JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

Pentafluorophenyl Transfer Reaction: Preparation of Pentafluorophenyl [60]Fullerene Adducts through Opening of Fullerene Epoxide Moiety with Trispentafluorophenylborane

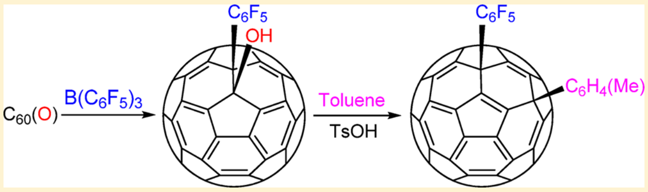
Sisi Liang,† Liang Xu,† Zhenshan Jia,† and Liangbing Gan*,†,‡

†Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

‡State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China

Supporting Information

ABSTRACT: Unlike the extensively studied perfluoroalkyl fullerene adducts, perfluorophenyl fullerene adducts are quite difficult to prepare by known methods. Trispentafluorophenylborane was found to react with fullerene epoxide to form the 1,2-perfluorophenylfullerenol. The method can be applied to both the simple epoxide $C_{60}(O)$ and fullerene multiadducts containing an epoxide moiety. Single crystal X-ray structure analysis confirmed the addition of the pentafluorophenyl group.



INTRODUCTION

Perfluoroalkyl fullerene derivatives have been extensively studied[1] since its first synthesis by the reaction of perfluoropropionyl peroxide or perfluoroalkyl iodides with C_{60}.[1a] Long-chain perfluoroalkyl-substituted C_{60} derivatives were investigated as field-effect transistor (FET)[2] and the active acceptor materials in OPV cell.[3] Compared with perfluoroalkyl fullerenes, perfluorophenyl fullerene adducts are rarely studied. Several partially fluorinated-phenyl cyclopentadienyl type fullerene adducts have been reported including the 3,4,5-trifluorophenyl adduct.[4] The reported method failed to introduce *ortho*-fluorophenyl or pentafluorophenyl group on to the fullerene cage.[4c] Pentafluorophenylmethyl adduct $C_{60}(CH_2C_6F_5)_2$ has been reported, which shows a favorable intermolecular face-to-face interaction between a perfluoroaromatic ring and the π surface of fullerene, allowing the molecule to be utilized for high-performance organic photovoltaic devices.[5] The pentafluorophenyl group directly attached 1,4-adduct $C_{60}(C_6F_5)(C_6H_4CF_3)$ was studied as the electron-transporting layer in bulk-heterojunction solar cells,[6] but full characterization of this compound was not possible because of low solubility, and it might be a mixture of isomers with partially nonfluorinated phenyl groups as suggested by the authors.

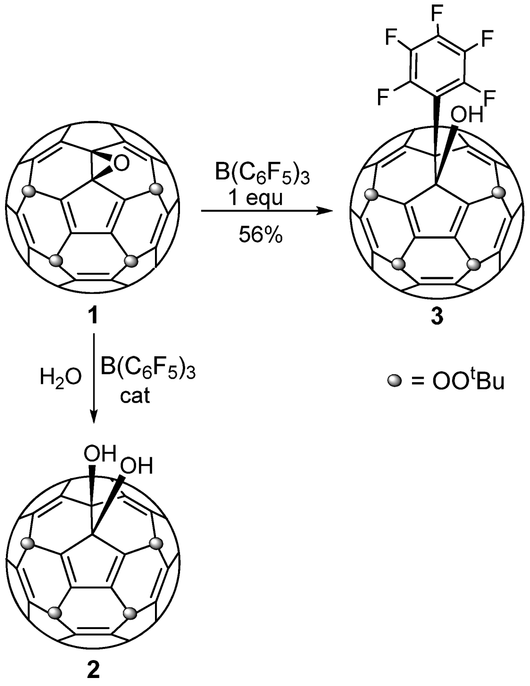
Even though there is no fully characterized fullerene adduct with a directly bound pentafluorophenyl group, there are numerous classical organic compounds containing the pentafluorophenyl group. Trispentafluorophenylborane $B(C_6F_5)_3$ is probably one of the best known pentafluorophenyl containing compound.[7] As a boron-based Lewis acid it can efficiently catalyze various organic reactions such as the stereoselective transformation of epoxides[8] and ring-opening reactions of nonactivated aziridines.[9] Unlike most other boranes $B(C_6F_5)_3$ is relatively stable toward moisture. Cleavage of the $B-C_6F_5$ bond is relatively rare. Transfer of pentafluorophenyl groups from boron to nickel was reported in the reaction between $B(C_6F_5)_3 \cdot 3H_2O$ and a nickel complex.[10] A pentafluorophenyl transfer reaction was observed in the photolysis of isoquinolinium hydroxytris(pentafluorophenyl)borate.[11] The $B(C_6F_5)_3$-induced cyclization reactions of 1,2-bis(phenylethynyl)benzenes resulted in pentafluorophenyl transfer to the cyclized product dibenzopentalene framework.[12] 1,1-Carboboration reactions of alkynes with $B(C_6F_5)_3$ have been proven as effective methods to make alkenylborane products, which formally involves a pentafluorophenyl transfer process.[13] Herein we report the synthesis of pentafluorophenyl containing fullerene adduct by using $B(C_6F_5)_3$ as a pentafluorophenyl transfer reagent.

