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1,6-DISUBSTITUTED TRIPTYCENES

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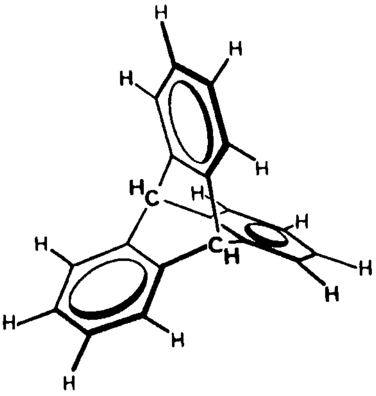
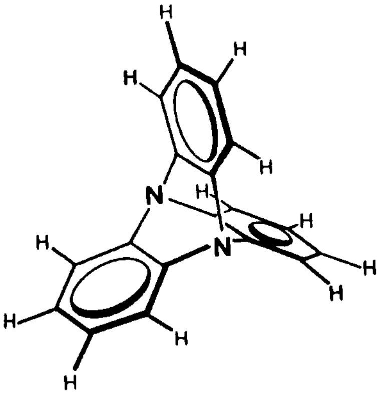
I. Introduction

In comparison with the vast number of known organic compounds, carbon forms few fully three-dimensional "cage" molecules, some common exceptions being cubane, adamantane, and triptycene. By applying the isostructural principle, chemists have built up an imposing array of adamantanes substituted with a variety of other nontransition elements, but until recently triptycene has strongly resisted most attempts to tinker with its structure in this way.

The 1,6-, or bridgehead, carbon atoms in the beautifully symmetric molecule (**I**) can theoretically be substituted with any elements capable of (roughly) tetrahedral coordination, the most likely candidates being in Groups III, IV, V, and VI of the periodic table (see Fig. 1). The problem of their study is almost entirely one of synthesis, not stability. Although the first member of the series, 1,6-diazatriptycene (**II**), was apparently synthesized more than 100 years ago, (*1*) progress has been slow because only the 1,-6-diarsatriptycene skeleton can be built up in a stepwise fashion from stable intermediates (*2*). Special techniques must be devised for the other triptycenes and thus far, with one exception, only Group V derivatives have been synthesized.



(I)



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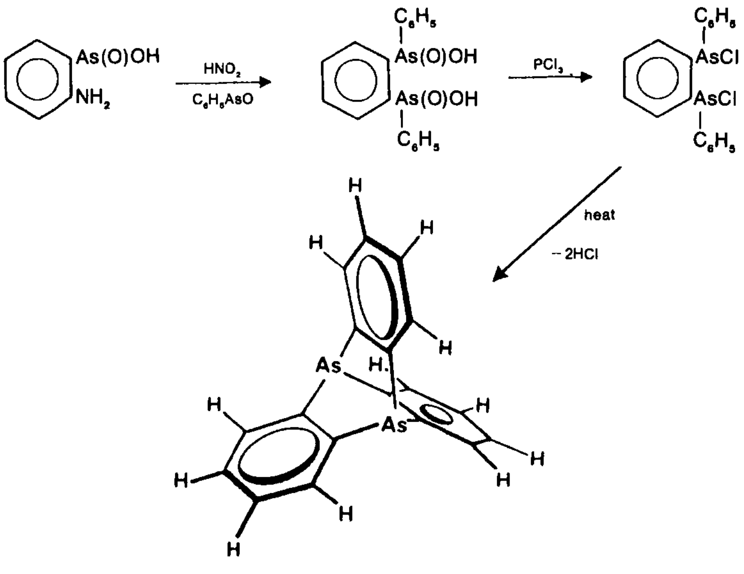


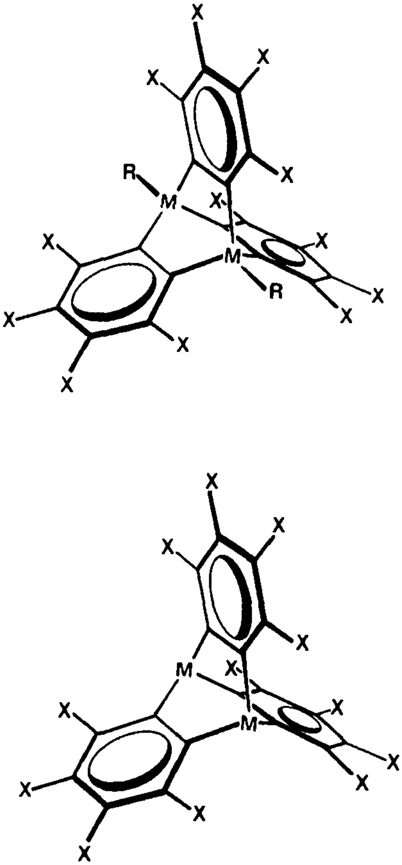
II. Synthesis

The simple method of direct synthesis in a heated, sealed tube is applicable to the more thermally stable triptycenes:

$$1,2\text{-}X_2C_6H_4 + M \longrightarrow M_2(C_6H_4)_3 \qquad M = P, X = Cl\ (3);\ M = As, X = I\ (4)$$

$$1,2\text{-}I_2C_6F_4 + M \longrightarrow M_2(C_6F_4)_3 \qquad M = P\ (4), As\ (4, 5), Sb\ (4\text{–}7), Bi\ (8)$$

$$1,2\text{-}I_2C_6Cl_4 + M \longrightarrow M_2(C_6Cl_4)_3 \qquad M = As\ (9), Sb\ (6, 9), Bi\ (9)$$



Group III: M = B, Al, Ga, In, Tl
R = Lewis base

Group IV: M = Si, Ge, Sn, Pb
R = alkyl, aryl, H

Group VI: M = Se?, Te
R = alkyl, aryl

Group V: M = N, P, As, Sb, Bi

FIG. 1. Some of the theoretically possible disubstituted triptycenes. The X groups may or may not all be identical; in the triptycenes known at the present time they are usually hydrogen, fluorine, or chlorine.

but the method fails for thermally fragile species such as $Sb_2(C_6H_4)_3$ and $Bi_2(C_6H_4)_3$. However, by utilizing the known stabilizing effect of fluorine substituents on the aromatic rings, a "mixed" direct synthesis showed that 1,6-distibatriptycenes carrying C_6H_4 groups were possible (*5*) (Fig. 2):

$$1,2\text{-}I_2C_6F_4 + 1,2\text{-}I_2C_6H_4 + Sb \longrightarrow$$
$$Sb_2(C_6F_4)_3 + Sb_2(C_6F_4)_2(C_6H_4) + Sb_2(C_6F_4)(C_6H_4)_2$$

It was only after some years of further research that $Sb_2(C_6H_4)_3$ was

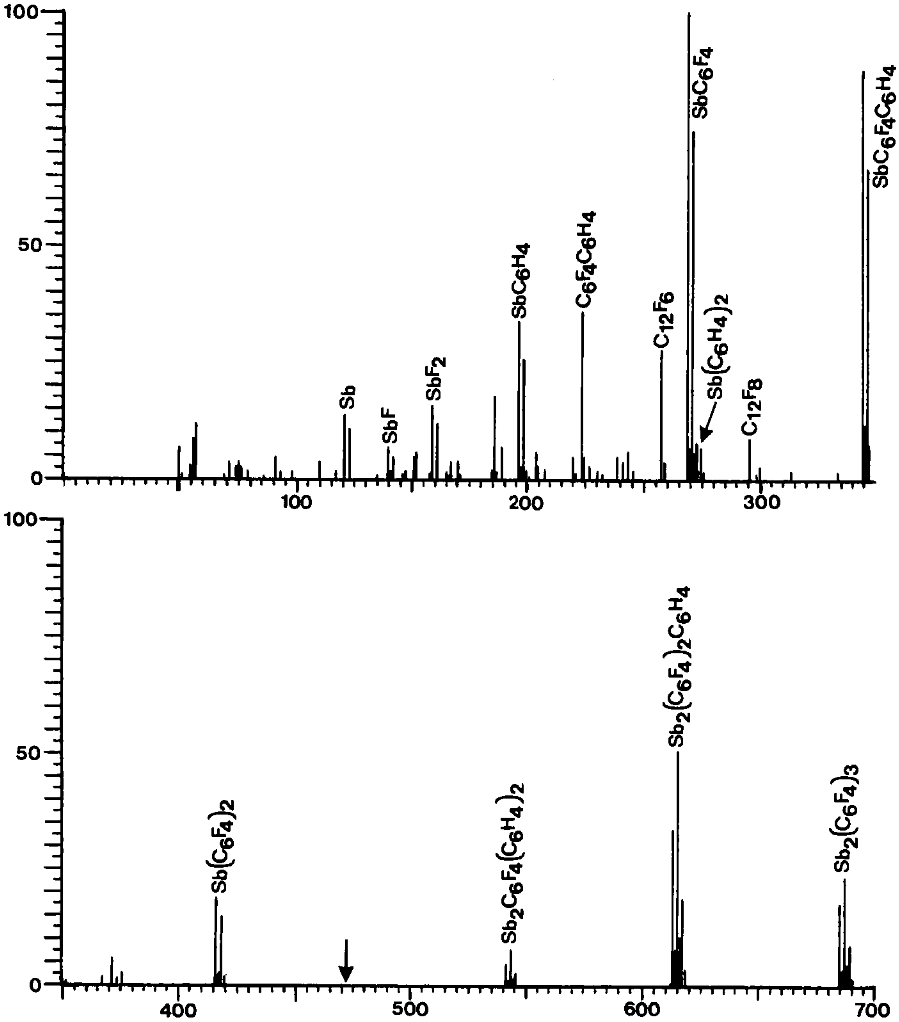
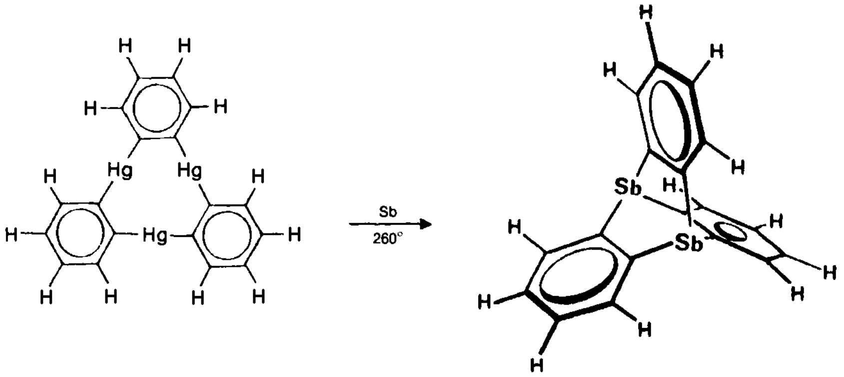
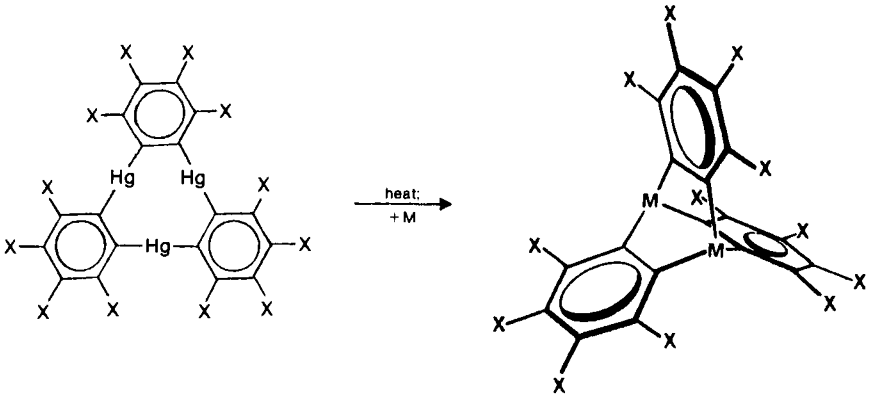


FIG. 2. Mass spectrum of the products formed by heating antimony with a mixture of 1,2-$I_2C_6H_4$ and 1,2-$I_2C_6F_4$. Note the absolute lack of $Sb_2(C_6H_4)_3$ at 472 mass units even though the mixed H/F species $Sb_2(C_6F_4)_2C_6H_4$ and $Sb_2(C_6F_4)(C_6H_4)_2$ are well in evidence.

finally synthesized, albeit in very low yield, by heating an intimate mixture of *ortho*-phenylenemercury with finely powdered antimony (*9, 10*):



