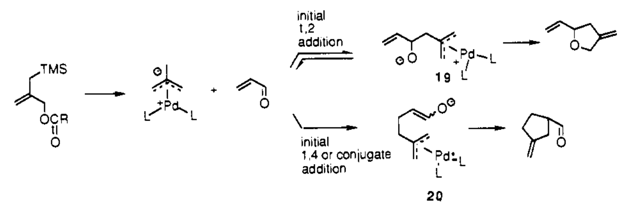
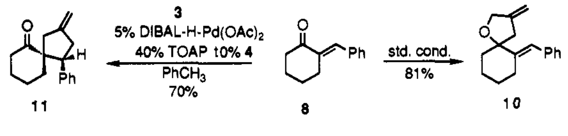
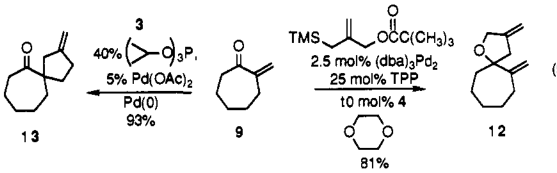
Scheme I. A Mechanistic Rationale



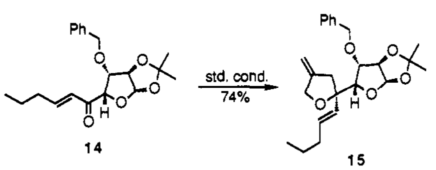
Enones **8** and **9**, which are particularly prone to conjugate addition, can be diverted from exclusive 1,4 addition ($\mathbf{11}^6$ and $\mathbf{13}^6$) to exclusive 1,2 addition ($\mathbf{10}^6$ and $\mathbf{12}^6$) (eqs 4 and 5) by the addition of the indium cocatalyst. Carbohydrates that bear many Lewis basic sites can also lead to good 1,2 selectivity and diastereoselectivity (>20:<1) under our standard conditions in the presence of the indium cocatalyst ($\mathbf{14}^6 \rightarrow \mathbf{15}$,[6] eq 6; 1,2 vs 1,4 4:1). However, steric hindrance may inhibit 1,2 addition as in the case of the galactopyranose **16**, which gives predominantly the 1,4 adduct (**17**:**18**, 1:4.2) under our standard conditions (eq 7).



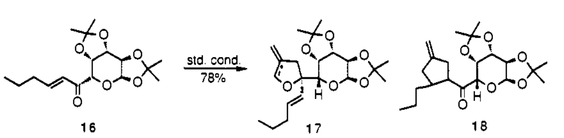
(4)



(5)



(6)



(7)

A reasonable explanation of the source of the indium effect derives from consideration of both the rate of 1,2 vs 1,4 addition as well as the rate of ring closure (see Scheme I). The absence of any coordinating group to stabilize an oxyanion disfavors 1,2 addition in the usual Pd-catalyzed TMM cycloaddition, thereby precluding formation of zwitterion **19**. On the other hand, the charge delocalization of the zwitterion **20** permits its formation with the ultimate production of the carbocycle. The presence of an oxyanion stabilizing group such as In^{3+} promotes attack at the more electrophilic carbonyl carbon to give the In^{3+}-stabilized zwitterion **19**. Since the counterion of the oxyanion has also proven to be important in its reaction with (π-allyl)palladium complexes,[8] In^{3+} may also promote the collapse of **19** to the methylenetetrahydrofuran. The fact that increasing the reaction temperature by going from THF to dioxane at reflux increases the ratio of 1,2 vs 1,4 addition products suggests that reversal of the 1,2 adduct **19** is competitive with cyclization and that the higher temperatures favor cyclization. While this scheme accounts for all of our current observations, we cannot rule out the involvement of some bimetallic palladium-indium complex as the active entity.[9] This dramatic chemoselectivity switch by indium complexes may prove useful in other nucleophilic reactions.[10]

Acknowledgment. We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for their generous support of our programs. Postdoctoral fellowships were provided by NSERC of Canada for S.S. and DFG for T.S. Mass spectra were provided by the UCSF Mass Spectrometry Facility sponsored by the NIH Division of Research Resources.

