

Synthesis, Basicity, and Dynamics of a Perfluorocyclohexenyl Anion

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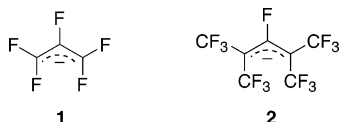
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Electron transfer to perfluoro-1,3-dimethylcyclohexane in moist THF has yielded two quite different products. Tetrabutylammonium iodide irradiated with ultraviolet light gives a tetrabutylammonium enolate, but potassium fluorenone ketyl affords a cyclohexenyl anion. This allylic anion was isolated as its conjugate acid, a rather strong carbon acid. Ring inversion in the anion, measured by ^{19}F NMR line shape analysis, is characterized by these activation parameter values: $\Delta H^\ddagger = 8.84 \pm 0.14$ kcal/mol and $\Delta S^\ddagger = 0.81 \pm 0.6$ cal mol $^{-1}$ K $^{-1}$.

Introduction

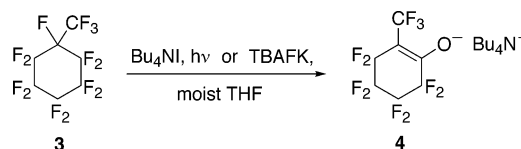
Perfluoroalkylcarbanions are ordinarily generated by fluoride ion addition to perfluoroalkenes or deprotonation of monohydroperfluoroalkanes. Although most of these species are rather unstable, a variety of tertiary examples have been isolated as tris(dimethylamino)sulfonium (TAS) or cesium salts.^{1–3} They enjoy stabilization by negative hyperconjugation with $\text{C}_\alpha\text{--F}$ bonds, as well as by the inductive and field effects of fluoro substituents.^{2,4} Their stability depends importantly on the nature of the counterion, for if the positive charge is neither diffuse nor buried the cation assists fluoride ion loss to give alkene(s).

Pentafluoroallyl anion (**1**) has been investigated computationally⁵ and perhaps also generated in a mass spectrometer,⁶ but the only perfluoroallylic anion to be synthesized and studied in solution prior to the present work is **2**, isolated as a TAS salt.⁷ In the course of a study of fluorocarbon functionalization, we have accidentally discovered the first example of a perfluorocyclohexenyl anion. Its mode of formation is novel.



Functionalization of saturated perfluorocarbons is challenging because they are highly inert and because the vigorous conditions required for successful attack

upon them generally result in wholesale destruction of the molecule.^{8–10} Powerful electron donors induce loss of a fluoride ion, and since the resulting intermediates are more easily reduced than the starting material, a reaction cascade ensues with hemorrhaging of fluoride ions.¹¹ We have developed methods for stopping the cascade at an early stage by placing a negative charge on the molecule, thus inhibiting further assault by an electron donor.¹² For example, perfluoromethylcyclohexane (**3**) can be transformed into the tetrabutylammonium enolate **4** either photochemically or “thermally” at room temperature. Irradiation of tetrabutylammonium iodide in THF



excites a charge-transfer-to-solvent (CTTS) transition,¹³ and the solvated electrons reduce **3** to perfluoro-1-methylcyclohexene (**5**) via initial loss of the most vulnerable fluorine, the tertiary one (Scheme 1). Hydroxide ion resulting from the presence of a small amount of water intercepts the alkene in an addition–elimination reaction, and deprotonation of the resulting enol yields **4**. The

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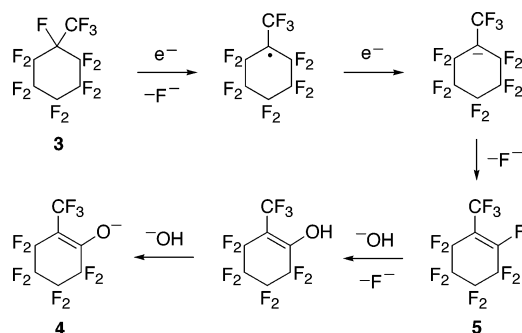
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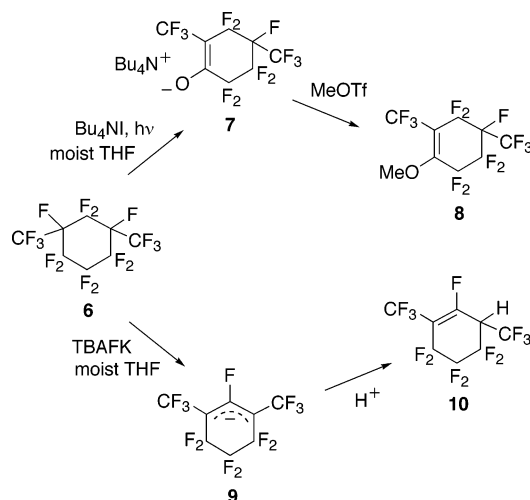
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SCHEME 1



