Table XVII. Exponents for the Uncontracted Oxygen (5,2;5,2) and Nitrogen (5,2;5,2) Auxiliary Basis Sets

O (5,2;5,2)	N (5,2;5,2)
628.647 540 00	485.065 720 00
143.997 618 00	110.512 210 00
40.085 904 00	30.500 452 00
11.984 937 60	9.032 932 60
1.456 047 48	1.129 675 60
4.741 407 60	3.638 609 20
0.405 997 92	0.326 227 20
210.000 000 00	162.000 000 00
47.999 207 00	36.837 400 00
13.361 968 00	10.166 817 00
3.994 991 30	3.010 977 50
0.485 349 20	0.376 558 50
1.580 469 20	1.212 869 70
0.135 332 64	0.108 742 40

the hydrogen bond is calculated to be too short, in each system studied, using the VWN functional. This is in agreement with the suggestions of Hill et al.,[71] who observed that including gradient corrections caused a marked increase in the hydrogen-bond length in the formic acid–methylamine complex. The results of the vibrational analysis, calculated with the inclusion of gradient corrections, are also in closer accord with experiment than the results obtained using the VWN functional. In each system where both the PERDEW and BP functionals were used, it was found that the BP functional gave results which were in slightly better agreement with experiment.

In general, the results obtained are closer to those obtained using traditional ab initio methods which include electron correlation, for example, the calculated binding energy for the water dimer, and the results of the vibrational analyses. Predicted structures, although not perfect (errors in the hydrogen-bond lengths are about 0.1 Å), are of comparable quality to those predicted by correlated ab initio methods, and this lends optimism that further work on the functionals will lead to improved quantitative results. Therefore, we expect that density functional techniques will become increasingly useful in the study of hydrogen-bonded systems. Their relatively low cost, compared to traditional ab initio methods which include electron correlation, should make them particularly useful in the study of the larger, more biologically important systems.

Acknowledgment. F.S. thanks Steven Chin and Hans Mikosch for extremely useful discussions. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. We are grateful to the Natural Sciences and Engineering Research Council of Canada, to the Fonds FCAR (Québec), to Hitachi, and to Kodak for support. We thank the Services Informatiques de l'Université de Montréal and Cray Canada for access to the Cray XMP at Dorval. A.St-A. thanks NSERC for a 1967 Science and Engineering Scholarship. D.R.S. thanks the Canada Council for a Killam Research Fellowship.

Appendix

In Table XVI are shown the exponents and contraction coefficients for the N(5211/411/1) and O(5211/411/1) orbital basis sets. In Table XVII are shown the exponents for the uncontracted N(5,2;5,2) and O(5,2;5,2) auxiliary basis sets used in these calculations.

Registry No. H_2O, 7732-18-5; $H_2NC(O)H$, 75-12-7; $HO_2CC(O)H$, 298-12-4; $H_2C{=}C(OH)C(O)H$, 927-76-4.

Communications to the Editor

"Living" Polymerizations as Mechanistic Probes. Stereoselection in the Nickel-Catalyzed Polymerization of Chiral Isocyanides

Timothy J. Deming and Bruce M. Novak*[1]

Department of Chemistry
University of California at Berkeley and the
Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received September 17, 1991

From a synthetic perspective, the ideal chain growth polymerizations are "living" and proceed without chain-transfer or chain-termination steps.[2] The benefits provided by living polymerizations are manifold and include the synthesis of polymers possessing controlled molecular weights and narrow polydispersities,[2] di- and triblock copolymers,[3] and telomers with defined endgroups.[4] We intend to show that, in addition to these extensive synthetic advantages, well-defined living systems can be used as probes to help elucidate the mechanistic details of polymerization reactions that are normally very difficult or impossible to detect using alternative approaches. Specifically, we report herein the use of living isocyanide polymerizations utilizing $[(\eta^3\text{-}C_3H_5)Ni(O_2CCF_3)]_2$,[5] I, to identify and quantify the deviation from absolute stereoselection in the polymerization of chiral isocyanides.

