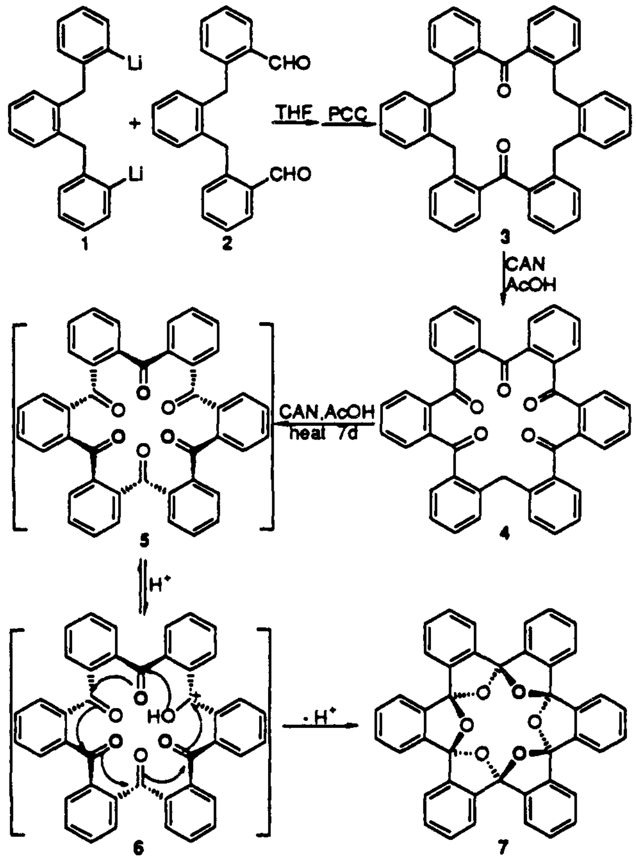
Scheme I



geometry is presented in Figure 1. The polyketal **7** contains a 12-crown-6 moiety incorporated with a $[1_6]$orthocyclophane inside the macrocycle. The up-down-up conformation of the six oxygen atoms gives rise to a preorganized spherical cavity of diameter 1.02 Å. The six benzylic carbon atoms in **7** form a plane (rms 0.0085 Å), from which oxygen atoms deviate by about 0.8 Å.

Inspection of the CPK model of hexaketone **5** indicates that the preferred conformation has an up-down-up arrangement of the six carbonyl functions, causing serious steric strain in the molecule. It appears therefore that, as soon as it is produced, **5** undergoes rapid rearrangement, probably via the oxonium ion **6**, resulting in sp^2-to-sp^3 rehybridization in each ketonic carbon to give the strain-free **7**. This is an unprecedented reaction. The cyclic hexaketal **7** is a novel coronand containing the 2*n*-crown-*n* moiety. When viewed from above, the oxygen atoms of **7** form a six-pointed star. Although a number of coronands have been synthesized[8] during the last two decades, in most cases the oxygens are separated by hydrocarbon spacers having two or more bridging atoms, such as dimethylene, trimethylene, or *o*- or *m*-phenylene units. The 2*n*-crown-*n*-type coronands, whose oxygens are separated from one another by one carbon atom, have not been reported. Although $(CH_2O)_n$ cyclic structures (e.g., paraformaldehyde) are labile, the polyketal **7**, which is composed of $(CR_2O)_6$ units incorporated with a $[1_6]$orthocyclophane, is stable. Generation of homologs of the star-shaped coronand **7** can be anticipated from oxidation of other even-number $[1_n]$orthocyclophanes.