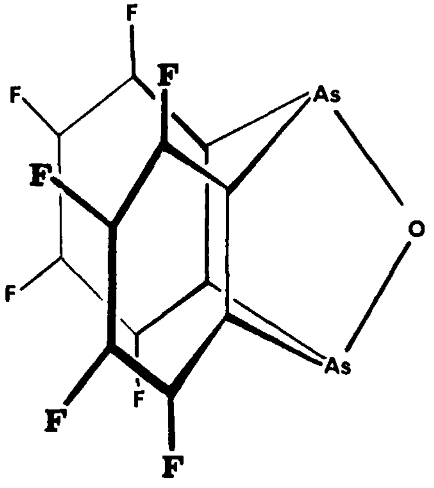
This transmetallation method also gave (*9*) $Bi_2(C_6H_4)_3$, but only in amounts analyzable by infrared and mass spectrometry. These low yields result from a simultaneous thermal decomposition which occurs during synthesis—both compounds are stable indefinitely in air at room temperature. Transmetallations with perfluoro- and perchlorophenylenemercury give much better yields of the very thermally stable perhalotriptycenes:



M = As, Sb; X = F

M = As, Sb, Bi; X = Cl

During the formation of $As_2(C_6F_4)_3$ via either direct synthesis or transmetallation, virtually unavoidable oxide impurities in the arsenic produce small amounts of a substance having a parent ion $As_2C_{12}F_8O^+$ in its mass spectrum (Fig. 3). Fractional crystallization and an X-ray study showed (*11*) this compound to be the epoxide $OAs_2(C_6F_4)_2$ (III). Although the above two methods of synthesis can give yields of up to 60% in some cases, they are obviously restricted to the 1,6-disubstituted



(III)

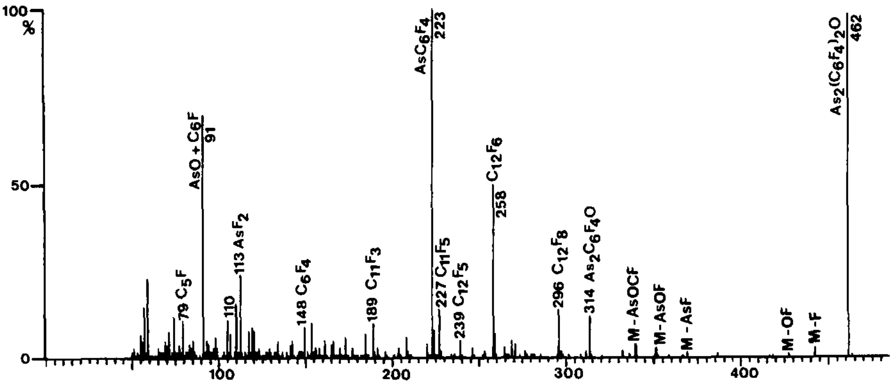
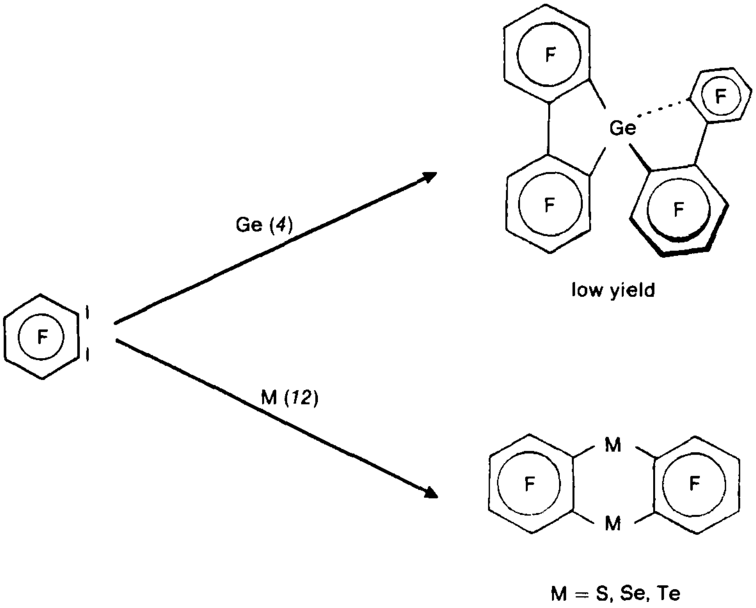


FIG. 3. Mass spectrum of the impurity, $OAs_2(C_6F_4)_2$, occurring in $As_2(C_6F_4)_3$ made by heating arsenic (containing traces of As_2O_3) with 1,2-diiodotetrafluorobenzene.

triptycenes of P, As, Sb, and Bi; the only possible variation is that of "mixed direct synthesis" typified by $AsSb(C_6F_4)_3$ (see Fig. 4), but problems then arise from separation of three products formed simultaneously. The lack of a suitable substituent with which the bridgehead atoms can satisfy their stereochemical needs results in a different type of product when direct synthesis is attempted with Group IV or VI elements (*4, 12*):



Cullen and Wu (*13*) have shown one way out of the preparative dilemma by demonstrating the use of a 1,2-dilithiobenzene derivative to make Group V triptycenes:

$$1,2\text{-}I_2C_6F_4 + 2MeLi \longrightarrow 1,2\text{-}Li_2C_6F_4 + 2MCl_3 \longrightarrow$$
$$M_2(C_6F_4)_3 \qquad M = As, Sb, Bi$$

Such dilithium reagents should make available many of the triptycenes suggested in Fig. 1, but the recent withdrawal of (the very expensive) 1,2-diiodotetrafluorobenzene from commercial catalogs is regrettable. Unfortunately, 1,2-dilithiobenzene cannot be prepared from the reaction of 1,2-dihalobenzenes with either lithium or alkyllithium reagents due to the exceedingly rapid formation of "benzyne"

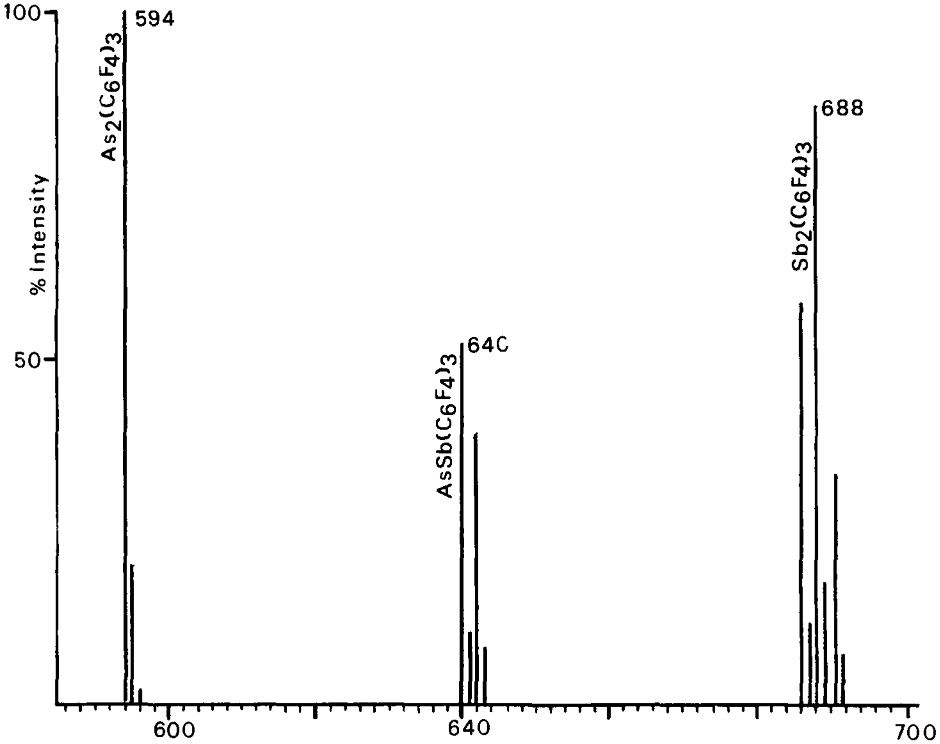


FIG. 4. Molecular ions of the three products formed in a "mixed" direct synthesis using Sb and As and 1,2-$I_2C_6F_4$.

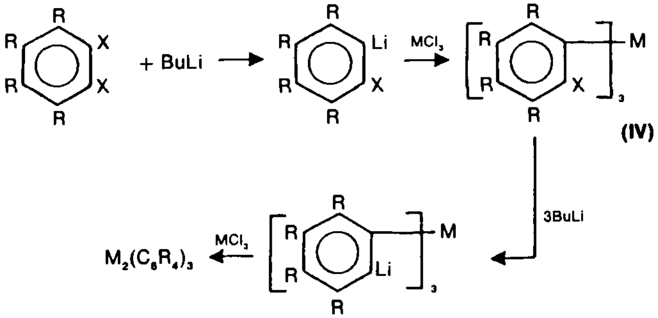
even at low temperatures; it has been synthesized from *ortho*-phenylenemercury via transmetallation (*14*):

$$(C_6H_4Hg)_3 + 6Li \longrightarrow 3Hg + 3Li_2C_6H_4$$

The present relative inaccessibility of the mercurial (*15*) is a major problem to even gram-scale reactions. A cheaper and simple synthesis of *ortho*-phenylenemercury starting from benzene is currently under investigation in the author's laboratory:

$$\begin{tikzcd}
C_6H_6 + Hg(O_2CMe)_2 \arrow[r] & C_6H_5Hg(O_2CMe) \arrow[r] & \underset{\text{(mainly ortho)}}{C_6H_4(HgO_2CMe)_2} \arrow[dl, "NaCl"] \\
(C_6H_4Hg)_3 & C_6H_4(HgCl)_2 \arrow[l, "KI"'] &
\end{tikzcd}$$

Failing the ready availability of the key 1,2-dilithiobenzenes, the following stepwise buildup of the triptycene skeleton might be considered:

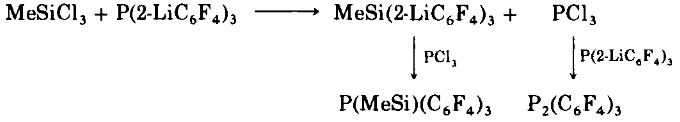


Such a synthesis has been achieved (*16*) when R = F and X = Br but, although very high yields of the intermediate (**IV**) are obtained, the final coupling to the triptycenes occurs in only about 2–4% yield. When R = H, benzyne formation is rapid during the attempted formation of 2-lithiohalobenzene; by starting with 2-chloroiodobenzene and stabilizing the intermediate lithium reagent with tetramethylethylenediamine we have obtained $M(2\text{-}ClC_6H_4)_3$ derivatives in yields approaching 90% (*17*). Unfortunately, these chloro species give only complex mixtures when treated with butyllithium and MCl_3, possibly because Li–Cl exchange does not readily occur; attempts to make the more amenable $M(2\text{-}BrC_6H_4)_3$ in the same manner have failed. Notwithstanding the low final yields obtained when R = F, the above stepwise reaction allows the formation both of triptycenes substituted by other than Group V elements and of "mixed" triptycenes (*16*)

$$(2\text{-}LiC_6F_4)_3SiMe + MeSiCl_3 \longrightarrow 3LiCl + (MeSi)_2(C_6F_4)_3$$

$$(2\text{-}LiC_6F_4)_3M + M'Cl_3 \longrightarrow 3LiCl + MM'(C_6F_4)_3$$

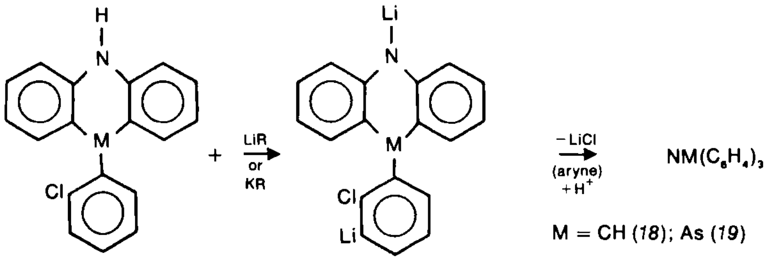
Care has to be taken when carrying out mixed reactions because transmetallation can occur in some instances. When $P(2\text{-}LiC_6F_4)_3$ is treated with $MeSiCl_3$, two triptycenes can be detected in the products using mass spectrometry (*8*): $P_2(C_6F_4)_3$ and $P(MeSi)(C_6F_4)_3$. The diphosphatriptycene apparently arises from the intermediate formation of some phosphorus trichloride:



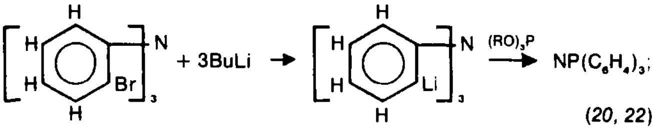
$$\begin{array}{ccccc} \mathrm{MeSiCl_3 + P(2\text{-}LiC_6F_4)_3} & \longrightarrow & \mathrm{MeSi(2\text{-}LiC_6F_4)_3} & + & \mathrm{PCl_3} \\ & & \Big\downarrow{\scriptstyle \mathrm{PCl_3}} & & \Big\downarrow{\scriptstyle \mathrm{P(2\text{-}LiC_6F_4)_3}} \\ & & \mathrm{P(MeSi)(C_6F_4)_3} & & \mathrm{P_2(C_6F_4)_3} \end{array}$$

The addition sequence is thus important and $MeSi(2\text{-}LiC_6F_4)_3$ must be added to PCl_3 in order to achieve the formation of pure $P(MeSi)(C_6F_4)_3$. The occurrence of $As_2(C_6F_4)_3$ and $Sb_2(C_6F_4)_3$ in the reactions of $Sb(2\text{-}LiC_6F_4)_3$ with $AsCl_3$ and of $Sb(2\text{-}LiC_6F_4)_3$ with $MeSiCl_3$, respectively, is presumably due to similar transmetallations.

