JOC Article

New Syntheses and Chemistry of Hexafluorotropone

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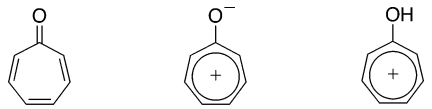
Two new routes to hexafluorotropone have been developed, one from hexachlorotropone and a superior synthesis from hexafluorobenzene. Hexafluorotropone was found to be a very weak base, with a conjugate acid pK_a of -6.2 ± 0.5. The tropone adds in [6 + 4] fashion to cyclopentadiene and photocyclizes to hexafluorobicyclo[3.2.0]hepta-3,6-dien-2-one. Lithium hydroxide in benzene transforms the tropone into pentafluorotropolone, which functions as a bidentate ligand.

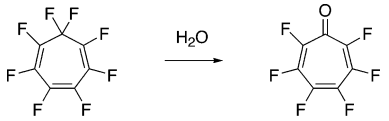
Introduction

With a conjugate acid pK_a of -1.02, tropone (**1**) is a million times more basic than typical ketones.[3] It can be regarded as a hybrid of forms **1** and **1a**, where **1a** plays a minor role (~16%) based on X-ray and electron diffraction results that reveal substantial bond alternation in a nearly planar ring.[4] The impressive basicity thus reflects the stability of the tropylium ion (**2**) formed upon protonation. Tropone displays unusual and interesting chemistry in both ground and excited states.



1 **1a** **2**

Hexafluorotropone (**3**) is an appealing molecule to study not only because it is an anomaly among perfluoroketones but also because its behavior bears on the question of balance between σ-electron withdrawal and π-electron donation in fluorine's schizoid nature.[5] Since the former tendency weakens and the latter strengthens the basicity of the ketone, a comparison of base strength between **3** and its parent would reveal which effect is dominant. Hexafluorotropone has been prepared by hydrolysis of octafluorocyclohepta-1,3,5-triene (**4**), which occurs even in moist air.[6,7] Synthesis of **4** from the parent triene was only possible in very low yield, however, and the authors of the work commented that "real progress in the perfluorotropone field will only come when a route from much more accessible compounds has emerged".[7] With the goal of exploring its chemistry and comparing it with the parent ketone, we undertook an investigation of alternative synthetic approaches to hexafluorotropone.

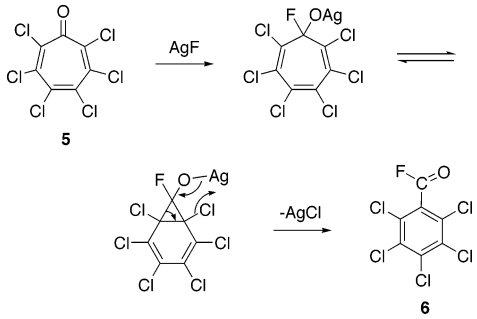


4 **3**

Results and Discussion

New Routes to the Tropone. Hexachlorotropone (**5**) was a promising precursor for its fluorinated analogue, as it can be made in quantity via a several-step route from readily available hexachlorocyclopentadiene and trichloroethylene.[8,9] At the outset, we attempted to replace the chlorines of **5** with fluorines by means of addition–elimination reactions employing KF, CsF, and AgF. At elevated temperatures, KF produced mixtures of chlorofluorobenzene derivatives; AgF aromatized the ketone even at room temperature, giving pentachlorobenzoyl fluoride (**6**) as the sole product.[10] A possible mechanism is shown in Scheme 1.

SCHEME 1



5 **6**

Saturation of the triene system with fluorine followed by reductive elimination of the chlorines was a possible alternative way to effect the **5** → **3** transformation.