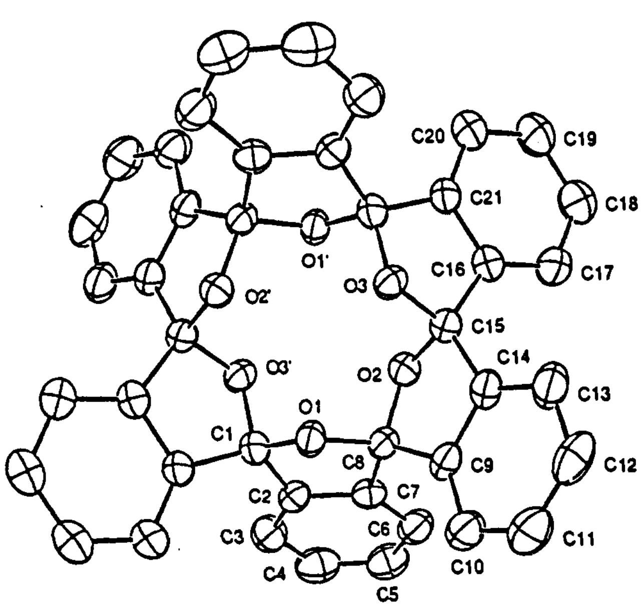


Figure 1. ORTEP diagram of 7.

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Supplementary Material Available: NMR and EIMS spectra for 1,2-bis(2-bromobenzyl)benzene, **3**, **4**, and **7** and an IR spectrum, crystallography data, and ORTEP, and a stereoview for **7** (31 pages); tables of structure factors for **7** (48 pages). Ordering information is given on any current masthead page.

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(7) X-ray analysis: **7** crystallizes in the monoclinic space group $P2_1/c$ (No. 14); $a = 15.813(6)$, $b = 13.108(1)$, $c = 20.257(7)$ Å; $\beta = 109.35(2)°$; $V = 3961.6$ Å^3; $d_{calcd} = 1.25$ g/cm^3; $Z = 4$. Data were collected on an Enraf-Nonius CAD4 diffractometer. Of the 5142 unique data collected with Mo Kα radiation ($\lambda = 0.71073$ Å), the 4212 with $F_o > 1.0\sigma(F)$ were used in the least-squares refinement to yield $R = 5.2\%$, $R_w = 6.9\%$ after an empirical absorption correction based on Ψ-scan data was applied.

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Electrocrystallization and ESR Spectra of the Single Crystal $[N(P(C_6H_5)_3)_2]\cdot C_{60}$

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Since the discovery of superconductivity at 18 K for K_3C_{60},[1] the alkali-metal fullerides have been the object of considerable research. So far, however, the solid-state properties of fulleride single-crystals have not yet been clarified. The preparation of

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appropriate single crystals is difficult for several reasons, principally the extreme air sensitivity of the material. Thus, the solid C_{60} anion has not yet been thoroughly characterized, and the nature of its salt is not well understood.

Characterization of chromium(III)-coordinated $C_{60}^{\bullet-}$ was recently carried out by ESR measurements[2] and the structure of the ferromagnetic 1:1 salt of TDAE–C_{60} studied by the Rietveld method.[3] Although preparation of fulleride anion radical salts has been described by Wudl et al.,[4] the resulting microcrystalline powder sample was not suitable for single-crystal X-ray analysis. The powder X-ray diffraction studies on alkali-metal-doped C_{60} did not reveal enough details for an elucidation of the character and structure of the C_{60} anion.[5] In addition, single crystals of clathrate C_{60} complexes[6] as well as some metal–C_{60} coordination compounds[7] were obtained. However, these C_{60} compounds do not seem to exhibit the nature of the real fulleride anion radical. Very recently X-ray crystal structure analyses of neutral C_{60} have been reported for twinned crystals[8a] and benzene-solvated single crystals.[8b]

In order to trap "buckyballs" we used a bulky cation, [bis(triphenylphosphoranylidene)]ammonium cation, $N[P(C_6H_5)_3]_2^+$ (PPN^+), and succeeded in obtaining single crystals of the fulleride anion salts for studying the solid-state properties of fulleride salts. We report herein our first ESR measurements on single crystals of the C_{60} anion radical salts, as well as preliminary results concerning its crystal structure.

