due to H_α and H_β of the vinylcarbene moiety, respectively. Similar ^1H NMR patterns have been observed for the analogous vinylcarbene complexes $Cp_2Ti(PMe_3)(=C(H)CH=CPh_2)$,[9] $Cp_2Zr(PMe_3)(=C(H)CH=CPh_2)$,[9] and $(ArN)WCl_2(P(OMe)_3)_2(=C(H)CH=CPh_2)$,[10] which were prepared by the addition of 3,3-diphenylcyclopropene to the corresponding reduced precursors. Although not directly comparable, the ^{13}C chemical shift of C_α of **1** at 288.9 ppm is in the same range as those found for a variety of known bis(triphenylphosphine)ruthenium(II) and -osmium(II) carbene complexes.[11] The ^{31}P chemical shift at 28.2 ppm for the coordinated triphenylphosphines is similar to that observed at 27.2 ppm for the phosphorous ligands of the recently reported vinylidene complex $(Ph_3P)_2RuCl_2(=C=C(H)^tBu)$.[12] X-ray diffraction data from a single crystal of **1** further confirmed the structural assignment (Figure 1). Unfortunately, the vinylcarbene moiety is disordered about a 2-fold axis, thus preventing an accurate determination of bond lengths and bond angles for this fragment.[13]

In the solid state, complex **1** is stable indefinitely under an inert atmosphere and for several minutes in air. The complex is stable for weeks in organic solvents in the absence of oxygen. Surprisingly, **1** is also stable for several days in CH_2Cl_2/C_6H_6 in the presence of water, alcohol, or a diethyl ether solution of HCl. This unusual stability is consistent with the functional-group tolerance of group VIII metathesis catalysts. As expected, **1** will not undergo Wittig-type reactions with either a ketone or an aldehyde.[14] In preliminary experiments, the ligand environment of **1** was modified by substitution of the chlorides with selected anionic ligands.[15]

Complex **1** polymerizes norbornene in a 1:8 mixture of CH_2Cl_2/C_6H_6 at room temperature to yield polynorbornene.[16] A new signal, attributed to H_α of the propagating carbene, was observed by ^1H NMR spectroscopy at 17.79 ppm.[17] Its identity and stability were confirmed by preparing a block polymer with 2,3-dideuterionorbornene and perprotionorbornene. When 2,3-dideuterionorbornene was added to the propagating species, the new carbene signal vanished and then reappeared when perprotionorbnene was added for the third block (Scheme I). These experiments demonstrate that the active polymer is stable and that chain termination and transfer are extremely slow relative to propagation, thus satisfying the sole criterion for a "living polymer".[18]

Although initiation is slower than propagation, a complete conversion of the parent vinylcarbene to the propagating carbene can be achieved.[19] The propagating carbene, generated from the reaction of **1** with norbornene, is quite stable in the presence of water or ethanol (up to 1000 equiv per catalyst molecule in a 1:9 mixture of CH_2Cl_2/THF; unfortunately, **1** is not soluble in either pure water or alcohol). Protic solvents do not slow down the polymerization activity of the catalyst, and to a first-order approximation, the rate of norbornene polymerization in organic media is comparable to that observed in the presence of protic solvents.

The above observations demonstrate that carbene complexes (metallaolefins) are viable intermediates in the ROMP of bicyclic monomers with group VIII metals, since an isolated, well-characterized ruthenium carbene complex shows all the characteristic reactions that are required for such intermediates. The potential for solvent variation and ligand modification holds great promise for fine-tuning the reactivity of the catalyst.

Acknowledgment. Financial support from the National Science Foundation and Du Pont is gratefully acknowledged. L.K.J. thanks the NSF for an NSF Predoctoral Fellowship. S.T.N. thanks the Department of Defense, Office of Army Research, for an NDSEG Predoctoral Fellowship and Caltech for an Institute Fellowship. Funds for the purchase of the Siemens R3m/V diffractometer system were made available from the National Science Foundation under Grant CHE-85-14495. We thank Dominic V. McGrath for helpful discussions.

