile also resulted in no reaction. Impressively. trifluoroacetic and even concentrated sulfuric acid failed to react with the propellane. So **40** is immune to assault by both electron-deficient free radicals and powerful electrophiles.

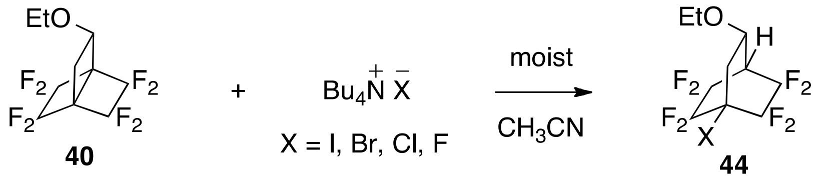
The story with nucleophiles is very different. Treatment of propellane **40** with tetrabutylammonium iodide and iodine in acetonitrile at r.t. produced diiodide **43** (Scheme 20). Attack by iodide ion opened the central bond, and the resulting anion was captured

Scheme 20



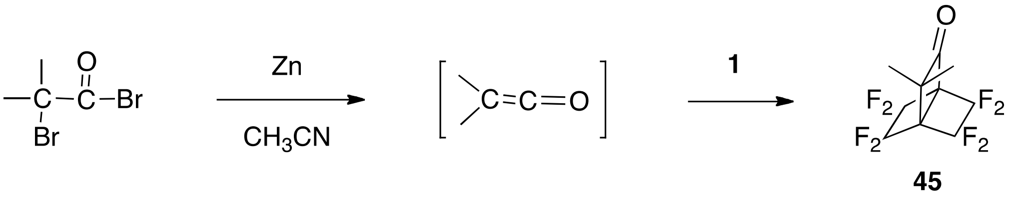
by iodine. When iodine was omitted and the solvent was not dry, the product was HI adduct **44** (X = I), as the intermediate anion was protonated by water (Scheme 21). The reaction was regiospecific, and a NOESY experiment revealed that halide had attacked distal to the oxygen. Thus, stabilization of the intermediate anion by oxygen's electronegativity was more important in determining the course of reaction than the relative electron density at the bridgehead carbons in the starting material. Tetrabutylammonium bromide, chloride, and fluoride gave **44** (X = Br, Cl, and F, respectively) under similar conditions.[27]

Scheme 21



The ability of fluorine substituents to stabilize a [2.2.2]propellane suggested that other electron-withdrawing groups such as carbonyl might have a similar effect. Dimethylketene, generated by reduction of α-bromoisobutyryl bromide with zinc,[28] reacted *in situ* with alkene **1** below r.t. to yield [2.2.2]propellanone **45** (Scheme 22). The X-ray crystal structure and data for this ketone are presented in the Supporting

Scheme 22

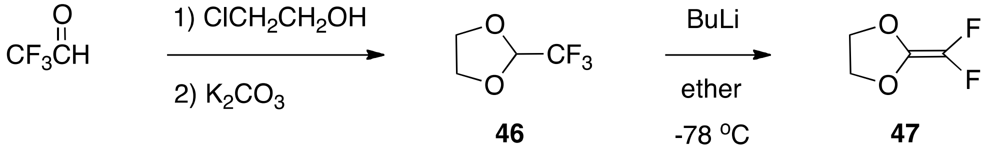


Information. We were surprised to find that a solution of **45** in $CDCl_3$ was unchanged after > 4 months at rt. Then, when a neat sample was heated at 120 °C for 5 h in a sealed tube, 38% of the propellanone survived.

Initial efforts to combine even more electron-deficient addends with **1** were unsuccessful. An attempt to add the elusive difluoroketene, formed *in situ* from bromodifluoroacetyl chloride and zinc in acetonitrile, produced a complex mixture, and the highly electron-deficient bis(trifluoromethyl)ketene failed to react with **1** even after 10 h at 80 °C.[29] Addition to **1** of tetrafluoroethylene would yield a particularly interesting compound, perfluoro[2.2.2]propellane, but the two alkenes failed to react even after 4 h at 120 °C. Irradiation at wavelengths down to 210 nm gave the same result.

We surmised that substitution of one or more fluorines of tetrafluoroethylene by oxygen, the second most electronegative element, could create a promising addend because of oxygen's π-donor ability. While that ability would facilitate the addition to **1**, in the resulting propellane only oxygen's electron-withdrawing power would be expected to influence the thermal stability. So ketene acetal **47** was chosen as a target for synthesis. Treatment of trifluoroacetaldehyde with 2-chloroethanol afforded a hemiacetal which was cyclized with potassium carbonate to give the known ketal **46** (Scheme 23).[30]

Scheme 23



Dehydrofluorination of **46** to obtain **47** proved challenging because a variety of bases and conditions resulted in polymerization of the very sensitive alkene. Success was finally achieved with butyllithium in ether at -78 °C followed by low temperature vacuum

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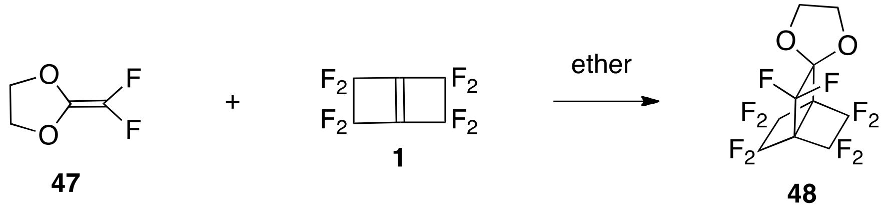
transfer at 60 mTorr. The resulting ketene acetal **47** in ether solution (50-70% yield) was quickly destroyed by moisture, and it polymerized in the presence of both acids and bases. It reacted immediately and quantitatively with **1** to produce propellane ketal **48** (Scheme 24).[2]

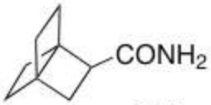
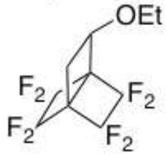
Scheme 24



The X-ray crystal structures of propellanes **45** and **48** reveal that the length of the central C-C bond is 1.558 and 1.573 Å, respectively, very similar to that of the C-C bonds in cyclobutane (1.548 Å).[31] Ketal **48** is even more stable thermally than **45**. A solution of **48** in $CDCl_3$ suffered no decomposition after several months at rt. When a sample was heated in a sealed tube at 100 °C for 10 h, no decomposition was detected; after 5 h at 140 °C, 45% of the propellane remained unchanged. Thermal stability data for the four known [2.2.2] propellanes are summarized in Table 3.

Fluorine substituents are known to stabilize cyclobutane rings, and the phenomenon has been attributed to relief of nonbonded repulsion within the rings.[32] The distances between opposite carbons in the three four-membered rings in **48** are all ~2.2 Å, far less than the sum of the van der Waals radii (3.4 Å). Electron-withdrawing substituents diminish the repulsion by decreasing electron density inside the rings. Thus, the ability of fluorine to stabilize [2.2.2] propellanes may stem principally from this effect.

Table 3. Thermal stability of [2.2.2] propellanes.

Propellane	No.	Temperature ((°C)	Half-Life (min)
	**36**	25	28
	**39**	21	2400
	**45**	120	~210
	**48**	140	~260

Despite its thermal robustness, **48** is extremely susceptible to attack by nucleophiles, electron-rich radicals, and electron donors, all of which cleave the central bond.[2] Interestingly, neither the LUMO nor the LUMO + 1, in which the central bond lies along a node, is suited for nucleophilic attack on that bond (Figure 2). However, the LUMO + 2, which lies 10.2 kcal/mol above the LUMO, has large lobes projecting from the central carbons. The larger of the two controls the direction of nucleophilic attack, consistent with the observed regiochemistry that places developing negative charge at the more electron-deficient end of the central bond. For comparison, the corresponding orbital (LUMO + 2) for the yet unknown [2.2.2] perfluoropropellane is also shown in Figure 2.