SCHEME 2



same tetrabutylammonium enolate can be prepared without light using tetrabutylammonium fluorenone ketyl (TBAFK) as the source of electrons.

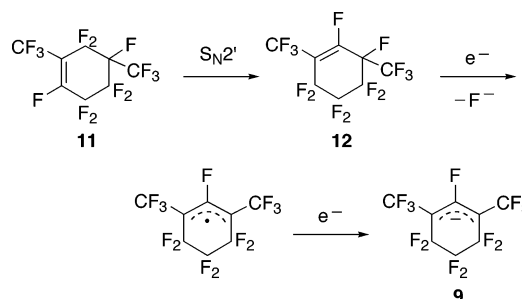
Results and Discussion

When the reductive functionalization reaction was carried out photochemically with perfluoro-1,3-dimethylcyclohexane (**6**), enolate **7** was obtained, free of the isomeric ion oxygenated at the 2-position of **6** (Scheme 2).¹² The selectivity of this reaction may be attributable to a steric effect, as the bulky tetrabutylammonium ion may approach C5 more easily than C2 to assist loss of fluoride ion. Enolate **7** was isolated as its methyl enol ether **8**.

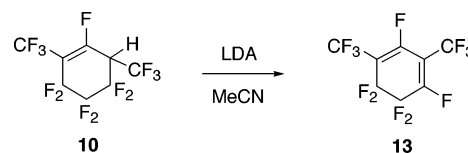
Under the thermal conditions, however, no **7** was observed. Instead, the ^{19}F NMR spectrum of the reaction mixture showed that a species with 2-fold symmetry had been formed. Its stability under the reaction conditions suggested the presence of a negative charge, and it became clear that the species was the allylic anion **9**. Protonation of **9** with sulfuric acid yielded hydroperfluorocyclohexene **10**, isolated in ~87% overall yield. Now the reduction was run photochemically in the absence of water, and **9** was again the product. Apparently, if hydroxide ion fails to capture the initially formed alkene **11**, leading to enolate **7**, the alkene undergoes fluoride ion-catalyzed isomerization to **12**. Calculations at the B3LYP/6-31G* level of theory¹⁴ indicate that alkene **12**^{15a} is only slightly lower in energy than **11**¹⁵ ($\Delta E = 0.60$ kcal/mol¹⁶), but it is more susceptible to reduction because

of the presence of a tertiary fluorine in an allylic position. Attack by two successive electrons then gives the robust anion **9** as its tetrabutylammonium salt.

The contrast in reaction course in moist THF between the photochemical and thermal conditions probably reflects a difference in hydroxide ion concentration during reaction. As a better electron donor than base, the fluorenone radical anion may be quite selective in attacking fluorocarbon in preference to water, whereas solvated electrons readily reduce both. Just as the negative charge on enolate **7** protects the molecule from further reduction, the charge on anion **9** plays the same role.



Since hydrofluorocarbon **10**, a potent electrophile, was quickly destroyed by dissolution in methanol, attempts to measure its acidity were carried out in nonhydroxylic solvents. Addition of strong, hindered amine bases such as triethylamine or Proton Sponge to **10** in acetonitrile gave stable solutions of the anion **9**. However, lithium diisopropylamide (LDA) transformed **10** quite cleanly into diene **13**, reflecting the ability of lithium ion to facilitate fluoride ion loss. Rapid, ill-defined decomposition was observed with a variety of weak bases such as dichloroacetate ion and the enolates of dimedone and triacetyl-methane.