RESULTS AND DISCUSSION

We have reported that the epoxy moiety in the fullerene-mixed peroxide derivative **1** can be opened into the diol compound **2** in the presence of water and catalytic amount of $B(C_6F_5)_3$.[14] In the absence of water, compound **1** was found to react with one equivalent of $B(C_6F_5)_3$ to form the pentafluorophenyl containing adduct **3** (Scheme 1). The NMR spectra clearly showed the C_s symmetry. On the ^1H NMR spectrum there are two *t*-butyl signals at 1.40 and 1.46 ppm. The hydroxyl proton appears at 4.46 ppm. The ^{13}C NMR spectrum also showed the C_s pattern with four sp^3 fullerene skeleton signals at 84.35, 82.44, 81.09, 57.64 ppm, the last of which can be assigned to the pentafluorophenyl bound cage carbon. Carbon signals for the pentafluorophenyl group could not be conclusively assigned

Received: April 26, 2014
Published: May 27, 2014

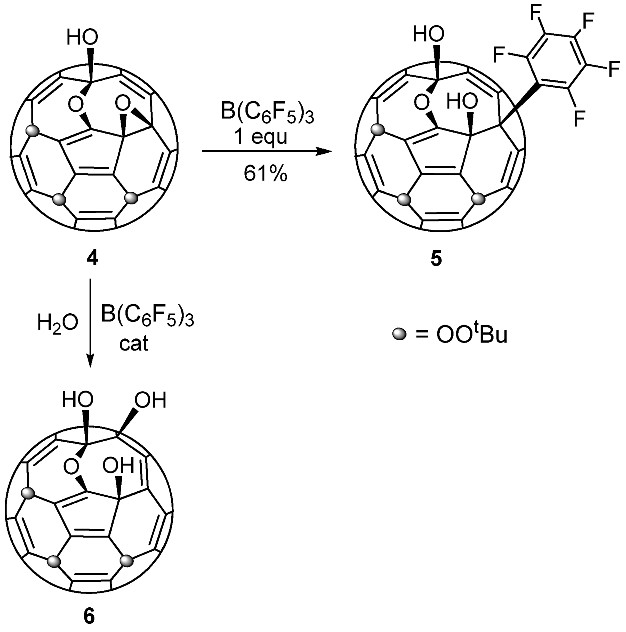
Scheme 1. Epoxide Opening Reactions of 1 with $B(C_6F_5)_3$ as Catalysis and Reactant



due to complicated coupling with the fluorine atoms. HRMS showed the expected molecular ion peak.

Under the same dry conditions the epoxy moiety in compound **4** was opened to form compound **5** (Scheme 2).

Scheme 2. Epoxide Opening Reactions of 4 with $B(C_6F_5)_3$ as Catalysis and Reactant



Presence of the hemiketal hydroxyl group has little effect judging from the comparable yields of **3** and **5**. But the $B(C_6F_5)_3$ catalyzed hydrolysis of compound **4** followed a S_N2' type mechanism to form compound **6** as shown previously.[15] The color of **6** is dark brown, whereas the color of both **4** and **5** is orange. Location of the double bond on the 7-membered ring containing the hydroxyl groups appears to have significant effect on the π-conjugation system of the cage.