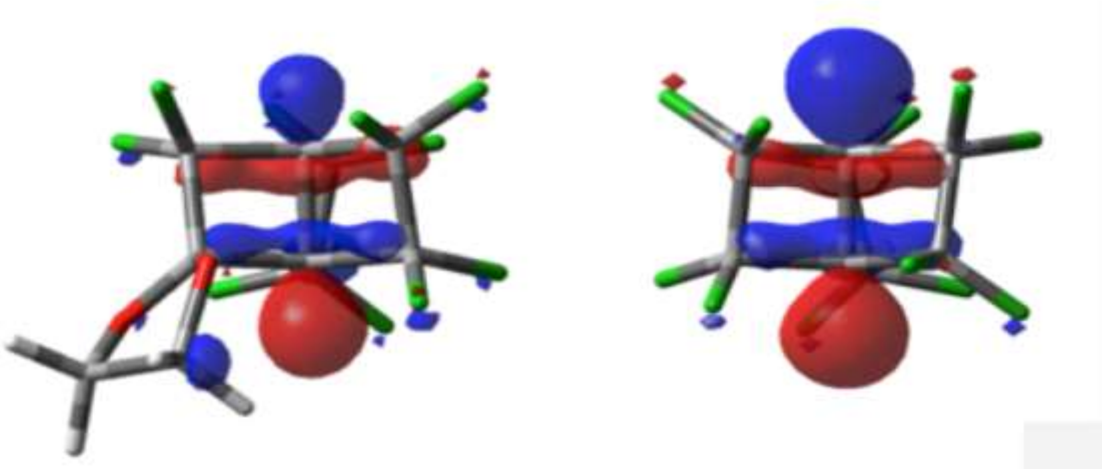
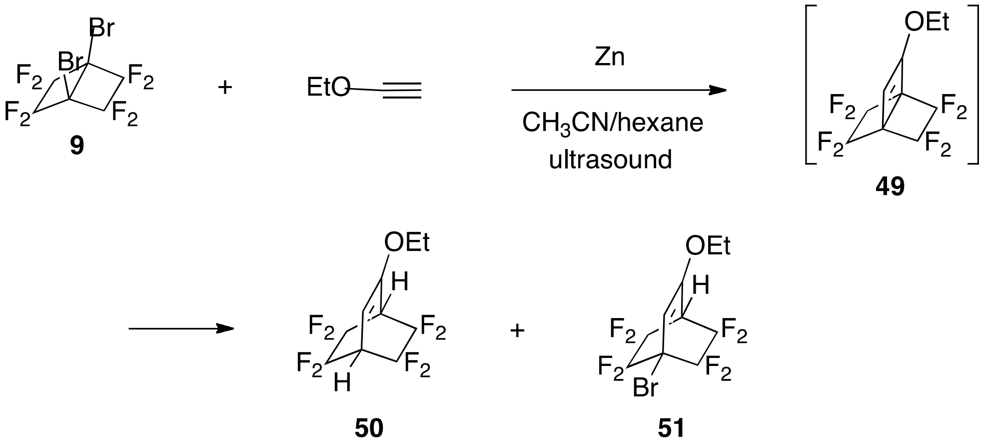


Figure 2. LUMO+2 of **48** (left) and LUMO+2 of the unknown [2.2.2] perfluoropropellane (right) at the B3LYP/cc-pVDZ level of theory. Isocontour = 0.006.

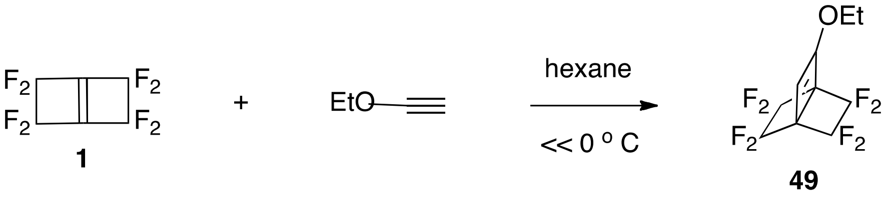
When **1** was generated from dibromo precursor **9** in the presence of ethoxyacetylene, the major product was bicyclic alkene **50**, accompanied by bromo analogue **51** (Scheme 25). [2 + 2] Cycloaddition must have occurred to create the very strained [2.2.2] propellene **49**, which was reduced by zinc to produce **50** via proton and perhaps hydrogen atom abstraction from the hexane/acetonitrile solvent. Opening of the central bond of the propellene by bromide ion followed by proton abstraction explains the formation of **51**.

Scheme 25

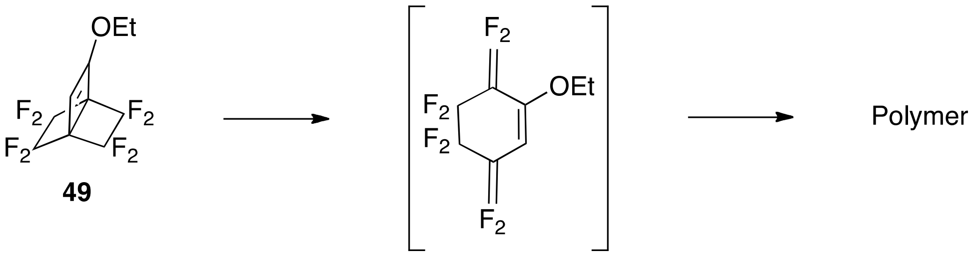


Isolated **1** was found to react readily with ethoxyacetylene at temperatures far below 0 °C to yield propellene **49** (Scheme 26). Its ^{19}F NMR spectrum, measured at -70 °C, comprised two AA'XX' patterns. Warming of the reaction mixture to r.t. resulted in polymerization of **49**, perhaps as shown in Scheme 27, but the propellene could be trapped in the cold as HI adduct **52** by addition of a slightly moist solution of tetrabutylammonium iodide in acetonitrile (Scheme 28). The regiochemistry of the reaction was confirmed by an NOE measurement that revealed close proximity of the bridgehead hydrogen to ethyl hydrogens. That formation of **49** is another orbital

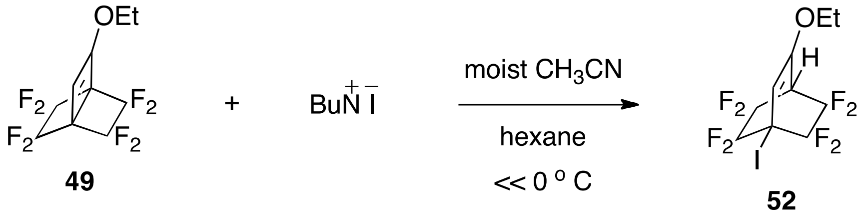
Scheme 26



Scheme 27



Scheme 28



topology-forbidden process[10] makes its occurrence at very low temperatures all the more remarkable. We did find a closed shell intermediate that lies *below* the reactants: ΔH_{298K} = -4.1 kcal/mol, ΔG_{298K} = 10.1 kcal/mol (G3MP2B3, Figure 3). For the corresponding triplet diradical, ΔH_{298K} = 7.0 kcal/mol, ΔG_{298K} = 19.8 kcal/mol. (An open shell singlet diradical at the triplet geometry is even higher in energy.)