Supplementary Material Available: Experimental details and spectroscopic data for complex **1** and its derivatives, additional information regarding the stability of **1**, description of the X-ray diffraction experiment, ORTEP drawings of the molecule showing the disordered components and a stereoview of the molecule, and tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles (19 pages); listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

---

(9) Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610-611.

(10) Johnson, L. K.; Grubbs, R. H. Manuscript in preparation.

(11) In assigning the oxidation state of these complexes, the carbene moiety was considered to be neutral. See: (a) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411-447. (b) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 563-565. (c) Clark, G. R.; Hodgson, D. J.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1552-1554. (d) Wright, A. H.; Roper, W. R. Unpublished results.

(12) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604-9610.

(13) Single crystals of **1** were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution. The molecule crystallized in a monoclinic unit cell, space group $C2/C(C_{2h}^6$; No. 15) with $a = 13.466$ (5) Å, $b = 14.188$ (6) Å, $c = 22.62$ (2) Å, $\beta = 104.50$ (6)°, $V = 4183.0$ (4) $Å^3$, and $D_{calcd} = 1.41$ g cm^{-3} for $Z = 4$, $T = 178$ K.

(14) For more information on the stability of **1**, please refer to the supplementary material.

(15) For additional details, please see the supplementary material.

(16) At room temperature, 2 mg of **1** polymerizes 70 equiv of norbornene in 0.5 mL of a 1:8 CD_2Cl_2/C_6D_6 solvent mixture in 3 h. The polymer was about 90% trans by ^1H NMR spectroscopy. The classical $RuCl_3$ systems also give a high amount (>90%) of trans polymer.[1a,b]

(17) The parent vinylcarbene shows a quartet at 17.86 ppm in this solvent mixture.

(18) This system is living because the propagating alkylidene is stable on the time scale of the reaction and, as is demonstrated by the blocking experiment, will continue to polymerize quantitatively on addition of further aliquots of monomer several hours after the original amount of norbornene is consumed. See: (a) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Wiley-Interscience: New York, 1968. (b) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87-143.

(19) For example, when 70 equiv of norbornene was added to **1** in a 1:8 CD_2Cl_2/C_6D_6 solvent mixture, after 50 min only 80% of the parent vinylcarbene was converted to the propagating carbene. Approximately 70% of the monomer was polymerized at this point.

Unprecedented Stereochemistry of the Electrophilic Arylation at Chiral Phosphorus

Toshiyuki Oshiki and Tsuneo Imamoto*

Department of Chemistry, Faculty of Science
Chiba University, Inage
Chiba 263, Japan

Received January 13, 1992

Electrophilic alkylation or arylation reactions of chiral tetracoordinate organophosphorus compounds having a P-H bond are known to proceed with retention of configuration at the phosphorus atom, and to our knowledge, inversion of configuration is unprecedented in this class of reactions.[1] We report herein the first example of inversion in an electrophilic arylation reaction at chiral phosphorus, and in addition, we wish to describe dramatic solvent

---

(1) (a) Farnham, W. B.; Murray, R. K.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 5809. (b) Van den Berg, G. R.; Platenburg, D. H. J. M.; Benshop, H. P. *J. Chem. Soc., Chem. Commun.* **1971**, 606. (c) Donohne, J.; Mandel, N.; Farnham, W. B.; Murray, R. K.; Mislow, K.; Benshop, H. P. *J. Chem. Soc., Chem. Commun.* **1972**, 120. (d) Van den Berg, G. R.; Platenburg, D. H. J. M.; Benshop, H. P. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 929. (e) Michalski, J.; Skrzypczynski, Z. *J. Organomet. Chem.* **1975**, *97*, C31. (f) Mikolajczyk, M.; Krzywanski, J. *J. Org. Chem.* **1977**, *42*, 190. (g) Michalski, J.; Skrzypczynski, Z. *J. Chem. Soc., Chem. Commun.* **1977**, 66. (h) Skrzypczynski, Z.; Michalski, J. *J. Org. Chem.* **1988**, *53*, 4549. (i) Zhang, J.; Xu, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1606. (j) Zhang, J.; Xu, Y.; Huang, G.; Guo, H. *Tetrahedron Lett.* **1988**, *29*, 1955. (k) Xu, Y.; Wei, H.; Zhang, J.; Huang, G. *Tetrahedron Lett.* **1989**, *30*, 949.

