the acetate samples derived from the *R* isomer of ethylphosphonate had predominantly the *S* configuration (*F* value[12] 39.7 = 36% ee *S*), whereas the acetate from the *S* ethylphosphonate contained an excess of *R* isomer (*F* value 59.1 = 32% ee *R*). Hence, the replacement of the phosphonate group by a hydrogen occurs in a retention mode.

The enantiomeric purity of the methyl groups in the product is substantially lower than that of the starting material. Although the enantiomeric excess of the substrate itself was not determined, a reference value was obtained by reacting an aliquot of the intermediate ethyl mesylate of *S* configuration with $LiEt_3BH$ to give ethane which was subjected to the same degradation as the enzymatically generated samples. The *F* value of the resulting acetic acid was 28.1, corresponding to 75% ee *S*.[8] Since the two steps of the transformation of ethyl mesylate to ethylphosphonate are not likely to involve significant racemization, it follows that the C-P lyase reaction must be accompanied by more than 50% racemization at the reacting carbon atom. This provides support for a mechanism involving a carbon-based radical intermediate, i.e., an ethyl radical.[15] The lifetime of the radical intermediate must be long enough for an apppreciable fraction of this species to undergo configurational inversion by rotation around the carbon–carbon bond prior to its acquisition of a hydrogen atom from a source in close proximity to the departed phosphonate group.

Acknowledgment. We are indebted to Mr. Allen Kastelle for the careful execution of the configurational analyses of the chiral acetate samples and to the National Institutes of Health for financial support (research Grants GM 32333 to H.G.F. and GM 20011 to C.T.W.).

---

(13) Arigoni, D. *Ciba Found. Symp.* **1978**, *60*, 243.

(14) Floss, H. G.; Tsai, M.-D. *Adv. Enzymol.* **1979**, *50*, 243.

(15) Charged intermediates, i.e., a carbocation or a carbanion, presumably would have a much higher barrier to inversion by rotation around the carbon–carbon bond due to interaction with counterions in the enzyme active site.[16]

(16) Poulter, C. D.; Rilling, H. C. *Acc. Chem. Rev.* **1978**, *11*, 307.

Regiochemistry of the Bisosmylation of C_{60}: "Ortho, Meta, and Para" in Three Dimensions

Joel M. Hawkins,[*,†] Axel Meyer,[†] Timothy A. Lewis,[†]
Uwe Bunz,[†] Rudi Nunlist,[†] Graham E. Ball,[†]
Thomas W. Ebbesen,[‡] and Katsumi Tanigaki[‡]

Department of Chemistry
University of California at Berkeley
Berkeley, California 94720
Fundamental Research Laboratory
NEC Corporation, Tsukuba 305, Japan

Received June 15, 1992

The polyfunctionalization of C_{60} through multiple addition reactions can potentially lead to a vast array of novel compounds and materials. To obtain pure compounds from these reactions, both stoichiometry and regiochemistry must be controlled. With the osmylation of C_{60}, we learned how to control stoichiometry with the ligands on osmium.[1,2] Here we report an analysis of the regiochemistry of the bisosmylation of C_{60}, including the first characterization of difunctionalized C_{60} frameworks.[3] Coupling constants show that the bond alternation character of C_{60} is maintained in these derivatives with band-shaped π-systems.

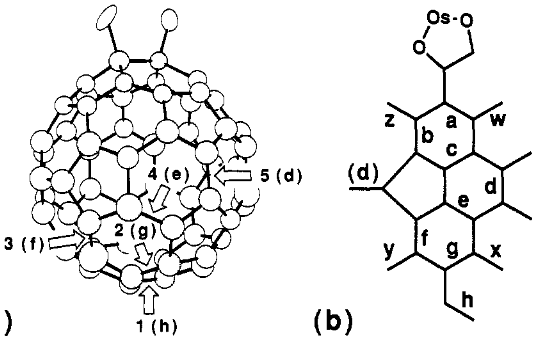

Figure 1. (a) Positions for the second osmyl group in the five regioisomers of $C_{60}(OsO_4L_2)_2$: isomers **3** and **5** are rigorously assigned; isomers **1**, **2**, and **4** are consistent with the observed symmetries and elution orders. (b) Unique cluster bonds in $C_{60}(OsO_4L_2)$ showing the possible second osmylation sites indicated in Table I. Bonds a–h are 6,6 ring fusions; bonds w–z are 6,5 fusions corresponding to C_S isomers.

If totally random, the bisosmylation of C_{60} would yield 54 regioisomers. We know from crystallography[1] and NMR[4] that the first OsO_4 adds to the fusion of two six-membered rings (6,6), reducing the number of possibilities to 24. We observe five regioisomers,[1,5] and to account for this selectivity, we propose that the second OsO_4 also adds to a 6,6 ring fusion (reducing the number of possibilities to eight) and that the hemisphere containing the first osmyl group is sterically inaccessible (reducing the number of possibilities to five) (Figure 1).

