fact that only scalar coupling is observed in the Ta complexes whereas exchange coupling is predominant in the case of Nb derivatives. A more refined calculation of the vibrational frequencies (including electron correlation) and a more detailed model for the coupling (with a three-dimensional and three-particle treatment) would be needed to give a more quantitative account of the observed phenomena.

In conclusion, two differences clearly appear between the Nb and Ta trihydrides: the existence in the Nb complex of first a thermally accessible dihydrogen state and second a low-frequency vibration which can account for the exchange coupling observations. These two facts seem to be intuitively related and are in agreement with the observed fluxionality at "high temperature" (−100 to +100 °C according to the compounds) of the trihydride complexes exhibiting exchange coupling.[1-3] A dihydrogen intermediate is likely to be involved in the fluxional processes. In contrast, the tantalum derivatives are not fluxional.[3] In order to establish a tighter connection between our two findings a more complete study of the potential surface including electron correlation is needed. Work in this field is presently in progress.

Acknowledgment. Thanks are due to Drs. F. N. Tebbe and O. Eisenstein for useful discussions and to K. Zilm for helpful comments.

Metalloporphyrin-Catalyzed Cooxidation of Olefin in the Singlet Oxygenation of Sulfide

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The photooxygenation of sulfides is responsible for the loss of activity of several important enzymes which are damaged in photodynamic action.[1,2] Much attention has been devoted to the structures and reactivities of initially formed reactive intermediates such as persulfoxide **1**, diradical **2**, and thiadioxirane **3** intermediates in singlet oxygenation of sulfides (Scheme I).[3-11] To our knowledge, no interaction between a sulfide–oxygen adduct and a metal ion, however, has been known. Meanwhile, a high-valency iron oxo species as an active oxidant in the cytochrome P-450 mediated monooxygenases is thought to be involved in the model systems employing iron(III) porphyrin and chemical oxidants such as iodosylbenzene[13] (PhIO) and peracids.[14] We report here the first example of an oxygen atom transfer from a peroxidic intermediate generated in singlet oxygenation of sulfide to metal ion affording metal oxo species, which is responsible for epoxidation.

Scheme I

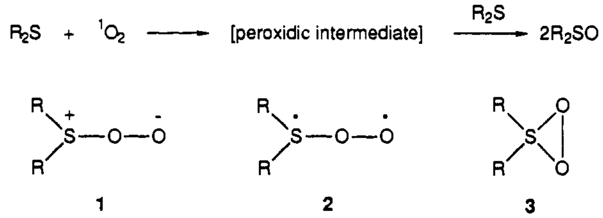
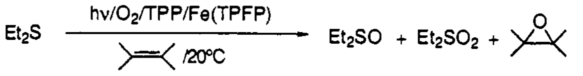


Table I. Cooxidation of Olefin in the Photooxidation of Diethyl Sulfide in the Presence of Fe(TPFP)



run	reactn conditns[a]	olefin (amt, equiv)	Et_2S[b] conv, %	epoxide yield,[c] %	catalyst[d] turnover
1	CH_2Cl_2/2 h	cyclooctene (25)	36	20	23
2	CH_2Cl_2/4 h	cyclooctene (50)	45	30	54
3	C_5H_5N/4 h	cyclooctene (50)	36	14	20
4	no solvent/10 h	cyclooctene (50)	15	20	80
5	CH_2Cl_2/4 h	norbornene (50)	42	48	101
6	CH_2Cl_2/4 h	*cis*-2-heptene (50)	50	28[e]	51
7	CH_2Cl_2/5 h	*trans*-2-heptene (50)	48	5[f]	9
8	CH_2Cl_2/1 h	*cis*-stilbene (100)	75	nd[g]	–
9	CH_2Cl_2/2 h	styrene (50)	64	0.1[g]	(<1)

[a] The ratio of reactants, olefin/sulfide/porphyrin, is 10000/200/1 (run 1 is 3000/120/1, run 8 is 2000/200/1, run 4 is 2000/400/1). Reactions were carried out in 20 mL, porphyrin concentration = 5×10^{-4} M (runs 6 and 7 in 10 mL, porphyrin concentration = 2×10^{-4} M; run 8 in 6 mL, porphyrin concentration = 8×10^{-5} M). [b] In each case, Et_2SO and Et_2SO_2 were also obtained. [c] Yields are based on sulfide consumed; nd is not detected. [d] Epoxide produced/porphyrin used. [e] The ratio of *cis*- and *trans*-epoxide is 82/18. [f] Only *trans*-oxide was obtained. [g] Benzaldehyde was not detected.