Supplementary Material Available: Listings of characterization data for **6a–c**, **7c**, **10–13**, and **15** (2 pages). Ordering information is given on any current masthead page.

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[8] Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230. Santon, S. A.; Felman, S. W.; Parkhurst, C. S.; Godleski, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 1964. Stork, G.; Poirier, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 1073. Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 1778, 8277. Keinan, E.; Seth, K. K.; Lamed, R. *J. Am. Chem. Soc.* **1986**, *108*, 3474. Keinan, E.; Sahai, M.; Roth, Z.; Nudelman, A.; Herzig, J. *J. Org. Chem.* **1985**, *50*, 3558.

[9] Cf. Yoshida, Y.; Shinohara, H.; Hanari, I. Jpn. Kokai Tokyo Koho 8000328; *Chem. Abstr.* **1980**, *92*, 129610c.

[10] Subsequent to initiation of our work on indium, several reports of its potential in other aspects of synthesis have appeared. Catalysis: Mukaiyama, T.; Ohno, T.; Nishimura, T.; Han, J. S.; Kobayashi, S. *Chem. Lett.* **1990**, 2239. Stoichiometric: Nomura, R.; Miyazaki, S.; Matsuda, H. *J. Am. Chem. Soc.* **1992**, *114*, 2738. Li, C. J.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 7017. Araki, S.; Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 727. Araki, S.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1991**, *415*, 7. Araki, S.; Ito, H.; Katsumara, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291. Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831.

How Crystalline Environment Can Provide Outstanding Stability and Chemistry for Arylnitrenes

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Elucidation of the chemical behavior of reactive intermediates in the solid state ought to give mechanistic information which is important in controlling topochemical reactivities.[1] Continuous interest in one-centered diradicals, such as carbenes or nitrenes,[2] as reactive intermediates prompts us to study the chemical reactivity and/or magnetic interaction of these species in the solid state. As an extension of our effort on diarylcarbenes along this line,[3] here we describe how the crystalline environment provides outstanding stability and reactivity for arylnitrenes, especially for (4-carboxyphenyl)nitrene, when they are generated in host crystals of aryl azides.[4]

UV photolysis on powdered crystals of aryl azides **1a–c** afforded arylnitrenes **2a–c** at cryogenic temperatures. The temperature dependence of the triplet ESR signals[5] of nitrenes was carefully

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† On leave from Ecole Polytechnique, France.

[1] (a) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217. (b) Gavezzotti, A.; Simmonetta, M. *Chem. Rev.* **1982**, *82*, 1. (c) Ramamurthy, V.; Venkasetan, K. *Chem. Rev.* **1987**, *87*, 433.

[2] Chemical behavior of carbenes and nitrenes in the gas phase or in solution is extensively investigated. See: (a) *Tetrahedron Symposia-in-Print*; Platz, M., Guest Ed.; *Tetrahedron* **1985**, *41*, 1423–1612. (b) Wentrup, C. *Tetrahedron Lett.* **1974**, *30*, 1301. (c) Lehman, P. A.; Berry, R. S. *J. Am. Chem. Soc.* **1973**, *95*, 8614. (d) Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443. (e) Costantino, J. P.; Richter, H. W.; Lee Go, C. H.; Waddell, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1744. (f) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5229. (g) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782.

[3] (a) Sugawara, T.; Tukada, H.; Izuoka, A.; Murata, S., Iwamura, H. *J. Am. Chem. Soc.* **1986**, *108*, 4272. (b) Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293.

[4] A fortuitous finding was reported on a remarkably stable nitrene generated by photolysis of crystals of cyanuric triazide. See: Moriarty, R. M.; Rahman, M.; King, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 842.

[5] The triplet signal carries a hyperfine coupling of a_N = 1.8 mT.