The ^1H and ^{13}C NMR spectra of compound **5** showed the C_1 symmetry. The hydroxyl protons appear at 4.85 and 4.90 ppm. The hemiketal carbon and the pentafluorophenyl bound cage carbon appear at 108.11 and 61.89 ppm, respectively. The NMR data could not assign the structure of compound **5** conclusively because of its C_1 symmetry. To get more information, we obtained single crystals of compound **5** from slow evaporation of its CH_2Cl_2 solution. The structure shows the pentafluorophenyl plane adopts a direction far away from the adjacent hydroxyl group (Figure 1). The dihedral angle between the pentafluorophenyl plane and the plane containing the two adjacent fullerene sp^3 carbons and the hydroxyl oxygen atom is 68.8°. The bond distance (1.610(4) Å) between the two adjacent fullerene sp^3 carbons is the longest single bond on the fullerene cage. The two double bonds (1.327(4) and 1.333(4) Å) on the central pentagon have the shortest bond distance on the cage. The hydroxyl group on the central pentagon shows an intramolecular H-bond with the oxygen atom of an adjacent peroxo group. The hemiketal hydroxyl group forms intermolecular H-bond with an adjacent molecule. In the unit cell there are 8 molecules (4 pairs of enantiomers). The fullerene cages show multiple intermolecular contacts with adjacent molecules.

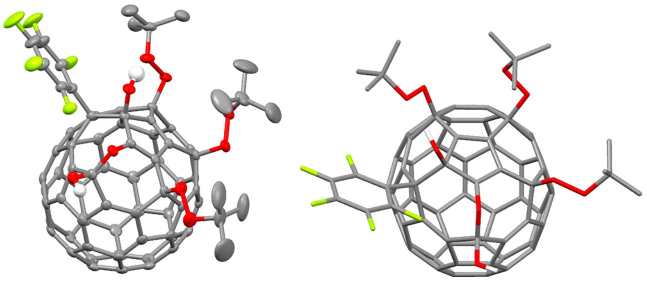
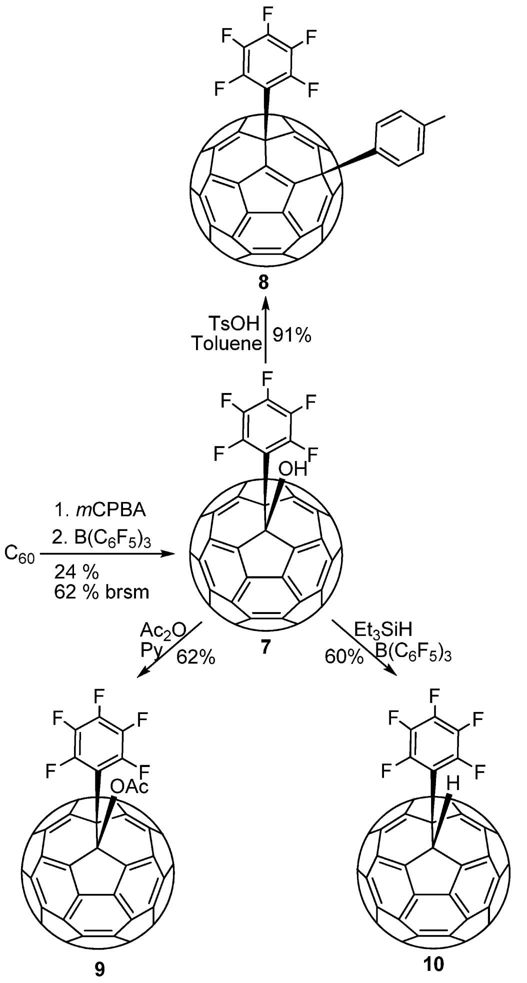


Figure 1. Two views of the X-ray structure of **5**. For clarity solvent molecules and hydrogen atoms on the *t*-butyl groups were not drawn. Ellipsoids were at 50%. Color scheme: gray = C, green = F, red = O, white = H.

