performed to detect heterodimer radical cation $[\mathbf{1}\cdot\mathbf{4}\cdot Sc_2(OTf)_5]^+$ at *m*/*z* 1364 (Figure 1 d). Control experiments of substrate **1** and product **3** in the presence of $Sc(OTf)_3$ showed no signals that could be assigned to the proposed radical intermediate in the case of the heterodimer radical complex ion. In the case of the monomer radical complex ion, the substrate **1** showed signals that can be assigned to this ion, possibly by homolytic cleavage of the C–I bond in the heated capillary. However, the intensity of these signals is only about one tenth of that in the case of the reaction.

[27] The water and diethyl ether adduct complex ions ($[M\cdot Sc(OTf)_2\cdot H_2O]^+$, $[M\cdot Sc(OTf)_2\cdot Et_2O]^+$) indicate two special features: a rising front peak flank and a negative mass shift. Both phenomena are observed only with quadrupole ion trap analyzers and with particularly unstable (easily fragmentable) ions.

[28] W. B. Motherwell, D. Crich, *Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, **1992**, pp. 179–212.

[29] C. Chatgilialoglu in *Radicals in Organic Synthesis* (Eds. P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, pp. 28–49.

[30] Glutarate **6** (20 μmol, $1\cdot10^{-3}$ M), scandium triflate (24 μmol, 1.2 equiv), and *tert*-butyl iodide (80 μmol, 4 equiv) were dissolved in diethyl ether (20 mL). The solution was cooled to 0 °C and saturated with air by using a glass syringe. A solution of triethyl borane (50 μmol, 2.5 equiv) and tris(trimethylsilyl)silane (80 μmol, 4 equiv) was prepared in diethyl ether (20 mL) under argon. The reaction and measurement were performed as described in refs. [23] and [26]. The MS/MS spectrum of *m*/*z* 654 ($[\mathbf{8}\cdot Sc(OTf)_2]^+$, Figure 2 b) and of *m*/*z* 1400 ($[\mathbf{6}\cdot\mathbf{8}\cdot Sc_2(OTf)_5]^+$, Figure 2 c) were obtained. Control measurements of substrate **6** and product **7** in the presence of $Sc(OTf)_3$ showed no signals that can be assigned to the monomeric and heterodimeric radical complex ions.

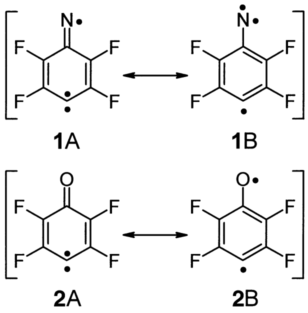
[31] The shape of the peak at *m*/*z* 597 provides unambiguous evidence for the addition of diethyl ether to the complex ion with *m*/*z* 524; see also ref. [27].

2,3,5,6-Tetrafluorophenylnitren-4-yl: A Quartet-Ground-State Nitrene Radical[**]

Hans Henning Wenk and Wolfram Sander[*]

Dedicated to Professor Walter Siebert
on the occasion of his 65th birthday

The interaction of unpaired electrons coupled by conjugated π-systems has been studied intensively during the last decade.[1–3] Also, a few heterospin systems combining different spin-carrying units within one molecule have been described. As these studies were aimed at the development of molecular magnets,[4] stable organic radicals were utilized, which were coupled to photochemically generated nitrene[5, 6] or carbene[7–9] units through *m*- or *p*-phenylene linkers. Systems containing highly reactive radicals (e.g. the phenyl radical) in addition to a nitrene or carbene have not been investigated so far. A molecule of this type is 2,3,5,6-tetrafluorophenylnitren-4-yl (**1**), which is formally generated by substituting a nitrogen atom for an oxygen atom in tetrafluorooxocyclohexadienylidene (**2**).