The inherent high stability of aromatic nitrogen derivatives and their extensive range of possible substitution reactions has allowed two approaches to the synthesis of "mixed" azatriptycenes denied to the other Group V elements:



M = CH (*18*); As (*19*)



(*20, 22*)

(multistage synthesis)

Perhaps a simpler route to tris(2-bromophenyl)amine would be to start directly from triphenylamine; bromination (*21*) of the latter occurs in two stages, giving first tris(4-bromophenyl)amine and then tris(2,4-dibromophyenyl)amine in yields of about 90%. Removal of the *para*-bromide atoms should occur readily and quantitatively with butyllithium:

$$\begin{tikzcd}
N(C_6H_5)_3 + 3Br_2 \arrow[r] & (4\text{-}BrC_6H_4)_3N \arrow[r, "3Br_2"] & (2,4\text{-}Br_2C_6H_3)_3N \arrow[dl, "3BuLi"] \\
(2\text{-}BrC_6H_4)_3N & (2\text{-}Br,4\text{-}LiC_6H_3)_3N \arrow[l, "H_2O"'] &
\end{tikzcd}$$

Hellwinkel (*22*) ingeniously removed the problem of para bromination by starting with tris(4-methylphenyl)amine, which exclusively brominates in the required three ortho positions. Unfortunately, although ortho dimetallation occurs when diphenylamine is treated with alkyllithium reagents, triphenylamine is lithiated in the meta positions (*23*) presumably due to the steric effects; the triphenyls of other Group V elements cleave when reacted with LiR derivatives.

III. Molecular Structure of Substituted Triptycenes

Dreiding models depict triptycenes as totally rigid systems, but several 1- and mixed 1,6-derivatives (as well as triptycene) show considerable distortion from their expected threefold symmetry. In fact, the molecules appear to behave as three rigid benzenoid rings *flexibly* connected to the bridgehead atoms (*24*). The observed distortions in the crystalline state occur both as slight displacements of the bridgehead atoms from the planes of the aromatic rings and as varying angles between the three rings (Table I). It is thought likely that most, if not

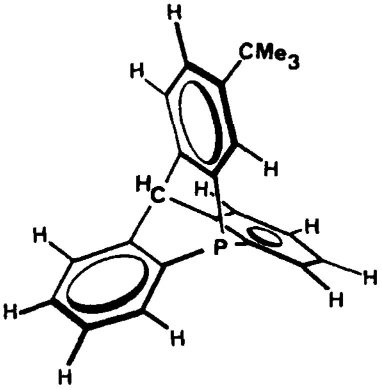
TABLE I

DISTANCES OF THE BRIDGEHEAD ATOMS FROM THE PLANES OF THE BENZENE RINGS, AND ANGLES BETWEEN THE BENZENE RINGS (*25, 26*)

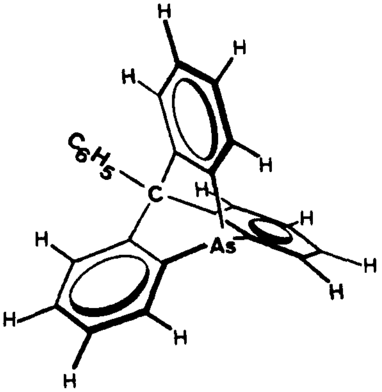
		Distance (Å) of bridgehead atoms from benzene plane			Angles (degrees) between the benzene rings		
Triptycene		Ring 1	Ring 2	Ring 3	(1)–(2)	(1)–(3)	(2)–(3)
(V)	P	0.023	0.040	0.029	119.4	122.5	118.0
	C	0.093	0.003	0.005	—	—	—
$P_2(C_6H_4)_3$	P	0.071	0.093	0.003	114.3	123.3	124.3
	P	0.093	0.071	0.003	—	—	—
(VII)	P	0.017	0.030	0.037	122.3	123.4	114.3
	N	0.034	0.122	0.078	—	—	—
(VII)	P	0.017	0.089	0.009	120.9	120.2	118.9
	N	0.005	0.047	0.052	—	—	—
$As(CH)(C_6H_4)_3$	—	—	—	—	115	122	122
$P(CH)(C_6H_4)_3$	—	—	—	—	115	121	124

all, of the distortion in these molecules is caused by asymmetric crystal forces (*24*). Structural studies (*25*) on $P(CH)(C_6H_4)_3$ and $As(CH)(C_6H_4)_3$ were made difficult because of orientational disorder in the crystals; by destroying their molecular symmetry with ring (*26*) or bridgehead (*24*) substituents the possibility of similar orientational disorder was removed, thus allowing much more precise details of the heterocycles (V) and (VI) to be obtained. Crystal disorder has so far frustrated our efforts to solve the structures of $Sb_2(C_6F_4)_3$ and $Bi_2(C_6F_4)_3$; a further problem with X-ray studies on the perfluorotriptycenes is that they form relatively unstable hemisolvates with all the common solvents (*6*) and hence unsolvated crystals have to be grown by sublimation.

An unusual structural feature, occurring in all the triptycenes so

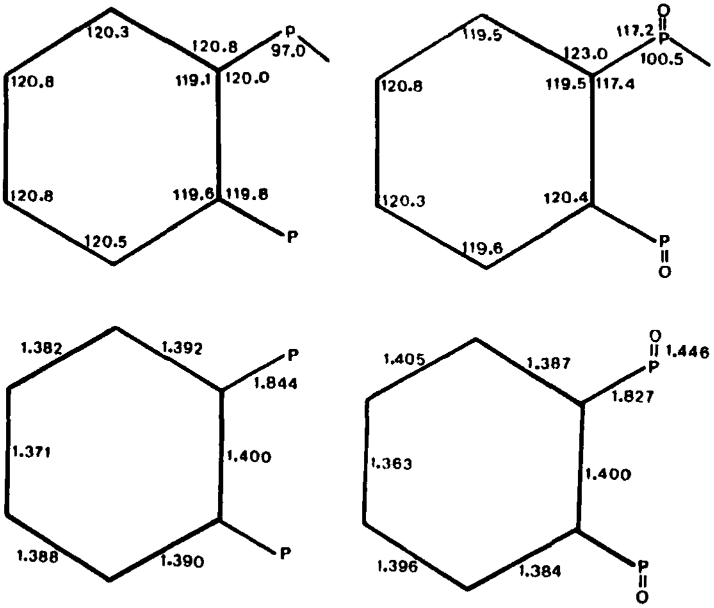


(V)



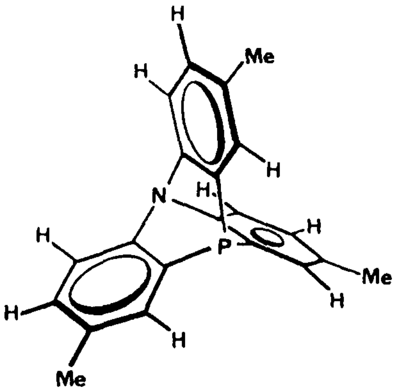
(VI)

far studied, is that the "inner" C–C bonds of the aromatic rings are longer than the "outer" bonds. For example, in $P_2(C_6H_4)_3$ (*27*) and $(OP)_2(C_6H_4)_3$ (*27*) the main parameters are as follows:

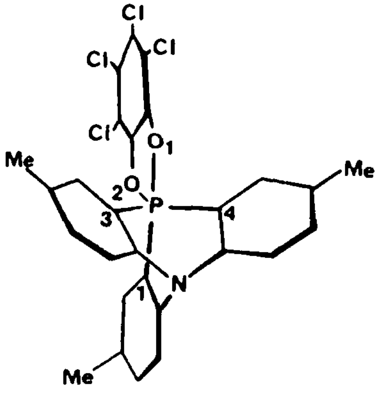


The changes in C–C bond lengths are obviously not associated with distortions in the ring bond angles [as they appear to be in biphenylenes (*28*), for example] and remain to be satisfactorily explained. The P═O bond is considerably shorter than that in Me_3PO (1.479 Å), where the CPC angle is 106.0°, and this is thought (*27*) to be due to the higher *s* character of this bond in the triptycene oxide; an increase in *s* character of the P–C bonds in $(OP)_2(C_6H_4)_3$ relative to $P_2(C_6H_4)_3$ may also account for the observed shortening of this bond.

To investigate the effect of further distortions in the $M(C{-}C)_3M$ cage, the structure of the trimethyl-substituted phosphaazatriptycene (VII) has been elucidated (*29*). Not unnaturally, nitrogen tries to adopt CNC angles (107.0° average) close to the tetrahedral value which reduces the CPC angle to 93.3°. Contrary to the *s* character arguments mentioned above for diphosphatriptycene and its oxide, the P–C bond in (VII) is surprisingly short at 1.823 Å; the mean N–C distance is 1.460 Å.



(VII)



(VIII)

The reaction between (VII) and *ortho*-tetrachloroquinone produced a chelate complex with the phosphorus (*30*), thus raising the intriguing question as to the possible geometry about that atom. Somewhat unexpectedly, an X-ray structural analysis of the complex showed that the whole system distorted in an attempt to generate trigonal bipyramidal coordination about the phosphorus (*30*) (VIII):

1. Angles C(3)PC(4), O(2)PC(3), and O(2)PC(4) are 100.8°, 134.2°, and 124.9°
2. Angles O(1)PC(3), O(2)PO(1), and O(1)PC(4) are 89.0°, 86.2°, and 91.9
3. Angle O(1)PC(1) is 172.9°

Notwithstanding these steric changes at phosphorus, the nitrogen atom still manages to retain CNC angles close to the tetrahedral value (105.4°, 108.2°, and 110.6°). The inner C–C bonds appear to be larger than the outer ring bonds but the difference in this molecule is close to the confidence limit of 3σ. Only one quaternary triptycene has so far been studied crystallographically: $[(CH_3As)(CH)(C_6H_4)_3]^+Cl^- \cdot H_2O$ (*31*). Relative to (VI) the CAsC angles have opened up to an average value of 97.7° [91.5° in (VI)] as would be expected; the decrease of the As–C distance from 1.948 Å in (VI) to 1.905 Å in the chloride could thus be a reflection of the increased *s* character in these bonds on quaternization. There is virtually no deviation from threefold symmetry of the aromatic rings relative to the bridgehead atoms, the ring planes making angles with each other of 120.4°, 120.4°, and 119.3°.