Inspired by the above results, we then tried to apply the method to the simple fullerene epoxide $C_{60}(O)$ without any other additions on the cage. To avoid the lengthy purification process, we treated the mixture of $C_{60}/C_{60}(O)$ directly with slightly excess amount of $B(C_6F_5)_3$. Under the condition C_{60} remained unchanged and could be easily separated from the epoxide opened product **7** (Scheme 3) by flash column chromatography on silica gel. Reactivity of the hydroxyl group in the present 1,2-adduct **7** is similar to the hydroxyl group in the 1,4-adducts reported in the literature.[16] Thus, heating a toluene solution of **7** in the presence of TsOH resulted in the replacement of the hydroxyl group by a toluenyl group to form the 1,4-adduct **8**. Acetylation of the hydroxyl group was easily achieved under standard condition to form **9**. In our previous study we found that hydroxyl group in fullerenols could be converted to the triethylsiloxy group by treating with $Et_3SiH/B(C_6F_5)_3$ or replaced by a hydrogen atom depending on the local structure.[17] The hydrogen adduct **10** was obtained in the present case, which is analogous to the classical reduction of alcohol to alkane.[7a,18]

The HRMS mass spectra showed the molecular ion signals for compounds **7**−**10**, confirming the presence of the

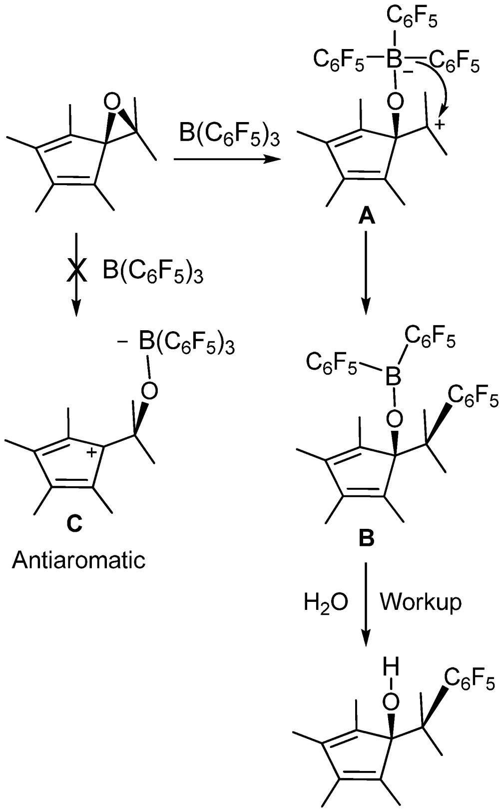
Scheme 3. Epoxide Opening Reaction of $C_{60}(O)$ and Related Further Reactions



pentafluorophenyl group. The 1,2-addition pattern of compounds **7**, **9** and **10** are confirmed by their ^{13}C NMR spectra, which showed 30 sp^2 fullerene cage carbon signals as expected for a C_s symmetric molecule (a few signals were overlapped). The C_1 symmetric compound **8** showed more than 60 signals in the range from 130 to 157 ppm for the aryl groups and the sp^2 fullerene cage carbons. A few broad doublets of triplets were present, which may be due to the carbon atoms on the pentafluorophenyl group. The two sp^3 fullerene carbons were not detected for compounds **7** and **9**. Only one sp^3 fullerene carbon was shown at 62.72 ppm for compound **10**. There are two sp^3 fullerene carbon signals at 61.44 and 53.84 ppm for compound **8**. The different rotation barrier for the pentafluorophenyl group in compounds **7**−**10** is probably responsible for this phenomenon. Fluorine atoms on the phenyl group could show remote weak coupling to the fullerene cage carbons close to the pentafluorophenyl group in the right configuration, thus splitting them into broad multiple signals, which are difficult to be detected. UV−vis spectra of compounds **7**−**10** provided further support for the structural assignments. Compounds **7**, **9** and **10** showed the characteristic absorption band for 1,2-adduct at around 430 nm, whereas compound **8** showed the typical broad absorption at 450 nm for a 1,4-adduct.

A possible mechanism is shown in Scheme 4 for the pentafluorophenyl transfer reaction of compounds **1** and **4**.

Scheme 4. Proposed Mechanism for the Pentafluorophenyl Transfer Reaction



Because of the antiaromatic nature of **C**, the first step forms the zwitterions intermediate **A** exclusively. In the absence of a nucleophile, transfer of a C_6F_5 group to the adjacent fullerene carbon cation becomes the only possible route to reduce the steric hindrance around the boron atom. Water in the work-up procedure probably hydrolyzed intermediate **B** into the final product. Such an intramolecular transfer pathway favors the 1,2-product instead of the isomeric S_N2' type product. The formation of **7** from $C_{60}(O)$ should follow a similar mechanism with no regioselectivity concerns.