For compound **2**, a triplet ground state has been determined experimentally by using ESR[10] and IR spectroscopy[11], as well as theoretically based on quantum-chemical calculations. The electronic structure of **2** can be described by the resonance structures **2A** (carbene) and **2B** (phenyl/phenoxyl diradical). For the nitrene radical **1**, which bears an additional unpaired electron, DFT calculations predict a quartet ground state 2.7 kcal mol^{-1} below the lowest doublet state (UB3LYP/6-311G(d,p) + ZPE). The electronic structure of **1** is also qualitatively represented by two resonance structures: structure **1A** corresponds to a combination of a carbene with an iminyl radical, structure **1B** to that of a nitrene and a phenyl radical. Two electrons are localized in the σ plane, one at the nitrogen atom (iminyl radical), the other at the C4 atom of the phenyl ring (phenyl radical). The third unpaired electron is delocalized over the π system and exhibits high spin densities at the nitrogen atom as well as at the C4 atom. Thus, **1** can be represented by the electronic structure of a delocalized carbene (**1A**) and a delocalized nitrene (**1B**), which share a common π electron. Both carbenes and nitrenes have similar structures: open-shell systems with triplet ground states, and thus the parallel alignment of the spins of all three electrons is energetically most favorable; this leads to a quartet ground state.

Photolysis of aryl azides in cryogenic matrices is a well-established method for the generation of triplet aryl nitrenes.[12–14] Short-wavelength irradiation of aryl iodides has recently been applied to generate various fluorinated phenyl radicals and didehydrobenzenes, which were studied by matrix-isolation spectroscopy.[15, 16] Therefore, 4-iodo-2,3,5,6-tetrafluoroazidobenzene (**7;** see Scheme 2) was used as a precursor for **1**. The perfluorinated system was chosen because, in contrast to the unsubstituted phenylnitrene (**3**),[12, 17] for 2,6-difluorinated phenylnitrene derivatives the irreversible ring expansion to the corresponding didehydroazepine (**4**; Scheme 1) was not observed under the conditions of matrix isolation.[13, 14, 18] Instead, 2,6-difluorophenylnitrene and pentafluorophenylnitrene (**5**) react reversibly to the azirine derivatives (**6**) upon irradiation with light of wavelength 444 nm.[14]

The IR spectrum of **7**, matrix isolated in solid argon at 3 K, exhibits the characteristic ν(NN) vibration of the azido group at 2131 cm^{-1} (Figure 1 a). The absorptions of **7** disappear upon

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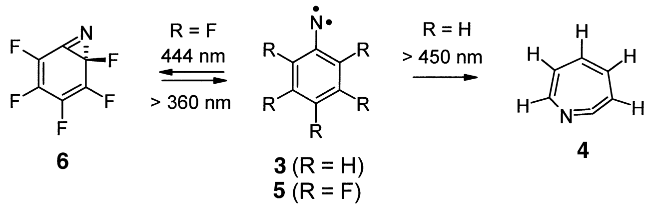


Scheme 1. Difference in reactivities between unfluorinated and fluorinated phenylnitrenes.

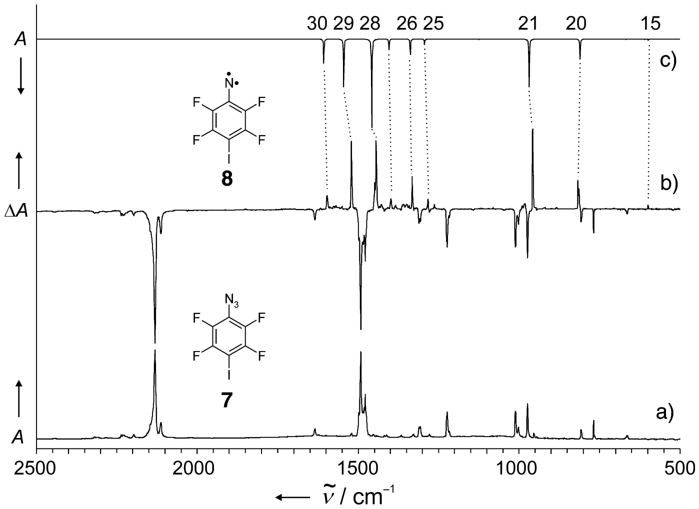
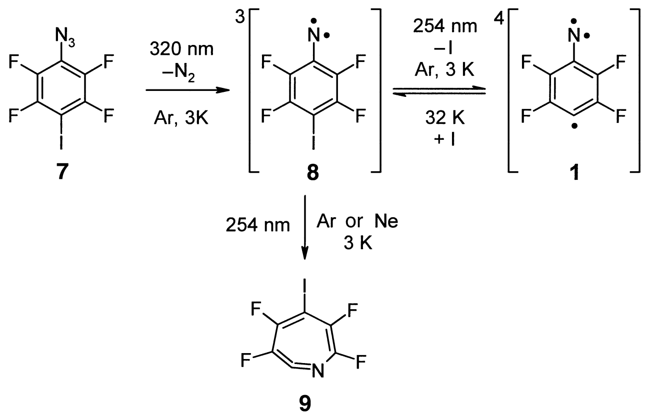