Polyisocyanides[6] have long been the subject of intense research due to the stable, helical conformation adopted by isocyanides possessing bulky substituents.[7] In the design of biomimetic polymers[8] and optically active helical polymers[9] based on these materials, a pivotal premise has been that the polymerizations of racemic mixtures of chiral isocyanides proceed stereoselectively[10]

---

(1) Alfred P. Sloan Fellow, 1991–1993; Presidential Young Investigator, 1991–1996.

(2) For a general overview of living polymerizations and criteria, see: (a) Szwark, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656. (b) Szwark, M. *Nature* **1956**, *178*, 1168. (c) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561. (d) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87. (e) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91. (f) Fetters, L. J. Monodisperse Polymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley-Interscience: New York, 1987; Vol. 10, p 19.

(3) Noshay, A.; McGrath, J. E. *Block Copolymers*; Academic Press: New York, 1977.

(4) Goethals, E. J., Ed. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, 1989.

(5) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 326.

(6) (a) Millich, F. *Chem. Rev.* **1972**, *72*, 101. (b) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Wiley: New York, 1969. (c) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225.

(7) Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932.

(8) (a) Nolte, R. J. M.; van Beijnen, A. J. M.; Neevel, J. G.; Zwikker, J. W.; Verkley, A. J.; Drenth, W. *Isr. J. Chem.* **1984**, *24*, 297. (b) Neevel, J. G.; Nolte, R. J. M. *Tetrahedron Lett.* **1984**, *25*, 2263. (c) van der Linden, J. H.; Schoonman, J.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 260. (d) van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 255.

(9) Kamer, P. C. J.; Cleij, M. C.; Nolte, R. J. M.; Harada, T.; Hezemans, A. M. F.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 1581.

0002-7863/92/1514-4400$03.00/0

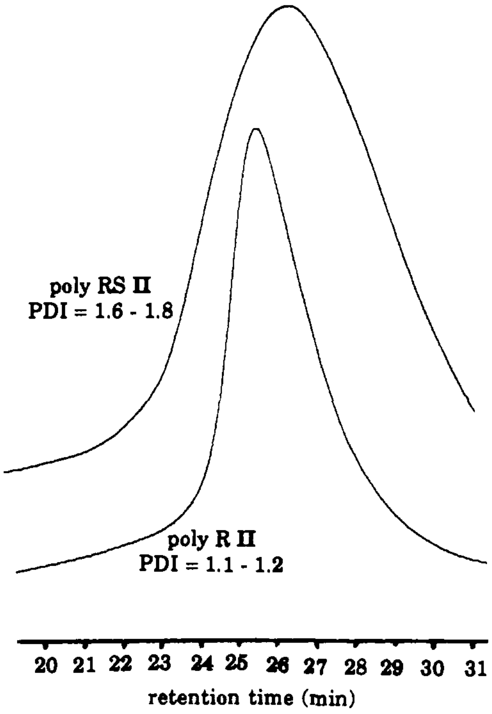


Figure 1. GPC traces of poly(R/S-II) and poly(R-II) prepared under identical conditions using I.

