

stance is consistent with the calculated isotopic composition.

Compound I is assigned an octahedral structure (Figure 1a) consistent with its 14 cage valence electrons (two from each (η^5 -C₅H₅)Co group, two from each BH group, and one from each "extra" H atom), corresponding to a ($2n + 2$)-electron system.^{1,4} The equivalence of the three C₅H₅ and the three BH groups on the NMR time scale is shown in the ¹H and ¹¹B spectra; the lone B-H doublet in the ¹¹B spectrum collapses to a singlet on proton decoupling. The area 2 singlet at τ 24.48 in the proton spectrum is assigned to the "extra" hydrogens which are assumed to undergo rapid tautomeric movement through face-bonding locations on the polyhedral surface. In this respect the molecule resembles its cage-isoelectronic analogue CB₅H₇,⁵ whose face-bridging proton has recently been defined in an electron-diffraction study.⁶

Compound II contains no "extra" hydrogens and thus is a $2n$ -electron system (7 framework atoms and 14 electrons). A capped octahedron is the expected geometry based on the similar case of Os₇(CO)₂₁⁷ and on the general observation⁷⁻⁹ that $2n$ -electron cages adopt capped polyhedral structures. The NMR indications of equivalent (C₅H₅)Co groups, three equivalent BH units, and a unique BH suggest a threefold symmetry axis; such a situation would exist if the unique BH group capped either the B₃ or the Co₃ face on the octahedron. The extremely low field ¹¹B signal of the lone BH unit strongly supports the Co₃-capped geometry shown in Figure 1b.

Compound III is also a $2n$ -electron system and might be expected to exhibit a capped pentagonal bipyramidal structure;⁹ however, the NMR data show that all borons are equivalent, as are all of the (C₅H₅)Co moieties. The dodecahedral *D*_{2d} geometry (Figure 1c) satisfies these observations. Although the $2n + 2$ rule would normally require two additional electrons to stabilize such a geometry, it is quite conceivable that stabilization could be achieved by partial bonding interactions between the formally nonbonded metal atoms 2 and 4, and similarly between 1 and 7. Alternatively, the static structure may be a capped pentagonal bipyramid (Figure 1d) which undergoes fluxional rearrangement in solution by breaking the Co(1)-B(3) bond and forming a Co(4)-B(8) link, thereby producing the dodecahedron (Figure 1c) as a time-averaged geometry. Although several eight-vertex boranes¹⁰ and carboranes^{11,12} have been postulated to undergo fluxional rearrangement in solution, such a process seems less likely for III with its relatively bulky (C₅H₅)Co groups, and we favor the fixed *D*_{2d} structure.

Structures I-III are novel in several respects. Compounds I and III are the first metalloboron cage compounds having as many metal as boron atoms, and III is the first with four metal atoms. Furthermore, II is the only known polyhedral boron cage having an "isolated" boron (bound to no other boron atoms) and is related to the tricobalt-carbon clusters, RCo₃(CO)₉.¹³ Studies of these materials are continuing and we shall present a full report at a later date.

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References and Notes

- (1) (a) K. Wade, *Chem. Br.*, **11**, 177 (1975) and references therein; (b) D. M. P. Mingos, *Nature (London)*, *Phys. Sci.*, **236**, 99 (1972); R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).
- (2) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973).
- (3) The proposed² structure of 2-(η^5 -C₅H₅)CoB₄H₈ has been confirmed by an x-ray diffraction study: L. G. Sneddon, private communication. We thank Professor Sneddon for this information.
- (4) (a) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972); (b) K. Wade, *J. Chem. Soc. D*, 792 (1971).
- (5) (a) T. Onak and J. B. Leach, *Chem. Commun.*, 76 (1971); (b) E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg.*

- Chem.*, **10**, 2770 (1971).
- (6) E. A. McNeill and F. R. Scholer, *Inorg. Chem.*, **14**, 1081 (1975).
- (7) R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, **95**, 3802 (1973).
- (8) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975).
- (9) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, in press.
- (10) (a) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muettterties, *Inorg. Chem.*, **6**, 1271 (1967); (b) E. L. Muettterties, E. L. Hoel, C. G. Salentine, and M. F. Hawthorne, *ibid.*, **14**, 950 (1975).
- (11) H. Hart and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1070 (1968).
- (12) M. L. Thompson and R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
- (13) B. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, **6**, 73 (1973).

Vernon R. Miller, Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Intercalate of Xenon Hexafluoride in Graphite. A Potential Mild Fluorinating Agent of Aromatic Compounds

Sir:

Recent discoveries that several halogen fluorides form intercalation compounds with graphite¹⁻³ prompted us to attempt the preparation of an analogous intercalate with xenon hexafluoride. Xenon hexafluoride does indeed form a spontaneous layer compound with graphite of nominal composition C_{19.1±0.2}XeF₆. The study of such a compound and its formation is of particular interest, because xenon hexafluoride is unique among the 16 known and readily isolable hexafluorides in that it does not possess a regular octahedral structure in the gas phase.⁴⁻⁶ It also possesses many other unusual physical and chemical properties not common to other hexafluorides.⁷ In some respects, though, it resembles the halogen fluorides in its ability to form salts containing either cationic or anionic derivatives of the parent molecule. In spite of the extremely aggressive fluorinating properties of XeF₆, the moderating influence of the graphite makes the intercalate a novel and useful fluorinating agent in aromatic systems.