Figure 1. Photochemistry of 7. a) IR spectrum of 7 (Ar, 3 K). b) Difference spectrum. Bands pointing upwards appear, bands pointing downwards disappear upon irradiation with light of wavelength 320 nm for 17 h. c) Calculated (UB3LYP/6–311G(d,p), unscaled) spectrum of 4-iodo-2,3,5,6-tetrafluorophenylnitrene T-**8**.

photolysis with light of 320 nm wavelength, while a new compound with intense IR bands at 958, 1445, and 1522 cm^{-1} is formed concurrently. In the UV/Vis spectrum the reaction is accompanied by decrease of the absorption of **7** at 238 nm and the formation of new bands at 257, 293, and 310 nm, as well as two broad absorptions in the 320–360 nm and 390–460 nm region. The new species does not exhibit the characteristic IR absorptions of a didehydroazepine[12, 17] or an azirine[14] (which are potential photoproducts of phenylnitrene derivatives), however it does show the typical ESR signals of a triplet nitrene[19] with the zero-field parameters $|D/hc| = 1.103$ cm^{-1} and $|E/hc| = 0.012$ cm^{-1}. Therefore, the spectrum of the newly formed compound is assigned to the triplet 4-iodo-2,3,5,6-tetrafluorophenylnitrene T-**8** (Scheme 2). This interpretation is supported by the calculated IR spectrum, which nicely reproduces the experimental data (Figure 1 b,c, Table 1).

Subsequent monochromatic short-wavelength irradiation with light of wavelength 254 nm results in a decrease of the bands of T-**8** and formation of new absorptions, which are assigned to two sets of bands A and B by comparison of the relative intensities in several experiments (Figure 2 a). Data set A exhibits IR absorptions in the region from 948 to 1546 cm^{-1} which decrease again upon annealing of the matrix at 32 K, reforming T-**8**. The UV spectrum does not yield additional information because of rapid deterioration of the optical quality of the matrix upon short wavelength irradiation. The reversibility of the reaction upon annealing of the



Scheme 2. Photoreaction of **7** and the subsequent chemistry.

Table 1. IR spectroscopic data of T-**8**.

Mode	Symmetry	$\tilde{\nu}_{\text{exp.}}$ [cm^{-1}][a]	$I_{\text{rel.,exp.}}$[a,b]	$\tilde{\nu}_{\text{calcd}}$ [cm^{-1}][c]	$I_{\text{rel.,calcd}}$[b,c]
15	a_1	599.4	0.07	599.1	0.01
16	b_1	–	–	610.4	0.00
17	a_2	–	–	644.3	0.00
18	b_1	–	–	669.3	0.00
19	b_2	–	–	738.1	0.00
20	a_1	817.3	0.37	811.8	0.23
21	b_2	958.0	1.00	969.8	0.54
22	a_1	–	–	1125.3	0.00
23	b_2	–	–	1146.8	0.00
24	b_2	–	–	1287.1	0.00
25	a_1	1283.5	0.14	1294.1	0.06
26	a_1	1332.2	0.42	1338.8	0.18
27	a_1	1398.2	0.14	1404.1	0.13
28	b_2	1444.7	0.85	1458.2	1.00
29	b_2	1521.6	0.85	1545.9	0.54
30	a_1	1597.3	0.18	1607.3	0.27

[a] Argon matrix, 3 K. [b] Relative intensity based on the most intense absorption. [c] Calculated at the UB3LYP/6–311G(d,p) level of theory, unscaled. The assignment is tentative and is based on band positions and intensities.