(i.e., a racemic monomer mixture is kinetically resolved into *all-R* polymer molecules and *all-S* polymer molecules to form polyisocyanides in which the pendant groups are assumed to be stacked in regular arrays).[11] During our investigations into the preparation of polyisocyanides of defined molecular weights and polydispersities, we discovered that the homogeneous polymerization of enantiomerically pure (R)- or (S)-α-methylbenzyl isocyanide, R-II or S-II, catalyzed by complex I, displayed all of the characteristics of a living system.[12] Living polymerizations are expected to produce polymers possessing narrow molecular weight distributions, characterized by a statistical Poisson distribution (i.e., the polydispersity index (PDI = $\bar{M}_w/\bar{M}_n$) values should approach 1.0).[2] This behavior was indeed observed in the polymerizations of R-II or S-II (PDI $\approx$ 1.1); however, when we polymerized racemic monomer, R/S-II, polymer molecular weight distributions[13] were found to be quite broad, with PDI values typically ranging from 1.6 to 1.7 (Figure 1). Subsequent experimentation revealed that the (R/S-II)/I system fulfilled all of the criteria required of a living polymerization, except for the lack of monodispersity.[12] This anomalous behavior can be rationalized by the invocation of catalytic centers with different propagation rates. Each nickel center in I is able to coordinate more than one isocyanide monomer under polymerization conditions;[12] hence, many distinct active species may exist in a racemic polymerization through coordination of different combinations of R and S monomers. Each of these combinations will generate a different catalyst center with its own propagation rate constant, leading to a broadened polydispersity, as observed. Conversely, in the polymerization of a pure enantiomer, all catalyst centers are stereochemically identical, and so the polydispersity remains narrow.

One important ramification of the observed data is that the effect (i.e., PDI) of mechanistic changes seen when switching from pure enantiomer to racemic monomer is immediately visualized under living polymerization conditions, whereas it remained undetected in a nonliving system: polymer samples derived from R-II, S-II, and R/S-II using heterogeneous, literature procedures[14] all had PDI $\approx$ 3–4. Furthermore, these data imply a significant degree of antipodal coordination to catalytic centers bound to chains of a given (R or S) configuration. This result raises the alarming possibility that these antipodal monomers could insert into the polymer chain, rendering impossible the absolute stereoselectivity proposed for the polyisocyanides.

In the belief that the broad range of PDI values in samples of poly(R/S-II) is indeed the result of variations in rate constants among catalytic sites, we sought to perform a detailed study of the kinetics of this system. Since the polymerization is living for both pure enantiomers and racemic monomer, there exists a defined number of active chain ends during the polymerization, and we were therefore able to quantitatively compare kinetic data (normally an equivocal exercise in an ill-defined heterogeneous system). We observed that, under both N_2 and O_2,[15] the pure enantiomers polymerized approximately 3 times faster than the racemic mixture (under N_2 (298 K), $k_{R/S\text{-II}} = 3.7\ (1) \times 10^{-2}$ L·mol^{-1}·s^{-1} vs $k_{S\text{-II}} = 1.2\ (1) \times 10^{-1}$ L·mol^{-1}·s^{-1}; under O_2 (298 K), $k_{R/S\text{-II}} = 5.1\ (1) \times 10^{-2}$ s^{-1} vs $k_{S\text{-II}} = 2.4\ (1) \times 10^{-1}$ s^{-1}). In order to quantify the energetics of this stereodiscrimination, we determined the thermodynamic activation parameters with both optically active and racemic monomers under a variety of conditions. From Eyring plots, the difference in the free energy of activation between the racemate and pure enantiomers ($\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}_{RS} - \Delta G^{\ddagger}_{S}$) was calculated at 298 K to be 0.8 (2) and 0.5 (2) kcal/mol for the reactions under O_2 and N_2, respectively. Similarly, we found that 1-(naphthyl)ethyl isocyanide (R-III or S-III vs R/S-III) yields a $\Delta\Delta G^{\ddagger}$ of 0.6 (2) kcal/mol under O_2.

From an examination of the Eyring data it is apparent that some degree of stereoselection is present in this system; the small magnitudes of the $\Delta\Delta G^{\ddagger}$'s, however, indicate that this stereoselection must be far from absolute.[16] In an effort to confirm this suspicion, we sought evidence of R/S stereocopolymer formation through a detailed examination of the physical properties of the polymers. DSC traces of pure poly(R-II), poly(S-II), and a blend of both all show a T_d at 246 °C, while poly(R/S-II) shows a T_d at 256 °C. Likewise, retention times for the pure poly(R-II) and poly(S-II) on a chiral HPLC column (Diacel Chiralcel-OA column, $CHCl_3$, 0.3 mL/min at 23 °C) are 10.3 and 10.6 min, respectively. In contrast, the material produced from the polymerization of R/S-II does not resolve into these two fractions but runs as one compound and displays its own unique retention time of 11.0 min. It should be noted that the above data hold true not only for the polymers prepared using I but also for polymer samples prepared using heterogeneous procedures.[14] Therefore, this lack of stereoselection appears to be a consequence of monomer–polymer interactions rather than any specific qualities of the Ni catalyst employed (polymer samples derived from R-II or S-II using either heterogeneous conditions[14] or I displayed identical optical rotations).