Weighed quantities of graphite in preweighed Kel-F reaction vessels sealed with Kel-F valves were allowed to react with excess XeF₆.⁸ The XeF₆ was prepared and purified as described previously.⁹ After prolonged contact, the excess XeF₆ was pumped off at room temperature until the reactor contents attained constant weight. No noncondensable gases were released during the reaction other than occasional negligible quantities of xenon gas. Results of numerous experiments showed that the ratio of weight increase to amount of graphite starting material is constant. Assuming that the weight increase is due solely to XeF₆ we obtain a stoichiometry: C_{19.1±0.2}XeF₆, which was supported by chemical analysis. Identical results were obtained with native graphite powder from BDH or with GTA grade Grafoil from the Union Carbide Co. The reaction is accompanied by a change of the original glossy, black appearance of the Grafoil to a mottled dark gray color. Graphite powder assumes a slightly brownish hue upon reaction with XeF₆. X-Ray patterns of the intercalate obtained with copper radiation showed the complete absence of the original strong graphite line at $d = 3.35$ Å, and the appearance of a new pattern containing very broad, diffuse peaks centered at approximately 3.97 and 4.55 Å.

Preliminary wide line ¹⁹F nuclear magnetic resonance spectra of the intercalate at room temperature performed at 15 and 35 MHz reveal the presence of a singlet-doublet

(coupling constant about 0.4 G) centered at about -48 ppm relative to CF_3COOH . The line widths of the peaks (0.1–0.15 G) seem to indicate the presence of fluorine in intercalated molecules capable of translatory motion, but additional inferences about the structure are unwarranted at present.

A thermogravimetric analysis of the intercalate was carried out on a Mettler thermoanalyzer. The compound begins to lose weight slowly around 80° , but rapid weight loss occurs only at 450° and appears to be complete at 575° . Appreciable quantities of CF_4 (24%) and C_2F_6 (12%) were observed in addition to xenon (64%) in a mass spectrometric analysis of the gases collected under vacuum in a separate experiment. Not all the xenon in the original sample was recovered. It was possibly retained in the graphite in the form of an extremely stable "residue compound". The x-ray pattern of the residue gave a very intense peak at $3.48 \text{ \AA}$, indicative of graphite with a slightly expanded lattice. No xenon fluorides were liberated upon heating. It is thus difficult to ascertain whether " $\text{C}_{19}\text{XeF}_6$ " is a true intercalation compound in the same sense as $\text{C}_{8.7}\text{IF}_5$ which again liberates IF_5 upon heating above 80° .^{1,3} On the other hand, the intercalate $\text{C}_{10}\text{AsF}_5$ has been found to liberate both AsF_5 and AsF_3 upon heating, the latter particularly at higher temperatures.¹⁰ It can therefore be expected that a strong fluorinating agent such as XeF_6 would fluorinate graphite at higher temperatures to yield carbon fluorides.

After removal of excess XeF_6 , the intercalate can be easily handled outside the vacuum line and gives off HF only very slowly. Presumably, the intercalated XeF_6 is eventually hydrolyzed to the explosive XeO_3 . Upon standing at room temperature in the open for 1 week, the material neither showed noticeable change nor was shock sensitive. A certain amount of caution is advised, however, in handling the material. This ease of handling may lend it useful and facile fluorination properties in organic chemistry. Indeed, treatment of phenanthrene in dichloromethane solution with 1 mole equiv of the XeF_6 -graphite intercalate at 0 – 25°C under anhydrous conditions in an open system, yielded fluorine substitution and addition products. The ^{19}F NMR spectrum of the crude reaction mixture (after aqueous sodium bicarbonate work-up) contained the following signals:¹¹ δ 194.6 (relative area 13), 152.8 (3), 125.2 (55), 122.4 (6), 118.8 (3), 115.6 (7), 113.3 (3), 110.3 (6), and 107.9 (3). Careful column chromatography on silica gel, petroleum ether (40 – 60°) serving as eluent, afforded 9-fluorophenanthrene as colorless needles, mp 51 – 53° , in 34% yield. It was identified by melting point (lit.¹² 51 – 52°), elemental analysis, mass spectrum, and the ^{19}F NMR spectrum¹¹ (δ 125.2, doublet of doublets (dd), $J_1 = 11.9 \text{ Hz}$, $J_2 = 2.0 \text{ Hz}$; lit.^{13,14} δ 125.3, dd, $J_1 = 11.8 \text{ Hz}$; $J_2 = 2.0 \text{ Hz}$).