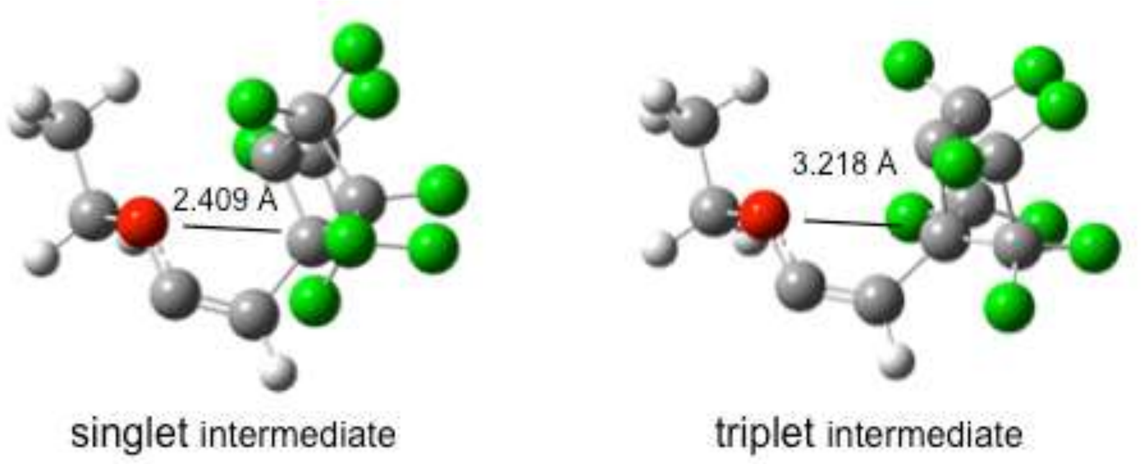
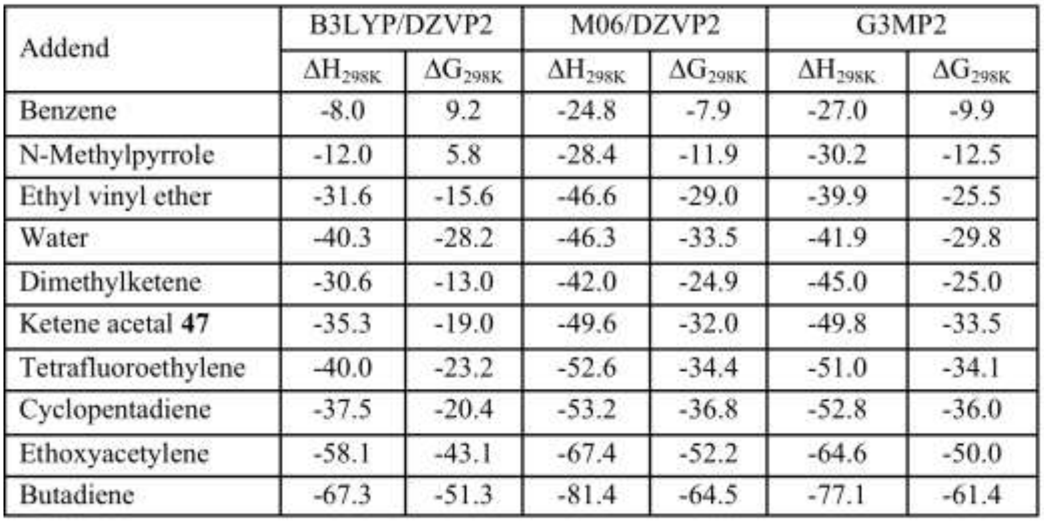


Figure 3. Closed shell singlet intermediate in the reaction of ethoxyacetylene with alkene **1**, and the corresponding triplet.

Heats and free energies of reaction with alkene **1** for a selection of addends are compiled in Table 4. They are arranged in order of increasing exothermicity as computed at the G3MP2 level of theory. All are strongly exothermic, including the five leading to the [2.2.2] propellane skeleton that fall in the range -40 to -65 kcal/mol.

Table 4. Heats and free energies of reaction with alkene **1** for selected addends.[a]



Addend	B3LYP/DZVP2		M06/DZVP2		G3MP2	
	ΔH_{298K}	ΔG_{298K}	ΔH_{298K}	ΔG_{298K}	ΔH_{298K}	ΔG_{298K}
Benzene	-8.0	9.2	-24.8	-7.9	-27.0	-9.9
N-Methylpyrrole	-12.0	5.8	-28.4	-11.9	-30.2	-12.5
Ethyl vinyl ether	-31.6	-15.6	-46.6	-29.0	-39.9	-25.5
Water	-40.3	-28.2	-46.3	-33.5	-41.9	-29.8
Dimethylketene	-30.6	-13.0	-42.0	-24.9	-45.0	-25.0
Ketene acetal **47**	-35.3	-19.0	-49.6	-32.0	-49.8	-33.5
Tetrafluoroethylene	-40.0	-23.2	-52.6	-34.4	-51.0	-34.1
Cyclopentadiene	-37.5	-20.4	-53.2	-36.8	-52.8	-36.0
Ethoxyacetylene	-58.1	-43.1	-67.4	-52.2	-64.6	-50.0
Butadiene	-67.3	-51.3	-81.4	-64.5	-77.1	-61.4

[a] in kcal/mol.

Conclusions

Though very stable thermally, perfluoroalkene **1** is highly reactive and boasts a rich chemistry. Water adds spontaneously across the double bond, and our calculations indicate that it does so via a pseudopericylic cycloaddition of the water dimer. Radical chain addition to that alkene double bond occurs readily; e.g., with benzaldehyde promoted by light. Ene reaction with alkenes and dienes takes place at r.t., and with 1,3-cyclohexadiene ene reaction dominates over Diels-Alder addition. The fact that reaction of **1** with butadiene results in Diels-Alder addition and not [2+2] cycloaddition constitutes strong evidence that the reaction occurs concertedly. Diazo compounds undergo 1,3-dipolar cycloaddition reactions with **1**, yielding pyrazolines. Their photolysis with elimination of nitrogen produces 1,3-diradicals that, instead of ring closing to create extremely strained [2.2.1] propellanes, opt for ring opening to generate carbenes. [2 + 2] Cycloadditons of **1** have been successful at or below r.t. with both electron-donor alkenes and a ketene. All three of the [2.2.2] propellanes (including the propellanone) derived from **1** are much more stable thermally than the sole [2.2.2] propellane in the literature that has a hydrocarbon skeleton, and the stability increases with the degree of electron withdrawal from the skeleton. This effect is probably attributable primarily to a decrease in C-C nonbonded repulsion within the interior of the molecules. Like alkene **1**, the fluorinated propellanes display both of the commonly antithetical qualities of robustness and high reactivity. Reaction of **1** with ethoxyacetylene afforded the first [2.2.2] propellene, a fragile compound that formed readily at temperatures far below 0 °C in an orbital topology-forbidden reaction. Calculations carried out for many of the addition reactions of alkene **1** reveal them all to be strongly exothermic, some extremely so.

Experimental Section

The ^{19}F NMR spectra were recorded at 282.2 or 470.3 MHz on a 300 or 500 MHz spectrometer. Chemical shifts are reported on the δ scale (ppm from internal standard trichlorofluoromethane, upfield negative). ^{1}H NMR spectra were recorded at 300 or 500 MHz on the same spectrometers 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. x 1/8 in., 10% OV 101 on Chromosorb-P acid washed, and the standard program was: det. 200 ºC, inj. 200 ºC, column temperature as noted in text. All analytical GC was done using a 25 m methyl silicone capillary column and flame ionization detector. The standard program was: carrier pressure 25 p.s.i.; detector 200 ˚C; injector 150 ˚C; $temp_1$= 50 ˚C; $temp_2$ = 250 ˚C; $time_1$= 5 min. @ 50 ˚C then 15 ˚/min to 250 ˚C. Solvents used in this work were reagent grade. Acetonitrile was distilled from calcium hydride, and tetrahydrofuran from potassium/benzophenone. Zinc dust was purified according to Shriner and Neumann.[33]

The initial geometry optimization calculations for all structures were performed using Jaguar[9] at the level of density functional theory[34] with the B3LYP exchange-correlation functional[35,36] and the cc-pVDZ+ basis set.[9b] Subsequently, the structures were reoptimized with the B3LYP, BP86,[37,38] PW91,[39,40,41] PBE,[42,43] M06,[44] and SVWN[45,46] functionals with the DZVP2[47] basis set for the benzene adduct formation from **1**. In addition, calculations for that reaction were done at the G3MP2 level[48] starting from the B3LYP/DZVP2 geometries. Nearly all other calculations were performed only at the DFT B3LYP//DZVP2 and MO6/DZVP2 levels and at the G3MP2 level. All but the initial geometry optimizations were done with Gaussian 09[49] by D.A.D. and M.V.