To illustrate that the above mentioned physical differences are due to antipodal insertion of R- and S-II into the same chains, we prepared polymer samples from 98% ^{13}C enriched (isocyanide carbon) R^*/S^*-II and a 50:50 mixture of 98% ^{13}C enriched S^*-II

---

(10) (a) Pino, P. *Adv. Polym. Sci.* **1965**, *4*, 393. (b) Ledwith, A.; Sherrington, D. C. In, *Reactivity, Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D., Ledwith, A., Eds.; Wiley-Interscience: London, 1974. (c) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.

(11) (a) van der Eijk, J. M.; Nolte, R. J. M.; Richters, V. E. M.; Drenth, W. *Biopolymers* **1980**, *19*, 445. (b) Roks, M. F. M.; Visser, H. G. J.; Zwikker, J. W.; Verkley, A. J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4507. (c) Visser, H. G. J.; Nolte, R. J. M. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 419; (d) **1983**, *102*, 417. (e) Visser, H. G. J.; Nolte, R. J. M.; Zwikker, J. W.; Drenth, W. *J. Org. Chem.* **1985**, *50*, 3133; (f) **1985**, *50*, 3138. All in ref 8.

(12) (a) Deming, T. J.; Novak, B. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 455. (b) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 6043.

(13) Determined by gel permeation chromatography (GPC) relative to polystyrene standards.

(14) All monomers were polymerized neat at 23 °C using $NiCl_2·6H_2O$ (0.2 mol %) under a N_2 atmosphere. Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30 and references contained therein.

(15) Under O_2, there is a change in the rate-determining step and the reaction becomes zero order in monomer. Nevertheless, the polymerization remains living. See ref 5 and 12.

(16) Stereoselection in isocyanide polymerizations has been questioned previously. See: Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C. *Macromolecules* **1988**, *21*, 1839.

and natural abundance *R*-II (poly(S^*/R^*-II) and poly(S^*/R-II)).[12] ^{13}C CP MAS NMR spectra of poly(S^*/R^*-II) and poly(S^*/R-II) gave imine carbon resonances (165 ppm) with widths at half-height at 493 and 327 Hz, respectively. This peak narrowing can be attributed to a reduction in the ^{13}C–^{13}C dipole–dipole relaxation mechanism in the singly labeled sample as opposed to the doubly labeled sample due to ^{13}C spin dilution along the individual polymer chains.[17] Hence, the singly labeled sample must have ^{13}C (*S*) carbons bound to ^{12}C (*R*) carbons, demonstrating that poly(*R*/*S*-II) is, in fact, a stereocopolymer.

Contrary to reports in the literature, we have shown that stereoselectivity is realized only to a limited degree in the polymerizations of II and III, with the $\Delta\Delta G^*$ values obtained representing an upper limit to this process. In light of the fact that poly(II) is the most widely studied polyisocyanide[18] and often serves as a point of reference for other polyisocyanides,[11,19] the absence of absolute stereoselectivity in polymerizations of II places the universally presumed absolute stereoselectivity of less sterically encumbered polyisocyanides in serious doubt.

Acknowledgment. This work was supported by University of California "Start-up Funds", the National Science Foundation (Grant No. CHE-9023253), and generous contributions from E. I. du Pont de Nemours and Company, the Exxon Corporation, Amoco, Kodak, and Chevron Research, T.J.D. gratefully acknowledges the NSF for a graduate fellowship. We thank Dr. David Duff for assistance with the ^{13}C CP MAS NMR spectra.