The ^{19}F NMR signal at 194.6 (doublet of triplets, $J_1 = 50.1 \text{ Hz}$, $J_2 = 15.6 \text{ Hz}$) is indicative of a fluorine addition product, possibly 9,9,10-trifluoro-9,10-dihydrophenanthrene. This tentative suggestion is consistent with the prominent signal at m/e 234 ($\text{C}_{14}\text{H}_9\text{F}_3^+$) in the mass spectrum of the crude reaction mixture.¹⁵ On the basis of the results outlined above, the xenon hexafluoride-graphite intercalate may become a useful mild fluorinating agent of aromatic systems.

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References and Notes

- (1) A. S. Opalovskii, A. S. Nazarov, A. A. Uminskii, and Yu. V. Chigagov, *Russ. J. Inorg. Chem.*, (Engl. Transl.), **17**, 1227 (1972).
- (2) A. A. Opalovskii, A. S. Nazarov, and A. A. Uminskii, *Russ. J. Inorg. Chem.*, (Engl. Transl.), **17**, 1366 (1972).
- (3) H. Selig and O. Gani, *Inorg. Nucl. Chem. Lett.*, **11**, 75 (1975).

- (4) L. S. Bartell and R. M. Garvin, *J. Chem. Phys.*, **48**, 2460, 2466 (1968).
- (5) H. H. Claassen, G. L. Goodman, and H. Kim, *J. Chem. Phys.*, **56**, 5042 (1972).
- (6) U. Nielsen, R. Haensel, and W. H. E. Schwarz, *J. Chem. Phys.*, **61**, 3581 (1974).
- (7) N. Bartlett and F. O. Sladky in "Comprehensive Inorganic Chemistry", Vol. I, J. C. Bailar, Ed., Pergamon Press, Oxford, 1973, p. 213.
- (8) It is recommended to carry out the reaction between graphite and XeF_6 vapor only. Direct contact of graphite with solid XeF_6 may lead to violent reactions or explosions, accompanied by release of large quantities of xenon gas and carbon fluorides.
- (9) J. G. Malm, F. Schreiner, and D. W. Osborne, *Inorg. Nucl. Chem. Lett.*, **1**, 97 (1965).
- (10) C.-H. Lin, H. Selig, M. Rabinovitz, I. Agranat, and S. Sarig, *Inorg. Nucl. Chem. Lett.*, **11**, 601 (1975).
- (11) The ^{19}F NMR spectra were recorded in dichloromethane at 94.1 MHz. ^{19}F chemical shifts (δ) are reported in ppm, upfield from CCl_3F .
- (12) M. A. Goldberg, E. P. Ordas, and G. Carsch, *J. Am. Chem. Soc.*, **69**, 260 (1947).
- (13) (a) M. J. S. Dewar, R. C. Fahey, and P. J. Grisdale, *Tetrahedron Lett.*, 343 (1963); (b) M. J. S. Dewar and J. Kelemen, *J. Chem. Phys.*, **49**, 499 (1968).
- (14) (a) K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta, Part A*, **23**, 1715 (1967); (b) K. D. Bartle, D. W. Jones, and R. M. Matthews, *Tetrahedron*, **27**, 270 (1969).
- (15) Similar results were obtained in the fluorination of phenanthrene with xenon difluoride. Cf. (a) R. Filler et al., Abstracts, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975, FLUO-13; (b) H. Selig et al., Abstracts, 43rd Annual Meeting of the Israel Chemical Society, Beer Sheva, Oct 1975, p. 144.

Henry Selig,* Mordecai Rabinovitz
Israel Agranat, Chun-Hsu Lin

Institute of Chemistry, Hebrew University
Jerusalem, Israel

Lawrence Ebert

Exxon Corporation
Linden, New Jersey 07036

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Fluorine Control of Regioselectivity in Photocycloaddition Reactions. The Direct Functionalization of Uracil via a Novel 1,4-Fragmentation

Sir:

While photochemical cycloaddition reactions of α,β -unsaturated systems have been extensively employed in organic synthesis,¹ the lack of regioselectivity in additions of simple olefins^{1d,2} detracts from the reaction's general utility. In connection with synthetic studies of nucleic acid bases,³ we encountered the above problem and wish to report here the powerful influence of a fluoro-substituent in controlling regioselectivity. In addition, a novel 1,4-fragmentation reaction has been uncovered which amplifies the utility of 5-fluorouracil as a photochemical synthon for the 5-uracil carbanion.³ Extension of these observations to enone photocycloaddition reactions would offer a rational method for controlling regioselectivity in these systems also.

Regarding regioselectivity, uracil, thymine, and 6-methyluracil show unexceptional behavior in their photocycloaddition reactions to isobutylene (Table I). Thus, the steric effect of the vinylic methyl has little influence on regioselectivity, and the modest preference for the 8,8- vs. the 7,7-dimethyl compound (3.4:1) is reminiscent of that noted for the cyclohexenone-isobutylene system (3.3:1).^{2a} Strikingly, 5-fluorouracil shows complete regioselectivity in its acetone-sensitized reaction with isobutylene (**2**), methylenecyclopentane (**4a**), methylenecyclohexane (**4b**), and methylenecycloheptane (**4c**). In each case only one product was observed by VPC and TLC. This material could be obtained analytically pure in high yield by simple recrystallization.