In a typical experiment, a dichloromethane solution of diethyl sulfide (8.5×10^{-2} M) and norbornene (50 equiv) was photoirradiated at 20 °C with tetraphenylporphine (TPP, 5.5×10^{-4} M) as sensitizer under an oxygen flow by employing a catalytic amount of (tetrakis(pentafluorophenyl)porphyrinato)iron(III) chloride (Fe(TPFP)). The resulting mixture was subjected to analytical GLC and GC–MS. Norbornene oxide was apparently produced in 48% yield, together with diethyl sulfoxide (90%) and diethyl sulfone (5%) (Table I, run 5). Very similar results were also obtained with cyclooctene (runs 1–4). Control reactions reveal that all of the components, the sulfide, singlet oxygen ($^1O_2$),[15] and Fe(TPFP),[16] are essential for epoxidation. Addition of a radical trap (triphenylmethane) did not have any influence on epoxidation. The results are summarized in Table I.

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(1) Straight, R. C.; Spikes, J. D. In *Singlet O_2*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 4, Chapter 2, p 91.

(2) Sysak, P. K.; Foote, C. S.; Ching, T.-Y. *Photochem. Photobiol.* **1977**, *26*, 19.

(3) For reviews, see: Ando, W.; Takata, T. In *Singlet O_2*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 3, Chapter 1, p 1 and references cited therein.

(4) (a) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085. (b) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *J. Am. Chem. Soc.* **1988**, *110*, 494. (c) Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696.

(5) (a) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478. (b) Foote, C. S.; Jensen, F. *J. Am. Chem. Soc.* **1988**, *110*, 2368. (c) Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 1909.

(6) (a) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787. (b) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 8212. (c) Clennan, E. L.; Yang, K. *J. Am. Chem. Soc.* **1990**, *112*, 4044.

(7) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677.

(8) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

(9) Corey, E. J.; Quannēs, C. *Tetrahedron Lett.* **1976**, 4263.

(10) (a) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154. (b) Ando, W.; Akasaka, T.; Takata, T. *J. Synth. Org. Chem., Jpn.* **1986**, *44*, 97 and references cited therein.

(11) Ando, W.; Miyazaki, H.; Akasaka, T. *Tetrahedron Lett.* **1982**, *23*, 2655.

(12) For reviews: (a) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; Chapter 1, p 1. (b) Mansuy, D. *Pure Appl. Chem.* **1987**, *59*, 759.

(13) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) Lindsay Smith, J. R.; Sleath, P. R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1009. (c) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786. (d) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243. (e) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (f) Mansuy, D.; Battioni, P.; Renaud, J. P.; Guērin, P. *J. Chem. Soc., Chem. Commun.* **1985**, 155. (g) Collman, J. P.; Kodadek, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2588. (h) Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 3625. (i) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770.

(14) (a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884. (b) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8443.

(15) Proof for reagent $^1O_2$ was obtained by testing oxygenation in the absence of a sensitizer and light and by adding Dabco: Foote, C. S.; Peterson, E. R.; Lee, K.-W. *J. Am. Chem. Soc.* **1972**, *94*, 1032.

(16) Preliminary results show that manganese and cobalt porphyrins also act as catalysts for epoxidation under the same conditions; details will be reported elsewhere.