Eventually, a hindered base was found that caused minimal decomposition and was close enough in basicity to **9** to allow for quantitative comparison: the 2,6-dinitroresolate ion (**14**). Measurements of the acidity of **10** were made in acetonitrile- d_3 with variable excesses of triethylamine and 2,6-dinitroresol (**15**). They were car-

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(16) This value is for 0 K, uncorrected for zero-point energy difference.

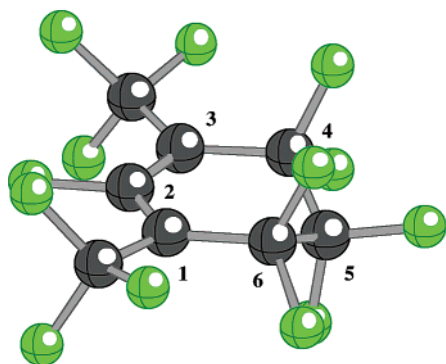


FIGURE 1. Structure of perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**) calculated at the B3LYP/6-31G* level of theory.

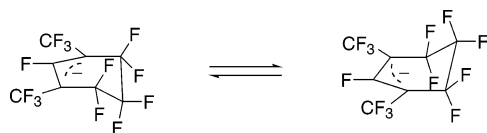
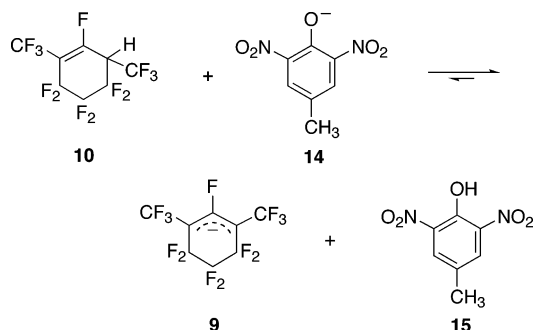


FIGURE 2. Ring inversion in perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**).

ried out at -45°C to limit exchange broadening (see below) and to slow decomposition. Ratios of anion **9** to its conjugate acid **10** were determined by ^{19}F NMR integration. In this way, cyclohexene **10** was found to be 53 ± 4 times more acidic in acetonitrile than cresol **15**, the $\text{p}K_{\text{a}}$ of which is 4.23 in water.¹⁷ This acidity ratio was calculated on the assumption that the decomposition of **9** does not consume base, and the acidity of **10** is somewhat greater yet if it does.¹⁸ Clearly, cyclohexene **10** is a strikingly acidic fluorocarbon.



The ^{19}F NMR spectrum of anion **9** in THF comprised four signals: narrow multiplets at $\delta -49.6$ (two CF_3 s) and -106.7 (vinyl F) and very broad singlets at $\delta -107.9$ (two CF_2 s) and -138.2 (CF_2). The breadth of the latter resonances indicated that a dynamic process was occurring at an intermediate exchange rate on the NMR time scale. B3LYP/6-31G* calculations ascribe C_s symmetry to the anion, with five of the ring carbons coplanar and the CF_3 carbons just $4\text{--}5^{\circ}$ out-of-plane (Figure 1). C5 is bent strongly out-of-plane in the other direction (flap angle 42°), and the dynamic process revealed by NMR is ring inversion involving that carbon (Figure 2). Thus, the anion exists in a “half-chair” conformation, but one that differs from the cyclohexene half-chair in which two carbons lie outside the plane of the other four.

As the temperature was lowered, the methyl and methine fluorine resonances of **9** changed very little, but

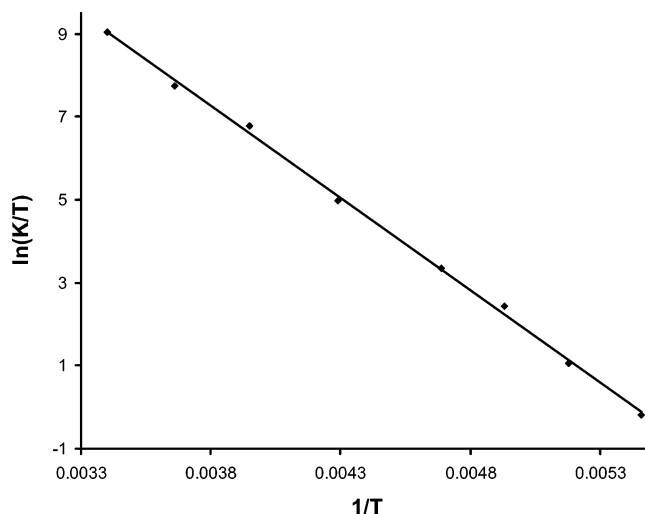


FIGURE 3. Eyring plot for ring inversion of perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**).