---

(17) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1987.

(18) (a) See ref 6a. See p 112 in this review and ref 109 therein. (b) Millich, F.; Baker, G. K. *Macromolecules* **1969**, *2*, 122. (c) Millich, F. *Adv. Polym. Sci.* **1975**, *19*, 117. (d) Millich, F. *Macromol. Rev.* **1980**, *15*, 207. (e) Huang, S. Y.; Hellmuth, E. W. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1974**, *15*, 499. (f) Huang, S. Y.; Hellmuth, E. W. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1974**, *15*, 505.

(19) (a) van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1980**, *13*, 1386. (b) King, R. B.; Borodinsky, L. *Macromolecules* **1985**, *18*, 2117. (c) King, R. B.; Greene, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 907.

(Trifluoromethyl)copper: A Useful CF_2 Transfer Reagent. A Novel Double Insertion of Difluoromethylene into (Pentafluorophenyl)copper

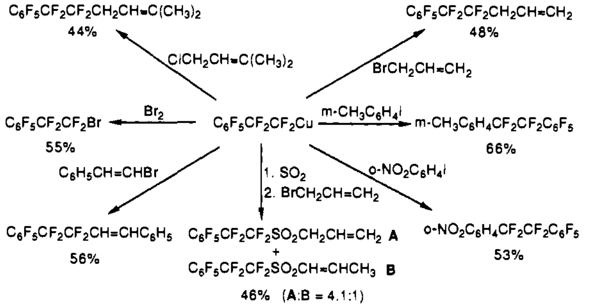
Zhen-Yu Yang, Denise M. Wiemers, and Donald J. Burton*

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

Received January 9, 1992

(Trifluoromethyl)copper has been demonstrated to be one of the most important reagents for the introduction of a trifluoromethyl group into organic molecules.[1] Previous preparations of this copper reagent have been achieved via the reaction of trifluoromethyl iodide, (trifluoromethyl)mercury, or iododifluoromethane sulfonyl fluoride with copper, but these methods have either employed expensive reagents or required high temperatures.

Scheme I



Recently, we reported a low-temperature pregenerative route to (trifluoromethyl)copper by the in situ metathesis of (trifluoromethyl)cadmium or -zinc reagents with cuprous halides.[2] The requisite cadmium and zinc reagents were prepared from the reaction of difluorodihalomethane with cadmium or zinc.[3] Although two different copper species can be formed in DMF solution, both slowly decompose at room temperature to afford (pentafluoroethyl)copper in quantitative yield.[2,4] The mechanism of the decomposition reaction has not been investigated in detail, but it is obvious that a CF_2 unit inserts into the carbon–copper bond. Since (trifluoromethyl)copper appeared to be a CF_2 transfer reagent, we were interested in determining whether (trifluoromethyl)copper could insert CF_2 units into other organometallic reagents or only insert into itself.

We report herein the preliminary results of a novel and efficient double insertion reaction of CF_2 into the carbon–copper bond of C_6F_5Cu generated from the metathesis of C_6F_5CdX with CuBr at room temperature. When a DMF solution of (pentafluorophenyl)copper was added to a DMF solution of (trifluoromethyl)copper at −30 °C and the resulting mixture was warmed to room temperature with stirring, $C_6F_5CF_2CF_2Cu$[5] was formed in 70–80% yields by ^{19}F NMR analysis of the reaction mixture. Since the exchange reaction of (perfluoroorgano)cadmium or -zinc reagents with cuprous halides occurs rapidly,[2] this insertion reaction could be simplified by in situ generation of the copper reagents. Thus, when 2 equiv of the (trifluoromethyl)cadmium or -zinc reagent and 1 equiv of C_6F_5CdX[6] were stirred with 3 equiv of CuBr in DMF at room temperature for 40 min, $C_6F_5CF_2CF_2Cu$ was observed in 70–80% yields.