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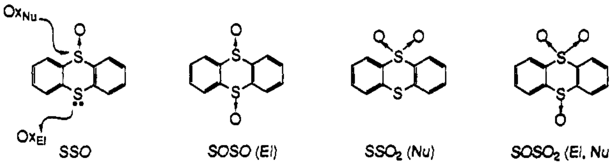
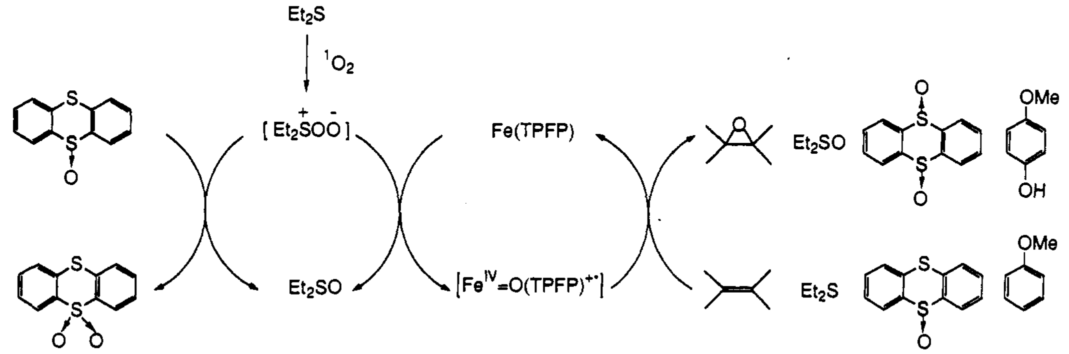
Table II. Nucleophilic Character (X_{Nu}) of Oxygen-Transfer Agents Derived from Thianthrene 5-Oxide



run	oxygen-transfer reaction	total yield, %	abs yield,[a] μM SSO$_2$, n_{Nu}	SOSO, n_{El}	SOSO$_2$, n_{Nu}, n_{El}	X_{Nu}[b]
1[c]	H_2O_2/1 N NaOH/C_6H_6/20 °C	0.25	0.886			1.00
2	$Et_2S/{}^1O_2/CH_2Cl_2$/20 °C	5.31	46.0			1.00
3	$PhIO/CH_2Cl_2$/20 °C	10.2	47.8	20.7	20.9	0.70
4	Fe(TPFP)/$Et_2S/{}^1O_2/CH_2Cl_2$/20 °C	5.26	33.2	78.2	trace	0.68
5[c]	*m*-CPBA/CH_2Cl_2/20 °C	27.0	22.4	42.7	2.48	0.36
6	Fe(TPFP)/PhIO/CH_2Cl_2/20 °C	15.6	29.6	78.2	29.0	0.28
7[c]	H_2O_2/1 N HCl/Et_2O/20 °C	3.27	0.652	15.0	0.298	0.06

[a] Represents amount of conversion of thianthrene 5-oxide into SSO$_2$, SOSO, and SOSO$_2$ products determined by GLC on a fused silica capillary column, using diphenyl sulfone as internal standard. [b] Mole fraction of amount of nucleophilic attack, i.e., $n_{Nu}/(n_{Nu} + n_{El})$; SOSO$_2$ represents double-oxygen-transfer product either via the sequence SSO (Ox$_{El}$) → SOSO (Ox$_{Nu}$) → SOSO$_2$ or via the sequence SSO (Ox$_{Nu}$) → SSO$_2$ (Ox$_{El}$) → SOSO$_2$, so that the yield of SOSO$_2$ is equally added to n_{Nu} and to n_{El}. [c] Reference 18.