In summary the present results showed that pentafluorophenyl group can be transferred from $B(C_6F_5)_3$ to the fullerene cage through opening of an epoxide moiety. The regioselective reaction probably follows a 1,4-shift mechanism from the boron atom to one of the epoxide-bound fullerene cage atoms. Further work is in progress to prepare fullerene adducts containing multiple pentafluorophenyl groups by using $B(C_6F_5)_3$ as the pentafluorophenyl source.

■ EXPERIMENTAL SECTION

All reagents were used as received. Dichloromethane (DCM) was distilled from phosphorus pentoxide. Other solvents were used as received. The reactions were carried out under atmosphere condition. The NMR spectra were obtained at 25 °C with 400, 500, and 600 MHz spectrometers (^{1}H and ^{13}C NMR spectra for the same compound were obtained with different spectrometers and different solvents in some cases). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-FT-ICR-HRMS spectra were recorded either in the positive- or negative-mode. Chromatographic purifications were carried out with silica gel of mesh 200−300.

Caution! *A large amount of peroxides is involved in some of the reactions. Care must be taken to avoid possible explosion.*

Compound 3. To a solution of compound **1** (120 mg, 0.11 mmol) in 60 mL of dry DCM was added $B(C_6F_5)_3$ (55 mg, 0.11 mmol) in the dark. The resulting solution was stirred at room temperature for 30 min. The solution was chromatographed on a silica gel column eluting with toluene. The first red band was collected and evaporated to give compound **3** (77 mg, 0.061 mmol, 56%) as an orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 1H), 1.46 (s, 18H), 1.40 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.48, 151.07, 150.65, 150.63, 149.24, 148.88, 148.72, 148.52, 148.40, 148.17, 147.68, 147.61, 147.46, 147.39, 147.09, 146.98, 145.66, 145.11, 145.09, 145.01, 144.56, 143.91, 143.85, 143.69, 142.75, 142.25, 141.25, 84.35, 82.44, 82.16 ($C(CH_3)_3$), 81.80 ($C(CH_3)_3$), 81.09, 57.64, 26.85 (CH_3), 26.58 (CH_3) (Carbon signals for the pentafluorophenyl group could not be conclusively assigned due to complicated coupling with the fluorine atoms); ESI-FT-ICR-HRMS-Positive $C_{82}H_{41}F_5NO_9$ (M + NH_4^+) calculated 1278.2696, found 1278.2694.

Compound 5. To a solution of compound **4** (92 mg, 0.089 mmol) in 45 mL of dry DCM was added $B(C_6F_5)_3$ (45 mg, 0.088 mmol) in the dark. The resulting solution was stirred at room temperature for 2 to 3 min. The solution was chromatographed on a silica gel column eluting with toluene/ethyl acetate (100:1). The first band was some byproduct, and the second red band was collected and evaporated to give compound **5** (65 mg, 0.054 mmol, 61%) as an orange solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H), 4.85 (s, 1H), 1.44 (s, 9H), 1.41 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.45, 150.45, 150.43, 149.98, 149.50, 149.43, 149.22, 149.16, 148.92, 148.77, 148.73, 148.60, 148.36, 148.27, 148.04, 147.98, 147.95, 147.93, 147.79, 147.71, 147.54, 147.49, 147.16, 146.99, 146.48, 145.56, 145.22, 144.83, 144.47, 144.29, 144.08, 144.05, 143.82, 143.37, 142.59, 142.56, 142.50, 142.43, 142.29, 140.80, 140.62, 140.12, 140.01, 139.76, 139.74, 139.36, 138.49, 136.84, 136.76, 128.24, 108.11, 84.41, 83.19 ($C(CH_3)_3$), 82.58, 81.99 ($C(CH_3)_3$), 81.98 ($C(CH_3)_3$), 81.26, 78.98, 61.89, 26.73 (CH_3), 26.70 (CH_3), 26.43 (CH_3) (Carbon signals for the pentafluorophenyl group could not be conclusively assigned due to complicated coupling with the fluorine atoms); ESI-FT-ICR-HRMS-Positive $C_{78}H_{33}F_5NO_9$ (M + NH_4^+) calculated 1222.2070, found 1222.2084.