2,2,3,3,5,5,6,6-Octafluorobicyclo[2.2.0]hexane (10) and 2,2,3,5,5,6,6-Heptafluorocyclohex-3-ene-1,1-diol (6). 1,4-Dibromoperfluorobicyclo[2.2.0]hexane (70 mg, 0.18 mmol) was dissolved in 3 mL of acetonitrile in a 25 mL round-bottom flask. After nitrogen had been bubbled in for 5 min, zinc dust (0.2 g, 3 mmol) and water (1 drop) wre added to the flask, which was then stoppered and rocked in an ultrasound bath for 4 h. ^{19}F NMR revealed two products, dihydro compound **10** and diol **6** the ratio 2 : 1.

For **10**: δ -111.3, -112.7 (AB q, *J* = 225 Hz, 8F). ^{1}H NMR: δ 2.0, 2H). MS: m/z 207 (M$^+$-F), 157 (base, $C_5F_5H_2^+$). For **6**, ^{19}F NMR: δ -105.7 (2F), -120.4 (2F), 121.8 (1F), -133.3 (2F), ^{1}H NMR: δ 5.9 (vinyl, 1H), 4.0 (2H). MS(CI): m/z 258 (MNH_4^+), 220 (M$^+$-HF), 175 (base). IR (cm^{-1}): 1627 ($\nu_{C=C}$), 3500 (br, ν_{OH}).

Ethyl 2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.0]hexane-1-carboxylate (13). N-Benzylpyrrole adduct (350 mg, 0.92 mmol) was subjected to FVP to generate alkene **1**, to which was added ether (3 mL) and ethyl formate (130 mg, 1.8 mmol, 2 eq). The solution was stirred 4 h at r.t. to generate adduct **13** cleanly by ^{19}F NMR. Purification was achieved by preparative GC at 150 °C to afford **13** as a colorless oil. ^{19}F NMR: δ -112.0, -115.7 (AB q, J = 226 Hz, 4F); -114.1, -124.2 (AX, *J* = 216 Hz, 4F). ^{1}H NMR: δ 3.83 (q, *J*= 7.2 Hz, 2H), 3.69 (m, bridgehead, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). MS: m/z 269 (M$^+$ - C_2H_5), 194, 175, 144, 113, 100 69, 29 (base, $C_2H_5^+$).

(2,2,3,3,5,5,6,6-Octafluorobicyclo[2.2.0]hexan-1-yl)(phenyl)methanone (15). To a Pyrex tube (1 x 10 cm) was added alkene **1** (0.16 g, 0.71 mmol), benzaldehyde (0.228 g, 2.15 mmol) and 3 mL of dry acetonitrile. The solution was irradiated with a 450 W medium-pressure mercury lamp at 15 °C under nitrogen for 1 h. After solvent removal, the residue was purified by flash chromatography on neutral alumina (pentane/CH_2Cl_2, 25:1) to afford **15** as colorless crystals (0.19 g, 0.58 mmol, 82%). Mp 97-98 °C. ^{19}F NMR: δ -111.4, -112.9 (AB q, *J* = 222 Hz, 4F); -112.0, 112.7 (AB q, *J* = 222 Hz, 4F). ^{1}H NMR: δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 4.34 (m, 1H). ^{13}C NMR: δ 183.5, 135.8, 134.3, 129.5, 129.1, 115.4 (t, *J* = 295 Hz), 113.9 (t, *J* = 269 Hz), 63.9 (m), 49.4 (m). IR (film, cm^{-1}): 1688, 1598, 1453, 1345, 1264, 1225, 1160, 1103, 1063, 995. Anal. Calc. for $C_{13}H_6F_8O$: C, 47.29; H, 1.83; F, 46.03. Found: C, 47.02; H, 1.76; F, 46.30.

2,2,3,3,5,5,6,6-Octafluoro-1-(2-methylallyl)bicyclo[2.2.0]hexane (16). To a flame-dried, heavy-walled glass tube (1 x 20 cm, 4 mm ID) containing zinc dust (0.50 g, 7.7 mmol) was added dibromide **9** (0.40 g, 1.1 mmol) and 4 mL of dry acetonitrile. Isobutene (0.5 mL, ~6 mmol) was condensed into a graduated trap at -78 ^{o}C, and its volume was measured after warming to 0 ^{o}C. It was vacuum transferred into the reaction tube cooled to 77 K. The tube was sealed with a flame under vacuum, allowed to warm to rt, and placed in a water-cooled ultrasonic bath for 24 h. It was cooled again to 77 K, opened, and allowed to thaw. Water (20 mL) was added to the light brown solution, and the mixture was extracted with 3 x 10 mL of pentane. The extract was dried over $MgSO_4$, then concentrated to 1 mL. Ene product **16** was present in 81% yield by ^{19}F NMR. Preparative GC at 150 ^{o}C gave **16** as a colorless liquid. ^{19}F NMR: δ -111.4, -113.6 (AB q, J = 227 Hz, 4F); -111.7, -118.0 (AX, J = 220 Hz, 4F). ^{1}H NMR: δ 4.96 (s, vinyl. 1H), 4.81 (s, vinyl, 1H), 3.38 (bs, bridgehead, 1H), 2.60 (s, methylene, 2H), 1.81 (s, methyl, 3H). ^{13}C NMR: δ 138.7, 116.2, 114.3, 113.1, 57.0 (both bridgeheads), 32.0, 23.4. MS: m/z 280 (M^+), 167, 147, 127, 113 (base, $C_3HF_4^+$), 69, 41, 27. IR (CCl_4, cm^{-1}): 1653 ($\nu_{C=C}$), 1435, 1350. 1289, 1249, 1187, 1145, 1118, 1068, 973, 938, 901.

1-(Cyclohexa-2,4-dien-1-yl)-2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.0]hexane (17). Alkene **1** was obtained by FVP of the N-benzylpyrrole adduct (300 mg, 0.79 mmol). A solution of 1,4-cyclohexadiene (60 mg, 0.75 mmol) in ether (2 mL) was added, and the reaction mixture was allowed to stand at r.t. for 10 h. By ^{19}F NMR, the yield of **17** based on **1** was quantitative. ^{19}F NMR: δ -108.2, -114.0 (AX, J = 236 Hz, 2F);

-111.5, -117.7 (AX, *J* = 217 Hz, 2F); -112.2 to -113.3 (m, 2 overlapping AB q's, 4F). ^{1}H NMR: δ 6.02 (m, vinyl, 1H); 5.98 (m, vinyl, 1H); 5.86 (m, vinyl, 1H); 5.51 (m, vinyl, 1H); 3.64 (m, bridgehead, 1H); 3.14 (t, *J* = 14 Hz, 1H); 2.31, 2.28 (AB q, *J* = 4.5 Hz, 2H). MS m/z 304 (M^+), 253, 151, 113 ($C_3HF_4^+$), 79 (base, $C_6H_7^+$), 69, 40. Anal. Calcd. For $C_{12}H_8F_8$: C, 47.37; H, 2.63. Found: C, 47.25; H, 2.60.

1-(Cyclohexa-2,5-dien-1-yl)-2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.0]hexane (18) and 7,7,8,8,9,9,10,10-Octafluorotetracyclo[4.2.2.2^{2,5}.0^{1,6}]dodec-3-ene (19).

To a solution of alkene **1** (0.80 g, 3.6 mmol) in 20 mL of dry ether was added 1,3-cyclohexadiene (2.68 mL, 28.7 mmol). The solution was allowed to stand under N_2 at r.t. for 4 h. Solvent was evaporated and the residue was dissolved in 15 mL of dry CH_2Cl_2. The solution was cooled to -45 °C, Br_2 was added dropwise with stirring in the dark until its color persisted, and stirring was continued for 2 h. After removal of the solvent and excess Br_2, the volatile portion of the residue was vacuum transferred to afford adduct **19** (0.23 g, 21% yield). Mp 72-74 °C. ^{19}F NMR: δ ^{19}F NMR: δ -107.9, -110.8 (subsplit AB q, *J* = 228 Hz, 4F); -108.7, -113.4 (subsplit AB q, *J* = 222 Hz, 4F). ^{1}H NMR: δ 6.31 (m, vinyl, 2H); 3.13 (bs, bridgeheads, 2H); 2.17 (d, *J* = 10.5 Hz, 2H), 1.26 (d, *J* = 10.5 Hz, 2H). HRMS Calcd. for $C_{12}H_8F_8$: 304.0498, found: 304.0495.