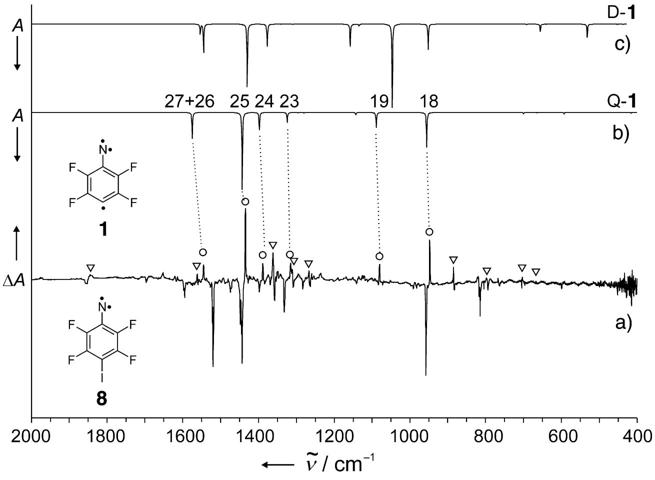


Figure 2. Photochemistry of T-**8**. a) Difference spectrum. Bands pointing upwards appear, bands pointing downwards disappear upon irradiation of T-**2** in an argon matrix at 3 K with light of wavelength 254 nm. Band set A is marked with circles, set B with triangles. b) Calculated (UB3LYP/6–311G(d,p), unscaled) spectrum of quartet nitrene radical Q-**1**. c) Calculated (UB3LYP/6–311G(d,p), unscaled) spectrum of doublet nitrene radical D-**1**.

matrix indicates cleavage of the C-I bond, and the observed IR spectrum is in excellent agreement with the calculated spectrum of quartet nitrene radical Q-**1** (Figure 2b, Table 2). In contrast, there is less agreement with the calculated data for the doublet state D-**1** (Figure 2c), especially in the region between 900 and 1100 cm^{-1}.

Table 2. IR spectroscopic data of the quartet nitrene radical Q-**1**.

Mode	Symmetry	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel.,exp.}$[a,b]	$\tilde{\nu}_{calcd}$ [cm^{-1}][c]	$I_{rel.,calcd}$[b,c]
18	b_2	948.0	0.52	956.4	0.45
19	a_1	1080.4	0.15	1089.6	0.20
20	b_2	–	–	1143.5	0.03
21	a_1	–	–	1280.6	0.01
22	b_2	–	–	1296.9	0.00
23	a_1	1315.2	0.19	1324.5	0.13
24	a_1	1389.0	0.15	1398.8	0.23
25	b_2	1434.7	1.00	1443.5	1.00
26	b_2	1545.5	0.15	1575.4	0.34

[a]–[c] See footnotes for Table 1

The second photoproduct B, which does not decrease upon annealing of the matrix, has a prominent absorption at 1854 cm^{-1}. The ν(C=N) vibration of didehydroazepine **4**, which arises upon photolysis of azidobenzene in cryogenic matrices in addition to phenylnitrene **3**, is observed at a similar frequency.[12, 17] When the experiment is carried out in a neon matrix, B is the exclusive product of the short-wavelength irradiation of T-**8**, while nitrene radical Q-**1** is not observed (Figure 3).[20] This allows us to unambiguously distinguish the absorption spectra of A and B. In particular, it can be discounted that the IR band at 884 cm^{-1}, the assignment of which to **1** would complicate the discrimination between doublet-**1** and quartet-**1** based on IR spectra, is caused by the nitrene radical.