Scheme II



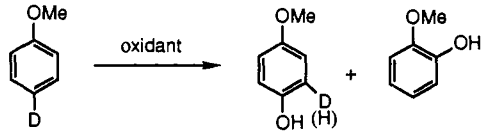
(Tetrakis(*p*-anisyl)porphyrinato)iron(III) chloride and its phenyl derivatives are also able to catalyze epoxidation of norbornene (epoxide: 40% and 30% yields, respectively). The high efficiency of Fe(TPFP) as a catalyst might be due to the greatly enhanced stability by fluorination of the porphyrin ring and formation of a more electrophilic oxene complex.[17]

Since less nucleophilic olefins such as stilbene and styrene were scarcely oxidized (Table I, runs 8 and 9), the active oxidizing reagent in the epoxidation reaction seems to have an electronic nature. Thianthrene 5-oxide was used as a useful chemical monitor for clarifying the electrophilic character of the oxygen-transfer agent.[18] As expected, the iron oxo species ($Fe^{IV}{=}O(TPFP)^{\bullet+}$) derived from the Fe(TPFP)/PhIO system[17] gave essentially electrophilic attack ($X_{Nu} \sim 0.28$) (Table II, run 6). In the singlet oxygenation of diethyl sulfide in the presence of Fe(TPFP), the 0.68 value of X_{Nu} (run 4) may suggest the intermediacy of both the persulfoxide intermediate ($X_{Nu} \sim 1$) (run 2) and an electrophilic oxidant.

It has been known that cis olefin is significantly more reactive than trans olefin in epoxidation caused by the intermediary high-valency iron oxo species ($Fe^{IV}{=}O(porph^{\bullet+})$) in iron(II) porphyrin/PhIO systems.[19] Thus, *cis*- and *trans*-2-heptene were epoxidized in 23% and 5% yields, respectively.

Moreover, Fe(TPFP) catalyzed the oxygen transfer from the persulfoxide intermediate to anisole-*4-*^2H to yield *p*-methoxyphenol. GC–MS analysis of the resulting *p*-methoxyphenol showed 63% content of deuterium, i.e., 63% of the NIH shift.[20] The marked NIH shift exhibited by this system, similar to those observed with microsomes[21] and iron(III) porphyrin/PhIO[17] systems (Table III), might confirm the intermediacy of $Fe^{IV}{=}O(TPFP)^{\bullet+}$.

Table III. Hydroxylation of Anisole and NIH Shift



oxidant	deuterium retention,[a] %	product ratios *o*	*m*	*p*	*o/p*
microsomes	60[b]	9.1	0	89.9	0.10[c]
Fe(TPFP)/$Et_2S/{}^1O_2$[d]	63	19.4	0	80.6	0.24
Fe(TPFP)/PhIO[e]	72	27.3	0	72.7	0.38
Fe(TPP)/PhIO[e]	60	16.7	0	83.3	0.20
Fenton's reagent	<5[f]	84.0	0	16.0	5.3[g]

[a] Reference 20. [b] Reference 21. [c] Daly, J. W.; Jerina, D. M.; Witkop, B. *Arch. Biochem. Biophys.* **1968**, *128*, 517. [d] The ratio of reactants, sulfide/porphyrin, is 200/1. The reaction was carried out in 3 mL of anisole-*4-*^2H, porphyrin concentration = 2×10^{-3} M. The D content of the starting material is 97%. [e] Reference 17. [f] Jefcoate, C. R. E.; Lindsay Smith, J. R.; Norman, R. O. C. *J. Chem. Soc. B* **1969**, 1013. [g] Norman, R. O. C.; Radda, G. D. *Proc. Chem. Soc.* **1962**, 138.

Consequently, the primary persulfoxide intermediate **1** is likely to transfer an outer oxygen atom to Fe(TPFP) to afford $Fe^{IV}{=}O(TPFP)^{\bullet+}$, which can oxidize olefin and sulfide to epoxide and sulfoxide (Scheme II).

The reactivity for the oxidation by the Fe(TPFP)/PhIO system increased in the expected order cyclooctene $<$ norbornene $\ll$

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(17) Chang, C. K.; Ebina, F. *J. Chem. Soc., Chem. Commun.* **1981**, 778.
(18) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020.
(19) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462.
(20) Kurata, T.; Watanabe, Y.; Katoh, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1988**, *110*, 7472.
(21) Daly, J. W.; Guroff, G.; Jerina, D. M.; Udenfriend, S.; Witkop, B. *Adv. Chem. Ser.* **1968**, *77*, 279.

diethyl sulfide (1:1.3:10). The competition reaction of sulfide and olefin, therefore, resulted in a somewhat low efficiency of epoxidation.