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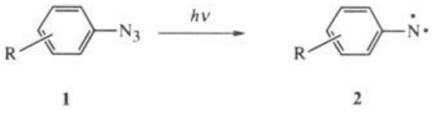
examined. Among the cases studied,[6] the result on (4-



1 2

a : R = *m*- COOH, **b** : R = *p*- CN, **c** : R = *p*- COOH

carboxyphenyl)nitrene **2c** shows the following outstanding features. First, nitrene **2c** photochemically generated in azide crystals of **1c** demonstrates unusual kinetic stability in crystals: *its half-life time at room temperature was found to be about 10 days*! Second, a distinct spectral change of the triplet signals of nitrene **2c** was observed with increasing temperature. The geminate nitrene, whose D value slightly decreases with raising the temperature ($D = 0.978$, $E = 1 \times 10^{-3}$ cm^{-1} at 4 K, $D = 0.960$, $E = 2 \times 10^{-3}$ cm^{-1} at 180 K), irreversibly disappears at temperatures higher than 200 K. New triplet signals start to appear at the expense of the geminate ones, which are entirely replaced by the former at 300 K: the new species is characterized by new zero-field parameters ($D = 0.970$, $E = 1 \times 10^{-3}$ cm^{-1} at 190 K). Although such temperature dependence of zero-field parameters has been reported on carbene species with bulky substituents,[7] almost no precedent is known for nitrene species. Third, a Curie plot for the nitrene shows a deviation from a straight line at lower temperatures ($T \leq 25$ K), suggesting the presence of appreciable intermolecular antiferromagnetic interaction between the nitrenes generated in crystals.[8] The latter two observations can be rationalized by assuming that a pair of nitrenes is generated efficiently through a photochemical process and that the nitrene signals are due to two weakly coupled triplets. Namely, the irreversible replacement of signals can be ascribed to the change of relative orientation of nitrenes in the dimeric pair.[9] The structural relaxation seems to occur in order to release the stress accumulated by the photochemical extrusion of nitrogen molecules within azide crystals.

Regardless of the structural change in the dimeric pair, the nitrenes survive up to room temperature. The photochemically generated nitrene **2c** starts to decay with an appreciable rate at temperatures higher than 340 K. An activation energy of the decay of photogenerated **2c** is evaluated to be 22 ± 2 kcal/mol between 300 and 370 K. The apparent decay rate becomes slower at temperatures higher than 370 K, and we do observe an increase in the intensity of the nitrene signals at temperatures higher than 380 K (Figure 1). This kinetic behavior may be interpreted in terms of a competition between the thermolysis of the remaining azide and the chemical decay of nitrene **2c**: the steady-state concentration becomes highest at around 390 K. The decay rate of thermally generated nitrenes eventually predominates over the formation rate at temperatures higher than 420 K.

The crystal structure of azide **1c** may be responsible for the unique chemical behavior of nitrene **2c** in crystals (Figure 2). The hydrogen-bonded dimers of **1c** are closely stacked in layers in the crystal: the density of the crystal is measured to be 1.51 g/cm^3. The tight packing suppresses translational or librational motions of the nitrenes which are generated in a restricted space surrounded by a benzene ring of the azide molecule above, a carboxyl oxygen atom of the molecule below, and by extruded nitrogen molecules.[10]

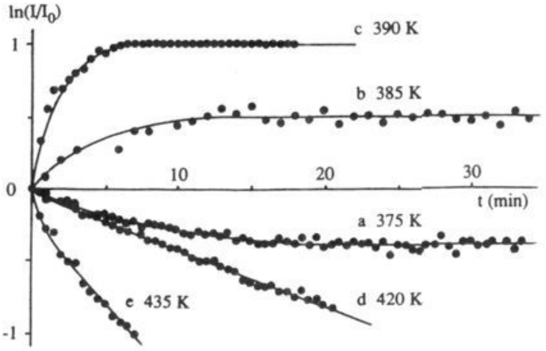


Figure 1. Time dependence of the ESR signal intensity of nitrene **2c** in a logarithmic scale at various temperatures.