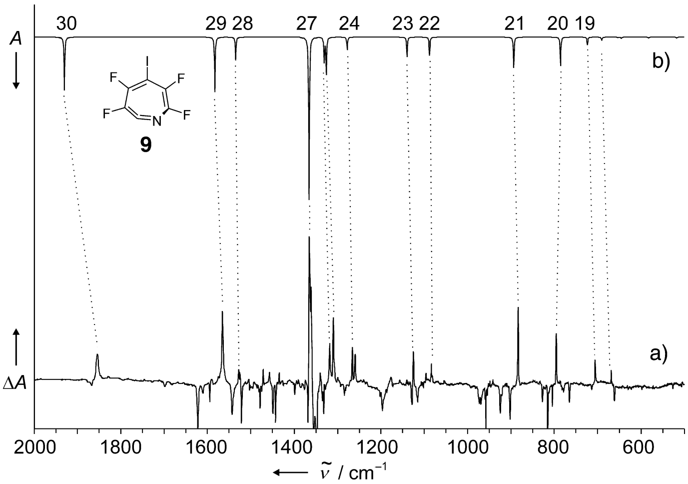


Figure 3. Photochemistry of T-**2**. a) Difference spectrum. Bands pointing upwards appear, bands pointing downwards disappear upon irradiation of T-**2** in a neon matrix at 3 K with light of wavelength 254 nm. b) Calculated (B3LYP/6–311G(d,p), unscaled) spectrum of didehydroazepine (**3**).

The absorption at 1854 cm^{-1} indicates rearrangement of T-**8** to the ring-expanded 5-iodo-3,4,6,7-tetrafluorodidehydroazepine (**9**; see Scheme 2) upon photolysis with light of wavelength 254 nm, although it was established by theoretical[18] as well as experimental[13, 14] studies that this reaction should not occur for 2,6-difluorinated phenylnitrenes in cryogenic matrices. In solution a significantly increased barrier for this reaction was observed with less fluorinated starting materials.[21] Nevertheless, comparison with the calculated spectrum of **9** confirms that the formation of the seven-membered ring is apparently possible in this case (Figure 3, Table 3). According to calculations (B3LYP/6-311G(d,p) + ZPE), the reaction T-**8** →**9** is endothermic by 7.5 kcal mol^{-1}.

Table 3. IR spectroscopic data of **9**.

Mode	$\tilde{\nu}_{exp.}$ [cm^{-1}][a]	$I_{rel.,exp.}$[a,b]	$\tilde{\nu}_{calcd}$ [cm^{-1}][c]	$I_{rel.,calcd}$[b,c]
18	669.1	0.05	691.1	0.02
19	706.1	0.13	724.2	0.05
20	795.9	0.31	786.3	0.18
21	883.7	0.50	894.5	0.19
22	1083.7	0.09	1088.2	0.11
23	1125.5	0.19	1141.0	0.12
24	1259.9	0.16	1278.7	0.08
		1266.1	0.21	
25	1310.1	0.43	1326.5	0.23
26	1318.5	0.24	1332.0	0.15
27	1361.2	0.64	1367.0	1.00
		1365.4	1.00	
28	1528.0	0.06	1535.7	0.14
29	1565.7	0.48	1583.7	0.34
30	1854.1	0.16	1930.3	0.33

[a] Neon matrix, 3 K. [b, c] See footnotes for Table 1.

Comparison of the calculated geometries of tetrafluorooxocyclohexadienylidene (**2**) and the nitrene radical **1** shows that there is not only a formal resemblance of both compounds (Figure 4). With the exception of the C=O and C=N bonds, the structures of **1** and **2** are almost identical, the differences in C–C bond lengths and bond angles being well below 0.1 Å and 2°, respectively. The spin-density distribution also reflects the similarity of both molecules, with differences appearing only at the nitrogen and oxygen atoms (Figure 4). In the carbene **2** the spin density at the oxygen atom is predominantly

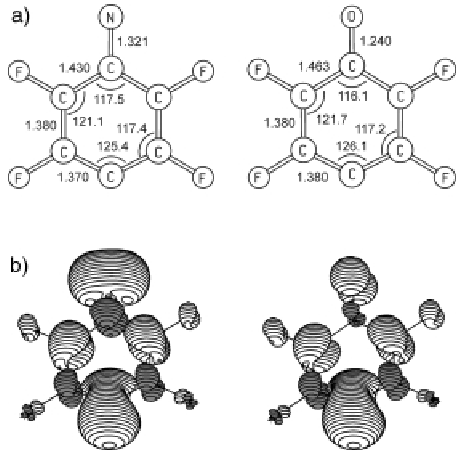


Figure 4. Comparison of the calculated geometries (a) and spin density distributions (b) in nitrene radical Q-**1** and carbene T-**2** (UB3LYP/6–311G(d,p)). Bond lengths [Å], bond angles [°].

localized in the p orbital perpendicular to the ring plane, while in **1** the highest spin density is in the ring plane.