The residue after vacuum transfer containing tetrabromide **20** was dissolved in 20 mL of dry THF and zinc dust (8.0 g, 0.12 mol) was added. The mixture was flushed with N_2 for 2 min, a small crystal of iodine was added, and the slurry was stirred for 2 h. After removal of zinc by filtration, solvent was evaporated and the residue was flash chromatographed on silica gel to give adduct **18** as a colorless liquid (0.30 g, 28% yield). ^{19}F NMR: δ -109.8, -119.0 (AX, *J* = 220 Hz, 4F); -112.7, -133.5 (AB q, *J* = 227 Hz, 4F).

^{1}H NMR: δ 5.88 (m, vinyl, 2H), 5.48 (m, vinyl, 2H), 3.57 (m, bridgehead, 1H), 3.40 (bs, 1H), 2.65 (m, 2H). HRMS Calcd. for $C_{12}H_8F_8$: 304.0498, found: 304.0496.

***cis*-3,4-Dibromo-7,7,8,8,9,9,10,10-octafluorotetracyclo[4.2.2.2^{2,5}.0^{1,6}]dodecane (21).** Alkene **19** (0.12 g, 0.40 mmol) was dissolved in 15 mL of dry CH_2Cl_2, and Br_2 (31 μL, 0.6 mmol) in 1 mL of dry CH_2Cl_2 was added. The solution was stirred at r.t. overnight exposed to ambient light. After removal of solvent, the residue was purified by flash chromatography on silica gel (pentane/CH_2Cl_2, 10 : 1) to obtain dibromide **21** as colorless crystals (0.93 g, 93%). Mp 120-122 °C. ^{19}F NMR: δ -105.1, -109.4 (AB q, *J* = 231 Hz, 4F); -105.2, -108.4 (AB q, *J* = 229 Hz, 4F). ^{1}H NMR: δ 5.07 (s, 2H), 2.73 (s, 2H), 2.47 (d, *J* = 10.0 Hz, 2H), 2.05 (d, *J* = 10.0 Hz, 2H). IR (film, cm^{-1}): 2965, 1486, 1346, 1223, 1155, 1059, 982, 902. Anal. Calcd. for $C_{12}H_8F_8Br_2$: C, 31.06; H, 1.74; Br. 34.44; F, 32.76. Found: C, 31.11; H, 1.73; Br, 34.56; F, 32.63.

7,7,8,8,9,9,10,10-Octafluorotetracyclo[4.2.2.2^{2,5}.0^{1,6}]dodecane (22). To alkene **19** (0.105 g, 0.345 mmol) in 20 mL of methanol was added 10% Pd/C (100mg). The mixture was cooled to -78 °C and purged by evacuating and filling with N_2 three times. A balloon filled with H_2 was attached to the apparatus, and the slurry was stirred at r.t. for 6 h. The catalyst was removed by filtration and washed with CH_2Cl_2. After evaporation of the solvent, the residue was purified by chromatography on silica gel with pentane to afford hydrofluorocarbon **22** as colorless crystals (87.5 mg, 83% yield). Mp 173-175 °C. ^{19}F NMR: δ -106.1, -111.0 (subsplit AB q, *J* = 230 Hz, 8F). ^{1}H NMR: δ 2.31 (s, 2H), 2.12 (d, *J* = 9.0 Hz, 4H), 1.58 (d, *J* = 9.0 Hz, 4H). IR (film, cm^{-1}): 2963, 1303, 1260, 1103, 982, 799. Anal. Calcd. for $C_{12}H_{10}F_8$: C, 47.07; H, 3.29; F, 49.64. Found: C, 47.09; H, 3.28; F, 49.74. See the Supporting Information for crystal structure data and ORTEP for **22**.

7,7,8,8,9,9,10,10-Octafluorotetracyclo[4.2.2.1^{2,5}.0^{1,6}]undec-3-ene (23). To alkene **1** obtained from N-benzylpyrrole adduct (200 mg, 0.53 mmol) was added a solution of freshly distilled cyclopentadiene (50 mg, 0.76 mmol). After 1 h, ^{19}F NMR showed that the yield of adduct **23** based on **1** was quantitative. Purification by preparative GC gave the adduct as a colorless crystalline solid. Mp 108.5-109 °C. ^{19}F NMR: δ -109.0, -113.2 (subsplit AB q, *J* = 227 Hz, 4F); -112.9, -117.5 (subsplit AB q, *J* = 230 Hz, 4F). ^{1}H NMR: δ 6.3 (d, *J* = 9 Hz, vinyl, 2H); 3.5 (s, 2H); 2.25, 1.85 (AX, *J* = 11 Hz, 2H). MS m/z 290 (M^+), 275 (M^+ - CH_3), 239, 221, 189, 169, 151, 127, 75, 66 (base, $C_5H_6^+$), 39. Anal. Calcd. for $C_{11}H_6F_8$: 45.52; H, 2.07. Found: C, 45.26; H, 2.10.

7,7,8,8,9,9,10,10-Octafluorotricyclo[4.2.2.0^{1,6}]dec-3-ene (24). To a flame-dried, heavy-walled glass tube (1 x 20 cm, 4 mm ID) containing zinc dust (0.50 g, 7.7 mmol) was added dibromide **9** (0.40 g, 1.1 mmol) and 4 mL of dry acetonitrile. 1,3-Butadiene (0.5 mL, ~6 mmol) was condensed into a graduated U-trap at -78 °C, and its volume was measured after warming to 0 °C. It was vacuum transferred into the reaction vessel cooled to 77 K. The tube was sealed with a flame under vacuum, allowed to warm to rt, and placed in a water-cooled ultrasonic bath for 24 h. The contents were frozen, the tube was opened, and the solid was allowed to thaw. Water (20 mL) was added to the light brown solution, and the mixture was extracted with 3 x 10 mL of pentane. After drying over $MgSO_4$, the extract was concentrated to 1 mL. White crystalline adduct **24** (95 mg, 31% yield) was obtained after subjection of this liquid to preparative GC. Mp 42.5-43 °C. ^{19}F NMR: δ -114.2, -118.2 (AB q, *J* = 220 Hz, 8F). ^{1}H NMR: δ 5.74 (t, *J* = 1.2 Hz, 2H), 2.48 (bs, 4H). IR (CCl_4, cm^{-1}): 1653 ($\nu_{C=C}$, vw), 1440, 1360. 1335, 1235, 1177, 1142, 1010, 968, 898, 801, 660. MS: m/z 278 (M^+), 263 (M^+ - CH_3), 237, 214, 163, 145, 127, 109, 75 (base, $C_3HF_2^+$), 51, 39. Anal. Calcd. for $C_{10}H_6F_8$: C, 43.18; H, 2.17; F, 54.64. Found C, 42.89; H, 2.20; F, 54.28.

6,6,7,7,8,8,9,9-Octafluoro-2,3-diazatricyclo[3.2.2.0^{1,5}]non-2-ene (27) and 6,6,7,7,8,8,9,9-Octafluoro-2,3-diazatricyclo[3.2.2.0^{1,5}]non-3-ene (29). To alkene **1** prepared from the N-benzylpyrrole adduct (350 mg, 0.92 mmol) was added 3 mL of an ethanol-free ether solution of diazomethane (~200 mg, 4.8 mmol). An instantaneous dipolar cycloaddition reaction took place to generate **27** cleanly as indicated by ^{19}F NMR. [This reaction is sensitive to the presence of both ethanol and water.] Adduct **27** decomposes at rt, and attempted purification by preparative GC (250 ^{0}C) led to isolation of rearranged isomer **29**. Compound **27**: ^{19}F NMR: δ -112.4, -119.4 (AB q, *J* = 220 Hz, 4F); -113.1, -113.9 (AB q, *J* = 220 Hz, 4F). ^{1}H NMR: δ 5.2 (s, 2H). MS: m/z 266 (M^+), 238 (M^+ -N_2), 219, 169 (base), 119, 75, 69. Compound **29**: ^{19}F NMR: δ -110.9, -116.0 (AB q, *J* = 220 Hz, 4F); -113.6, -117.8 (AB q, *J* = 212 Hz, 4F). ^{1}H NMR: δ 6.79 (bs, CH, 1H), 6.58 ((bs, NH, 1H). MS m/z 266 (M^+), 216, 197 (base), 166, 69.