Single crystals of **5** were obtained from slow evporation of its CH_2Cl_2 solution. Formula: $C_{79}H_{31}F_5O_9Cl_2$, T = 180.01(12) K, Orthormbic, space group *Pbca*. Unit cell dimensions: a = 14.9459(4) Å, b = 19.7129(5) Å, c = 36.9458(10) Å, $\alpha = \beta = \gamma$ = 90°. V = 10885.2(5) Å^3. Z = 8, ρ_{calcd} = 1.574 Mg/m^3. Reflections collected/unique 41418/10710 [R(int) = 0.0495]. Final R indices [$I > 2\sigma(I)$] R_1 = 0.0615, wR_2 = 0.1443. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-991336.

Compound 7. $C_{60}O$ was prepared following the method reported in the literature.[19] C_{60} (0.5 g, 0.69 mmol) was treated with *m*-chloroperoxybenzoic acid (3.4 g, 19.8 mmol) to afford a crude product (0.52 g) containing a mixture of C_{60}, $C_{60}O$ and small amount of $C_{60}O_2$ after silica gel purification. $B(C_6F_5)_3$ (140 mg, 0.27 mmol) was added to the crude product in 200 mL CS_2. The resulting solution was stirred at rt for about 7 min. The solution was chromatographed on a silica gel column eluting with CS_2. The first purple band was unreacted C_{60} (309 mg, 0.43 mmol). The second band was eluted with CS_2/toluene(1:1) to afford fullerenol **7** (148 mg, 0.164 mmol, 24% for two steps, based on recovered starting material 62%): ^{1}H NMR (500 MHz, CS_2/C_6D_6) δ 3.66 (s, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) δ 151.80, 151.78, 150.84, 148.61, 148.05, 146.77, 146.58, 146.40, 146.34, 146.31, 145.75, 145.75, 145.58, 145.41, 144.86, 144.32, 144.20, 143.25, 142.83, 142.50, 142.38, 142.06, 141.71, 141.56, 141.47, 139.97, 139.61, 137.09; ESI-FT-ICR-HRMS-Negative $C_{66}F_5O$ (M − H)$^-$ calculated 902.9864, found 902.9865; MALDI-TOF $C_{66}HF_5O$ calculated 904.0, found 904.1.

Compound 8. To a solution of compound **7** (59 mg, 0.065 mmol) in 110 mL of Tol/CS_2 (10:1) was added *p*-toluenesulfonic acid monohydrate (110 mg, 0.58 mmol). The resulting solution was heated and stirred in an oil bath preset at 80 °C for 11 h. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column eluting with CS_2 to afford compound **8** (58 mg, 0.059 mmol, 91%). Some unreacted fullerenol **7** (5 mg, 0.0055 mmol) was recovered by eluting with CS_2/toluene (1:1): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 8.01−7.99 (d, J = 10 Hz, 2H), 7.35−7.33 (d, J = 10 Hz, 2H), 2.46 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 156.73, 152.07, 149.72 (triplet with two other signals at 149.74, 149.70), 149.06, 148.73, 148.11, 147.95, 147.67, 147.44, 147.29 (triplet with two other signals at 147.31, 147.28), 147.25, 147.23, 147.11, 146.93, 146.69, 145.72, 145.71, 145.67, 145.25, 144.94, 144.83, 144.58, 144.55, 144.49, 144.44, 144.31, 144.29, 144.11, 144.10, 143.93, 143.91, 143.90, 143.87, 143.57, 143.50, 143.40, 143.38, 143.33, 143.22, 143.14, 143.13, 143.12, 143.05, 142.78, 142.65, 142.53, 142.49, 142.35, 141.89, 141.24, 140.85, 139.72, 139.25, 138.44, 138.02 (triplet with two other signals at 138.04, 138.00), 137.23, 137.20, 130.44, 126.89, 61.44, 53.84, 21.45, (CH_3); ESI-FT-ICR-HRMS-Positive $C_{73}H_7F_5$ (M^+) calculated 978.0462, found 978.0447.