the broad NMR signals representing the methylene fluorines decoalesced. When the spectrum finally re-sharpened at -100°C , the signal at $\delta -107.9$ had resolved into a pair of doublets ($J = 262$ Hz) at $\delta -90.8$ and -126.0 , and the $\delta -138.2$ peak had become a pair of doublets ($J = 247$ Hz) at $\delta -125.2$ and -152.9 . Line shape analysis over the temperature range -100 to $+21^{\circ}\text{C}$ gave a set of rate constants, and the resulting Eyring plot (Figure 3) revealed these activation parameter values: $\Delta H^{\ddagger} = 8.84 \pm 0.14$ kcal/mol and $\Delta S^{\ddagger} = 0.81 \pm 0.6$ cal mol $^{-1}$ K $^{-1}$. The barrier lies between the ring inversion barrier for perfluorocyclohexene ($\Delta H^{\ddagger} = 7.2 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = 2.6 \pm 1.6$ cal mol $^{-1}$ K $^{-1}$)¹⁹ and that for perfluorocyclohexane ($\Delta G^{\ddagger} = 10.9$ kcal/mol at 25°C).²⁰ The only other barrier reported for ring inversion in a cyclohexenyl system is that for 1,2,3,4,5,6-hexamethylcyclohexenyl cation ($E_{\text{a}} = 8.9$ kcal/mol, $\log A = 10.8$ s $^{-1}$).²¹ Based on their activation parameter values, ring inversion of **9** is calculated to be 160 times faster than that of this cation at 25°C .

The calculated geometry of anion **9** reflects the role of negative hyperconjugation in stabilizing its charge, for the length of the 10 methyl and methylene C–F bonds flanking C1 and C3 correlate nicely with their degree of alignment with the allylic π system (Figure 1). For example, the quasiaxial C–F bonds at C4 and C6, misaligned by only 7.5° , are 1.393 Å long, but the quasiequatorial bonds, misaligned by 53° , are 1.379 Å in length. For comparison, the C–F bonds at C5, where hyperconjugation cannot occur, average 1.363 Å in length.

Experimental Section

NMR spectra were performed on 300 and 500 MHz machines. ^{19}F NMR spectra were recorded at 282.2 and 470.3

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MHz, with trichlorofluoromethane as internal standard. ^{13}C NMR spectra were recorded at 125.7 MHz. GC was performed using a $\frac{1}{4}$ in. \times 10 ft column packed with 10% OV-101 on Chromasorb-W-AW-DMCS 60/80. The UV source for photoreaction was a Vycor-filtered 450 W Hanovia medium-pressure mercury arc contained in a quartz water jacket.

THF was distilled from potassium benzophenone ketyl, and acetonitrile was distilled from calcium hydride. After distillation, technical perfluoro-1,3-dimethylcyclohexane was further purified by GC as a mixture of *cis* and *trans* isomers. The mixture was 90% pure by GC. Caution should be taken in handling methyl triflate, as it is very poisonous.