Mass spectroscopically pure C_{60} was obtained from fullerene-enriched soot using a graphite column[9a] and a subsequent alumina column.[9b] In an H-cell with Pt electrodes, 4 mg (3.1×10^{-4} M) of pure C_{60} and 30 mg (2.9×10^{-3} M) of PPN^+Cl^- were electrolyzed (0.7 μA) in a degassed solvent mixture (18 mL) of 5:1 chlorobenzene/THF for ca. 2 weeks. Metallic lustrous rod-type black crystals as long as ca. 4 mm grew on the surface of the platinum cathode.[10] The SEM micrograph of the compound shows clearly the needle shape of the crystals. As we noticed the air, light, and moisture sensitivity of these salts during our experiments, electrocrystallization was carried out in the dark at room temperature. The single crystals showed no electric conductivity at room temperature. The compound was insoluble in almost all organic solvents except for pyridine and nitrobenzene.

The most intriguing feature of the crystalline compound is its electronic structure. Electroreductively generated fulleride species, C_{60}^{n-} (n = 1–6), have so far only been prepared in solution.[11] The ESR spectrum for the freshly isolated PPN·C_{60} single crystal is shown in Figure 1a. The g-value calibrations were made using DPPH, and the magnetic field calibration was made using manganese ion and nitroxide radical. The broad signal at room temperature (peak-to-peak line width ca. 35 G) is assigned to the $C_{60}^{\bullet-}$ species ($g = 1.999_2$ at room temperature) on the basis of the results for PPh_4^+ salts of $C_{60}^{\bullet-}$.[4] This broad signal became significantly narrower with decreasing sample temperature, and finally a sharp signal (peak-to-peak line width ca. 5 G) was obtained at 77 K. This behavior is consistent with the previous observations on $PPh_4^+C_{60}^{\bullet-}$.[4] Parts b–d of Figure 1 show the time dependence of the ESR spectra of the same sample. The broad signal (A) decreased gradually, whereas the sharp signal (B) superimposed on the broad signal became stronger.

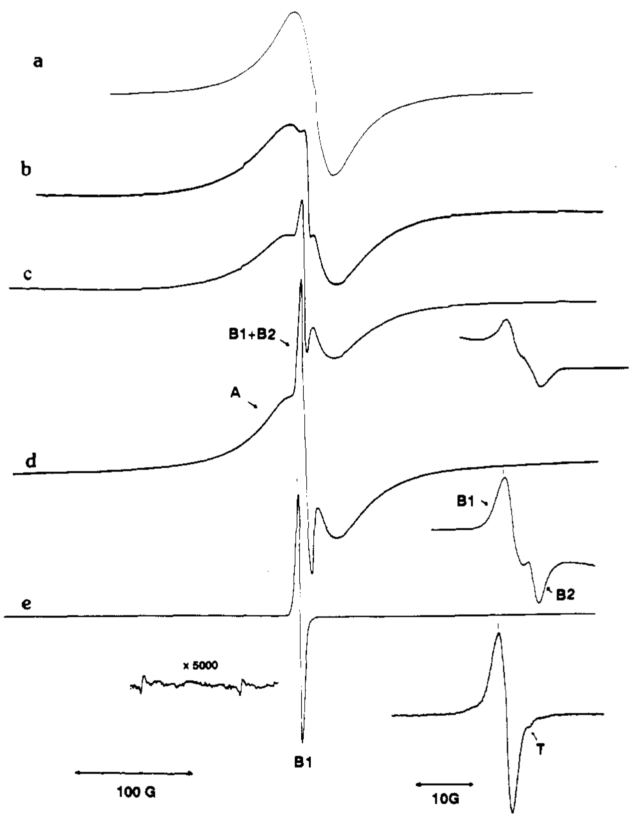

Figure 1. Time course of ESR signals of PPN·C_{60}. Magnetic fields were near 336 ± 25 mT and modulation was 0.5 mT for all spectra. Spectrum a depicts the signal for freshly isolated PPN·C_{60} (at 5 h after isolation from the Pt electrode). At times less than 1 day the signal had the form shown in b. After this the signal gradually developed as shown in c after 7 days), d (after 12 days), and e (after 45 days). The central part of the sharp signal is enlarged for c and d (modulation 0.05 mT) and e (modulation 0.1 mT). The broad signal (A) completely disappeared for e. The B2 signal is clearly visible in the c and d enlargements, whereas the existence of C_{60}^{2-} (T), superimposed on B1, is apparent in the e enlargement. For an explanation of the abbreviations A, B1, B2, and T, see the text.