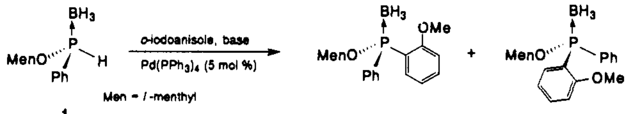
0002-7863/92/1514-3975$03.00/0

Table I. Palladium-Catalyzed Reaction of (S_P)-(Menthyloxy)phenylphosphine–Borane ($\mathbf{1}_S$) with *o*-Iodoanisole[a]

entry	solvent	base	temp (°C)	time (h)	yield (%)	$\mathbf{2}_S$:$\mathbf{2}_R$
1	CH_3CN	K_2CO_3	50	16	96	100:0
2	CH_3CN	K_3PO_4	20	16	72	100:0
3	CH_3CN	Ag_2CO_3	30	2	61	99:1
4	DMF	K_2CO_3	50	16	39	80:20
5	THF	K_2CO_3	50	48	76	4:96
6[b]	THF	K_2CO_3	90	2	59	6:94
7	THF	CH_3COOK	50	48	55	3:97
8	THF	K_2CO_3/18-crown-6	50	48	36	24:76
9	THF	Li_2CO_3	50	24	23	16:84
10	THF	Na_2CO_3	50	68	60	25:75
11	THF	K_3PO_4	50	16	76	47:53
12	THF	DBU	50	68	24	35:65
13	THF	NaH	50	0.5	21	82:18
14	THF	Ag_2CO_3	50	12	67	99:1
15	tetrahydropyran	K_2CO_3	50	48	56	13:87
16	dioxane	K_2CO_3	50	16	61	10:90
17	toluene	K_2CO_3	50	16	17	22:78
18	toluene	Ag_2CO_3	40	4	56	100:0

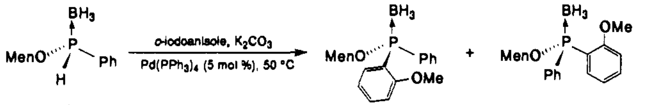
[a] All reactions were carried out with a molar ratio of $\mathbf{1}_S$:*o*-iodoanisole:base:$Pd(PPh_3)_4$ = 1:2:2:0.05. [b] The reaction was carried out in a sealed tube.

Scheme I



$\mathbf{1}_S$ $\mathbf{2}_S$ $\mathbf{2}_R$

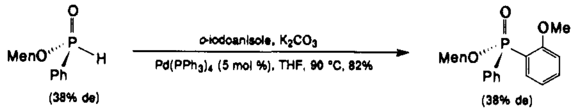
Scheme II



$\mathbf{1}_R$ $\mathbf{2}_R$ $\mathbf{2}_S$

Solvent	Time (h)	Yield (%)	$\mathbf{2}_R$: $\mathbf{2}_S$
CH_3CN	16	98	100 : 0
THF	48	67	4 : 96

Scheme III



3 4

effects on the stereochemistry of the reaction.

Previously, we reported that optically active secondary phosphine–boranes reacted with iodomethane with complete retention of configuration at phosphorus.[2] On the basis of these results, we have examined palladium-catalyzed cross-coupling reactions of secondary phosphine–boranes with aromatic iodides.[3] Our initial investigation was undertaken with diastereomerically pure (S_P)-(menthyloxy)phenylphosphine–borane ($\mathbf{1}_S$) and *o*-iodoanisole (Scheme I).