Photochemical Synthesis and Methylation of Perfluoro-2,4-dimethylcyclohex-1-enolate (7). Perfluoro-1,3-dimethylcyclohexane (**6**) (0.60 g, 90% pure, 1.5 mmol), water (18 mg, 1.0 mmol), tetrabutylammonium iodide (1.38 g, 3.74 mmol), and THF (10 mL) were placed in a 25 mL quartz tube. It was sealed with a septum and attached to the jacket surrounding the lamp. The whole assembly was immersed in water contained in a large beaker. Cooling water was introduced to the beaker continuously, and a pan with a draining hose contained the overflow. The mixture was irradiated for 20 h while being stirred with a motor-driven horseshoe magnet placed close to the quartz tube outside the beaker. Formation of perfluoro-2,4-dimethylcyclohex-1-enolate (**7**) was observed by NMR. Treatment with excess methyl triflate transformed the enolate into its *O*-methyl ether (**8**), which was purified by preparative GC. Yield: 0.28 g, 50% based on perfluoro-1,3-dimethylcyclohexane. ^1H NMR (CDCl_3): δ 4.2 (t, poorly resolved, CH_3). ^{19}F NMR (CDCl_3): (The labels “*cis*” and “*trans*” in the assignments locate fluorine atoms relative to the CF_3 group at C4. Assignments were made with the help of NOE measurements.) δ -59.08 (s, 3F, CF_3 on C2); -70.45 (s, 3F, CF_3 on C4); -98.53, -105.38 (ABq, J = 307 Hz, 2F; A, *cis*, C3; B, *trans*, C3); -105.04 (dd, J = 24, 301 Hz, 1F, *trans*, C6); -119.51 (d, 289 Hz, 1F, *cis*, C5); -125.09 (d, 301 Hz, 1F, *cis*, C6); -135.92 (d, 289 Hz, 1F, *trans*, C5); -183.87 (s, 1F, C4). IR (neat, cm^{-1}): 2977, 1664, 1470, 1382, 1340, 1282, 1223, 1157, 1079, 1017, 940, 894, 671. HRMS: calcd for $\text{C}_9\text{H}_3\text{F}_{13}\text{O}$ 373.9976, found 373.9976.

“Thermal” Synthesis of Perfluoro-1,3-dimethylcyclohex-2-enyl Anion (9) and 3H-Perfluoro-1,3-dimethylcyclohexene (10). The following operations were done under nitrogen protection, and glassware was dried in an oven at 120 °C overnight. Tetrabutylammonium bromide (3.87 g, 12 mmol), fluorenone (2.16 g, 12 mmol), potassium (0.48 g, 12 mmol), and THF (40 mL) were added to a 60 mL dropping funnel with a fritted filter plate. The mixture was magnetically stirred overnight, and then nitrogen pressure was applied to force tetrabutylammonium fluorenone ketyl solution through the filter plate into a 50 mL flask. Potassium bromide was thus removed by filtration, and the deep red ketyl solution was transferred to a 50 mL syringe. Perfluoro-1,3-dimethylcyclohexane (**6**) (0.74 g, 90% pure, 1.9 mmol) was added to a 100 mL two-neck round-bottom flask. The ketyl solution was slowly added to the above flask over the course of 8 h, controlled by a syringe pump. Formation of perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**) was observed by NMR. ^{19}F NMR (CD_3CN): δ -48.53 (m, narrow, 6F, two CF_3 s), -105.39 (m, narrow, 1F, C2), -106.50 (s, broad, 4F, C4 and 6), -136.90 (s, broad, 2F, C5).

Triglyme (freshly distilled, 40 mL) was added to the above mixture, and THF was removed under vacuum. Concentrated sulfuric acid (10 mL) was added while the mixture was stirred and cooled in a water bath. The resulting 3H-perfluoro-1,3-dimethylcyclohexene (**10**) was vacuum transferred to a liquid nitrogen-cooled U-trap. Yield: 0.54 g, 85%. ^1H NMR (CDCl_3):

δ 4.16 (m, broad, 1H). ^{19}F NMR (CDCl_3): δ -58.67 (narrow m, 3F, C1), -61.36 (s, 3F, C3), -88.98 (s, broad, 1F, C2), -102.54 (d, 294 Hz, 1F), -120.35 (d, 273 Hz, 1F), -122.73 (d, 294 Hz, 1F), -125.15 (d, 267 Hz, 1F), -128.07 (d, 273 Hz, 1F), -147.77 (d, 267 Hz, 1F). ^{13}C NMR (^{19}F decoupled, CDCl_3): δ 157.70 (d, 10 Hz, C2), 120.76 (d, 10 Hz, CF_3 on C3), 119.26 (s, CF_3 on C1), 110.77 (m, CF_2 , C4, 5, or 6), 110.23 (m, C1), 109.64 (m, CF_2 , C4, 5, or 6), 107.43 (s, CF_2 , C4, 5, or 6), 48.60 (d, 137 Hz, C3). IR (neat, cm^{-1}): 1704, 1390, 1223, 1164, 1023, 898. HRMS: calcd for C_9HF_{13} 343.9871, found 343.9871.