(1) Walter H. Stockmayer Fellow, 2001–2002.
(2) Present address: Wyeth-Ayerst Research, 401 N. Middletown Rd, Pearl River, NY 10965.
(3) Hosoya, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1414.
(4) Lloyd, D. *Non-Benzenoid Conjugated Carbocyclic Compounds*; Elsevier: New York, 1984; p 70.
(5) See, for example, Smart, B. E. In *Chemistry of Organic Fluorine Compounds II*; Hudlicky, M., Pavlath, A. E., Eds.; ACS Monograph 187; American Chemical Society: Washington, D.C., 1995; p 979.
(6) Dodsworth, D. J.; Jenkins, C. M.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1972**, 803. The facile hydrolysis clearly reflects the stability of the aromatic heptafluorotropylium ion.
(7) Dodsworth, D. J.; Jenkins, C. M.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1984**, *24*, 41.

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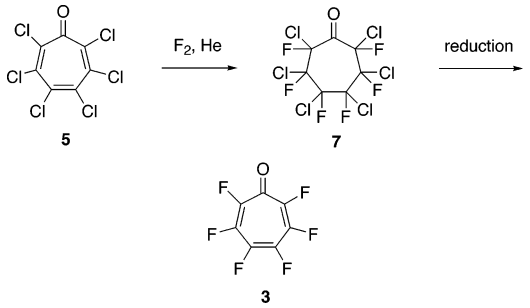
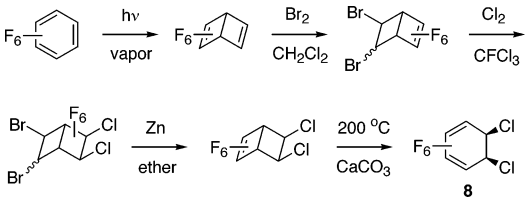


Treatment of tropone **5** with a fluorine/helium mixture in Freon 113 ($CF_2ClCFCl_2$) gave a complex array of chlorofluoroketones (**7**), which could be reduced under very mild conditions. Copper bronze in refluxing acetonitrile or in dimethyl sulfoxide at room temperature produced the desired tropone **3**, as did even sodium iodide in acetone at room temperature. Prolonged contact with excess reducing agent had to be avoided, for it destroyed the tropone. Unfortunately, the combined yield for the fluorination and reduction steps was only 10−25%. The presence of an insoluble dark solid remaining after reduction suggested that oligomerization/polymerization had happened during fluorination, a common occurrence in the fluorination of C=C double bonds.[11] In an effort to minimize the opportunity for a carbon radical intermediate to find a C=C double bond to attack before being intercepted by a fluorine molecule, starting material was introduced very slowly via syringe pump with good mechanical stirring into a solution kept saturated with fluorine. However, the yield of tropone after reduction was not significantly improved by this technique. Invariably accompanying **3** in the reduction product were minor amounts of chloropentafluorotropones, separation of which from **3** required liquid or preparative gas chromatography.

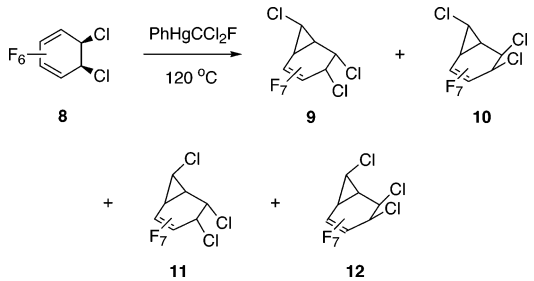
Since every step of the reaction sequence leading to **3** is scalable, it is practical to obtain gram quantities of the tropone by this route despite the low yield from the final steps. Given the room for improvement, though, we decided to try an entirely different synthetic approach, described below.

Cyclohexadiene **8** is synthesized from hexafluorobenzene in five steps in an overall yield of 65% (Scheme 2).[12]

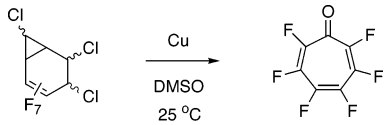
SCHEME 2



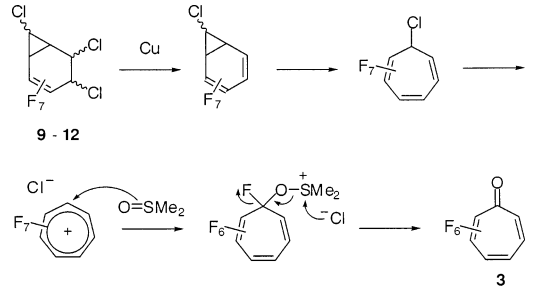
Heating **8** with a slight excess of $PhHgCFCl_2$[13] in 1,2,4-trichlorobenzene at 120 °C gave a stereoisomeric mixture of chlorofluorocarbene adducts (**9**−**12**) in about 70% yield by NMR. The temperature was critical, as the adducts underwent vinylcyclopropane rearrangement.[14] As could be anticipated on steric grounds, the relative amounts of adduct diminished in the order shown, with dominant products **9** and **10** in the ratio 4:1.