The reaction was carried out in the presence of 5 mol % of $Pd(PPh_3)_4$ under various conditions. The results are summarized in Table I. The stereospecificity of the reaction depended largely on the solvent and the base used. The reaction in acetonitrile proceeded with almost complete retention of configuration (entries 1–3).[4] Similary, predominant retention occurred in dimethylformamide (DMF) (entry 4). Contrary to these findings, inversion of configuration was observed in ethereal solvents or toluene. Reactions in tetrahydrofuran (THF) in the presence of K_2CO_3 or CH_3CO_2K proceeded with a remarkably high degree of stereospecificity (entries 5–7), while use of a stronger base such as K_3PO_4 or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) resulted in lower levels of specificity (entries 11 and 12), and retention of configuration occurred when NaH or Ag_2CO_3 was employed (entries 13, 14, and 18).

The diastereomer, (R_P)-(menthyloxy)phenylphosphine–borane ($\mathbf{1}_R$), was next allowed to react with *o*-iodoanisole under similar conditions. Representative results are shown in Scheme II. Complete retention occurred in acetonitrile, whereas nearly complete inversion was observed in THF. These results, which are almost the same as those of the reaction of $\mathbf{1}_S$, clearly indicate that the stereochemistry of the reaction is not affected by the chirality of the *l*-menthyl group.[5]

The inversion of configuration and dramatic solvent effects found in this study result from the characteristic reactivities of phosphine–boranes.[6,7] The mechanism accounting for the observed stereochemical outcome is not yet fully understood, but we suppose that the configuration of the product is determined in the transmetalation step in the catalytic cycle.

In summary, we have found that the stereochemistry of the palladium-catalyzed cross-coupling reaction of secondary phosphine–boranes ranges from almost complete retention to inversion by changing the solvent and the base.[8] By this method, both diastereomers of the coupled product can be synthesized from one diastereomer, $\mathbf{1}_S$ or $\mathbf{1}_R$.

---

(2) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

(3) Palladium-catalyzed cross-coupling reactions of organophosphorus compounds with aromatic or vinylic halides have been reported. For reactions of optically active organophosphorus compounds, see ref 1i–k. For reactions of achiral or racemic phosphorus compounds, see the following: Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 909. Xu, Y.; Li, Z.; Xia, H.; Guo, H.; Huang, Y. *Synthesis* **1983**, 377. Xu, Y.; Li, Z.; Xia, H.; Guo, H.; Huang, Y. *Synthesis* **1984**, 781. Xia, J.; Guo, H. *Synthesis* **1986**, 691. Holt, D, A.; Erb, J. M. *Tetrahedron Lett.* **1989**, *30*, 5393. Casalnuovo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324.

(4) Reaction temperature also affected the stereospecificity. The following diastereospecificities were observed in the reaction of $\mathbf{1}_S$ in acetonitrile in the presence of $K_2CO_3/Pd(PPh_3)_4$: 100% de (50 °C), 95% de (60 °C), 87% de (70 °C), and 69% de (82 °C).

(5) In order to evaluate the generality of this method, we examined the reactions of (S_P)-methylphenylphosphine–borane with *o*-, *m*-, or *p*-iodoanisole under various conditions. Similar solvent and base dependence of the stereochemistry were observed in these reactions.

(6) To compare the stereochemistry of the reaction of $\mathbf{1}_S$, (R_P)-menthyl phenylphosphinate (**3**) (38% de), whose structure resembles $\mathbf{1}_S$, was allowed to react with *o*-iodoanisole (2 equiv) under the same conditions as in entry 6 in Table I. ^1H NMR (500 MHz) analysis of the product by comparison with the spectra of authentic samples indicated that the reaction proceeded with retention (Scheme III). This result is in accordance with the previously reported results of the palladium-catalyzed reaction of optically active isopropyl methylphosphinate with aromatic or vinylic halides.[1i–k]

(7) Reactions in the presence of triethylamine as the base are worthy of note. Treatment of $\mathbf{1}_S$ with *o*-iodoanisole (2 equiv) in the persence of Et_3N (2 equiv) and $Pd(PPh_3)_4$ (5 mol %) in CH_3CN at 50 °C for 16 h afforded no trace of coupled product. Contrary to this result, cross-coupling reactions of phosphinates are known to proceed smoothly in the presence of Et_3N.[1i–k]

(8) It was reported that the stereochemistry of the palladium-catalyzed cross-coupling reaction of chiral alkylsilanes with aryl triflates could be controlled from almost complete retention to inversion by varying the reaction temperature and the solvent: Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on a Priority Area of Organic Unusual Valency No. 02247104 from the Ministry of Education, Science and Culture, Japan. We thank H. Seki and R. Hara, Chemical Analysis Center of Chiba University, for the measurements of ^{1}H NMR (500 MHz) spectra.