$$C_6F_5Cu + 2CF_3Cu \xrightarrow[-30\ ^\circ C\ \text{to RT}]{} \underset{70\text{–}80\%}{C_6F_5CF_2CF_2Cu}$$

$$\underset{M\,=\,Cd,\ Zn}{C_6F_5CdX + 2CF_3MX} \xrightarrow[RT]{CuBr} \underset{70\text{–}80\%}{C_6F_5CF_2CF_2Cu}$$

Multiple insertion of CF_2 units into C_6F_5Cu was not observed even when a large excess of CF_3Cu was utilized. When 3–9 equiv of CF_3Cu was slowly added to a solution of C_6F_5Cu, only $C_6F_5CF_2CF_2Cu$ and CF_3CF_2Cu were formed; no $C_6F_5(CF_2)_nCu$ ($n > 2$) was detected by ^{19}F NMR analysis of the reaction mixture. Insertion of CF_2 into the primary copper reagent, $C_6F_5CF_2CF_2Cu$, is slower than insertion into the more reactive CF_3Cu.

Previous reports have demonstrated that the formation of (trifluoromethyl)cadmium or -zinc reagents from difluorohalomethane involved difluorocarbene as an intermediate,[3] and $(CF_3)_2Cd$ has been used to produce difluorocarbene which can be trapped by alkenes.[7] Although the product was formed, apparently from the double insertion of difluoromethylene into the carbon–copper bond, no evidence was obtained for a free di-

---

(1) (a) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921. (b) Kobayashi, Y.; Kumadaki, I. *Tetrahedron Lett.* **1969**, 4095. (c) Kobayashi, Y.; Kumadaki, I.; Sato, S.; Hara, N.; Chidami, E. *Chem. Pharm. Bull.* **1970**, *18*, 2334. (d) Kobayashi, Y.; Kumadaki, I.; Hanzawa, Y. *Chem. Pharm. Bull.* **1977**, *25*, 3009. (e) Kobayashi, Y.; Yamamoto, K.; Kumadaki, I. *Tetrahedron Lett.* **1979**, 4071. (f) Kobayashi, Y.; Kumadaki, I. *J. Chem. Soc., Perkin Trans. 1* **1980**, 661. (g) Kobayashi, Y.; Yamamoto, K.; Asai, T.; Nakano, M.; Kumadaki, I. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2755. (h) Kondratenko, N. V.; Vechirko, E. P.; Yagupolskii, L. M. *Synthesis* **1980**, 932. (i) Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. *Chem. Lett.* **1981**, 1719. (j) Suzuki, H.; Yoshida, Y.; Osuka, A. *Chem. Lett.* **1983**, 135. (k) Carr, G. E.; Chambers, R. D.; Holmes, T. F. *J. Chem. Soc., Perkin Trans. 1* **1988**, 921. (l) Chen, Q.-Y.; Wu, S.-W. *J. Chem. Soc., Chem. Commun.* **1989**, 705. (m) Chen, Q.-Y.; Wu, S.-W. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2385. (n) Urata, H.; Fuchikami, T. *Tetrahedron Lett.* **1991**, *32*, 91. MacNeil, J. G.; Burton, D. J. *J. Fluorine Chem.*, in press.

(2) Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 832.

(3) (a) Burton, D. J.; Wiemers, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 5014. (b) Dolbier, W. R., Jr.; Wojtowicz, H.; Burkholder, C. R. *J. Org. Chem.* **1990**, *55*, 5420.

(4) Willert-Porada, M.; Burton, D. J.; Baenziger, N. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1633.

(5) $C_6F_5CF_2CF_2Cu$: ^{19}F NMR (DMF, vs $C_6H_5CF_3$) −39.0 (t, J = 29.3 Hz, 2 F), −44.6 (s, 2 F), −77.2 (m, 2 F), −90.1 (m, 1 F), −101.1 (m, 2 F).

(6) Heinze, P. L.; Burton, D. J. *J. Fluorine Chem.* **1985**, *29*, 359.

(7) Krause, L. J.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 671.