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 \((C_5H_5)\) group, two from each BH group, and one from each "extra" H atom), corresponding to a \((2n + 2)\)-electron system.\(^6\) The equivalence of the three \(C_5H_5\) 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 \(r = 24.48\) in the proton spectrum is assigned to the "extra" hydrogens which are assumed to undergo rapid tautomer movement through face-bonding locations on the polyhedral surface. In this respect the molecule resembles its cage-isoelectronic analogue \(CB_3H_7\),\(^5\) 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 \(OS_5(\text{CO})_{27}\) and on the general observation\(^7\) that \(2n\)-electron cages adopt capped polyhedral structures. The NMR indications of equivalent \((C_5H_5)Co\) 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 \(B_3\) or the \(Co_3\) face on the octahedron. The extremely low field \(^{11B}\) signal of the lone BH unit strongly supports the \(Co_4\)-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 \((C_5H_5)Co\) 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) that 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 boranes\(^10\) and carbonaboranes\(^11,12\) have been postulated to undergo fluxional rearrangement in solution, such a process seems less likely for III with its relatively bulky \((C_5H_5)Co\) 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, \(RCCo_3(\text{CO})_9\).\(^3\) Studies of these materials are continuing and we shall present a full report at a later date.

Acknowledgment. This work was supported in part by the Office of Naval Research.

References and Notes

(3) The proposed structure of \(2\times(\text{C}_5\text{H}_5)(\text{CO})_2\text{CoB}_3\) has been confirmed by an x-ray diffraction study; L. G. Sneddon, private communication. We thank Professor Sneddon for this information.

Communications to the Editor
Appreciable quantities of CF4 (24%) and C2F6 (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 compound has been found to liberate both xenon and fluorine substitution and addition products. The 19F NMR spectrum of the crude reaction mixture (after aqueous sodium hydroxide treatment) showed a prominent signal at -48 ppm (chemical shift 194.6, J1 = 2.0 Hz; J2 = 11.9 Hz, J1 = 11.8 Hz, J2 = 2.0 Hz). The 19F NMR signal at 194.6 (doublet of triplets, J1 = 50.1 Hz, J2 = 15.6 Hz) is indicative of a fluorine addition product, possibly 9,9,10-trifluoro-9,10-dihydroxenanthrene. This tentative suggestion is consistent with the prominent signal at m/e 234 (C10H12F8+) in the mass spectrum of the crude reaction mixture. On the basis of the results outlined above, the xenon hexafluoride-graphite intercalate may become useful in catalyzing fluorinating reactions.

Acknowledgment. We gratefully acknowledge financial support from the Israel Commission for Basic Research.

References and Notes

8. It is recommended to carry out the reaction between graphite and XeF6 vapor only. Direct contact of graphite with solid XeF6 may lead to violent reactions or explosions, accomplished by release of large quantities of xenon gas and carbon fluorides.
11. The 19F NMR spectra were recorded in dichloromethane at 94.1 MHz. The chemical shifts (δ) are reported in ppm, upfield from CC13F.

Henry Selig, Mordecai Rabinovitz
Israel Agranat, Chun-Hsu Lin
Institute of Chemistry, Hebrew University
Jerusalem, Israel

Lawrence Ebert
Exxon Corporation
Linden, New Jersey 07036
Received September 22, 1975

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, the lack of regioselectivity in additions of simple olefins to double bonds of double bonds occurs at about −48 ppm relative to CF3COOH. 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 °C, but rapid weight loss occurs only at 450 °C and appears to be complete at 575 °C. Appreciable quantities of CF4 (24%) and C2F6 (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 Å, indicative of graphite with a slightly expanded lattice. No xenon fluorides were liberated upon heating. It is thus difficult to ascertain whether "C10XeF6" is a true intercalation compound in the same sense as C8I2F5 which again liberates IF5 upon heating above 800 °C. On the other hand, the intercalate C10AsF5 has been found to liberate both AsF3 and AsF5 upon heating, the latter particularly at higher temperatures. It can therefore be expected that a strong fluorinating agent such as XeF6 would fluorinate graphite at higher temperatures to yield carbon fluorides.

After removal of excess XeF6, the intercalate can be easily handled outside the vacuum line and gives off HF only very slowly. Presumably, the intercalated XeF6 is eventually hydrolyzed to the explosive XeO3. 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 XeF6-graphite intercalate at 0-25 °C under anhydrous conditions in an open system, yielded fluorine substitution and addition products. The 19F NMR spectrum of the crude reaction mixture (after aqueous sodium bicarbonate work-up) contained the following signals: 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 °C) serving as eluent, afforded 9-fluorophenanthrene as colorless needles, mp 51-53 °C, in 34% yield. It was identified by melting point (lit. 51-52 °C), elemental analysis, mass spectrum, and the 19F NMR spectrum (δ 125.2, doublet of doublets (dd), J1 = 11.9 Hz, J2 = 2.0 Hz; lit. 51-52 °C, elemental analysis, mass spectrum, and the 19F NMR spectrum δ 125.3, dd, J1 = 11.8 Hz, J2 = 2.0 Hz). The 19F NMR signal at 194.6 (doublet of triplets, J1 = 50.1 Hz, J2 = 15.6 Hz) is indicative of a fluorine addition product, possibly 9,9,10-trifluoro-9,10-dihydroxenanthrene. This tentative suggestion is consistent with the prominent signal at m/e 234 (C10H12F8+) in the mass spectrum of the crude reaction mixture. On the basis of the results outlined above, the xenon hexafluoride-graphite intercalate may become a useful mild fluorinating agent of aromatic systems.

Acknowledgment. We gratefully acknowledge financial support from the Israel Commission for Basic Research.

References and Notes

8. It is recommended to carry out the reaction between graphite and XeF6 vapor only. Direct contact of graphite with solid XeF6 may lead to violent reactions or explosions, accomplished by release of large quantities of xenon gas and carbon fluorides.