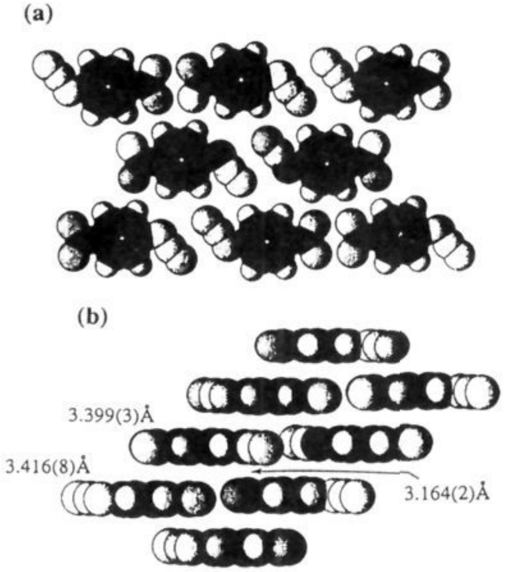


Figure 2. Crystal structure of *p*-carboxyphenyl azide **1c**: (a) crystal packing normal to the molecular plane (along the [$\bar{1}$ 2 2] direction); (b) side view of the stacking of the molecules. The univalent nitrogens in the generated nitrenes are shown schematically as black balls. Crystal data: triclinic with space group $P\bar{1}$, $a = 6.782$ (3), $b = 10.825$ (1), $c = 5.6000$ (3) Å, $\alpha = 94.47$ (2)°, $\beta = 108.99$ (3)°, $\gamma = 70.93$ (2)°, $V = 367.3$ (1) Å^3, and $Z = 2$. The final R value was 0.044 for 1203 independent reflections.

The distance between the univalent nitrogen and the oxygen is only 3.16 Å, which suggests significant electronic interaction between these two sites. This specific environment prevents nitrenes from isomerizing[11] or collapsing to form final products. At elevated temperatures, almost exclusive formation of the azo compound was confirmed by HPLC analysis after an annealing procedure. This reactivity is also consistent with the crystal structure discussed above.

In summary, the extraordinary stability of nitrene **2c** in crystals allows us to observe a subtle structural change and a unique kinetic behavior of **2c**. A close investigation of reactive intermediates in the solid state seems to be of great importance in understanding topochemical reactivity in organic solids.

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[6] The zero-field parameters for **2a** and **2b** are $D = 0.981$, $E = 1 \times 10^{-3}$ cm^{-1} and $D = 0.959$, $E = 1 \times 10^{-3}$ cm^{-1}, respectively. Their triplet ESR signals irreversibly bleach at temperatures higher than 60 and 250 K, respectively.

[7] (a) Wasserman, E.; Kuck, V. J.; Yager, W. A.; Hutton, R. S.; Greene, F. D.; Abegg, V. P.; Weinshenker, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6335. (b) Nazran, A. S.; Gabe, E. J.; LePage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Am. Chem. Soc.* **1983**, *105*, 2912. (c) Tukada, H.; Sugawara, T.; Murata, S.; Iwamura, H. *Tetrahedron Lett.* **1986**, *27*, 235.

[8] The energy gap between the ground-state singlet and excited triplet for a pair of the relaxed nitrenes is evaluated to be 10 cal/mol, which corresponds to −2 J of the antiferromagnetic exchange interaction.

[9] Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. For instance, the observed difference in zero-field parameters between the geminate and relaxed species can be reproduced by a change of ca. 15° in the angle between the long axes of the nitrene pair.

[10] Preliminary analysis suggests that extruded nitrogen molecules sit in a cage even after gentle annealing up to room temperature. See: (a) McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304. (b) McBride, J. M. *Adv. Photochem.* **1990**, *15*, 279.

[11] Cryogenic photolysis of 4-carboxyphenyl azide **1c** was also monitored by IR spectroscopy. Characteristic absorption bands for neither azacycloheptatetraene nor azirine derivatives were detected. See: (a) Chapman, O. L.; Le Roux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282. (b) Chapman, O. L.; Sheridan, R. S.; Le Roux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 6245. (c) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499. (d) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1192.

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Registry No. 1c, 6427-66-3; 2c, 66740-69-0.