6,6,7,7,8,8,9,9-Octafluoro-4,4-dimethyl-2,3-diazatricyclo[3.2.2.0^{1,5}]non-2-ene (28). Alkene **1** generated from the N-benzylpyrrole adduct (350 mg, 0.92 mmol) was combined with 3 mL of a dried solution of 2-diazopropane (200 mg, 2.9 mmol) in ether.[50] An immediate reaction occurred to afford adduct **28** cleanly, as judged by ^{19}F NMR. This reaction is sensitive to the presence of water, and the adduct decomposed both at r.t. and upon attempted purification by GC. ^{19}F NMR: δ -104.2, -104.8 (AB q, *J* = 229 Hz,

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4F); -112.7, -119.9 (AB q, J = 220 Hz, 4F). ^{1}H NMR: δ 1.76 (m, 6H). MS: m/z 266 (M$^+$ -N$_2$), 251 (base, M$^+$ - N$_2$, CH$_3$), 69.

1,1,2,2,4,4,5,5-Octafluoro-3-methylenecyclohexane (33). A freshly prepared ether solution (2 mL) of pyrazoline **27** was placed in a quartz tube (1 x 5 cm) and stirred magnetically while being irradiated with an unfiltered 450 W medium pressure mercury lamp for 4 h. An ^{19}F NMR spectrum of the resulting solution comprised only two signals, corresponding to **33**. ^{19}F NMR: δ -111.5 (s, 4F), -118.6 (s, 4F). MS: m/z 240 (M$^+$), 176, 171, 151, 113, 95, 75, 64, 43.

7-Ethoxy-2,2,3,3,5,5,6,6-octafluorotricyclo[2.2.2.0^{1,4}]octane (40). To a dry 2-necked 50 mL round-bottom flask was added zinc dust (4.08 g, 62.8 mmol), dibromide **9** (1.20 g, 3.13 mmol), and 20 mL of dry acetonitrile. The mixture was flushed with N$_2$ for 2 min, then ethyl vinyl ether (3.0 mL, 31 mmol) and a small crystal of iodine were added. The flask was mounted in a water-cooled ultrasound bath and sonicated for 30 min. Liquid was decanted and the residue was washed with 10 mL of CH$_2$Cl$_2$. Quick evaporation of the solvent left a brown oil that was subjected to purification by flash chromatography on neutral alumina using pentane/CH$_2$Cl$_2$ (50 : 1) as eluent. Propellane **40** was obtained as a colorless oil (0.71 g, 77%). ^{19}F NMR: δ -105.8, -113.4 (AX, J = 225 Hz, 2F); -107.8, -118.4 (AX, J = 217 Hz, 2F); -108.9, -119.0 (AX, J = 211 Hz, 2F); -110.5, -111.6 (AB q, J = 218 Hz, 2F). ^{1}H NMR: δ 4.63 (t, J = 8.0 Hz, 1H); 3.52, 3.51 (AB q of q, J = 7.0 Hz, J_{AB} = 9.3 Hz, 2H); 3.15 (m, 1H); 3.05 (m, 1H); 1.23 (t, J = 7.0 Hz, 3H). ^{13}C NMR: δ 115.9 (t of m, J = 306 Hz), 71.5, 64.9, 48.5, 38.1, 29.9, 14.6. HRMS: calcd. for C$_{10}$H$_8$F$_8$O 296.0447, found 296.0442.

3-(Ethoxymethylene)-1,1,2,2,4,4,5,5-octafluoro-6-methylenecyclohexane (41) and 3,6-Bis(difluoromethylene)-4-ethoxy-1,1,2,2-tetrafluorocyclohexane (42). A purified sample of propellane **40** was allowed to stand at r.t. for several days. The two products were separated by preparative GC. Compound **41**: ^{19}F NMR: δ -112.8 (s, 2F), -114.5 (s, 2F), -118.7 (s, 2F), -119.2 (s, 2F). ^{1}H NMR: δ 7.13 (s, 1H), 6.31 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). IR (neat, cm^{-1}): 3138, 2992, 2910, 1673, 1480, 1416, 1394, 1345, 1295, 1228, 1150, 1094, 1032. HRMS: calcd. for $C_{10}H_8F_8O$ 296.0447, found 296.0450. Compound **42**: ^{19}F NMR: δ -73.8 (m, 1F); -75.3 (s, 1F); -78.0 (m, 1F); -80.1 (s, 1F); -102.3, -126.4 (AX, *J* = 262 Hz, 2F); -108.1, -131.2 (AX, *J* = 258 Hz, 2F). ^{1}H NMR: δ 4.38 (s, 1H), 3.47 (m, 1H), 3.35 (m, 1H), 2.81 (m, 1H), 2.35 (m, 1H), 1.16 (t, *J* = 6.9 Hz, 3H). IR (neat, cm^{-1}): 2984, 2906, 1766, 1740, 1141, 1331, 1208, 1152, 1122, 1073. HRMS: calcd. for $C_{10}H_8F_8O$ 296.0447, found 296.0453.

7-Ethoxy-2,2,3,3,5,5,6,6-octafluoro-1,4-diiodobicyclo[2.2.2]octane (43). To a flask was added zinc dust (1.7 g, 26 mmol), dibromide **9** (0.50 g, 1.30 mmol), and 10 mL of dry acetonitrile. Flushing with N_2 followed (2 min), then ethyl vinyl ether (1.25 mL, 12.9 mmol) and a small crystal of iodine were introduced. The flask was placed in a water-cooled ultrasound bath and sonicated for 30 min. The mixture was filtered under N_2 through a pipet containing a cotton plug, and the residue was washed with 5 mL of dry acetonitrile. To the filtrate were added tetrabutylammonium iodide (2.4 g, 6.6 mmol) and iodine (6.60 g, 26.0 mmol). After the mixture stood under N_2 overnight, the solvent was evaporated to leave a brown oil that was purified by flash chromatography on silica gel with pentane/CH_2Cl_2 (50 : 3) as eluent. Diiodide **43** was obtained as a colorless oil (0.35 g, 46% yield). ^{19}F NMR: δ -100.1, -102.0 (subspit AB q, *J* = 252 Hz, 2F); -194.5, -108.8

(subsplit AB q, *J* = 247 Hz, 2F); -105.3, -108.3 (subsplit AB q, *J* = 247 Hz, 2F); -105.7, -107.6 (subsplit AB q, *J* = 244 Hz, 2F). ^{1}H NMR: δ 3.78 (m, 1H); 3.65, 3.58 (AB q of q, *J* = 7.0, J_{AB} = 9.3 Hz, 2H);), 2.90 (m, 1H), 2.70 (m, 1H); 1.26 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 110.8 (t of m, *J* = 276 Hz), 109.9 (t of m, *J* = 277 Hz), 75.3, 68.3, 45.9, 39.4, 36.2, 15.2. IR (neat, cm^{-1}): 2983, 1239, 1202, 1138. Anal. Calcd. for $C_{10}H_8F_8I_2O$: C, 21.84; H, 1.47. Found: C, 22.13; H, 1.43.