Treatment of these adducts with an array of reducing agents under a variety of conditions resulted in either no reaction or unpromising mixtures, with one remarkable exception. Copper bronze in dimethyl sulfoxide transformed the adduct mixture into hexafluorotropone (**3**) at room temperature. Since careful exclusion of moisture did not alter the result, the oxygen of the tropone originated with the solvent. A likely mechanism for the reaction is shown in Scheme 3. Isolated by chromatography and recrystallized, the tropone was obtained in 38% yield from cyclohexadiene **8**, i.e., 25% overall yield in seven steps from hexafluorobenzene. The rare ketone had finally become readily accessible.



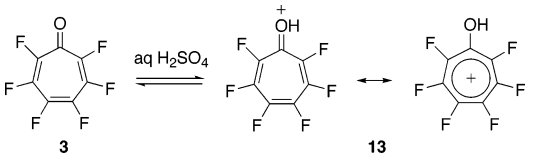
SCHEME 3



Chemistry of the Tropone. Hamor et al. obtained the X-ray crystal structure of hexafluorotropone and found it to be planar with somewhat less bond alternation in the ring but a significantly shorter C−O bond than that of the parent ketone (**1**).[15] A key question for us was the relative basicity of the two tropones. As noted above, the pK_a of the conjugate acid of **1** is −1.02, measured spectrophotometrically in aqueous sulfuric acid.[3] We

(8) (a) West, R.; Kusuda, K. *J. Am. Chem. Soc.* **1968**, *90*, 7354. (b) West, R. *Acc. Chem. Res.* **1970**, *3*, 130.
(9) Druecke, S.; Imming, P.; Kamplchen, T.; Seitz, G. *Chem. Ber.* **1988**, *121*, 1595.
(10) For analogous ring-contracting rearrangements of octachlorocycloheptatriene, see ref 8a.
(11) See, for example: Correa, R. A.; Jing, N.; Lemal, D. M. *J. Org. Chem.* **1993**, *58*, 6406.
(12) Dailey, W. P.; Correa, R. A.; Harrison, E.; Lemal, D. M. *J. Org. Chem.* **1989**, *54*, 5511.
(13) Seyferth, D.; Murphy, G. J. *J. Organomet. Chem.* **1973**, *49*, 117.
(14) Dailey, W. P.; Ralli, P.; Wasserman, D.; Lemal, D. M. *J. Org. Chem.* **1989**, *54*, 5516.
(15) Guy, J. J.; Hamor, T. A.; Jenkins, C. M. *J. Fluorine Chem.* **1975**, *5*, 89.

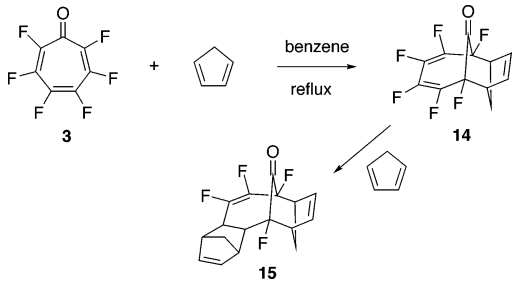
determined the pK_a of hexafluorotropone's conjugate acid (**13**) by ^{19}F NMR in the same medium, but found that much more concentrated sulfuric acid was required. Half protonation was attained at an H_0 value of -6.2 ± 0.5, which is therefore the pK_a. Hexafluorotropone's basicity turns out to be roughly 100 000 times less than that of the parent tropone. This striking finding demonstrates that the influence of σ-electron withdrawal completely overshadows that of π-electron donation in determining basicity in this system.