Photochemical Synthesis of Perfluoro-1,3-dimethylcyclohex-2-enyl Anion (9). Perfluoro-1,3-dimethylcyclohexane (**6**) (10 mg, 0.025 mmol), tetrabutylammonium iodide (46 mg, 0.125 mmol), and CD_3CN (1 mL) were added to a quartz NMR tube. It was sealed with a septum and attached to the jacket surrounding the UV source. The whole assembly was immersed in cooling water, as described above. The mixture was irradiated for 20 h. Perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**) was the major product, as shown by NMR.

Formation of Perfluoro-1,3-dimethylcyclohex-2-enyl Anion (9) from 3H-Perfluoro-1,3-dimethylcyclohexene (10). 3H-Perfluoro-1,3-dimethylcyclohexene (**10**) (15 mg, 0.044 mmol) and CD_3CN (0.5 mL) were added to an oven-dried NMR tube. Proton Sponge (46 mg, 0.044 mmol) dissolved in CD_3CN (0.5 mL) was added to the tube. Perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**) was formed quantitatively, as indicated by NMR.

Formation of Perfluoro-1,3-dimethylcyclohex-1,3-diene (13) from 3H-Perfluoro-1,3-dimethylcyclohexene (10). 3H-Perfluoro-1,3-dimethylcyclohexene (**10**) (20 mg, 0.058 mmol) and CD_3CN (0.5 mL) were placed in an oven-dried NMR tube. Lithium diisopropylamide (LDA) (29 μL , 2.0 M, 0.058 mmol) was added to the NMR tube. Perfluoro-1,3-dimethylcyclohex-1,3-diene (**13**) was formed cleanly, as indicated by NMR. ^{19}F NMR (CD_3CN): δ -62.08 (d, poorly resolved, 3F, CF_3), -63.83 (d, poorly resolved, 3F, CF_3), -102.20 (m, broad, 1F, C2), -125.29 (s, 2F, C5 or 6), -130.45 (s, 2F, C5 or 6), -160.31 (m, broad, 1F, C4). GC/MS (*m/e*): 324 (M^+).

Measurement of 3H-Perfluoro-1,3-dimethylcyclohexene (10) Acidity. 2,6-Dinitro-*p*-cresol (60.7 mg, 0.306 mmol) and triethylamine (\sim 15.4 μL , 0.113 mmol) were dissolved in CD_3CN (2.00 mL), total volume 2.06 mL. To an oven-dried NMR tube was added 3H-perfluoro-1,3-dimethylcyclohexene (**10**) (15.0 mg, 0.0436 mmol), dissolved in CD_3CN (0.5 mL). It was sealed with a septum and cooled to -15 °C in an ethylene glycol slush bath. Amine/phenol mixture (1.00 mL) was added to the NMR tube, and the contents were well mixed before NMR measurements were taken at -45 °C. The molar ratio of cresol/cresolate to triethylammonium ion was measured as 2.70:1.00 by ^1H NMR. The ratio of 3H-perfluoro-1,3-dimethylcyclohexene (**10**) to perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**) to decomposed fluorocarbon was 1.36:10.14:1.00, as revealed by ^{19}F NMR.

Another measurement was carried out, using 3H-perfluoro-1,3-dimethylcyclohexene (**10**) (15.0 mg, 0.0436 mmol) and 1.00 mL of a 3.08 mL mixture of 2,6-dinitro-*p*-cresol (151.8 mg, 0.766 mmol), triethylamine (\sim 26.9 μL , 0.183 mmol), and CD_3CN (3.0 mL). The molar ratio of cresol to triethylamine was measured as 4.10:1.00 by ^1H NMR. The ratio of 3H-perfluoro-1,3-dimethylcyclohexene (**10**) to perfluoro-1,3-dimethylcyclohex-2-enyl anion (**9**) to decomposed fluorocarbon was 1.32:7.48:1.00, as revealed by ^{19}F NMR.

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