IV. Mass Spectra

Triptycene is very stable under electron impact and both the doubly and triply charged molecular ions are present in the mass spectrum. The substituted derivatives $NP(C_6H_4)_3$ (*22*), $NAs(C_6H_4)_3$ (*19*), $P_2(C_6H_4)_3$ (*3*), $P_2(C_6F_4)_3$ (*8*), and $As_2(C_6F_4)_3$ (*8*) behave similarly (although the triply charged parent ion of the latter has not yet been observed). As the atomic weight of the bridgehead atoms increases, the stability falls and no doubly charged molecular ions can be detected in the spectra of $Sb_2(C_6F_4)_3$ and $Bi_2(C_6F_4)_3$; indeed, even the molecular ion of perfluorodibismuthatriptycene is of low intensity (~3% relative to the base ion, Bi^+). The ion $C_{12}H_8^+$, presumably ionized biphenylene, is prominent in the $M_2(C_6H_4)_3$ spectra (*8, 32*), with the peak due to $C_{18}H_{12}^+$ becoming more intense as M changes from P to Bi; Fig. 5 shows

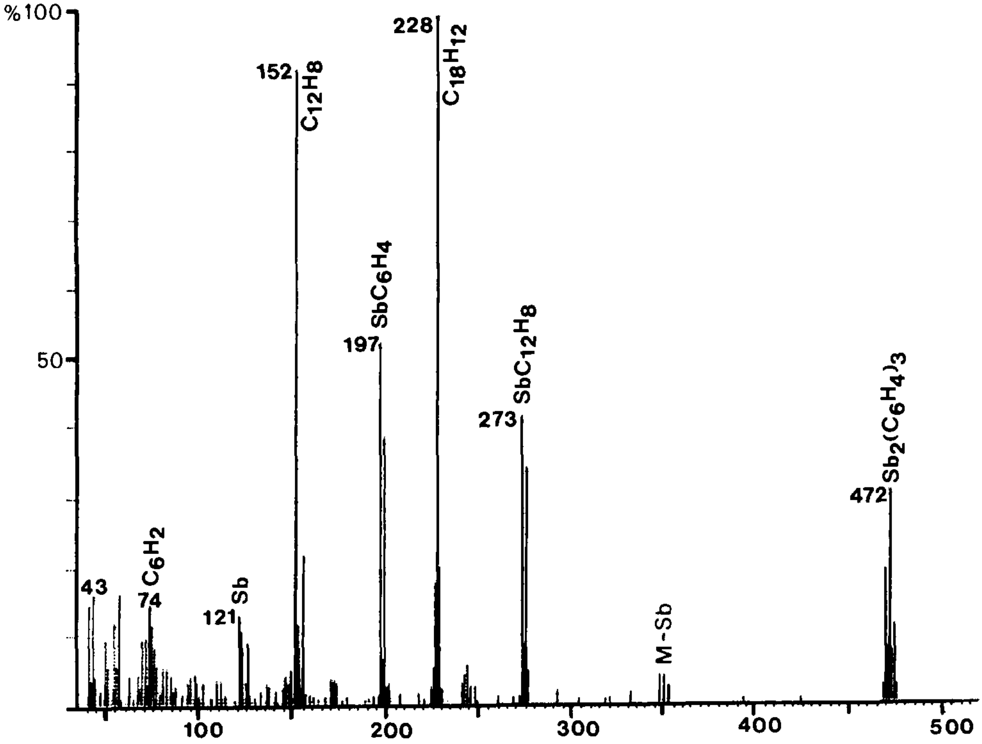
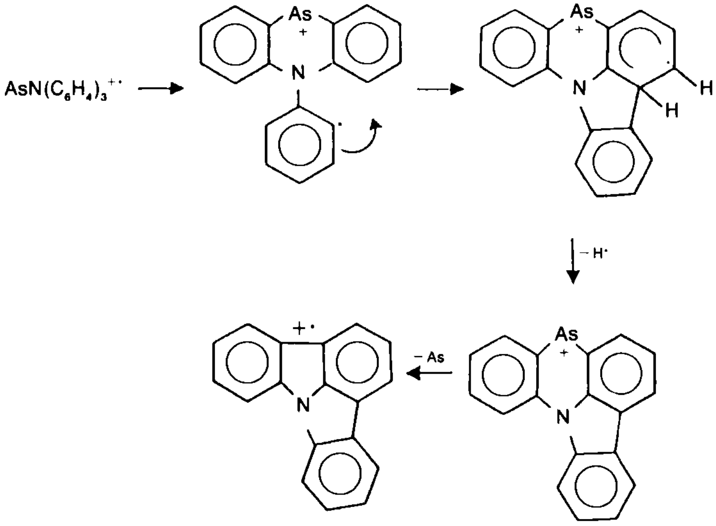


FIG. 5. Mass spectrum of 1,6-distibatriptycene showing the typical fragmentation pattern of $M_2(C_6H_4)_3$ species.

the mass spectrum of $Sb_2(C_6H_4)_3$ as a typical member of those species not containing nitrogen.

Triptycene, $C_{20}H_{14}$, in addition to showing an intense parent ion (100%) in its mass spectrum, readily loses one, or two, hydrogen atoms to give $C_{20}H_{13}^+$ (100%) or $C_{20}H_{12}^+$ (50%). Unexpectedly, deuteration studies revealed that these hydrogen atoms are lost from the aromatic rings, not from the bridgehead carbons. Similarly, the base peak in the spectrum of arsaazatriptycene is $(M - 1)^+$; the hydrogen atom in this case can only arise from one of the aromatic rings (*19*). When either carbon or nitrogen is present in bridgehead positions of a triptycene, facile rearrangement reactions involving multicyclic ring systems can occur to give fragment ions which have no analogs for elements outside the $n = 2$ shell of the periodic table. For example, the rearrangement involved in the formation of the $(M - 1)^+$ ion of $AsN(C_6H_4)_3$ probably proceeds via initial rupture of a carbon–arsenic bond (*19*):



Although flourine-migration reactions can occur, the three main M-containing ions in the mass spectra of perfluorotriptycenes containing Group V elements are directly analogous to those (*3, 8, 32*) in the hydrogen series: $M_2(C_4X_4)_3^+$, $M(C_6X_4)_2^+$, and $MC_6X_4^+$. A typical spectrum is shown in Fig. 6a for $Sb_2(C_6F_4)_3$, whereas Table II lists the detected meta-stable transitions. For comparison, the spectra of

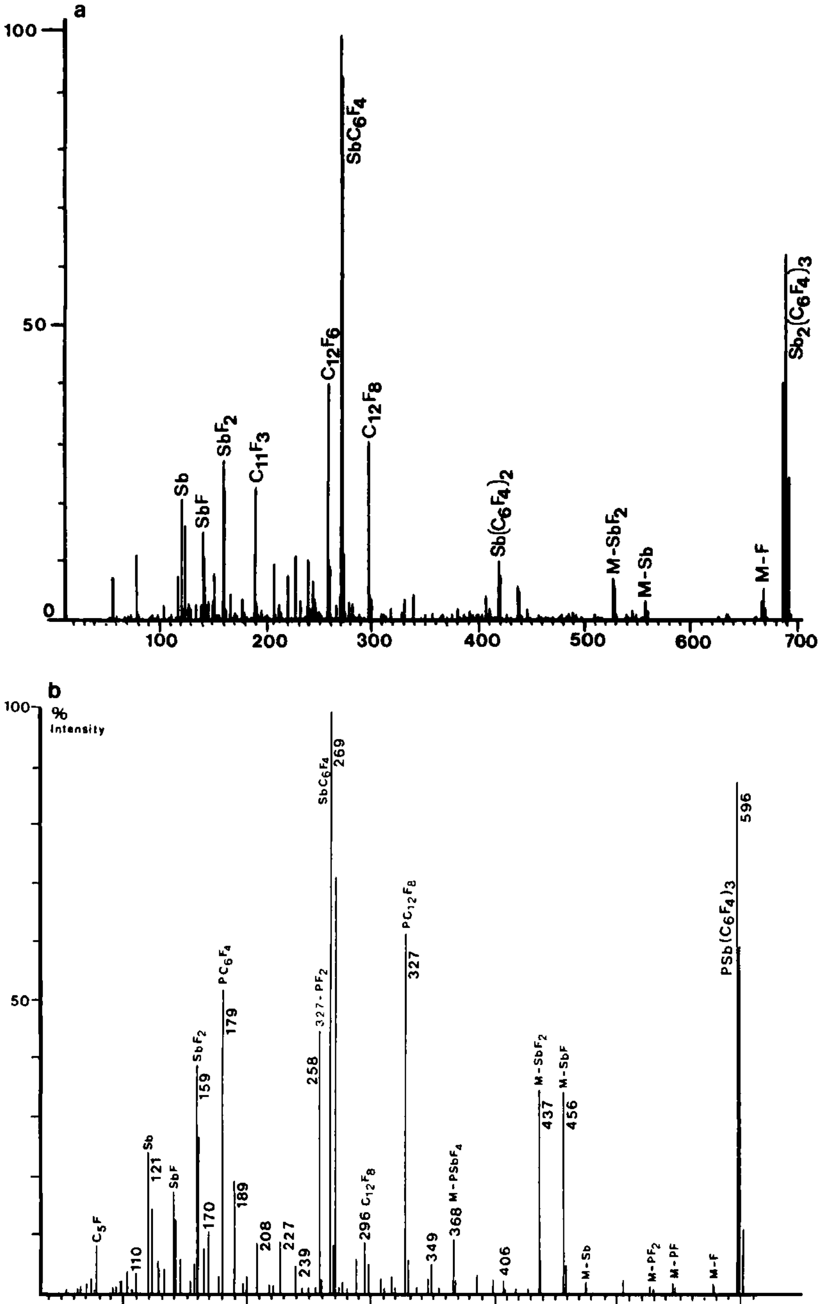


FIG. 6. (a) Mass spectrum of perfluorodistibatriptycene. (b) Mass spectrum of perfluorophosphastibatriptycene. (c) Mass spectrum of $(CH_3Si)_2(C_6F_4)_3$. (d) Mass spectrum of perchlorodistibatriptycene.

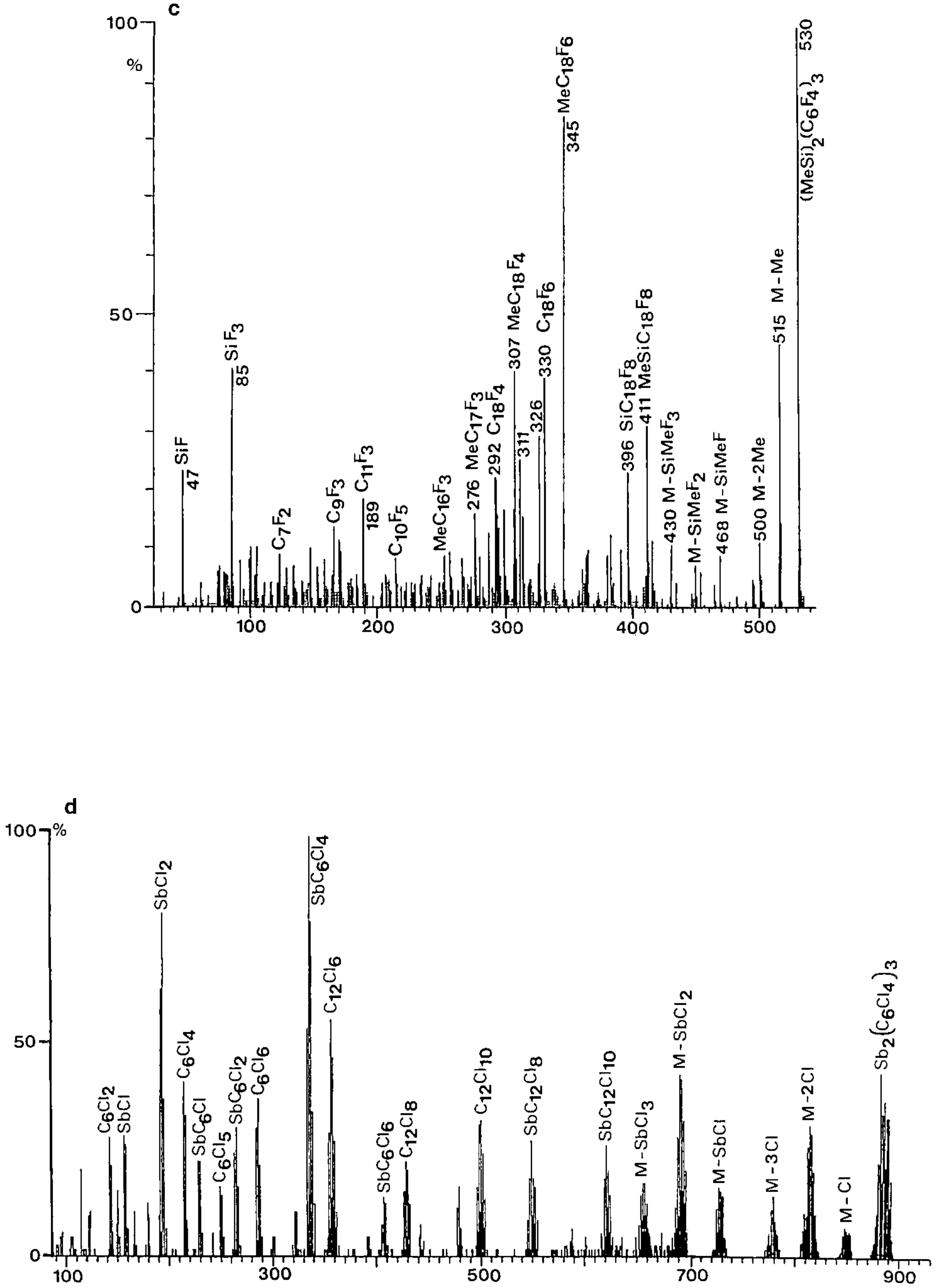


FIG. 6c and d. See legend on p. 17.