Supplementary Material Available: X-ray crystallographic data for 4-carboxyphenyl azide, including tables of positional and thermal parameters, bond distances, and bond angles (4 pages); table of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

Synthesis and Crystal Structure of Intramolecularly Coordinated Organobismuth Compounds and Edge Inversion at Trivalent Bismuth

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Received April 27, 1992

Inversion at the central atom has been recognized to be a slow process among group 15 elements[1] except the classical vertex inversion of nitrogen (6 kcal mol^{-1} for NH_3).[2] The vertex inversion barriers typified by PnH_3 (Pn = pnictogen) have been calculated to increase with increasing pnictogen atomic number.[3] On the other hand, edge inversion, recently proposed by Arduengo and Dixon, predicts the following: (1) inversion barrier decreases with increasing pnictogen atomic number, (2) σ-acceptors (electronegative substituents) stabilize the T-shaped transition state, and (3) coordination of an empty p-orbital appearing at the transition state with nucleophiles also stabilizes the transition state.[3,4] Hence, trivalent organobismuth compounds should be suitable to test for edge inversion. Although only a few papers concerning inversion at trivalent bismuth have been reported, none of them have estimated the barriers of inversion.[5] We report here a unique example of edge inversion.

1-(*p*-Methylphenyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxabismole (**1**)[6] was prepared from dichloro(*p*-methylphenyl)bismuth and dilithio reagent **2a**.[7] The ^{19}F NMR spectrum (acetone-d_6) of **1** shows a pair of quartets [δ −75.7, −78.3 (J = 8.7 Hz) (split width ($\Delta\nu$) 220 Hz)] for the CF_3 groups at room temperature,

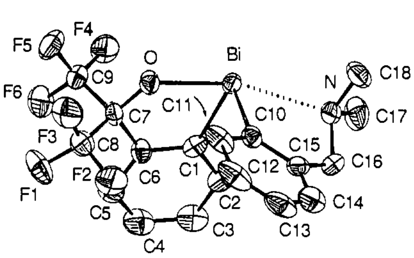
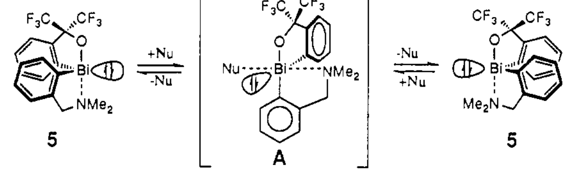


Figure 1. An ORTEP drawing of **5**.

Table I. Coalescence Temperatures (T_c) and Free Energies of Activation ($\Delta G^{\ddagger}_{Tc}$) in DMSO-d_6

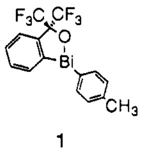
	compounds		
	1	**4**	**5**
T_c (°C)	175	125	55
$\Delta G^{\ddagger}_{Tc}$ (kcal mol^{-1})	21.2 ± 0.1	18.6 ± 0.1	15.4 ± 0.1

Scheme I. Nucleophilic Stabilization by the Intramolecular Substituent (NMe_2) and the Solvent (Nu: Pyridine in this case) for the Intermediate A in the Edge Inversion



demonstrating that the compound possesses a stable pyramidal configuration. At 175 °C in DMSO-d_6, coalescence of the two CF_3 groups was observed, and the energy for the inversion was calculated to be 21.2 kcal mol^{-1} (175 °C). Coalescence was not observed in *o*-dichlorobenzene and benzonitrile until 175 °C.

Surprisingly, ^{19}F NMR spectra (acetone-d_6) of **3** bearing electronegative substituents such as chlorine (**3a**),[8] acetoxy (**3b**),[8] and trifluoroacetoxy (**3c**)[8] groups show a singlet even at −50 °C. Hence, the inversion is much faster in **3** than in **1**. In contrast, the vertex inversion barrier of Me_2PCl (40.4 kcal mol^{-1}) is known to be higher than that of Me_3P (35.6 kcal mol^{-1}).[9] Thus, the result suggests that the inversion takes place via edge inversion. However, there is a possibility of inversion by an intermolecular process for **3** and also a possibility of an intramolecular process via a four-membered cyclic transition state by coordination of the carbonyl oxygen to the bismuth. Therefore, in order to investigate the possibility of an edge inversion process, we synthesized **4**[10] and **5**[11] by the reaction of **2b** or **2c** with **3a**.