Compound 9. To a solution of compound **7** (137 mg, 0.15 mmol) in 50 mL of CS_2 was added acetic anhydride (705 mg, 6.91 mmol) and pyridine (60 mg, 0.76 mmol). The resulting solution was stirred at room temperature for 1 day. The solution was washed with water (40 mL × 3), the organic layer was directly flash chromatographed on a silica gel column eluting with toluene. Then the solvents were removed under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with CS_2/toluene (4:1) and the first gray band was collected as compound **9** (89 mg, 0.094 mmol, 62%). Eluting with CS_2/toluene (1:1) gave the second gray band as unreacted compound **7** (50 mg, 0.0553 mmol): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 2.18 (s, 3H, CH_3CO); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 170.53 (CH_3CO), 151.24, 151.23, 148.61, 148.04, 147.69, 146.76, 146.61, 146.44, 146.35, 146.27, 145.78, 145.64, 145.55, 145.45, 144.91, 144.82, 144.61, 144.06, 143.27, 142.88, 142.78, 142.51, 142.48, 141.96, 141.60, 141.47, 141.02, 139.66, 139.56, 138.84, 21.09 (CH_3CO); FT-IR (microscope) 2922, 2850, 1757, 1649, 1521, 1491, 1431, 1366, 1305, 1214, 1190, 1163, 1086, 1010, 997, 980, 938, 886, 836, 799, 783, 702, 634 cm^{-1}; ESI-FT-ICR-HRMS-Negative $C_{68}H_3F_5O_2$ (M^-) calculated 946.0048, found 946.0004; MALDI-TOF $C_{66}F_5$ (M − CH_3COO) calculated 887.0, found 886.9.

Compound 10. To a solution of compound **7** (80 mg, 0.089 mmol) in 70 mL of CS_2 /DCM (1:1) was added 150 mg of $HSiEt_3$ (1.29 mmol) and $B(C_6F_5)_3$ (60 mg, 0.12 mmol). The resulting solution was stirred at room temperature for 6.5 h. The reaction was quenched by filtering through a short silica gel column eluting with toluene. Then the solvents were removed under reduced pressure. The resulting residue was chromatographed on a silica gel column eluting with petroleum ether to remove unreacted triethylsilane. Then the eluent was changed to CS_2 to afford the first gray band as compound **10** (47 mg, 0.053 mmol, 60%). Unreacted compound **7** (24 mg, 0.027 mmol) was eluted CS_2/toluene (1:1): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 6.75 (s, 1H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) δ 151.65, 150.39, 147.75, 147.42, 146.60, 146.56, 146.52, 146.34, 145.93, 145.88, 145.66, 145.54, 144.99, 144.87, 144.56, 143.48, 142.82, 142.78, 142.26, 142.22, 142.05, 141.82, 141.80, 141.41, 140.59, 139.97, 136.44, 62.72; ESI-FT-ICR-HRMS-Negative $C_{66}F_5$ (M − H)$^-$ calculated 886.9915, found 886.9942; MALDI-TOF $C_{66}HF_5$ calculated 888.0, found 888.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected spectroscopic data for all new compounds and crystallographic data for **5** including CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gan@pku.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support is provided by NNSFC (Grants 21272013 and 21132007) and MOST (2011CB808401).

■ REFERENCES

(1) (a) Fagan, P. J.; Krusic, P. J.; McEwen, C. N.; Lazar, J.; Parkert, D. H.; Herron, N.; Wasserman, E. *Science* **1993**, *262*, 404. (b) Yoshida, M.; Sultana, F.; Uchiyama, N.; Yamada, T.; Iyoda, M. *Tetrahedron Lett.* **1999**, *40*, 735. (c) Avent, A. G.; Boltalina, O. V.; Goryunkov, A. A.; Darwish, A. D.; Markov, V. Y.; Taylor, R. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2002**, *10*, 235. (d) Goryunkov, A. A.; Kuvychko, I. V.; Ioffe, I. N.; Dick, D. L.; Sidorov, L. N.; Strauss, S. H.; Boltalina, O. V. *J. Fluorine Chem.* **2003**, *124*, 61. (e) Dorozhkin, E. I.; Goryunkov, A. A.; Ioffe, I. N.; Avdoshenko, S. M.; Markov, V. Y.; Tamm, N. B.; Ignat'eva, D. V.; Sidorov, L. N.; Troyanov, S. I. *Eur. J. Org. Chem.* **2007**, 5082.