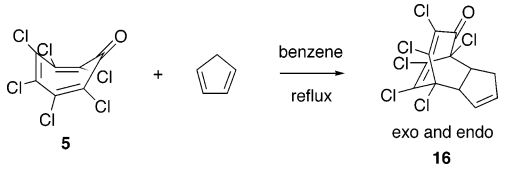
In the case of 1,2,3,4,5-pentafluorocyclopentadiene and the derived anion, lone pair-π repulsion should destabilize but σ-electron withdrawal stabilize the anion, reducing its basicity. Seppelt showed that the pK_a of the diene falls between 12.8 and 15.5, the value for the hydrocarbon cyclopentadiene.[16] Thus, the dominance of electron withdrawal in determining basicity is considerably greater in hexafluorotropone.

Parent tropone (**1**)[17] reacts with cyclopentadiene to give a [6 + 4] adduct with exo stereochemistry. Both the periselectivity and the stereochemistry are explainable in terms of HOMO−LUMO interactions. Whereas secondary orbital interactions between the frontier orbitals stabilize the endo transition state in a Diels−Alder reaction, those same interactions are antibonding in the transition state for a [6 + 4] cycloaddition; thus, the exo adduct is favored by default.[18,19]

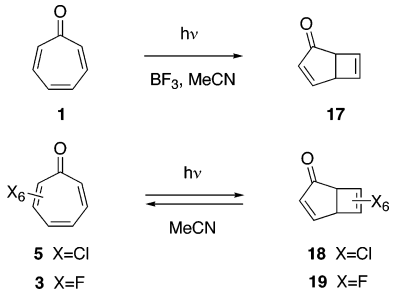
Hexafluorotropone parallels the behavior of its parent in reaction with cyclopentadiene, giving the exo [6 + 4] adduct **14**. The stereochemistry was confirmed by the X-ray crystal structure (see the Supporting Information). When the cycloaddition is carried out with excess cyclopentadiene at reflux in much more concentrated benzene solution, a second molecule of the diene adds in [4 + 2] fashion, giving **15**.



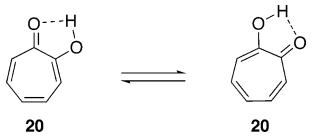
Interestingly, hexachlorotropone (**5**) gives a [4 + 2] adduct (**16**) with cyclopentadiene in benzene at reflux.[20] Perhaps the contrast in its behavior vis-à-vis that of the planar **3**[15] and nearly planar **1**[4] is attributable to the boat conformation of **5**,[21] in which the chlorines at the 2- and 7-positions may hinder approach of the diene in the [6 + 4] mannner.



The parent tropone displays a rich photochemistry. UV irradiation in acetonitrile yields a mixture of [6 + 4], [6 + 2], and [4 + 2] dimers,[22] and in dilute sulfuric acid a [6 + 6] dimer.[23] With boron trifluoride in acetonitrile, photocyclization to bicyclo[3.2.0]hepta-3,6-dien-2-one (**17**) occurs.[24] Hexachlorotropone (**5**) cyclizes analogously to **18** in acetonitrile with 254 nm light, and the reaction is reversible.[25] We have found that the fluorinated tropone **3** also gives the corresponding bicyclic ketone (**19**) reversibly when irradiated with a medium-pressure mercury arc. When benzophenone was introduced as a triplet sensitizer with irradiation at 254 nm, the cyclization was far slower and no new product was formed. Thus, formation of **19** is probably a singlet-state reaction.

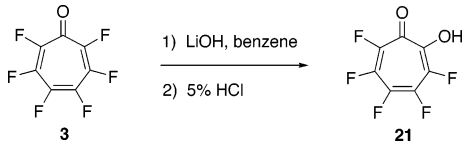


Tropolone (**20**) undergoes rapid tautomerization in solution and thus has time-averaged C_{2v} symmetry.[26] Tatlow et al. prepared pentafluorotropolone (**21**) from **3** by treatment with aqueous sodium hydroxide, isolation of the copper(II) complex of **21**, and regeneration with hydrogen sulfide.[27] This procedure was necessary because the 2-position of **3** was the least favored site of attack by the hydroxide ion. The 2-, 3-, and 4-hydroxy derivatives were obtained in 65% yield in the ratio 15:65:20, respectively. Like the parent, tropolone **21** displays C_{2v} symmetry on the NMR time scale.