Registry No. TPP, 917-23-7; Fe(TPFP), 36965-71-6; Fe^{IV}(=O)(TPFP), 137364-06-8; Et$_2$S, 352-93-2; Et$_2$SO, 70-29-1; Et$_2$SD$_\infty$, 597-35-3; O$_2$, 7782-44-7; cyclooctene, 931-88-4; norbornene, 498-66-8; *cis*-2-heptene, 6443-92-1; *trans*-2-heptene, 14686-13-6; *cis*-stilbene, 645-49-8; styrene, 100-42-5; cyclooctene oxide, 286-62-4; norbornene oxide, 278-74-0; *cis*-2-heptene oxide, 56052-93-8; *trans*-2-heptene oxide, 56740-07-9; (tetrakis(*p*-anisyl)porphyrinato)iron(III) chloride, 36995-20-7; (tetraphenylporphyrinato)iron(III) chloride, 16456-81-8.

Multiple, Reversible Chlorination of C$_{60}$

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It is of interest to us to explore the potential for oxidative chlorination of fullerenes, a class of compounds where rules of addition have only begun to be developed. We hope to learn how chlorination affects the chemistry of fullerene clusters and to explore substitution reactions on these systems. Fluorinated fullerenes have been reported recently.[1] In this communication we report initial results on reactions of C$_{60}$ with Cl$_2$ under conditions where multiple addition produces species containing 12–15 Cl/C$_{60}$. Chlorine is extracted from these products by thermal, chemical, and electrochemical means, with regeneration of C$_{60}$ in 50–80% isolated yield.

Solid C$_{60}$,[2] exposed to liquid chlorine at its normal boiling point in the absence of light, is converted to chlorinated products which are slightly soluble in the liquid. Quantitative conversions are achieved in about 1 day by passing liquid chlorine continuously over 30–150 mg of C$_{60}$ on a glass filter. The extract is collected and reddish-brown noncrystalline solids are isolated by evaporation of chlorine and drying under vacuum.

Mass spectra have been used to characterize alkylated[6] and fluorinated[1] derivatives of C$_{60}$. Mass spectra of chlorinated C$_{60}$ showed C$_{60}$ and Cl$_2$, but ions from C$_{60}$Cl$_x$ molecules were not detected. However, combustion analyses, IR spectra (ν C–Cl, 850 cm^{-1}, br), and carbon and chlorine binding energies from XPS spectra (Cl 2p 201.2 eV; C 1s 286.1 eV with fwhm of 3.0 eV) are consistent with the presence of species with C–Cl interactions.

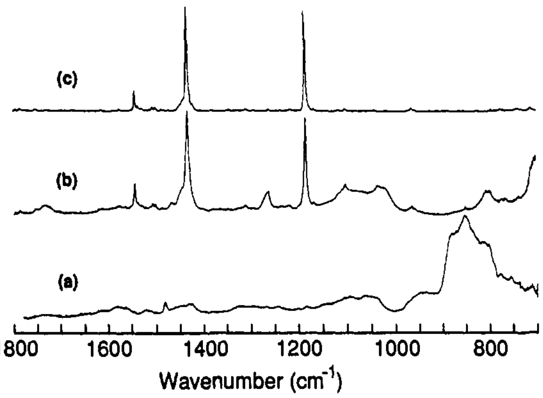

Figure 1. IR spectra: (a) C$_{60}$Cl$_{12.0}$, deposited on KBr from C$_6$H$_6$, at ambient temperature; (b) C$_{60}$Cl$_{12.0}$, after heating 1 h under vacuum at 200 °C; (c) authentic C$_{60}$.