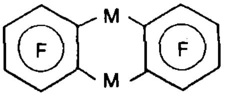
TABLE II

META-STABLE TRANSITIONS OCCURRING IN THE MASS SPECTRUM OF DODECAFLUORODISTIBATRIPTYCENE, $Sb_2(C_6F_4)_3$

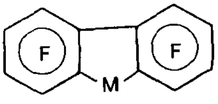
$Sb_2(C_6F_4)_3^+ \rightarrow SbC_6F_4^+ + Sb(C_6F_4)_2$	(very strong)
$SbC_{18}F_{10}^+ \rightarrow C_{18}F_{10}^+ + Sb$	
(i.e., M-SbF_2)	
$SbC_{18}F_{10}^+ \rightarrow C_{18}F_8^+ + SbF_2$	
$Sb(C_6F_4)_2^+ \rightarrow C_{12}F_6^+ + SbF_2$	(very strong)
$Sb(C_6F_4)_2^+ \rightarrow C_{12}F_8^+ + Sb$	
$SbC_6F_4^+ \rightarrow SbC_6F_2^+ + F_2$	
$SbC_6F_4^+ \rightarrow Sb^+ + C_6F_4$	(two peaks at 54.5 and 55.8)
$SbC_6F_4^+ \rightarrow SbF_2^+ + C_6F_2$	(two peaks at 94.0 and 95.6)
$C_{12}F_6^+ \rightarrow C_{12}F_5^+ + F$	
$C_{12}F_6^+ \rightarrow C_{11}F_4^+ + CF_2$	
$C_{12}F_6^+ \rightarrow C_{11}F_3^+ + CF_3$	
$C_{12}F_5^+ \rightarrow C_{11}F_3^+ + CF_2$	
$C_{12}F_4^+ \rightarrow C_{11}F_2^+ + CF_2$	
$C_{11}F_2^+ \rightarrow C_{11}F^+ + F$	

a "mixed" triptycene, $PSb(C_6F_4)_3$, and the Group IV derivative, $(MeSi)_2(C_6F_4)_3$, are shown in Figs. 6b and 6c, respectively.

Fluorine-radical loss from the parent ions is relatively unimportant as shown by the very low intensities of $(P - F)^+$ ions. A more important mechanism of fluorine loss appears to be via migration to a bridgehead atom followed by loss of MF or MF_2; a study of the "mixed" triptycenes shows that such abstractions occur more readily for antimony than for either phosphorus or arsenic. The parent ion can also lose one aromatic ring to give (IX), but a more favorable fragmentation is the loss of MC_6F_4 to yield (X). In this latter process it is found that the C_6F_4 group

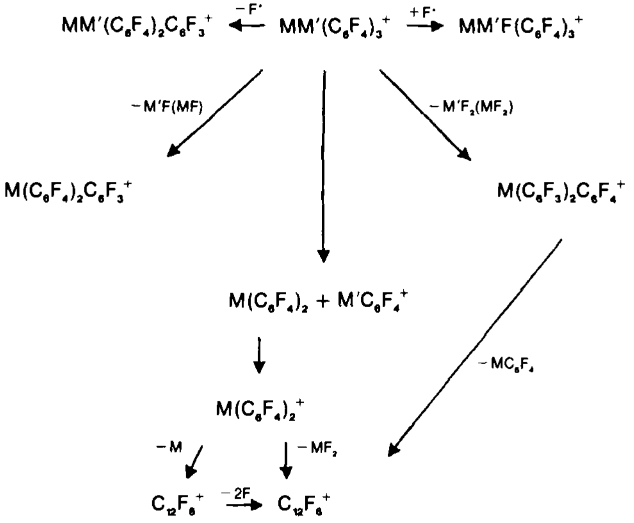


(IX)



(X)

remains with the heavier element in spectra of $MM'(C_6F_4)_3$ mixed species. Very similar spectra, but with slightly differing ion intensities, are obtained under fast-atom bombardment (FAB) conditions using sulfolane as the matrix solvent; the general scheme shown below has recently been suggested for the main fragmentation processes occurring in the FAB spectra of the perfluorotriptycenes (*33*):



Proof of the correct assignment of a molecular ion can, of course, be obtained from high-resolution mass measurements. In the case of $Sb_2(C_6F_4)_3$ a cross-check can be made by measuring the intensities of the isotopomeric species in the molecular ion cluster and comparing them with the calculated values for a $C_{18}Sb_2$ moiety containing ^{12}C, ^{13}C, ^{121}Sb, and ^{123}Sb isotopes (see Fig. 7). The method is only accurate to about 1% but the very characteristic pattern of C_xSb^+ and $C_ySb_2^+$ ion clusters nevertheless makes a useful visual aid when scanning the spectrum of a compound for the first time; for example, the presence of antimony in two of the three molecular ions shown in Fig. 4 is immediately apparent. It is not possible to use the comparative-intensity technique of Fig. 7 for a hydrogen-containing ion such as $Sb_2(C_6H_4)_3^+$ because fragmentation via loss of one or more hydrogen atoms can occur and will interfere with the intensity measurements; even so, the basic underlying pattern for two antimony atoms in the molecular ion cluster of $Sb_2(C_6H_4)_3$ is still obvious in Fig. 5.

The mass spectrum (Fig. 6d) of a perchlorotriptycene such as $Sb_2(C_6Cl_4)_3$ is exceedingly complex in appearance due to both the large number of fragment ions resulting from the relative weakness of the carbon–chlorine bonds and the isotopomeric ion clusters arising from the occurrence of two chlorine isotopes, ^{35}Cl and ^{37}Cl. Chlorine

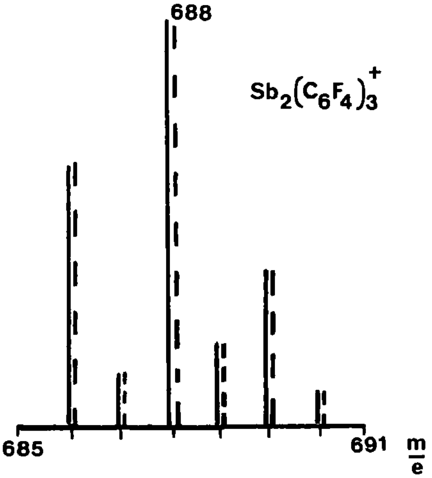


FIG. 7. Comparison of observed (solid line) and calculated (dashed line) peak intensity values for an ion cluster $Sb_2C_{18}F_{12}^+$.

migration reactions are common, shown by the presence of several "chlorine-rich" ions such as $C_{12}Cl_{10}^+$, $C_6Cl_6^+$, $C_6Cl_5^+$, and $SbC_{12}Cl_{10}^+$; furthermore, the antimony-containing species $SbC_6Cl_6^+$, $SbC_6Cl_2^+$, and SbC_6Cl^+ are present and have no counterparts in the spectra of the hydrogen and fluorine analogs. The molecular ion $Sb_2(C_6Cl_4)_3^+$ consists of 741 possible isotopomeric species, the sheer number of which makes selection of a single ion for accurate mass measurement very difficult. In cases like this the technique illustrated for a simple case in Fig. 7 becomes more useful; a good fit between the observed and computer-calculated peak intensities at each mass number under low resolution (when many of the isotopomeric peaks will overlap) may be taken as strong proof of identity for the chosen ion cluster.

V. Nuclear Magnetic Resonance Spectra

^1H or ^{19}F NMR spectra of the symmetrical triptycenes $M_2(C_6H_4)_3$ and $M_2(C_6F_4)_3$ can be considered as approximating to AA'XX' systems if it is assumed that there is no inter-ring coupling. When M is phosphorus, however, the situation is more complex due to the spin of $\frac{1}{2}$ possessed by the ^{31}P nucleus resulting in the presence of 16,384 (i.e., 2^{14}) theoretically possible energy levels for $P_2(C_6H_4)_3$ and $P_2(C_6F_4)_3$, because each contains 14 nuclei with $I = \frac{1}{2}$. Even though the high symmetry possessed by the $P_2(C_6H_4)_3$ molecule greatly simplifies the system, its proton NMR spectrum is too complex to be analyzed in the absence of ^{31}P decoupling. By treating the decoupled spectrum as an AA′XX′ system the coupling constants obtained (*3*) were $|J_{AA'}|$, $|J_{XX'}| = 7.4$, 0.4 Hz; $J_{AX} = \pm 7.4$ Hz and $J_{AX'} = \pm 1.2$ Hz, with the two resonances occurring at 7.94 and 7.21 ppm. The ^{31}P chemical shift of 43 ppm (upfield from an 85% H_3PO_4 external standard), and those of $PN(C_6H_4)_3$ (70–80 ppm) and $(CH)P(C_6H_4)_3$ (65 ppm), are thought (*3, 22, 34*) to reflect changes in the CPC angles as the opposite bridgehead atom is changed, the relationship being expressed by the following equation (*22*):

$$\delta(^{31}\mathrm{P}) = 4406.84 - 953.79 \ln(\text{angle CPC})$$

Similarly, a linear plot is obtained when the ^{13}C chemical shifts of the bridgehead carbon atoms are compared with the C–C(bridgehead)–C angle for four triptycenes (*22*). Thus by calculating CPC and C–C(bridgehead)–C angles in a variety of as yet unknown triptycenes, Hellwinkel (*22*) has been able to predict their ^{31}P and ^{13}C(bridgehead) chemical shifts.

A detailed, simultaneous analysis (*35*) of the proton-decoupled ^{13}C NMR spectrum and of the ^{13}C satellites in the proton-decoupled ^{31}P spectrum has allowed all the ^{31}P–^{31}P and ^{13}C–^{31}P coupling constants in 1,6-diphosphatriptycene to be evaluated (Table III). The large C(2)–P(1) coupling and small C(1)–P(6) coupling are considered to be strongly dependent on the orientation of the phosphorus lone-pair electrons and

TABLE III

^{13}C Chemical Shifts, ^{31}P–^{31}P and ^{13}C–^{31}P Coupling Constants in $P_2(C_6H_4)_3$(*35*)

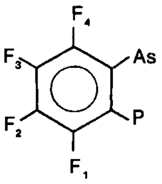
	From ^{13}C spectrum	From ^{13}C and ^{31}P spectra
δ(C1)	145.32 ppm (TMS)	—
δ(C2)	134.42	—
δ(C3)	128.24	—
$\|^3J(\mathrm{P1, P6})\|$	24.5 ± 0.5 Hz	24.2 ± 0.1 Hz
^1J(C1, P1)	-7.6 ± 2.0	—
^2J(C1, P6)	-3.9 ∓ 2.0	—
^2J(C2, P1)	$+44.1 \pm 0.6$	44.4 ± 0.15
^3J(C2, P6)	$+1.8 \mp 0.6$	$+1.4 \mp 0.15$
^3J(C3, P1)	$+12.5 \pm 2.0$	$+13.8 \pm 0.5$
^4J(C3, P6)	-0.1 ∓ 2.0	-1.4 ∓ 0.5

therefore, because of the rigid shape of the triptycene skeleton, these values represent the two extremes (i.e., the largest and the smallest, respectively) for two-bond $^{13}C-^{31}P$ coupling constants in aromatic phosphines.

The AA′ and XX′ components of the ^{19}F NMR spectrum of $Sb_2(C_6F_4)_3$ are shown in Fig. 8. The origin of the observed 10 lines in each component was decided upon using both the consistency in the derivation of L and the signs of the coupling constants, which were adjusted to be identical to those in similar compounds (*36*). The analysis, which assumed there was no F–F coupling between the rings, gave $J_{AA'} = +15.4$ Hz, $J_{XX'} = -17.5$ Hz, $J_{AX} = -22.2$ Hz, and $J_{AX'} = +5.0$ Hz; the similar magnitude of $J_{AA'}$ and $J_{XX'}$ arises from the low value of K (-2.08 Hz). The para $J_{AA'}$ coupling is considerably larger than that found in 1,2-dihalotetrafluorobenzenes [e.g., +7.9 Hz in 1,2-$Br_2C_6F_4$(*36*)], but such couplings can range from about +5 to +18 Hz in other polyfluoro aromatic derivatives (*36*). In the spectrum of $Bi_2(C_6F_4)_3$, peaks 5 and 6 (7 and 8) merge so that within the experimental error $K = 0$ Hz and hence $J_{AA'}$ and $J_{XX'}$ have identical magnitude: $J_{AA'} = +17.3$ Hz, $J_{XX'} = -17.3$ Hz, $J_{AX} = -24.6$ Hz, and $J_{AX'} = +3.2$ Hz. (The estimated error in these various coupling constants is ±0.3 Hz.)

The AA′ component in the ^{19}F spectrum of $(MeSi)_2(C_6F_4)_3$ presumably has the shape shown in Fig. 9 due to additional H–F coupling; as would be expected from this, complex splitting of the methyl resonance is observed in the proton spectrum. The ^{19}F NMR spectrum of $P_2(C_6F_4)_3$ exhibits a symmetrical doublet in the AA′ component due to phosphorus–fluorine coupling, each half of the doublet being identical to the XX′ component; $J_{^{31}P-^{19}F} = 60.2$ Hz.