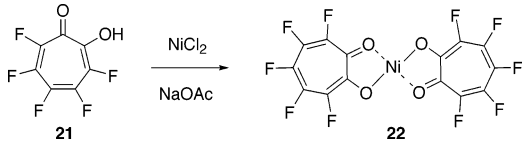


(16) Paprott, G.; Seppelt, K. *J. Am. Chem. Soc.* **1984**, *106*, 4060.
(17) Cookson, R. C.; Drake, B. V.; Hudec, J.; Morrison, A. *J. Chem. Soc., Chem. Commun.* **1966**, 15. Ito, S.; Fujise, Y.; Okuda, T.; Inoue, Y. *Bull. Chem. Chem. Soc. Jpn.* **1966**, *39*, 1351.
(18) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
(19) Mukherjee, D.; Watts, C. R.; Houk, K. N. *J. Org. Chem.* **1978**, *43*, 817.
(20) Akhtar, M.; Bratby, D. M.; Chadwick, J. C.; Fray, G. I. *Tetrahedron* **1976**, *32*, 2265.
(21) Dodge, R. P.; Sime, R. J.; Templeton, D. H. Private communication to Scherer, K. V., cited in *J. Am. Chem. Soc.* **1968**, *90*, 7352.
(22) Kende, A. S. *J. Am. Chem. Soc.* **1966**, *88*, 5026.
(23) Mukai, T.; Tezuka, T.; Akasaki, Y. *J. Am. Chem. Soc.* **1966**, *88*, 5025.
(24) Cavazza, M.; Zandomeneghi, M.; Pietra, F. *J. Chem. Soc., Chem. Commun.* **1990**, 1336.
(25) Scherer, K. V. *J. Am. Chem. Soc.* **1968**, *90*, 7352.
(26) Weiler, L. *Can. J. Chem.* **1972**, *50*, 1975.

We were interested in tropolone **21** as a potentially useful, electron-deficient bidentate ligand.[28] A more efficient synthesis was needed, and we found one by taking advantage of the carbonyl's coordinating ability to direct hydroxide attack to the neighboring carbons. Treatment with anhydrous lithium hydroxide in benzene, then acidification transformed tropone **3** into **21**, 85% pure, in 72% yield based on tropone consumed. Less than 10% of the 3-hydroxy and none of the 4-hydroxy derivative was present.



Addition of aqueous nickel chloride to a buffered acetone solution of tropolone **21** resulted immediately in a golden yellow precipitate of bis(pentafluorotropolonato)nickel (**22**). Its ^{19}F NMR spectrum comprises a very broad signal at Φ +8.9, a moderately broad one at −84.1, and a sharp singlet at −185.6 ppm, probably corresponding to the 2- and 6-, the 3- and 5-, and the 4-fluorine, respectively, the line breadth varying inversely with the distance from the nickel atom.



Conclusion

Hexafluorotropone (**3**) was prepared from hexachlorotropone, but a better synthesis has also been developed that proceeds from hexafluorobenzene in 25% overall yield. Like the parent tropone, **3** undergoes [6 + 4] cycloaddition to cyclopentadiene with exo stereochemistry. UV irradiation cyclizes **3** to its bicyclo[3.2.0] isomer. Synthesis of pentafluorotropolone has been greatly improved, and a nickel(II) complex has been prepared with this bidentate ligand.

Experimental Section

NMR spectra were obtained on 300 and 500 MHz machines. ^{19}F NMR spectra were recorded at 282.2 MHz, with trichlorofluoromethane as internal standard. Ultrasound treatment was carried out using a Bransonic 42 ultrasound cleaning bath. A 10 ft × 1/4 in. 10% SF-96 on Chromasorb W HP 80/100 column was used for preparative gas chromatography.