The five regioisomers of $C_{60}[OsO_4(py)_2]_2$ were separated by preparative HPLC, converted to their 4-*tert*-butylpyridine analogs, and analyzed by 1D NMR (Table I). The first (least retained) isomer is quite insoluble and could not be analyzed, but the other four isomers gave completely resolved ^{13}C spectra and almost completely resolved ^1H spectra. Either 30 or 32 cluster carbon peaks were observed, corresponding to C_2 symmetry (where none of the carbons lie on the axis of symmetry) or C_s symmetry (where four of the carbons lie on the plane of symmetry), respectively. In agreement with these symmetries, either two or three types of O-bonded carbons and two or three sets of 4-*tert*-butylpyridine resonances were observed. The three sets of peaks found for isomer **5** correspond to the positioning of one of the osmyl groups across the mirror plane. On the basis of these considerations, possible positions for the second osmyl group can be assigned for isomers **2–5** (Table I). All of the 6,5 ring fusions can be ruled out except those with C_S symmetry (w, x, y, and z).

To uniquely define two of the 2:1 adducts, we enriched the C_{60} with ^{13}C for 2D NMR analyses. To increase the ^{13}C content beyond the 5% level which we had previously obtained from cored, ^{13}C-packed rods,[4,6] we baked the packed rods at 900 °C at 0.1 mmHg for 24 h before vaporization in the simple contact-arc apparatus at Berkeley and routinely obtained a maximum of 12–14% ^{13}C. With its highly controlled plasma, the NEC instrument can give much higher levels of enrichment.[7] An average ^{13}C content of 11% was used for the 2D NMR experiments.

Isomers **3** and **5** were identified by 2D NMR (Figure 1, Table I). While the INADEQUATE pulse sequence was sufficient to assign the five types of carbons in C_{70}[8] and the 17 types of carbons

---

[†] University of California at Berkeley.

[‡] NEC Corporation.

(1) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312.

(2) Hawkins, J. M. *Acc. Chem. Res.* **1992**, *25*, 150.

(3) Fagan observes three isomers of $C_{60}[Pt(PEt_3)_2]_2$ by ^{31}P NMR with the trans isomer (cf. isomer **1**) showing a singlet. His crystal structure of $C_{60}[Pt(PEt_3)_2]_6$ shows that the unsubstituted carbons retain some of the short/long bond alternation of C_{60}: Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134. Balch recently obtained the crystal structure of an isomer of $C_{70}[Ir(CO)Cl(PPhMe_2)_2]_2$: Balch, A. L.; Lee, J. W.; Olmstead, M. M. Submitted for publication.

(4) Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770.

(5) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S. In *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*; Hammond, G. S., Kuck, V. J., Eds.; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992; Chapter 6. Isomers **1–5** correspond to HPLC peaks b–f, respectively. The ratios of the areas of these peaks measured at 410 nm are 3:18:28:13:39 for osmylation in the presence of pyridine.

(6) Hawkins, J. M.; Meyer, A.; Loren, S.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 9394.

(7) Ebbesen, T. W.; Tabuchi, J.; Tanigaki, K. *Chem. Phys. Lett.* **1992**, *191*, 336.

(8) Johnson, R. D.; Meijer, G.; Salem, J. R.; Bethune, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 3619.

0002-7863/92/1514-7954$03.00/0

Table I. 1D ^{13}C and ^{1}H NMR Spectra of Purified Regioisomers of $C_{60}[OsO_4(4\text{-}tert\text{-butylpyridine})_2]_2$

isomer	^{13}C peaks for C_{60} moiety[a]	C–O peaks	4-*tert*-butylpyridine signals[b]	symmetry	possible structures[c]
2	30 (equal intensity)	2	2	C_2	c, g (f)
3	30 (equal intensity)	2	2	C_2	f (c, g)
4	32 (4 half intensity)	2	2	C_s	a, b, e, w, x
5	32 (4 half intensity)	3 (ratio 1:1:2)	3 (ratio 1:1:2)[d]	C_s	d (y, z)

[a] See supplementary material for a complete peak listing. [b] All ^{13}C and ^{1}H NMR peaks resolve except as noted for isomer **5**. [c] Assignments in parentheses are consistent with 1D spectra but ruled out by 2D spectra. [d] C(2)-*H* shows two peaks (ratio 3:1) and the *tert*-butyl signals overlap.

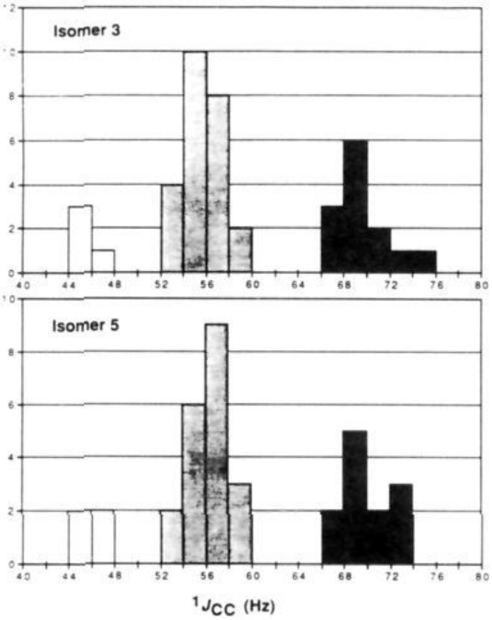

Figure 2. Histograms of coupling constants ($^1J_{CC}$) in isomers **3** and **5** showing distinction of C–C–O bonds (white), 6,5 ring fusions (shaded), and 6,6 ring fusions (black).