In spectra of mixed triptycenes, $MM'(C_6F_4)_3$, the expected four ^{19}F resonances are observed for the two "*ortho*" and two "*meta*" fluorine atoms; Fig. 10a shows the spectrum of $PSb(C_6F_4)_3$ together with the magnitude of the coupling constants determined by assuming that the system is approximately first order. The resonance due to F(1) in the spectrum of $PAs(C_6F_4)_3$ is split into a doublet by F–P coupling,



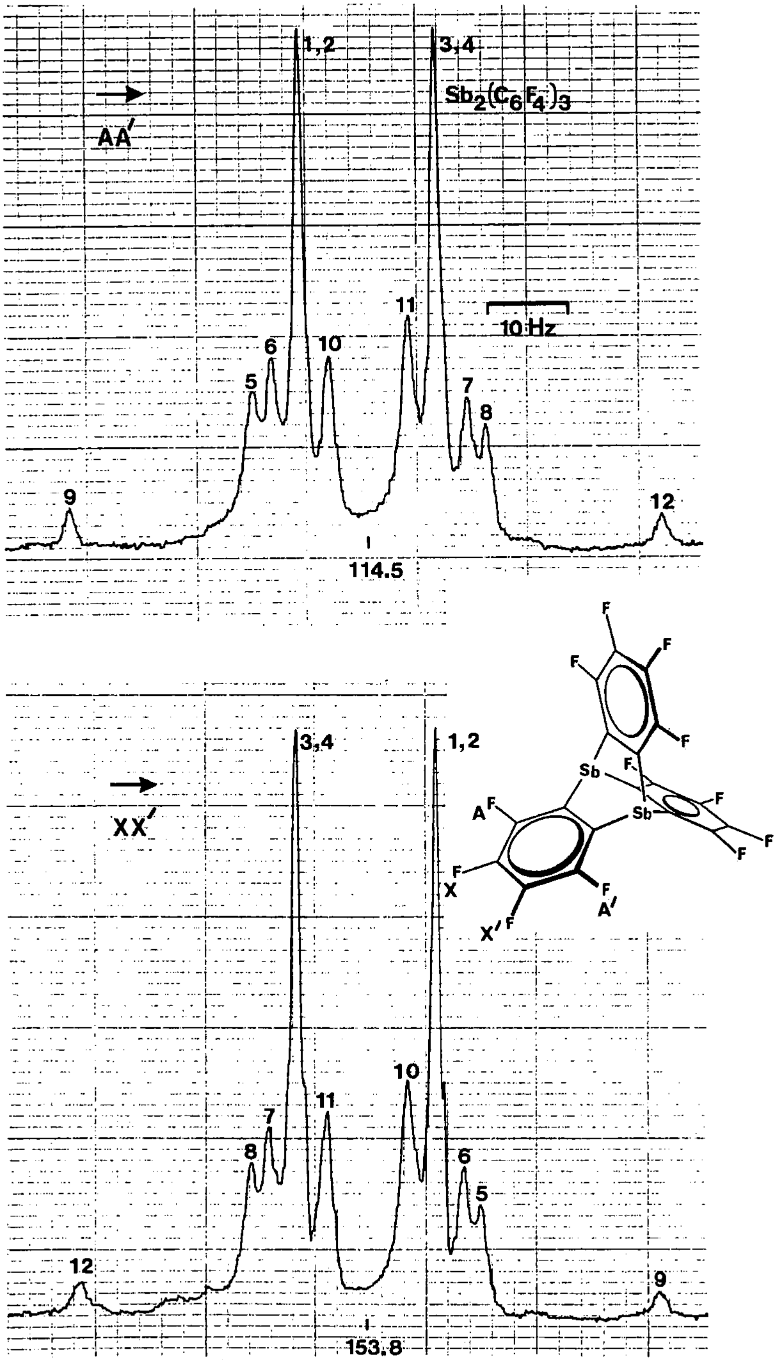


Fig. 8. The AA′ and XX′ components in the ^{19}F NMR spectrum of Sb$_2$(C$_6$F$_4$)$_3$.

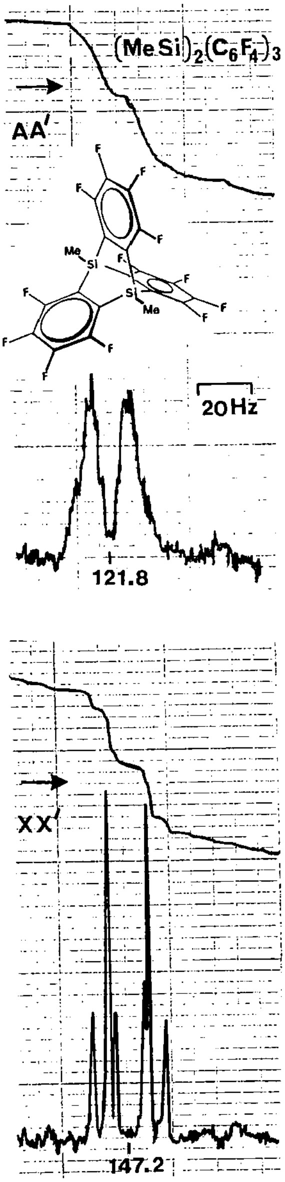


FIG. 9. The low-field (AA′) and high-field (XX′) components in the ^{19}F NMR spectrum of (MeSi)$_2$(C$_6$F$_4$)$_3$ showing the effects of proton coupling on the appearance of the AA′ peaks.

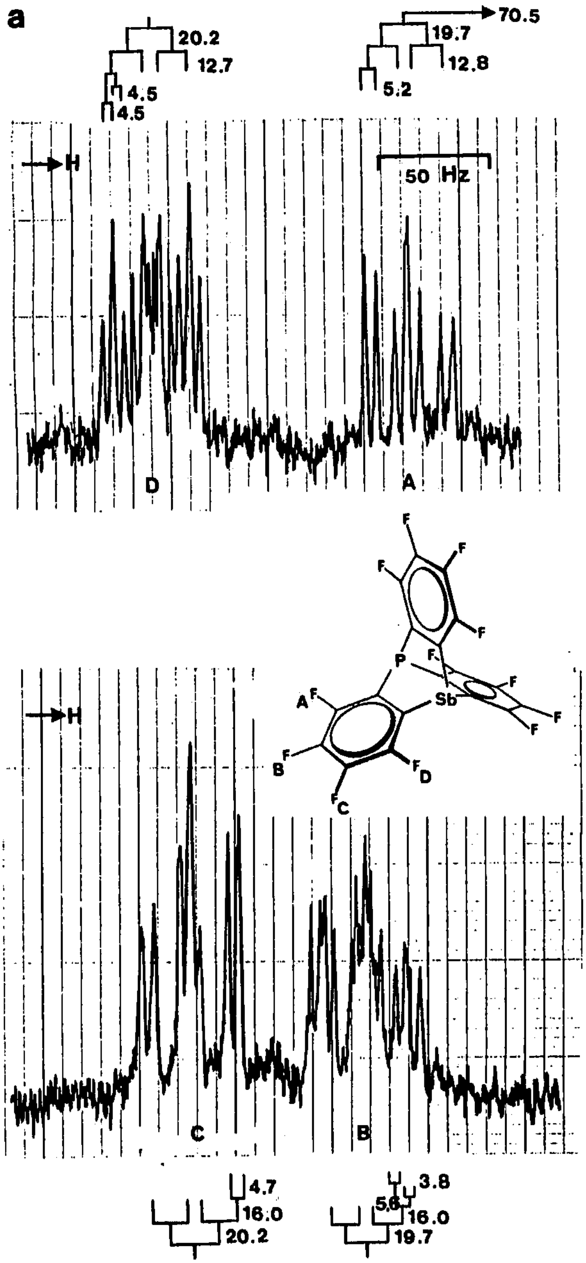


FIG. 10. (a) The four goups of lines in the ^{19}F NMR spectrum of perfluorophosphastibatriptycene showing the coupling constants derived by first-order analysis. Only one-half of the A doublet is shown; phosphorus–fluorine coupling is observable on all peaks except those due to the C fluorine atoms. (b) The four groups of lines in the ^{19}F NMR spectrum of perfluorphospharasatriptycene. The low-field half of the doublet arising from the A fluorine atoms lies under the D group.

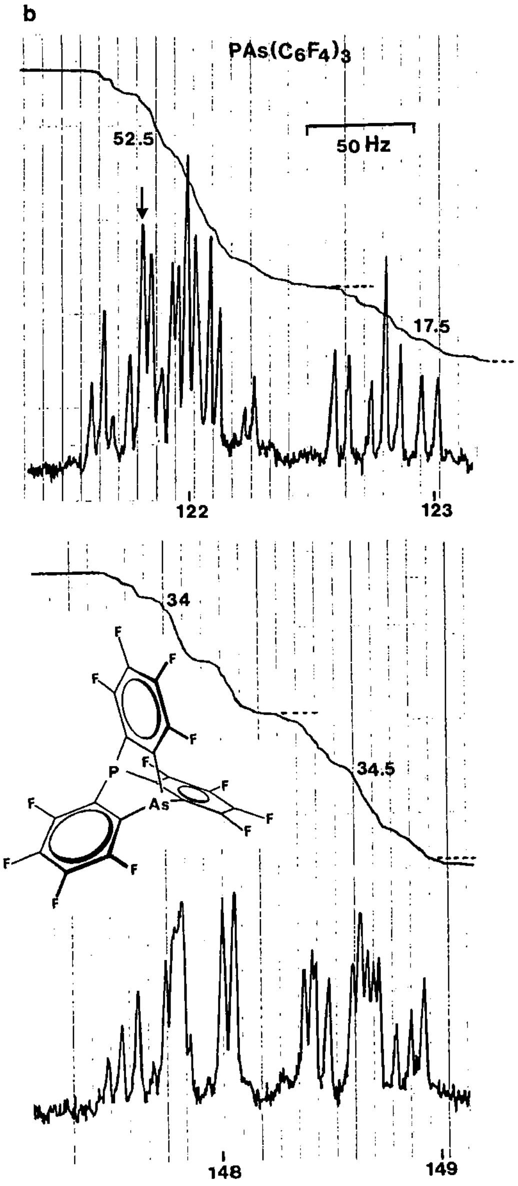
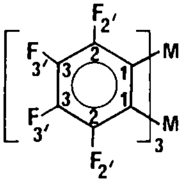


FIG. 10b.

one-half of which lies under the F(4) peak as shown by the intensity data marked on the spectrum (Fig. 10b). Although this spectrum partially resembles that of $PSb(C_6F_4)_3$, it is definitely more second order and has not been analyzed except for the F(1) resonance, which was treated as first order to give $J_{1-2} = (-)23.5$ Hz, $J_{1-4} = (+)16.5$ Hz, $J_{1-3} = \pm 6.1$ Hz, and $J_{F-P} = 110.0$ Hz. (The signs are inferred from the knowledge (*36*) that ortho couplings are always negative and para couplings are always positive, whereas meta couplings can be either sign in polyfluoroaromatic compounds.)

Symmetrical $M_2(C_6F_4)_3$ triptycenes show three ^{13}C resonances for the C_1, C_2, and C_3 types of carbon atom, the chemical shift of C_1 being



particularly sensitive to the identity of M, unlike those of C_2 and C_3 (Table IV). A fourth peak occurs in the proton-decoupled ^{13}C spectrum of $(MeSi)_2(C_6F_4)_3$ due to the methyl carbon atoms; this latter resonance has the form of a symmetrical septet which arises from $^{13}C-^{19}F$ coupling to the six F_2 fluorine atoms (see Figs. 11a and 11b). Due to the

TABLE IV

^{13}C NMR DATA FOR SOME TRIPTYCENES

		$Sb_2(C_6F_4)_3$	$Bi_2(C_6F_4)_3$	$(MeSi)_2(C_6F_4)_3$	$P_2(C_6H_4)_3$	$P_2(C_6F_4)_3$[a]
Chemical shift	C(1)	129.7	157.2	121.9	145.32	—
relative to TMS	C(2)	151.1	150.8	151.6	134.42	150.4
	C(3)	141.0	140.2	140.9	128.24	138.6
	C(4)	—	—	−4.8	—	—
Solvent		$(CD_3)_2CO$	$(CD_3)_2CO$	$CDCl_3$	CS_2-$(CD_3)_2CO$	
Doublet splitting[b] on		C(2) 235	C(2) 234	C(2) 244	—	
peaks due to $^{13}C-^{19}F$		C(3) 244	C(3) 246	C(3) 250	—	
coupling (Hz)						

[a] Calculated shifts using the substitution parameters given in J. D. Memory and N. K. Wilson, "NMR of Aromatic Compounds," Wiley, New York, 1982.

[b] Splitting measured as the distance between the two largest peaks in each doublet.