Photolysis of 4-iodo-2,3,5,6-tetrafluoroazidobenzene (**7**) offers an access to the until now unknown C_6F_4N potential energy surface and to the unusual high-spin nitrene radical **1**. The influence of different topologies and substituents on the spin state of nitrene radicals will be investigated in future studies.

Experimental Section

Matrix experiments were carried out according to standard techniques[22] using a Sumitomo Heavy Industries RDK-408D closed-cycle cryostat. The lowest temperature available with this system is 2.7 K. Matrices were produced by codeposition of a large excess of neon or argon (Messer-Griesheim, 99.9999 %) and the substance to be isolated on top of a cold CsI window. During deposition of argon matrices the temperature of the window was maintained at 30 K. Argon matrices for ESR spectroscopy were deposited at 13 K on a 2 mm OFHC-copper rod, cooled by an APD-HC2 closed-cycle cryostat. IR spectra were recorded with a Bruker Equinox 55 FTIR spectrometer with a resolution of 0.5 cm^{-1} in the range of 400–4000 cm^{-1}. ESR spectra were recorded with a Bruker Elexsys E500 spectrometer. Irradiations were carried out with a Gräntzel low-pressure mercury lamp (254 nm) and an Osram HBO-500-W/2 high-pressure mercury arc lamp in an Oriel housing with quartz optics, a dichroic mirror, and a Schott cutoff filter (320 nm). DFT calculations were performed with the Gaussian 98 suite of programs.[23]

4-Iodo-2,3,5,6-tetrafluoroaniline: Yellow HgO (12.8 g, 59.1 mmol) was added to a solution of 2,3,5,6-tetrafluoroaniline (12.8 g, 77.6 mmol) in ethanol (200 mL). The solution was vigorously stirred and iodine (19.8 g, 78.0 mmol) added. The mixture was stirred overnight and filtered over celite. After addition of Na_2SO_3 (1 g) the solution was concentrated to a residual volume of 50 mL using a rotary evaporator. Water (200 mL) was added and the precipitate was filtered off. Recrystallization from 25 % ethanol in water and subsequent drying in vacuo yielded 4-iodo-2,3,5,6-tetrafluoroaniline (16.2 g, 55.7 mmol, 72 %) as dark crystals. MS: m/z(%): 291 (M^+, 100), 164 (50), 144 (25), 137 (60), 127 (30), 117 (25), 69 (20).

4-Iodo-2,3,5,6-tetrafluoroazidobenzene (**7**): 4-Iodo-2,3,5,6-tetrafluoroaniline (3.0 g, 10.3 mmol) was dissolved in trifluoroacetic acid (30 mL) and cooled to 0 °C. A solution of sodium nitrite (0.81 g, 11.7 mmol) in water (15 mL) was slowly added while stirring and cooling with an ice bath. The solution was stirred for further 15 min at 0 °C. A solution of sodium azide (0.75 g, 11.5 mmol) in water (15 mL) was added to the stirred solution, which was subsequently stirred for 1 h at room temperature. After addition of ether (100 mL) the organic phase was washed with water and dilute aqueous NaOH, dried (Na_2SO_4), and evaporated. Chromatography (silica/pentane) yielded **7** (2.18 g, 67 %) as a colorless oil. MS: m/z (%): 317 (M^+, 10), 289 (30), 162 (100), 127 (30), 117 (20), 112 (10), 98 (25), 69 (25). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 66.3$ (t, $J = 28.0$ Hz), 120.5 (tt, $J = 2.9$ Hz, 12.3 Hz), 140.0 (dm, 256.4 Hz), 147.2 ppm (dm, 248.1 Hz). IR (Ar, 3 K): $\tilde{\nu}$ (%): 2229.9 (5), 2196.8 (5), 2130.9 (100), 2112.4 (18), 1634.5 (10), 1492.2 (95), 1478.4 (49), 1307.6 (15), 1223.2 (31), 1012.1 (31), 1001.9 (13), 974.3 (39), 955.3 (6), 807.8 (11), 768.3 (22), 664.5 cm^{-1}(5).