8-Ethoxy-2,2,3,3,5,5,6,6-octafluoro-1-iodobicyclo[2.2.2]octane (44, X = I). Propellane **40**, prepared from dibromide **9** (0.50 g, 1.30 mmol) in 10 mL of acetonitrile as described above, was filtered into a small filter flask containing tetrabutylammonium iodide (2.40 g, 6.50 mmol) and 5 drops of water. After the solution stood at r.t. for 2 h, solvent was evaporated and the residue was purified on a silica gel column eluted with pentane/CH_2Cl_2 (50 : 3). Compound **44** was obtained as a colorless oil (0.47 g, 85% yield). ^{19}F NMR: δ -105.4, -108.9 (subsplit AB q, *J* = 261 Hz, 2F); -108.4, -110.6 (subsplit AB q, *J* = 244 Hz, 2F); -109.1, -112.4 (subsplit AB q, *J* = 244 Hz, 2F); -109.6, -114.2 (subsplit AB q, *J* = 256 Hz, 2F). ^{1}H NMR: δ 3.99 (br, 1H); 3.55, 3.45 (AB q of q, *J* = 7.0, J_{AB} = 9.3 Hz, 2H); 3.26 (br, 1H); 2.94 (m, 1H); 2.52 (m, 1H); 1.22 (t, *J* = 7..0 Hz, 3H). ^{13}C NMR: δ 113.0 (t of m, *J* = 261 Hz), 110.9 (t of m, *J* = 278 Hz), 69.4, 65.5, 47.2, 39.0, 37.7, 15.1. IR (neat, cm^{-1}): 2983, 1447, 1352, 1288, 1205, 1125, 1064, 1029. Anal. Calcd. for $C_{10}H_9F_8IO$: C, 28.32; H, 2.14; F, 35.84. Found: C, 28.66; H, 1.95; F, 35.94.

1-Bromo-8-ethoxy-2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.2]octane (44, X = Br). Propellane **40**, prepared from dibromide **9** (0.50 g, 1.30 mmol) in 10 mL of acetonitrile as above, was added to tetrabutylammonium bromide (3.35 g, 10.4 mmol) and 4 drops of water. Workup was the same as for **44 (X = I)**, affording the product as a colorless oil

(0.34 g, 68 % yield). ^{19}F NMR: δ -106.3, -109.5 (subsplit AB q, *J* = 261 Hz, 2F); -110.5, 114.3 (subsplit AB q, *J* = 258 Hz, 2F); -115.7, -116.7 (subsplit AB q, *J* = 250 Hz, 2F); -116.0, -119.3 (subsplit AB q, *J* = 256 Hz, 2F). ^{1}H NMR: δ 4.02 (br, 1H); 3.55, 3.47 (AB q of q, *J* = 7.1, J_{AB} = 8.9 Hz, 2H); 3.25 (br, 1H); 2.83 (br, 1H); 247 (m, 1H): 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR δ 112.3 (t of m, *J* = 265 Hz), 112.1 (t of m, *J* = 265 Hz), 68.4, 65.5, 57.9, 47.0, 36.5, 15.0. IR (neat, cm^{-1}): 2984, 1353, 1292, 1208, 1131, 1066. Anal. Calcd. for $C_{10}H_9F_8BrO$: C, 31.85; H, 2.40. Found: C, 32.16; H, 2.00.

1-Chloro-8-ethoxy-2,2,3,3,5,5,6,6-octafluorobicyclo[2.2.2]octane (44, X = Cl). Propellane **40**, prepared from dibromide **9** (0.50, 1.30 mmol) in 10 mL of acetonitrile as above, was combined with anhydrous tetrabutylammonium chloride (3.60 g, 13.0 mmol). Workup was the same as that for **44 (X = I)**, and it afforded the HCl adduct as a colorless oil (0.35 g, 83% yield). ^{19}F NMR: δ -106.3, -109.5 (subsplit AB q, *J* = 262 Hz, 2F); -110.6, -114.3 (subsplit AB q, *J* = 258 Hz, 2F); -115.9, -116.6 (subsplit AB q, *J* = 246 Hz, 2F); 116.0, -119.3 (subsplit AB q, *J* = 256 Hz, 2F). ^{1}H NMR: δ 4.01 (br, 1H); 3.55, 3.46 (AB q of q, *J* = 7.0, J_{AB} = 9.0 Hz, 2H); 3.26 (br, 1H); 2.84 (m, 1H); 2.47 (m, 1H); 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 112.3 (t of m, *J* = 265 Hz), 112.2 (t of m, *J* = 265 Hz), 68.4, 65.5, 57.7, 47.0, 36.5, 15.1. IR (neat, cm^{-1}): 2929, 1450, 1353, 1294, 1209, 1134. HRMS: calcd. for $C_{10}H_9F_8ClO$: 332.0214, found: 332.0212.

8-Ethoxy-1,2,2,3,3,5,5,6,6-nonafluorobicyclo[2.2.2]octane (44, X = F). Propellane **40** was prepared as above from dibromide **9 (**0.50 g, 1.30 mmol) and purified by flash chromatography on neutral alumina. It was added to an acetonitrile solution of anhydrous tetrabutylammoniium fluoride (3.40 g, 13.0 mmol). Workup, the same as for **44 (X = I)**, gave the HF adduct as a colorless oil (0.19 g, 46% yield). ^{19}F NMR: δ -108.9,

-111.5 (subsplit AB q, *J* = 264 Hz, 2F); -113.7, -115.2 (subsplit AB q, *J* = 261 Hz, 2F); -126, -128.1 (subsplit AB q, *J* = 249 Hz, 2F); -129.0, -131.0 (subsplit AB q, *J* = 248 Hz, 2F); -203.8 (s, 1F). ^{1}H NMR: δ 4.04 (br, 1H); 3.55, 3.47 (AB q of q, *J* = 7.0, J_{AB} = 8.8 Hz, 2H); 3.23 (br, 1H); 2.68 (m, 1H; 2.35 (m, 1H); 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR: δ 113.1 (t of m, *J* = 262 Hz), 112.1 (t of m, *J* = 263 Hz), 88.3, 66.8, 65.6, 46.9, 30.2, 15.1. IR (neat, cm^{-1}): 2951, 1452, 1329, 1209, 1141, 1068, 983. HRMS: calcd. for $C_{10}H_9F_9O$: 316.0509, found: 316.0513.

5,5,6,6,7,7,8,8-Octafluoro-3,3-dimethyltricyclo[2.2.2.0^{1,4}]octan-2-one (45). To a flame-dried 100 mL Schlenk flask was added zinc dust (3.0 g, 46 mmol), dry acetonitrile (10 mL), and alkene **1** (0.31 g, 1.4 mmol) in 5 mL of dry acetonitrile. The mixture was cooled to 15 °C and α-bromoisobutyryl bromide (0.84 g, 3.7 mmol) was introduced.[27] After the mixture was stirred at 15 °C for 1 h, it was cooled to 0 °C and residual dimethylketene was pumped off at 5 Torr. The mixture was filtered and the solid was washed with 20 mL of CH_2Cl_2. Solvent was evaporated and the residue was purified on a silica gel column (pentane/CH_2Cl_2, 10 : 1) to obtain the propellanone as colorless crystals (0.22 g, 54% yield). Mp 105-107 °C. ^{19}F NMR: δ -98.3, -107.1 (AB q, *J* = 224 Hz, 4F); -104.3, -108.9 (AB q, *J* = 220 Hz, 4F). ^{1}H NMR: δ 1.63 (d, J_{HF} = 4.5 Hz, 6H). ^{13}C NMR: δ 188.9, 117.1 (t of m, *J* = 293 Hz), 114.6 (t of m, *J* = 315 Hz), 53.0, 45.2, 30.0. 23.1 (d, J_{CF} = 10.4 Hz). IR (film, cm^{-1}): 2962, 1819, 1478, 1324. 1295, 1202. HRMS: calcd. for $C_{10}H_6F_8O$: 294.0291, found: 294.0292. Crystal structure data and ORTEP for **45** are available in the Supporting Information.