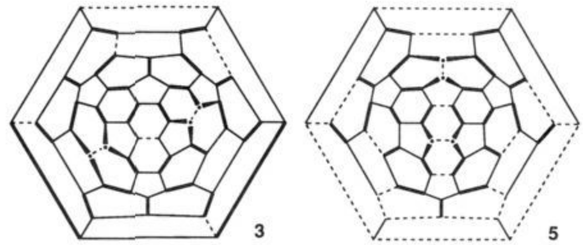

Figure 3. Pattern of coupling constants in isomers **3** and **5**: 45–47 Hz (wedges), 53–59 Hz (solid lines); 67–74 Hz (bold lines). Dots indicate O-bonded carbons; dashed lines indicate undiscernible couplings.

in monoosmylated C_{60},[4] we used the more powerful C–C HOHAHA technique[9] to assign the 30 and 32 types of carbons in bisosmylated isomers **3** and **5**.[10] The O-bonded carbons are the furthest upfield (103–105 ppm), the adjacent carbons tend to be downfield (149–157 ppm), and the remaining carbons are dispersed between 136 and 151 ppm (see supplementary material for complete assignments). Long-range couplings aided peak assignments. With isomers **3** and **5** identified, isomers **1**, **2**, and **4** can be tentatively assigned as shown in Figure 1 on the basis of the symmetries of isomers **2** (C_2) and **4** (C_S) and the elution order on HPLC (assuming that polarity increases as the angle between the osmyl groups decreases). These assignments agree with the steric and electronic control proposed above to account for the formation of five regioisomers of $C_{60}[OsO_4(py)_2]_2$, i.e., steric blocking of the hemisphere proximate to the first osmyl group and addition of the second osmyl group to a 6,6 ring fusion.

Coupling constants ($^1J_{CC}$) for isomers **3** and **5** indicate three types of bonds within the C_{60} clusters: bonds to the O–bonded carbons (45–47 Hz), 6,5 ring fusions (53–59 Hz), and 6,6 ring fusions (67–74 Hz) (Figure 2). Thus, these difunctionalized C_{60} derivatives with differently contoured band-shaped π-systems exhibit confined local distortion at the sites of osmylation, with the remainder of the carbon framework showing bond alternation corresponding to the two types of bonds in C_{60} (Figure 3).

Acknowledgment. J.M.H. is grateful to the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (Teacher–Scholar Award), the Merck Sharp & Dohme Research Laboratories (postdoctoral fellowship for A.M.), the Shell Oil Company Foundation (Shell Faculty Fellowship), Xerox Corporation, Monsanto Company, Hoffmann-La Roche Inc., and Eli Lilly and Company for financial support. U.B. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship. We thank Alessandro F. Moretto for assistance with the synthesis of ^{13}C-enriched C_{60} and Virginia A. Carlson for assistance in baking the packed carbon rods.

Note Added in Proof: 2D NMR analysis of isomer **2** confirms the assignment given in Figure 1.

Supplementary Material Available: Listing of ^{13}C and ^{1}H NMR peaks for isomers **2–5** including peak assignments for isomers **3** and **5** (2 pages). Ordering information is given on any current masthead page.

---

(9) Nunlist, R.; Ball, G. E.; Meyer, A.; Hawkins, J. M. Manuscript in preparation.

(10) 2D spectra were obtained of **3** (44 mg) and **5** (35 mg) in $CDCl_3$ at 100.627 MHz on a modified Bruker AM-400 using a 5-mm probe at 26 °C. A HOHAHA[11] sequence with 10 ms MLEV-17 mixing time was used. The spectral width was set to 7042 Hz in both dimensions; 4K or 8K points were sampled in F_2 and 1024 to 2048 points were sampled in F_1. The files were processed on a Bruker X32. After application of an exponential broadening of 4 Hz in F_2 and squared cosine multiplication in F_1, 4K points in F_2 and 1K points in F_1 were transformed with zero-filling to a final 4K × 4K complex matrix. Coupling constants were measured from individual rows.

(11) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *65*, 355.

Reaction of Disilanes with a *cis*-Platinum Dihydride: Novel Platinum Complexes with Terminal Disilanyl Groups and Bridging Disilene Ligands

Michael J. Michalczyk,*,† Craig A. Recatto,‡
Joseph C. Calabrese,† and Mark J. Fink*,‡

Du Pont Central Research, Experimental Station
P.O. Box 80356, Wilmington, Delaware 19880
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received March 16, 1992

Catalytic dehydrogenative coupling of polyhydrosilanes to polysilane oligomers and polymers has been a growing area of interest.[1,2] Recent work has focused on early transition metal

---

† Du Pont Central Research, Contribution no. 6178.
‡ Tulane University.

0002-7863/92/1514-7955$03.00/0