Registry No. **1*S***, 127686-94-6; **1*R***, 127759-69-7; **2*S***, 127686-93-5; **2*R***, 127759-68-6; **3**, 31352-60-0; **4**, 140150-04-5; DBU, 6674-22-2; K_2CO_3, 584-08-7; K_3PO_4, 7778-53-2; Ag_2CO_3, 534-16-7; CH_3COOK, 127-08-2; Li_2CO_3, 554-13-2; Na_2CO_3, 497-19-8; NaH, 7646-69-7; 18-crown-6, 17455-13-9; *o*-iodoanisole, 529-28-2.

Supplementary Material Available: Experimental details for the cross-coupling reaction and for the determination of the enantiomeric excess of the product (2 pages). Ordering information is given on any current masthead page.

Synthesis of a C_{60}-*p*-Xylylene Copolymer

Douglas A. Loy* and Roger A. Assink

Fuel Science Department and Physical Chemistry and
Mechanical Properties of Polymers Department
Sandia National Laboratories
Albuquerque, New Mexico 87185

Received December 27, 1991

Procedures allowing the preparation and purification of macroscopic quantities of buckminsterfullerenes,[1] or buckyballs, have ignited an explosion of research into their physical and chemical properties. Recently, it was discovered that C_{60} reacted with benzyl radicals to form polybenzylated fullerenes.[2] Substitution of a diradical species for the benzyl radicals would allow C_{60} molecules to be linked together, resulting in a polymeric material. Xylylene, a diradical analogue of a benzylic radical, is easily prepared by the flash thermolysis of paracyclophane and is known to readily react with itself to form poly(*p*-xylylene).[3] We report the first C_{60} copolymer prepared by reacting pure C_{60} with xylylene (Scheme I).[4]

The polymerizations were carried out using a slightly modified version of the apparatus used by Errede[3a] in generating poly(*p*-xylylene) from *p*-xylene or paracyclophane. In this experiment, paracyclophane was sublimed at 200 °C (under a 1-mbar vacuum) into a tube furnace set at 650 °C where the xylylene comonomer was formed. The xylylene was then swept into a reaction vessel containing a vigorously stirred solution of pure C_{60} in toluene cooled with a dry ice/acetone bath to −78 °C. Addition of the xylylene to the C_{60} was heralded by an immediate change in the color of the solution from purple to olive-green. When the solution was allowed to warm to room temperature, a brown precipitate formed. The insoluble precipitate was washed with toluene and diethyl ether before drying under vacuum (2 mbar).