Perchlorotropone (5).[9] A three-necked 1000 mL round-bottom flask equipped with a mechanical stirrer and a reflux condenser was immersed in an ultrasound bath. Well-ground octachlorocycloheptatriene (30 g, 82 mmol) was added through a powder funnel. A mixture of trifluoroacetic acid (500 mL) and distilled water (55 mL) was then introduced. The suspension was sonicated with stirring until all the solid went into the yellow greenish solution. The reaction mixture was placed in a refrigerator (~0 °C). Ketone **5** was obtained as bright greenish yellow crystals after suction filtration and further dried on the vacuum line. Yield: 18 g, 80%. Trifluoroacetic acid can be recovered by adding 100 mL of concentrated sulfuric acid, followed by distillation.

2,3,4,5,6,7-Hexachloro-2,3,4,5,6,7-hexafluorocycloheptanone (7). Hexachlorotropone (30 g, 103 mmol) was dissolved with Freon-113 ($CF_2ClCFCl_2$, 700 mL) in a 1000 mL three-necked round-bottom flask fitted with a mechanical stirrer and cooled in an ice bath. After the solution was purged with N_2 for 10 min, a mixture of F_2/He (30:70) was bubbled slowly through the yellow solution with efficient stirring. The bubbling was continued until the solution became colorless. Freon-113 was then recovered by distillation, and a viscous colorless liquid was left behind. This was chromatographed on a column of silica gel (200 g, Acros, 0.035−0.07 mm), with 12:1 hexane/ether as eluent. Product was eluted as the first band. Evaporating the solvent gave 30 g of **7** as a viscous liquid. Yield: 70%. ^{19}F NMR: many peaks between −70 and −140 ppm. GC/MS: many peaks giving a similar pattern of signals, *m/e* 391 ($C_7Cl_5F_6O^+$), 292 ($C_5Cl_4F_4O^+$), 179 ($C_3Cl_3F_2^+$), 163 ($C_3Cl_2F_3^+$), 132 ($C_2Cl_2F_2^+$), 101 (CCl_2F^+), 85 ($CClF_2^+$), 69 (CF_3^+), and 47 (CCl^+).

Hexafluorotropone (3) from Reduction of 7. Copper bronze (38 g, 0.59 mol) was added to a solution of **7** (22 g, 53 mmol) in 250 mL of DMSO. The resulting brown suspension was mechanically stirred under N_2 in an ultrasound bath for 1 h. After 300 mL of water was added to the reaction mixture, it was extracted with methylene chloride (4 × 150 mL). The combined organic layer was washed with water (2 × 80 mL) and saturated NaCl solution (2 × 80 mL) and then dried over $MgSO_4$. The dark liquid obtained after evaporating the solvent was chromatographed on a column of silica gel (150 g, Acros, 0.035−0.07 mm), with 1:4 ether/hexane as eluent. Product was collected as the second band. Evaporating the solvent gave a pale yellow solid, 2.5 g, crude yield 18%. Recrystallization from cyclohexane gave **3** as white needles, yield 2.1 g (15%), purity ~90%. A pure sample can be obtained by a second chromatography or preparative gas chromatography. ^{19}F NMR ($CDCl_3$): δ −124.9 (m, 2F), −136.4 (m, 2F), −142.0 (m, 2F). GC/MS (*m/e*): 214 (M^+), 186 ($C_6F_6^+$), 167 ($C_6F_5^+$). UV (acetonitrile, nm): λ_{max} 227 (22 800), 311 (6200).