(2) Chikamatsu, M.; Itakura, A.; Yoshida, Y.; Azumi, R.; Yase, K. *Chem. Mater.* **2008**, *20*, 7365.

(3) Karakawa, M.; Nagai, T.; Irita, T.; Adachi, K.; Ie, Y.; Aso, Y. *J. Fluorine Chem.* **2012**, *144*, 51.

(4) (a) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Hahn, I.; Kroto, H. W.; Langley, G. J.; O'Loughlin, J.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1121. (b) Sawamura, M.; Iikura, H.; Ohama, T.; Hackler, U. E.; Nakamura, E. *J. Organomet. Chem.* **2000**, *599*, 32. (c) Shang, W. L.; Zhang, J. M.; Chen, X. L.; Zou, Y. H.; He, S. S.; Zhao, J. W.; Zhu, S. Z. *Synthesis* **2012**, *44*, 2575.

(5) Li, C.-Z.; Matsuo, Y.; Niinomi, T.; Sato, Y.; Nakamura, E. *Chem. Commun.* **2010**, *46*, 8582.

(6) Varotto, A.; Treat, N. D.; Jo, J.; Shuttle, C. G.; Batara, N. A.; Brunetti, F. G.; Seo, J. H.; Chabinyc, M. L.; Hawker, C. J.; Heeger, A. J.; Wudl, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 5166.

(7) For a recent example, (a) Adduci, L. L.; McLaughlin, M. P.; Bender, T. A.; Becker, J. J.; Gagne, M. R. *Angew. Chem., Int. Ed.* **2014**, *53*, 1646. For reviews, (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345. (c) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (d) Melen, R. L. *Chem. Common.* **2014**, *50*, 1161.

(8) (a) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1995**, 721. (b) Chandrasekhar, S.; Reddy, C. R.; Babu, B. N.; Chandrashekar, G. *Tetrahedron Lett.* **2002**, *43*, 3801.

(9) Watson, I. D. G.; Yudin, A. K. *J. Org. Chem.* **2003**, *68*, 5160.

(10) Kalamarides, H. A.; Iyer, S.; Lipian, J.; Rhodes, L. F.; Day, C. *Organometallics* **2000**, *19*, 3983.

(11) Hewavitharanage, P.; Danilov, E. O.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 10653.

(12) (a) Kehr, G.; Erker, G. *Chem. Commun.* **2012**, *48*, 1839. (b) Chen, C.; Harhausen, M.; Liedtke, R.; Bussmann, K.; Fukazawa, A.; Yamaguchi, S.; Petersen, J. L.; Daniliuc, C. G.; Frohlich, R.; Kehr, G.; Erker, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 5992.

(13) Kehr, G.; Erker, G. *Chem. Common.* **2012**, *48*, 1839.

(14) Huang, S. H.; Wang, F. D.; Gan, L. B.; Yuan, G.; Zhou, J.; Zhang, S. W. *Org. Lett.* **2006**, *8*, 277.

(15) Xiao, Z.; Yao, J. Y.; Yu, Y. M.; Jia, Z. S.; Gan, L. B. *Chem. Commun.* **2010**, *46*, 8365.

(16) (a) Tajima, Y.; Hara, T.; Honma, T.; Matsumoto, S.; Takeuchi, K. *Org. Lett.* **2006**, *8*, 3203. (b) Chen, Z. X.; Wang, G. W. *J. Org. Chem.* **2005**, *70*, 2380. (c) Wang, G. W.; Lu, Y. M.; Chen, Z. X. *Org. Lett.* **2009**, *11*, 1507.

(17) (a) Zhang, G.; Zhang, Q. Y.; Jia, Z. S.; Liang, S. S.; Gan, L. B.; Li, Y. L. *J. Org. Chem.* **2011**, *76*, 6743. (b) Xin, N. N.; Yang, X. B.; Zhou, Z. S.; Zhang, J. X.; Zhang, S. X.; Gan, L. B. *J. Org. Chem.* **2013**, *78*, 1157.

(18) (a) Gevorgyan, V.; Lin, J. X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919. (b) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887. (c) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.

(19) Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 8926.