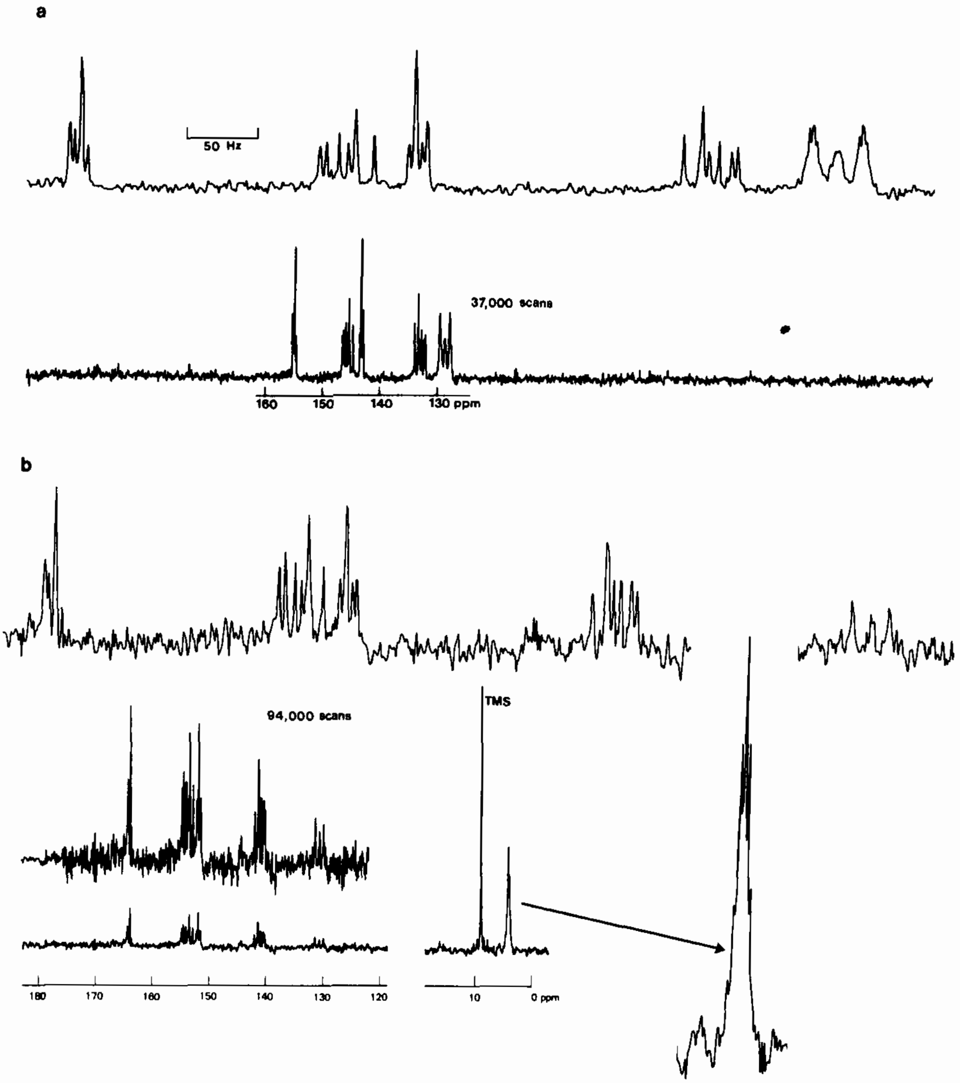


FIG. 11. (a) ^{13}C NMR spectrum of perfluorodistibatriptycene, $Sb_2(C_6F_4)_3$. (b) ^{13}C NMR spectrum of $(MeSi)_2(C_6F_4)_3$.

high symmetry of the molecule these fluorines act as a six-particle set, the observed splitting being the mean value of the individual coupling constants for the two components of the set in the $A_3A'_3X$ system. Since the value of $J_{A'-X}$ is probably very close to zero, J_{A-X} will simply be equal to half the observed splitting in the septet, ~1.2 Hz.

VI. Ultraviolet and Infrared Spectra

Triptycene shows two bands at 270 (log *e* = 3.54) and 278 nm (log *e* = 3.66) with a shoulder at 264 nm (log *e* ≅ 3.3); steadily increasing absorption, not plotted (*18*) below 330 nm (log *e* ≅ 3.8), is also present.

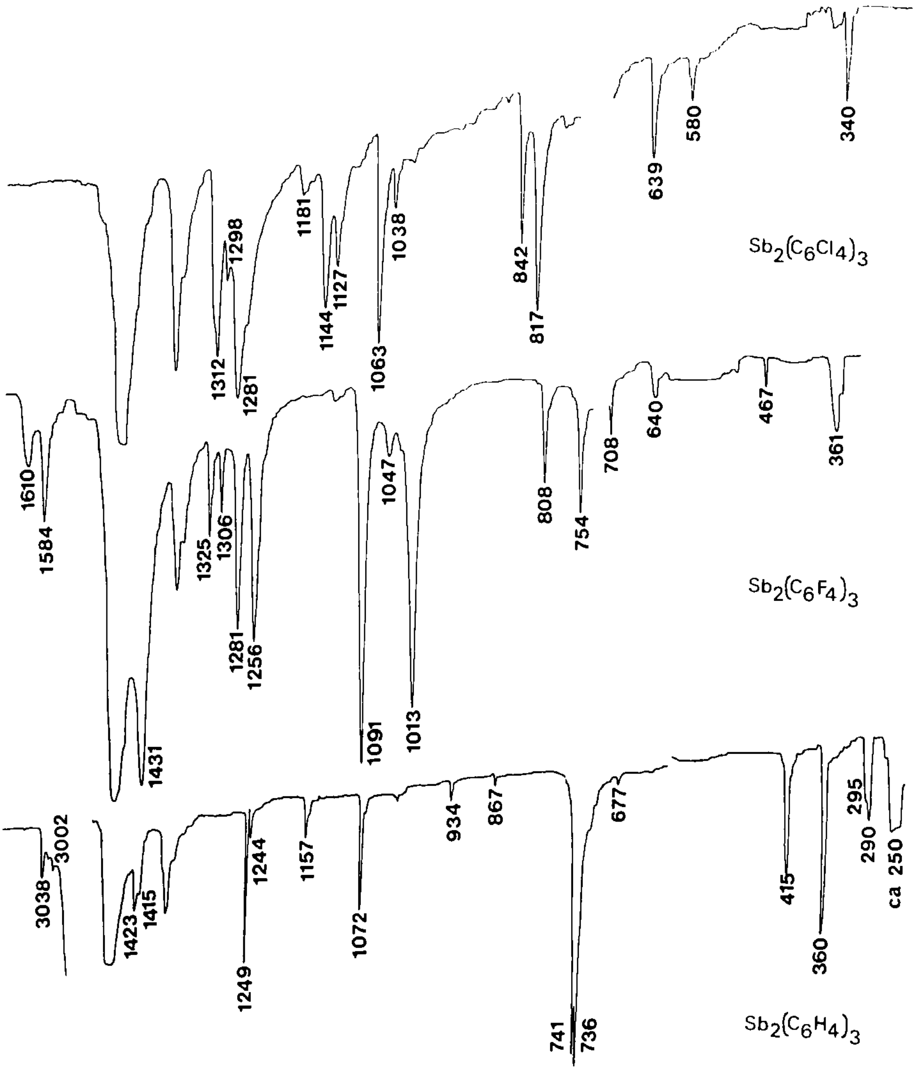


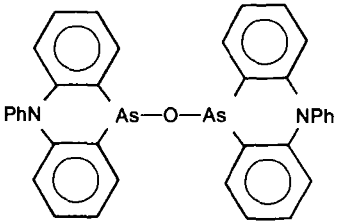
FIG. 12. Infrared spectra of a series of distibatriptycenes.

There is no evidence for interaction of the benzenoid rings either with or through the bridgehead atoms; 1-azatriptycene has a virtually identical ultraviolet spectrum (*18*). Arsazatriptycene, $AsN(C_6H_4)_3$ (*19*), has a very strong band at 218 nm (log $e = 4.69$) with no other distinct peaks (although at 270 nm log e is still about 3.48), whereas diphosphatriptycene displays peaks at 218 (log $e \cong 5.01$), 267 (log $e = 3.27$), 275 (log $e = 3.33$), and 283 nm (log $e = 3.36$). Again there appears to be no interaction between the aromatic rings and the bridgehead heteroatom.

The strongest infrared absorption for $M_2(C_6H_4)_3$ species occurs close to 750 cm^{-1} and can presumably be attributed to the in-phase, out-of-plane deformation of the four C–H bonds in each ring. This vibration shows up as a doublet with a separation which decreases steadily from $P_2(C_6H_4)_3$ ($\Delta = 25$ cm^{-1}) to $Bi_2(C_6H_4)_3$, where a single band with an unresolved shoulder occurs. Unfortunately, most authors have given sparse or, worse still, no infrared data for their products. Journal editors should be encouraged to ask for peak data (with indications of intensities) and should be willing to publish infrared traces of any new types of compounds; these latter are of immense help to the preparative chemist and amply worth the journal space involved. The spectra of $Sb_2(C_6X_4)_3$, X = H, F, or Cl, are displayed in Fig. 12; the strong peak at 1091 cm^{-1} in the spectrum of $Sb_2(C_6F_4)_3$ shows evidence of splitting on solvate formation. Two strong absorptions between 1000 and 1100 cm^{-1} are indicative of 1,2-disubstituted tetrafluorobenzenes and the lack of a medium-intensity band at about 950 cm^{-1} shows the absence of a $F_4C_6-C_6F_4$ bond. (A useful collection of infrared spectra is presented in ref. *37* for $(CH)_2(C_6H_4)_3$ and its $CX(CH)(C_6H_4)_3$ derivatives.)

VII. Chemistry

The triptycene skeleton is exceedingly stable; as Earley and Gallagher comment (*19*) "the outstanding feature of the chemistry of azarsatriptycene is its lack of reactivity" (toward reagents which normally cleave arylarsines). Although insoluble in cold hydrochloric or hydrobromic acids, $NAs(C_6H_4)_3$ dissolves on heating but separates out unchanged when the solutions are cooled; boiling with HCl/acetic acid or HBr/acetic acid mixtures also leaves the molecule intact. Strongly basic reagents such as refluxing sodium ethoxide in ethanol are without action and even Raney nickel under reflux for 2 hours gave only a 31% yield of triphenylamine, leaving 50% of the compound to be recovered. Little nitration occurs in boiling nitric acid, the triptycene instead being oxidized almost quantitatively to $N(AsO)(C_6H_4)_3$; this oxide is also formed when azarsatriptycene is treated with bromine in chloroform and the unstable bromide is hydrolyzed. Ready cleavage was achieved only with sodamide in hexamethylphosphoramide when the oxide (**XII**) resulted. A further unexpected feature in the chemistry of this compound is that quaternary salts cannot be obtained by (1) boiling with methyl iodide, (2) treatment with MeI/AgBF$_4$, or (3) heating to 180° with methyltoluene-*p*-sulfonate (*19*). In contrast, N(CH)(C$_6$H$_4$)$_3$ and As(CH)(C$_6$H$_4$)$_3$ readily quaternize (*18, 31*).



(XII)

The "tied-back" nature of the phenylene groups in triptycenes should make them good ligands, but so far there is only one report of this type of interaction. A bright yellow complex, [(C$_6$H$_4$)$_3$NAs]$_2$PdCl$_2$, readily forms when azarsatriptycene reacts with K$_2$PdCl$_4$; it is assumed that the nitrogen is inactive as a donor, leaving this complex as a monomer with Pd–As bonding (*19*).

1,6-Disubstituted triptycenes have a more varied chemistry when phosphorus is present as a heteroatom. Thus P$_2$(C$_6$H$_4$)$_3$ forms a monoquaternary salt when treated with benzyl bromide (*3*) and doubly protonates in fluorosulfonic acid (*34*) at $-60°$; oxidation with peracetic acid in ethyl acetate gives the dioxide (O=P)$_2$(C$_6$H$_4$)$_3$ (*3, 27*). The rise in the P=O stretching frequency from 1195 cm^{-1} in triphenylphosphine to 1233 cm^{-1} in (O=P)$_2$(C$_6$H$_4$)$_3$ is thought (*34*) to reflect increased O-to-P p_π–d_π bonding in the latter molecule. Elemental sulfur in refluxing carbon disulfide oxidizes diphosphatriptycene to the disulfide (SP)$_2$(C$_6$H$_4$)$_3$ (*3*).