[6 + 4] Adducts 14 and 15 from Hexafluorotropone (3) and Cyclopentadiene. Perfluorotropone (0.2 g, 0.9 mmol) and freshly cracked cyclopentadiene (2 mL) were dissolved in benzene (50 mL). After flushing with nitrogen, the mixture was gently refluxed with magnetic stirring overnight. The solvent was taken off by rotary evaporation. The brownish viscous residue was chromatographed on a column of silica gel (50 g, Acros, 0.035−0.07 mm), with 1:2 ether/hexane as eluent. The resulting yellow solid was sublimed at 70 °C/60 mTorr to give 1:1 adduct **14** as a white solid, mp 123−5 °C. Yield: 0.08 g (31%). ^{19}F NMR ($CDCl_3$): δ −142.6 (d, J_{app} = 21 Hz, 2F), −148.6 (s, 2F), −176.2 ppm (d, J_{app} = 21 Hz, 2F). ^{1}H NMR ($CDCl_3$): δ 6.28 (s, 2H), 3.62 (t, J = 5.5 Hz, 2H), 2.28, 2.21 (ABq, J = 13 Hz, 2H; high field signals each split into a quintet, J = 5 Hz). ^{13}C NMR ($CDCl_3$, proton-decoupled): δ 188.5 (t, J = 60 Hz), 141.4 (m), 137.8 (m), 135.4 (s), 97.0 (d of d, J = 811 and 74 Hz), 51.1 (d, J = 95 Hz), 34.5 (t, J = 29 Hz). IR (cm^{-1}, tetrachloroethylene): 1775, 1693, 1640. GC/MS (*m/e*): 280 (M^+), 260 ($C_{12}H_5F_5O^+$), 215 ($C_7F_7OH^+$), 186 ($C_6F_6^+$), 66 ($C_5H_6^+$). Anal. Calcd for $C_{12}H_6F_6O$: C, 51.44; H, 2.16; F, 40.69. Found: C, 51.39; H, 2.08; F, 40.83.

The 1:1 adduct **14** (10 mg) was dissolved in 1 mL of benzene. After cyclopentadiene (0.1 mL) was added, the mixture was heated at reflux for 8 h. The product **15** was difficult to separate from the dimer of cyclopentadiene. ^{19}F NMR ($CDCl_3$): δ −136.8 (d, J = 36 Hz, 1F), −144.0 (s, 1F), −148.6 (t, J = 36 Hz, 1F), −154.8 (d, J = 36 Hz, 1F), −157.2 (s, 1F), −172.1 (s, 1F). GC/MS (*m/e*): 346 (M^+), 280 ($C_{12}H_6F_6O^+$), 215 ($C_7HF_6O^+$), 66 ($C_5H_6^+$).

X-ray Crystal Structure of 14.[29] A crystal (approximate dimensions 0.38 × 0.20 × 0.20 mm) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker

(27) Allen, M. E.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1984**, *25*, 309.

(28) The English workers prepared a copper(II) complex with this ligand (ref 27).

CCD area detector diffractometer for a data collection at 173-(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrixes determined from 77 reflections. The data collection was carried out using Mo Ka radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 4.9 cm. The complete sphere of reciprocal space was surveyed to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of −28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[30] Final cell constants were calculated from the xyz centroids of 2957 strong reflections from the actual data collection after integration (SAINT 6.01, 1999).[31] Unit cell dimensions were as follows: a = 12.4672(10) Å, b = 6.8783(5) Å, c = 12.5205(10) Å; α = 90°, β = 103.958(1)°, γ = 90°. Z = 4.

The structure was solved using SIR92[32] and refined using SHELXL-97.[33] The space group $P2_1/n$ was determined on the basis of systematic absences and intensity statistics. A direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full-matrix least-squares refinement converged to R1 = 0.0328 and wR2 = 0.0840 (F^2, all data). Goodness of fit on F^2 = 1.035. The program PLATON[34] was used for checking the structure. The crystals are centrosymmetric; thus, the stereochemistry shown in the Supporting Information and the inverse are present equally in the crystal.

Hexafluorotropone (3) from Cyclohexadiene 8. Diene **8** (4.0 g, 16 mmol) was added to a suspension of (dichlorofluoromethyl)phenylmercury[13] (9.6 g, 21 mmol) in 1,2,4-trichlorobenzene (30 mL) in a 100 mL round-bottom flask attached to an efficient reflux condenser. The mixture was heated under nitrogen at 125 °C for 5 h. ^{19}F NMR showed about 60% conversion of starting material to **9**−**12** with less than 10% rearranged products. The mixture was vacuum transferred at 50 mTorr for 8 h to give a colorless liquid (10 g) that contained benzene, hexafluorobenzene, starting material, and trichlorobenzene in addition to desired product. The ^{19}F NMR spectrum was in accord with the reported values.[12]