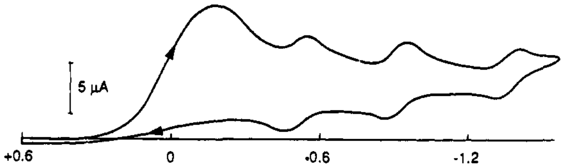

Figure 2. Cyclic voltammogram (Pt button; sweep rate 500 mV/s; Ag/AgCl reference electrode) of 0.5 mM C$_{60}$Cl$_{11.6}$ in dried CH$_2$Cl$_2$ with 0.1 M *n*-Bu$_4$NBF$_4$ (recrystallized from acetone and ether; dried under vacuum at 125 °C). Reduction of Cl$_2$ under these conditions occurs near +0.5 V.

In the absence of detailed information from mass spectra, we sought other means of determining whether chlorination yields products structurally related to C$_{60}$. When C$_{60}$Cl$_{12.0}$[7] was warmed under vacuum in an IR spectrometer, the characteristic four-band pattern of C$_{60}$[8] began to appear as the temperature reached 200 °C (Figure 1), and by 350 °C only C$_{60}$ was detected. On a synthesis scale, C$_{60}$Cl$_{12.0}$, heated under vacuum to 550 °C, released 80% of the chlorine as Cl$_2$, leaving a residue which was purified by passage through alumina using toluene as eluent. The eluted product, characterized as C$_{60}$, was isolated in 50% yield. Reversible addition of phenylthiyl radicals to C$_{60}$ has been reported.[6b]

Triphenylphosphine has been used to dehalogenate polychlorinated aromatics.[9] When toluene solutions of reddish-brown C$_{60}$Cl$_{12.0}$ and PPh$_3$ were combined, the color rapidly changed to reddish. After purification, C$_{60}$ was obtained in 80% yield.

Cyclic voltammetry of C$_{60}$Cl$_{11.6}$ in dichloromethane (Figure 2) on either glassy carbon or Pt working electrodes showed a broad irreversible wave near −0.2 V (vs Ag/AgCl) and three reversible waves characteristic of authentic C$_{60}$.[3b,10] Controlled potential reduction on the cathodic side of the broad wave (at −0.45 V vs Ag wire) consumed electricity (10.6 F/mol) equivalent to that required for conversion of 91% of the Cl in C$_{60}$Cl$_{11.6}$ to Cl$^-$. C$_{60}$ was produced in the electrochemical cell and was isolated in 54% yield.

Information obtained on reactivity of C$_{60}$ with metal complexes[11] and other studies[12] suggest that unsaturation in C$_{60}$ can

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(1) (a) Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III. *J. Am. Chem. Soc.* **1991**, *113*, 5475. (b) Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 966.

(2) Mixed fullerenes were made by evaporating carbon electrodes in an atmosphere of helium.[3] Products were separated by chromatography on alumina using hexanes eluent[4] with exclusion of light and air.[5] Chromatographed C$_{60}$ in benzene was passed through alumina to yield C$_{60}$ which after drying under vacuum contained small amounts of aliphatic hydrocarbon impurities detected by IR (Found: C, 98.68; H, <0.4). Chlorination produced C$_{60}$Cl$_{13.1}$ (Found: C, 60.96; H, <0.3; Cl, 39.4). Similar chlorinated compositions were generated from C$_{60}$ from which hydrocarbon impurities had been removed at 400 °C.[1a]

(3) (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) 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.

(4) (a) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. (b) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.

(5) Taylor, R.; Parsons, J. P.; Avent, A. G.; Rannard, S. P.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *Nature* **1991**, *351*, 277.

(6) (a) Bausch, J. W.; Surya Prakash, G. K.; Olah, G.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3205. (b) 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.

(7) The fractional quantity of Cl emphasizes that this is not a formula but a representation of the average composition derived from elemental analysis.

(8) (a) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. (b) Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Wahab Allaf, A.; Balm, S.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 412.

(9) Ballester, M. In *Advances in Physical Organic Chemistry*; Bethell, D., Ed.; Academic Press: San Diego, 1989; Vol. 25, pp 298–310.

(10) (a) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

0002-7863/91/1513-9900$02.50/0