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[1] a) H. Iwamura, *Adv. Phys. Org. Chem.* **1990**, 179–253; b) H. Iwamura, *J. Phys. Org. Chem.* **1998**, *11*, 299–304.
[2] D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88–94.
[3] A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893.
[4] *Magnetism: Molecules to Materials* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**.
[5] P. M. Lahti, B. Esat, R. Walton, *J. Am. Chem. Soc.* **1998**, *120*, 5122–5123.
[6] P. M. Lahti, B. Esat, Y. Liao, P. Serwinski, J. Lan, R. Walton, *Polyhedron* **2001**, *20*, 1647–1652.
[7] K. Matsuda, H. Iwamura, *Chem. Commun.* **1996**, 1131–1132.
[8] K. Matsuda, H. Iwamura, *Mol. Cryst. Liq. Cryst.* **1997**, *306*, 89–94.
[9] K. Matsuda, G. Ulrich, H. Iwamura, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1581–1588.
[10] H. H. Wenk, R. Hübert, W. Sander, *J. Org. Chem.* **2001**, *66*, 7994–7999.
[11] W. Sander, R. Hübert, E. Kraka, J. Grafenstein, D. Cremer, *Chem. Eur. J.* **2000**, *6*, 4567–4579.
[12] J. C. Hayes, R. S. Sheridan, *J. Am. Chem. Soc.* **1990**, *112*, 5879–5881.
[13] I. R. Dunkin, P. C. P. Thomson, *J. Chem. Soc. Chem. Commun.* **1982**, 1192–1193.
[14] J. Morawietz, W. Sander, *J. Org. Chem.* **1996**, *61*, 4351–4354.
[15] H. H. Wenk, A. Balster, W. Sander, D. A. Hrovat, W. T. Borden, *Angew. Chem.* **2001**, *113*, 2356–2359; *Angew. Chem. Int. Ed.* **2001**, *40*, 2295–2298.
[16] H. H. Wenk, W. Sander, *Chem. Eur. J.* **2001**, *7*, 1837–1844.
[17] O. L. Chapman, J. P. Le Roux, *J. Am. Chem. Soc.* **1978**, *100*, 282–285.
[18] W. T. Borden, W. L. Karney, *J. Am. Chem. Soc.* **1997**, *119*, 3347–3350.
[19] M. S. Platz in *CRC Handbook of Organic Photochemistry, Vol. II* (Ed.: J. C. Scaiano), CRC Press, Boca Raton, FL, USA, **1989**, S. 373–393.
[20] In contrast, photolysis of fluorinated diiodobenzene derivatives leads to the corresponding radicals and diradicals in solid neon but not in argon, see references [15,16].
[21] N. P. Gritsan, A. D. Gudmundsdottir, D. Tigelaar, Z. D. Zhu, W. L. Karney, C. M. Hadad, M. S. Platz, *J. Am. Chem. Soc.* **2001**, *123*, 1951–1962.
[22] I. R. Dunkin, *Matrix Isolation Techniques: A Practical Approach*, Oxford University Press, Oxford, **1998**.
[23] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**..

Conversion of Hexafluoropropene into 1,1,1-Trifluoropropane by Rhodium-Mediated C−F Activation[**]

Thomas Braun,[*] Daniel Noveski, Beate Neumann, and Hans-Georg Stammler

Interest in the activation of carbon–fluorine bonds by transition metal centers has been increasing dramatically over the last decade.[1] Recent discoveries include the stochiometric[2] and catalytic[3, 4] derivatization of aromatic compounds

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