This mixture was diluted with DMSO (25 mL), copper bronze (4.0 g, 62 mmol) was added, and the resulting suspension was stirred at room temperature for 7 h. Methylene chloride (100 mL) and water (100 mL) were added successively to the reaction mixture. The suspension was filtered to give two layers of clear solution. The aqueous layer was extracted again with methylene chloride (100 mL). The combined organic solution was washed once with water (100 mL) and dried over anhydrous Na_2SO_4. The brown residue from rotary evaporation was chromatographed on a column of silica gel (50 g, Acros, 0.035−0.07 mm) with 3:1 hexane/ether as eluent to give a pale yellow solid (1.7 g) that contained some 1,2,4-trichlorobenzene. Sublimation at 50 °C/ 50 mTorr afforded **3** as a white solid. Yield: 1.3 g, 38% from diene **8**, 100% pure by ^{19}FNMR.

Hexafluorobicyclo[3.2.0]hepta-3,6-dien-2-one (19). Perfluorotropone (40 mg) was dissolved in acetonitrile-d_3 (0.4 mL). The solution was placed in a quartz NMR tube and irradiated with a 450 W Hanovia lamp. Progress of the reaction was monitored by ^{19}F NMR. After 4 days, about 60% of the starting material had been converted into **19**. The resulting yellow solution was vacuum transferred to give **19** in acetonitrile-d_3. ^{19}F NMR: δ −115.3 (t, J = 11 Hz, 1F), −121.5 (m, 1F), −123.0 (d of t, J = 19 and 3 Hz, 1F), −152.2 (s, 1F), −183.6 (d of t, J = 21 and 11 Hz, 1F), −185.9 ppm (m, 1F). IR (neat, cm^{-1}): 1763, 1708. HRMS (m/e): 213.9853 (theor), 213.9851 (found).

Pentafluorotropolone (21). In a 50 mL round-bottom flask was dissolved hexafluorotropone (0.28 g, 1.3 mmol) in benzene (20 mL). Anhydrous lithium hydroxide powder (0.84 g, 35 mmol) was added, and the suspension was stirred at room temperature under nitrogen overnight. After filtration, the filtrate was evaporated to recover 0.03 g of unreacted tropone **3**. The filter cake was dissolved in 3 N HCl (∼100 mL), and the solution was extracted with ether (100 mL × 3). The ether solution was washed with water (100 mL) and dried over anhydrous sodium sulfate. After rotary evaporation, the brown solid residue was sublimed at 60 °C/50 mTorr to give 0.18 g of pentafluorotropolone as a white solid, ∼85% pure, 72% yield based on consumed tropone **3**. The ^{19}F NMR (acetone-d_6) spectrum was in good accord with literature values.[27]

Nickel(II) Complex (22) of Pentafluorotropolone. Pentafluorotropolone (50 mg, 0.24 mmol) was dissolved in a mixture of water (1 mL) and acetone (1 mL). In another vial, nickel(II) chloride hexahydrate (30 mg, 0.12 mmol) and sodium acetate (100 mg, 1.2 mmol) were dissolved in water (2 mL) to give a green solution, which was added into the tropolone solution. Upon mixing, golden yellow solid precipitated out. After being stirred at room temperature for 20 min, the suspension was filtered. The filter cake was washed with water and cold ether, dissolved in ether (15 mL), and dried with anhydrous sodium sulfate. After rotary evaporation, **22** was obtained as a golden yellow solid (35 mg). It was dried for 6 h at 100 °C/60 mTorr. ^{19}F NMR (acetone-d_6): δ +8.9 (very broad), −84.1 (moderately broad), and −185.6 ppm (sharp). Complex **22** was insoluble in water and hexane, slightly soluble in ether, and soluble in acetone. Mp > 280 °C. HRMS (m/e): 479.8990 (theor), 479.8997 (found).

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Supporting Information Available: Tables of X-ray crystallographic data and ORTEP for **14**; X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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