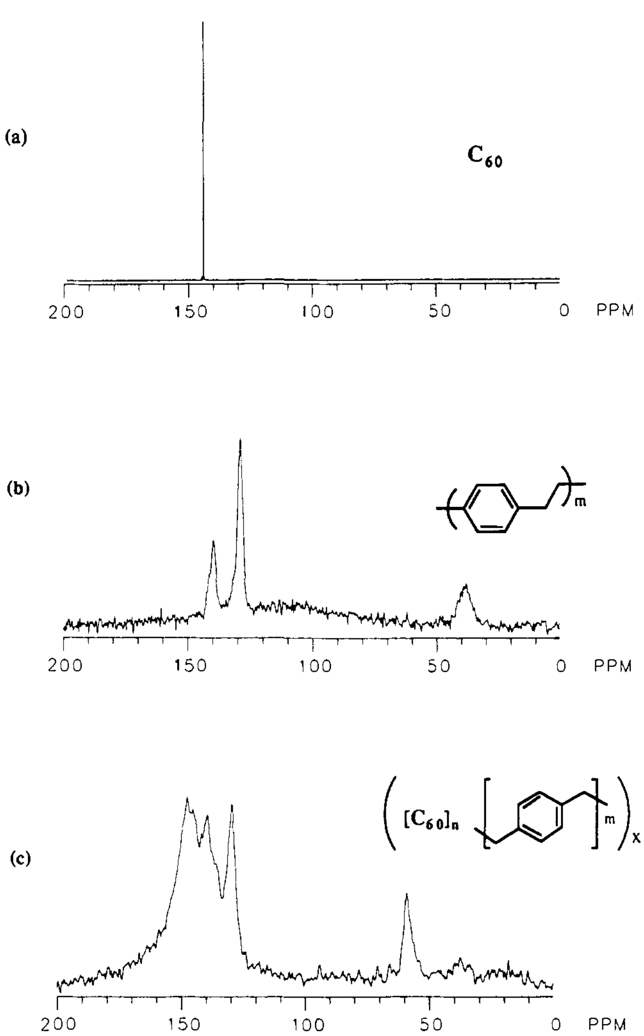
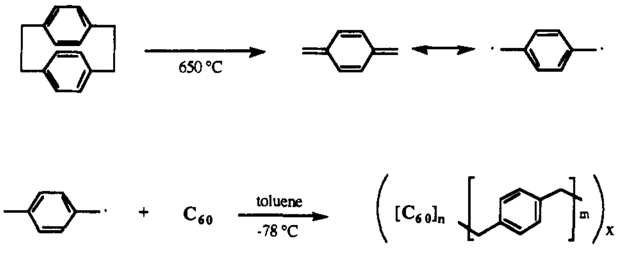


Figure 1. ^{13}C MAS NMR spectra of (a) C_{60} and (b) poly(*p*-xylylene). (c) ^{13}C CP MAS NMR spectrum of C_{60}-*p*-xylylene copolymer. Spectra were obtained at 50.17 MHz with a Chemagnetics console interfaced to a Nicolet 1280 data station. Samples were spun between 4 and 5 kHz in rotors. Direct pulse MAS experiments were carried with 16-s delays between 64 scans. Cross-polarized MAS experiments utilized a 1.5-ms cross polarization time with 4-s delays over 4096 averages.

Scheme I. Formation of Xylylene and Copolymerization with C_{60}



The C_{60}-xylylene copolymer was characterized using solid-state ^{13}C MAS NMR (Figure 1c). Pure C_{60} exhibited the expected resonance at 143.7 ppm (Figure 1a).[5] We also obtained the first reported ^{13}C NMR spectrum of poly(*p*-xylylene) (Figure 1b).[6]

---

(1) (a) Kratschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. (b) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (c) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634–8636. (d) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499–7503.

(2) (a) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274. (b) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.

(3) (a) Szwarc, M. *J. Polym. Sci.* **1951**, *6*, 319. (b) Errebe, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1960**, *82*, 5218.

(4) (a) We recently learned that polystyrene has been covalently modified with C_{60} at the University of Southern California: Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.*, in press. However, there are no reports of polymers derived from C_{60}. (b) The C_{60} fullerene was purified from toluene-soluble soot by chromatography on alumina as described by Allemand et al.: Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. The soot was obtained from Texas Fullerenes Corporation.

(5) In addition to the major resonance, a second peak was observed 0.7 ppm downfield due to molecular oxygen in the crystal lattice; complete details will be discussed in a forthcoming paper. The ^{13}C NMR resonance of C_{60} has been reported at 142.7 ppm: Bausch, J. W.; Prakash, G. K. S.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem. Soc.* **1991**, *113*, 3205–3206.

(6) The poly(*p*-xylylene) was prepared from paracyclophane using the same apparatus as for the copolymerization of C_{60} and xylylene, save that the xylylene was allowed to condense and polymerize on the quartz tube at room temperature.

0002-7863/92/1514-3977$03.00/0