2-(Trifluoromethyl)-1,3-dioxolane (46).[30] To a dried Schlenk flask equipped with a finger condenser (acetonitrile, -45 °C) was added 2-chloroethanol (15.0 g, 0.186

mol) and pentane (30 mL). The flask was cooled to -78 ^{o}C and gaseous trifluoroacetaldehyde [generated by dropwise addition of trifluoroacetaldehyde methyl hemiacetal (30.0 g, 0.230 mol) to polyphosphoric acid (110. 0 g) at 130-140 ^{o}C] was condensed in the flask. After all the aldehyde had been introduced, the sidearm of the flask was closed and the mixture was slowly warmed to r.t. with stirring. Potassium carbonate (25.0 g, 0.181 mol) was added slowly, and the mixture was stirred for 20 h under N_2. Water (100 mL) was added and the aqueous layer was extracted with pentane (3 x 70 mL). The dried pentane extract was fractionally distilled very carefully to afford dioxolane **46** as a colorless liquid, bp 88-91 ^{o}C (17.6 g, 67% yield). ^{19}F NMR: δ -83.6. ^{1}H NMR: δ 5.23 (q, $J = 4.5$ Hz, 1H), 4.12 (m, 2H), 4.08 (m, 2H).

2-(Difluoromethylene)-1,3-dioxolane (47). Into a flame-dried 50 mL Schlenk flask were placed anhydrous ether (6 mL) and dioxolane **46** (130 mg. 0.915 mmol). The solution was cooled to -78 ^{o}C and *n*-butyllithium (2.5 M in hexane, 2.0 mL, 5.0 mmol) was added. Stirred for 6 h at -78 ^{0}C, the mixture was then vacuum transferred in the cold at 60 mTorr with the distillate trapped at 77 K. [Caution: the Schlenk flask should be attached to a N_2 bubbler and have its contents quenched, e.g. with *t*-butanol, before warming.] Because ketene acetal **47** was found to have a boiling point close to that of ether, its ether/hexane solution was used directly in the next step. Yield: 50-70%. ^{19}F NMR (ether/hexane): δ -137.9 (s, 2F). GC/MS: m/z 122 (M^+), 103 (M^+ - F), 85, 43, 28 (base, $C_2H_4^+$).

3,3,5,5,6,6,7,7,8,8-Decafluorospiro[tricyclo[2.2.2.0^{1,4}]octane-2,2'-[1,3]dioxolane] (48). The solution of ketene acetal **47** from the previous step was added to alkene **1** (150 mg, 0.670 mmol) in 2 mL of anhydrous ether. ^{19}F NMR revealed that the reaction completed immediately and that all of the alkene **1** was consumed. Evaporation of the solvent gave propellane **48** (212 mg, 100% yield) as a colorless solid. Mp 48-50 °C. ^{19}F NMR: δ -104.1 (s, 2F); -106.6, -107.0 (AB q, *J* = 228 Hz, 4F); -106.7, -107.4 (AB q, *J* = 224 Hz, 4F). ^{1}H NMR: δ 4.25 (m, 2H), 4.21 (m, 2H). ^{13}C NMR (^{19}F decoupled): δ 119.6, 115.5, 115.0, 111, 66.9 (t, *J* = 154 Hz), 53.2, 51.5. IR (film, cm^{-1}): 2961, 1305, 1235, 949, 847. HRMS (CI): calcd for $C_{10}H_5F_{10}O_2$ (M + H$^+$) 347.0130, found 347.0127.

2-Ethoxy-5,5,6,6,7,7,8,8-Octafluorobicyclo[2.2.2]oct-2-ene (50) and 1-Bromo-3-ethoxy-5,5,6,6,7,7,8,8-Octafluorobicyclo[2.2.2]oct-2-ene (51).

To a flame-dried 10 mL round-bottom flask were added dibromide **9** (670 mg, 1.8 mmol), 6 mL of dry acetonitrile, 0.9 mL of a 40% solution of ethoxyacetylene in hexanes (0.36 g, 5.1 mmol), and zinc dust (1.0 g, 15 mmol). This mixture was placed in a water-cooled ultrasonic bath and shaken for 4 h using a modified kugelrohr motor (switching gears reduced the oscillation range to ~20°). ^{19}F NMR showed that the dominant product was bicyclooctene **50**, accompanied by <10% of bromobicyclooctene **51**. Preparative GC at 150 °C afforded both compounds as colorless oils. Compound **50**: ^{19}F NMR: δ -110.3 to -113.5 (2 overlapping AB quartets, 8F). ^{1}H NMR: δ 4.80 (d, vinyl, *J* = 6 Hz, 1H), 3.90 (q, methylene, *J* = 7 Hz, 2H), 3.48 (bs, bridgeheads, 2H), 1.37 (t, methyl, *J* = 7 Hz, 3H). MS: m/z 296 (M$^+$), 268 (M$^+$ - C_2H_4), 248 (M$^+$ - C_2H_4, HF), 168, 104 (base), 29 ($C_2H_5^+$). Anal. Calcd. for $C_{10}H_8F_8O$: C, 40.54; H, 2.70. Found: C, 40.23; H, 2.67. Compound **51**: ^{19}F NMR: δ -109.2, -111.4 (AB q, *J* = 251 Hz, 4F); -112.2, -115.0 (AB q, *J* = 242 Hz, 4F). ^{1}H NMR: δ 4.87 (s, vinyl, 1H), 3.90 (q, methylene, *J* = 7 Hz, 2H), 3.52 (bs,

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bridgehead, 1H), 1.37 (t, methyl, *J* = 7 Hz, 3H). MS: m/z 374 (M^+), 346 (M^+ - C_2H_4), 247, 182, 113, 75, 69, 29 (base, $C_2H_5^+$).

2-Ethoxy-5,5,6,6,7,7,8,8-Octafluorotricyclo[2.2.2.0^{1,4}]oct-2-ene (49) and 3-Ethoxy-5,5,6,6,7,7,8,8-Octafluoro-1-iodo-bicyclo[2.2.2]oct-2-ene (52).

To alkene **1** generated from its N-benzylpyrrole adduct (200 mg, 0.53 mmol) was added at 77 K a solution of ethoxyacetylene (300 μL of a 1 : 1 solution in hexanes, 1.8 mmol) in 2 mL of ether. The cold trap was allowed to warm to -78 °C, and a sample withdrawn for ^{19}F NMR was placed in a spectrometer precooled to -78 °C. The spectrum revealed two AX patterns corresponding to propellene **49**. Reaction was complete by the time the first spectrum was acquired. Upon warming to rt, the solution turned a bright red color, and the ^{19}F spectrum became very complicated with many peaks arising between -111 and -114 ppm simultaneous with disappearance of the propellene peaks. In another experiment, propellene **49** in ether solution at -78 °C was trapped by addition of a slightly moist acetonitrile solution of tetrabutylammonium iodide. An instant color change to brown occurred. The ^{19}F NMR spectrum of this mixture at r.t. showed a pair of quartets representing ring-opened HI adduct **52**. After extraction with water, the organic phase was dried over $MgSO_4$ and reduced in volume to 1 mL. Preparative GC at 150 °C of this solution gave **52** as a colorless oil. Propellene **49**: ^{19}F NMR: δ -100.9, -116.0 (AX, *J* = 215 Hz, 4F); -102.2, -115.2 (AX, *J* = 217 Hz, 4F). HI adduct **52**: ^{19}F NMR: δ -104.8, -108.7 (AB q, *J* = 233 Hz, 4F); -108.5, -110.1 (AB q, *J* = 257 Hz, 4F). ^{1}H NMR: δ 4.97 (s, vinyl, 1H), 3.86 (q, methylene, *J* = 7 Hz, 2H), 3.51 (bs, bridgehead, 1H), 1.34 (t, methyl, *J* = 7 Hz, 3H). MS: m/z 422 (M^+), 393 (M^+-C_2H_5), 374 (M^+-C_2H_5F), 294, 247, 230 (base), 167, 142, 113, 75.

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Supporting Information Available. ^{1}H and ^{19}F NMR spectra; total energies and Cartesian coordinates for all calculated structures; X-ray data (CIF) and ORTEPs for **22** and **45** (CCDC 1838646 and CCDC 1838647, respectively). The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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