Greaney and Gorun[12] reported an ESR spectrum of fullerene anions in a Bu_4NPF_6 solution as supporting electrolyte. Some

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(10) Elemental analysis data: C, 89.76 (91.57); H, 2.90 (2.40); N, 1.11 (1.11) (values in parentheses are calculated values (%) for $N[(P(C_6H_5)_3)_2]\cdot C_{60}$). Repeated elemental analyses indicated that the values obtained for carbon content are always less than the calculated ones, e.g., for an independent sample: C, 88.57; H, 2.93; N, 1.20. This discrepancy is due to the incomplete combustion of the "soot" (even at 1030 °C).

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ESR spectral features in various samples of our PPN·C_{60} in different time frames were quite similar to the reported spectrum. They suggested that there might be a facile electron exchange as follows:

$$C_{60}^- + C_{60} \rightleftarrows C_{60} + C_{60}^- \quad (1)$$

$$C_{60}^- + Bu_4N^+ \rightleftarrows Bu_4N^+C_{60}^- \quad (2)$$

$$Bu_4N^+C_{60}^- + C_{60} \rightleftarrows C_{60} + Bu_4N^+C_{60}^- \quad (3)$$

They also assigned a broad and a sharp signal to ion-paired $C_{60}^{\bullet-}$ and the free $C_{60}^{\bullet-}$, respectively.

However, on closer inspection it was noted that this sharp signal was due not to a single species but to two species, B1 and B2. Line widths of these sharp signals were nearly constant in the measured temperature range (293–77 K). The sharp signal (B1) may be tentatively assigned to the free $C_{60}^{\bullet-}$ ($g = 2.000_7$) on the basis of Greaney's report.[12] The other signal (B2) ($g = 1.999_5$) is not so amenable to saturation by microwave power as B1 and gradually disappeared with time. This species seems to be an intermediate one. The broad signal (A) is thus assignable to $PPN^+C_{60}^{\bullet-}$.

Dubois et al.[13] observed a concomitant sharp signal superimposed on the $C_{60}^{\bullet-}$ signal corresponding to A in a frozen electrolyte solution of C_{60}. Furthermore, they proposed the occurrence of a disproportionation as follows:

$$2C_{60}^{\bullet-} \rightleftarrows C_{60} + C_{60}^{2-} \quad (4)$$

In our case, we also cannot rule out the existence of triplet C_{60}^{2-} (Figure 1e, T), to which Dubois et al.[13] referred for the first time. Although we failed to observe a half-field resonance for C_{60}^{2-}, which would be conclusive evidence of the existence of a triplet state ($S = 1$), this fact is also consistent with the absence of the half-field signal in the experiment of Dubois et al.[13] After the broad signal (A) and the (B2) sharp signal disappeared completely, we invariably observed the signals due to C_{60}^{2-} (T). The C_{60}^{2-} species generated on photoexcitation[14] was also observed. As yet, we are not sure whether C_{60}^{2-} is present in the electrolyte solution from the beginning of crystal formation as a result of the disproportionation of $C_{60}^{\bullet-}$ or appears later in the solid state. Thus, taking the disproportionation into account, $C_{60}^{\bullet-}$ (PPN$^+$ adduct (A) and free (B1)) and C_{60}^{2-} generated due to the electron exchange in the neighborhood of the Pt electrode might randomly grow crystals of PPN·C_{60} on the electrode. Alternatively the electron exchange process (eqs 1 and 3) and the disproportionation (eq 4) might occur even in the solid state.