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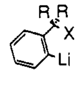
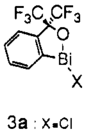
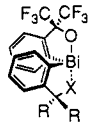


2a : R=CF_3 ; X=OLi
2b : R=CH_3 ; X=OMe
2c : R=H ; X=NMe_2



3a : X=Cl
3b : X=CH_3CO_2
3c : X=CF_3CO_2



4 : R=CH_3 ; X=OMe
5 : R=H ; X=NMe_2

The structures of **4** and **5** were shown to be quite similar by X-ray crystallography, and an ORTEP diagram of **5** is shown in Figure 1.[12] The distance between the nitrogen of the *N*,*N*-di-

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(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry* 4th ed.; John Wiley: New York, 1980; p 446. (b) Aylett, B. J. *Organometallic Compounds, Vol. 1, Part 2, Group IV & V*, 4th ed.; John Wiley: New York, 1979.

(2) Rauk, A.; Allen, L. C.; Clementi, E. *J. Chem. Phys.* **1970**, *52*, 4133.

(3) Dixon, D. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1987**, *109*, 338.

(4) (a) Dixon, D. A.; Arduengo, A. J., III; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 2461. (b) Arduengo, A. J., III; Dixon, D. A.; Roe, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 6821. (c) Arduengo, A. J., III; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 627. (d) Dixon, D. A.; Arduengo, A. J., III *J. Phys. Chem.* **1987**, *91*, 3195. (e) Arduengo, A. J., III; Dixon, D. A.; Roe, D. C.; Kline, M. *J. Am. Chem. Soc.* **1988**, *110*, 4437.

(5) (a) Bras, P.; Herwijer, H.; Wolters, J. *J. Organomet. Chem.* **1981**, *212*, C7. (b) Bras, P.; Van der Gen, A.; Wolters, J. *J. Organomet. Chem.* **1983**, *256*, C1.

(6) **1**: mp >300 °C; ^1H NMR (acetone-d_6) δ 2.24 (s, 3 H), 7.35 (d, J = 7.5 Hz, 2 H), 8.03 (d, J = 7.5 Hz, 2 H), 7.30–8.08 (m, 4 H); ^{19}F NMR (acetone-d_6) δ −75.7 (q, J = 8.7 Hz, 3 F), −78.3 (q, J = 8.7 Hz, 3 F). All of the important compounds gave correct elemental analyses: **1**, **3b**, **3c**, **4**, **5**, and **7**.

(7) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(8) **3a**: mp ca. 130 °C dec; **3a** was almost pure but did not give the correct elemental analysis. **3b**: mp 267–269 °C dec. **3c**: mp 185–186 °C.

(9) Rauk, A.; Andose, J. D.; Frick, W. G.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507.

(10) **4**: mp 234–235 °C; ^1H NMR ($CDCl_3$) δ 1.56–1.63 (m, 6 H), 3.80 (s, 3 H), 7.10–7.90 (m, 7 H), 8.10–8.20 (m, 1 H); ^{19}F NMR ($CDCl_3$) δ −72.6 (q, J = 8.6 Hz, 3 F), −75.9 (q, J = 8.6 Hz, 3 F).

(11) **5**: mp 194–195 °C; ^1H NMR (acetone-d_6) δ 2.75 (s, 6 H), 4.04 (d, J = 15 Hz, 1 H), 4.09 (d, J = 15 Hz, 1 H), 7.23–7.29 (m, 6 H), 8.00 (ddd, J = 7.3, 0.7, 0.4 Hz, 1 H), 8.22 (dd, J = 7.3, 1.1 Hz, 1 H); ^{19}F NMR (acetone-d_6) δ −73.1 (q, J = 8.3 Hz, 3 F), −76.5 (q, J = 8.3 Hz, 3 F).

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