We also propose the occurrence of concurrent crystal lattice degradation, because the ESR spectral changes should not be interpreted merely by the decomposition of $PPN^+C_{60}^{\bullet-}$. In samples left at room temperature for several weeks, we no longer observed the broad signal for $PPN^+C_{60}^{\bullet-}$, but instead, only sharp signals assignable to free $C_{60}^{\bullet-}$ (B1). The sharp signal (B2) superimposed on the free $C_{60}^{\bullet-}$ signal also disappeared. The total spin concentration also decreased to ca. 1% of the original content within 2 months. Irreversible degradation (the reverse reaction of ion pairing, e.g., eq 2) of the lattice of $PPN^+C_{60}^{\bullet-}$, as follows,

$$\underset{\text{A}}{PPN^+C_{60}^{\bullet-}} \rightarrow \underset{\text{B2}}{[PPN^+\text{---}C_{60}^{\bullet-}]} \rightarrow PPN^+ + \underset{\text{B1}}{C_{60}^{\bullet-}} \quad (5)$$

may even occur in the solid state.

Preliminary results of X-ray diffraction studies on the single crystal revealed that the structure demonstrated a zigzag arrangement composed of a discrete 1:1 PPN$^+$ salt of $C_{60}^{\bullet-}$ radical anion.[15] Surprisingly, the monoclinic lattice of PPN$^+$ and C_{60} appears to persist for a long time in spite of the gradual decrease of the X-ray peak intensities. Presumably this corresponds to the above mentioned degradation (eq 5).

However, for a comprehensive understanding of the intrinsic electronic "metastable" state of the crystal, it would be necessary to investigate the ESR spectra in more detail. This analysis is in progress right now.[16]

Acknowledgment. We thank Dr. M. Takayama (Toho University) for EIMS and Mr. H. Nakagawa (Newly Instruments Ltd.) for FTMS of pure C_{60} and PPN·C_{60}. We are indebted to Mr. H. Sakamura (Institute of Industrial Science, The University of Tokyo) for his assistance in obtaining a SEM micrograph of the crystal.

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(15) Crystal data for PPN·C_{60}: formula $C_{96}H_{30}NP_2$ (FW = 1259.15), crystal dimensions 0.45 × 0.3 × 0.3 (mm); crystal system, monoclinic, space group *Cc* (or *C*2/*c*), lattice constants, $a = 12.429(4)$ Å, $b = 27.433(6)$ Å, $c = 17.850(4)$ Å, $\beta = 90.45(2)°$, $V = 6086(3)$ Å^3, $Z = 4$. The preliminary *R* factor was 0.20 for 1880 observed unique reflections (at room temperature). Lattice constants designate the packing structure of this molecule with four molecules of PPN·C_{60} in one unit cell. The diameter of C_{60} (7.0 Å) and the separation of neighboring C_{60} molecules (10.5 Å, center-to-center) are well consistent with those of the crystal composed of a free C_{60} molecule (7.065 Å)[8a] and a center-to-center distance for adjacent C_{60} molecules (9.96 Å).[8b] C_{60} moieties seem to be tightly packed in the crystal structure. A detailed X-ray crystal structure analysis at low temperatures will be published elsewhere.

(16) Watanabe, T.; et al. To be submitted. We have found recently that these changes of ESR spectra were significantly facilitated by a gradual increase of the sample temperature up to 150 °C.

Four Carbon Component Coupling Reaction Based on Free-Radical Carbonylation: An Easy Access to β-Functionalized δ,ε-Unsaturated Ketones

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Free-radical carbonylation is now experiencing a renaissance.[1] Despite the large body of knowledge accumulated in the past three decades concerning transition-metal-catalyzed carbonylations,[2] the carbonylation of *alkyl* moieties remains a challenge.[3] Obviously, one of the most noteworthy aspects of free-radical carbonylation is that this conceptually different approach provides a simple solution to this long-standing problem. In this paper, we are pleased to report the accomplishment of a four-carbon connection process, where carbon monoxide is incorporated as one of the components. This new type of free-radical transformation couples the following four-carbon units in the sequence: R-X **1**, carbon monoxide, functionalized alkene **2**, and allylstannane **3** (Scheme I). In terms of the versatility in substrates and the importance of the products, the procedure leading to β-functionalized δ,ε-unsaturated ketones **4** has considerable synthetic potential.

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