Methyl iodide with PN(C$_6$H$_4$)$_3$ forms the P–methyl iodide on heating in a bomb; by treating this iodide with AgBF$_4$ in 1,2-dichloroethane it was transformed into the tetrafluoroborate (*22*). The phosphorus atom in [(PMe)N(C$_6$H$_4$)$_3$]I is found to be considerably more shielded [$\delta(^{31}P) = +4.75$ ppm] than that in [(C$_6$H$_5$)$_3$PMe]I [$\delta(^{31}P) = -19.4$ ppm] (*22*). Bromine oxidizes phosphazatriptycene to a yellow-red compound, presumably the dibromide, which gives (OP)N(C$_6$H$_4$)$_3$ on subsequent hydrolysis (*22*). The trimethyl derivative, PN(C$_6$H$_3$Me)$_3$, has a very similar chemistry (*22*); it also undergoes addition of several *ortho*-quinones to give 1:1 complexes in which the phosphorus atom attempts to adopt trigonal bipyramidal geometry (*22*) as in (**VIII**).

The diarsatriptycene skeleton also resists the action of boiling nitric acid and the oxide $(O{=}As)_2(C_6H_4)_3$ results when the acid is diluted with water (*2*). Bromine reacts with $As_2(C_6H_4)_3$ in chloroform to give the orange-red tetrabromide, which hydrolyzes to the above oxide (*2*) and decomposes on heating to give 1,2-dibromobenzene, $OAs_2(C_6H_4)_2$, and $As_2(C_6H_4)_3$ (*2*). Methyl bromide (*38*) and iodide (*2, 38*) are without action on diarsatriptycene but methyltoluene-*p*-sulfonate at 180° converts it into the monosulfonate (*38*). It is considered that the presence of the positive charge on one arsenic atom deactivates the second sufficiently to inhibit double quaternization (*38*). Conversely, the fact that $P_2(C_6H_4)_3$ did not form the doubly quaternized salt with benzyl bromide was attributed to the highly insoluble nature of the mono bromide which precluded further reaction (*2*); successful diprotonation (*34*) of $P_2(C_6H_4)_3$ in fluorosulfonic acid would appear to support this latter assumption in the case of diphosphatriptycene.

Since $Sb_2(C_6F_4)_3$ may be formed in about 60% yield by direct synthesis from antimony and 1,2-diiodotetrafluorobenzene, its chemistry has been somewhat extensively studied (*4–7*). Most unexpectedly, perfluorodistibatriptycene was found to separate from a variety of solvents as crystalline hemisolvates; typically, the hexane solvate slowly effloresces in the open air and loses about 98% of the hexane after 14 days. The retention of 0.5 mol of solvent was originally indicated by elemental analysis and then checked by accurate thermogravimetric analysis. A rather novel way of demonstrating solvate formation (*8*), but which cannot give the actual stoichiometry, is illustrated in Fig. 13. A sample of $Sb_2(C_6F_4)_3 \cdot 0.5$ hexane was introduced into a mass spectrometer via the direct insertion probe; as the probe slowly warmed up a series of mass scans was recorded, Fig. 13 giving the cross-scan report of total ion current (TIC) relative to several hexane fragment ions. The diagram shows conclusively that no significant amount of hexane is lost until the narrow band of mass scans between numbers 26 and 30; hence the first hump in the TIC curve represents the decomposition point of a specific solvate, the identity of the solvent being confirmed by the various ions originating from hexane and whose intensities follow very closely the contour of the TIC curve. Further heating gave the normal spectrum of $Sb_2(C_6F_4)$ as shown in Fig. 13 by the presence of the three major antimony-containing ions.

$Sb_2(C_6F_4)_3$ is a very robust molecule, being stable indefinitely in the open air at ambient temperatures. Near the melting point (258°), some

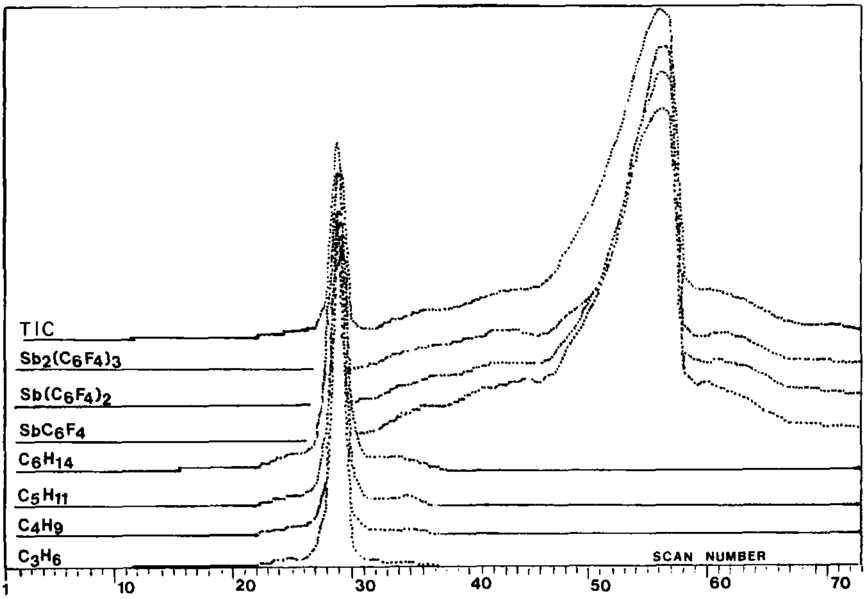
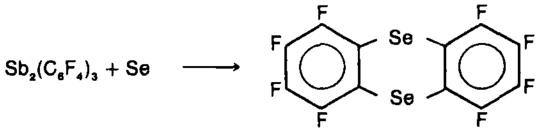


FIG. 13. Cross-scan report for the mass spectrum of the $Sb_2(C_6F_4)_3$-hexane solvate.

of the compound sublimes under atmospheric pressure to give beautifully formed crystals in the melting-point tube [surprisingly, even $Bi_2(C_6F_4)_3$ is stable enough to sublime in air just below its melting point of 314°]; vacuum sublimation in a sealed, evacuated tube held in a slight temperature gradient is the best way to grow large, solvent-free crystals. Slow thermal decomposition of $Sb_2(C_6F_4)_3$ occurs in a vacuum above 350° but water is without action up to 300°; this is to be contrasted with the ready hydrolysis of $Sb(C_6F_5)_3$ under ambient conditions in damp air. No quaternary salt was formed when perfluorodistibatriptycene was refluxed in methyl iodide for some hours. Transfer of C_6F_4 groups to selenium occurs in high yield on heating:



This reaction was used originally to demonstrate that tetrafluorophenyl groups were present in molecule.

Rapid oxidation of $Sb_2(C_6F_4)_3$ takes place when chlorine is passed through its solution in cold carbon tetrachloride (*6*); after about 10 sec the solution becomes turbid and begins to precipitate the tetrachloride $(Cl_2Sb)_2(C_6F_4)_3$. Hydrolysis of this chloride occurs readily on addition of distilled water but, although the product analyzes as "$O_2Sb_2(C_6F_4)_3$", its highly insoluble nature suggests it is polymeric; the ill-defined solid formed when bromine is allowed to stand in contact with $Sb_2(C_6F_4)_3$ again gives the oxide on hydrolysis, but in very inferior yield. Both the tetrachloride and oxide decompose on heating in sealed,evacuated tubes to give back some $Sb_2(C_6F_4)_3$ as one of the products; in a mass spectrometer the mass cutoff for $[O_2Sb_2(C_6F_4)_3]_x$ occurs at the ion $Sb_2(C_6F_4)_3^+$, presumably due to decomposition occurring on the probe. Iodine does not react with perfluorodistibatriptycene at the boiling point of carbon tetrachloride.

Perfluorodistibatriptycene is unaffected by cold, concentrated nitric acid but dissolves with oxidation on boiling (*6*); dilution of the solution with water results in the deposition of $Sb_2(C_6F_4)_3(NO_3)_2(OH)_2$ as needlelike, colorless crystals. This nitrate slowly hydrolyzes on repeated crystallization from water to give $Sb_2(C_6F_4)_3(OH)_4$; attempts to dehydrate this tetrahydroxo derivative to the above polymeric oxide have so far failed. The stereochemistry of these Sb(V)-substituted triptycenes would be of great interest but all the crystals yet studied have proved to be twinned.

Heating together antimony, antimony trioxide, and 1,2-diiodotetrafluorobenzene in a sealed tube failed to give the antimony analog of the arsenic epoxide (**III**); because some $Sb_2(C_6F_4)_3$ was formed in this system it is also obvious that the triptycene does not react with Sb_2O_3 at 260°.

$Bi_2(C_6F_4)_3$ can now be made in yields up to about 20% by heating finely powdered bismuth with 1,2-diiodotetrafluorobenzene (*8*) so that its chemistry can also be studied in some detail; earlier attempts at this synthesis, using granular bismuth, gave only a mixture of perfluoropolyphenylenes. Perfluorodibismuthatriptycene forms hemisolvates like $Sb_2(C_6F_4)_3$, but these dissociate more readily. Chlorine at room temperature cleaves the fluoro-aromatic groups and the product, presumably $BiCl_3$, gives only BiOCl on hydrolysis. Boiling water has no action on $Bi_2(C_6F_4)_3$, but hot, concentrated nitric acid causes complete decomposition. It would appear from these initial studies (*8*) that most attempts to prepare derivatives of $Bi_2(C_6F_4)_3$ will be foiled by the relative instability of the molecule; perhaps more surprising is the fact that it exists at all when one looks at the meager array of known organobismuth compounds.

The very low solubility of perchlorodistibatriptycene has considerably hindered attempts to explore its chemistry, and virtually the only known property is the formation of hemisolvates with those few solvents in which it is soluble, for example, dimethylformamide, diethylformamide, and nitrobenzene (*6*).

VIII. Conclusions and Suggestions for Further Work

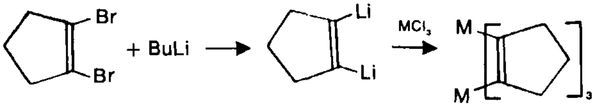
Before the chemistry of the 1,6-disubstituted triptycenes can be developed much further, a good, general method is required for their synthesis. One possible route to the Group V triptycenes which has not been explored is to treat alkali or alkaline earth pnictides with aryl halides:

$$6C_6F_6 + 2Li_3N \longrightarrow N_2(C_6F_4)_3 + 6LiF$$

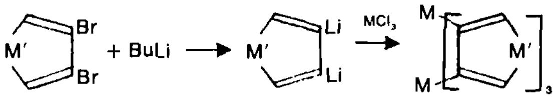
$$1,2\text{-}X_2C_6H_4 + Na_3P \longrightarrow P_2(C_6H_4)_3$$

$$1,2\text{-}C_6H_4(NHLi)_2 + C_6F_6 \longrightarrow 1,2\text{-}C_6H_4(NHC_6F_5)_2 \xrightarrow{2BuLi} N_2(C_6H_4)(C_6F_4)_2$$

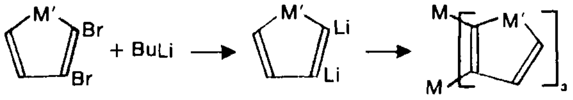
As indicated in the discussion on synthesis (Section II) the best reagents to use would appear to be 1,2-dilithoarenes once these become generally available. It is possible to study this mode of preparation by making compounds similar to the triptycenes but containing other cyclic species, rather than phenylene rings, because the relevant 1,2-dilithio reagents are relatively simple to make. For example, some preparations which might be tried involve the following reactions:



M = P; As, Sb, Bi



M = O, S, Se, Te



(two isomers)

Several of the Group V triptycenes should prove to be useful ligands toward transition metals since the organic groups are effectively tied back and so will partially relieve steric requirements at the donor atom. However, according to NMR chemical shift data the lone pair on phosphorus in $NP(C_6H_4)_3$ (*22*) and $P_2(C_6H_4)_3$ (*3, 34*) has high *s* character and this will decrease the ligand potential. The tying back of the phenylene groups in the rigid triptycene skeleton raises two further interesting questions which have yet to be answered fully. The first has already been hinted at and concerns the possible stereochemistry adopted by a Group V element in, for example, $Sb_2(C_6F_4)_3Cl_4$ and $As_2(C_6H_4)_3Br_4$, where the oxidation state of antimony and arsenic is +5. Boron triptycenes will no doubt be made shortly in which the Group III atom is stabilized in the "tetrahedral" conformation by a suitable donor molecule:

$$1,2\text{-}LiC_6X_4 + H_3NBF_3 \longrightarrow (H_3NB)_2(C_6X_4)_3$$

What happens to the boron stereochemistry and the molecular stability when attempts are made to remove the ammonia by reacting the diadduct with a stronger Lewis acid?

$$(H_3NB)_2(C_6X_4)_3 + 2BF_3 \longrightarrow 2H_3NBF_3 + B_2(C_6X_4)_3$$

In this way triptycenes could perhaps be used to explore the chemistry of severely nonplanar Group III elements.

As is obvious from this review the subject of 1,6-disubstituted triptycenes is very much in its infancy, but it is hoped that new workers will be attracted to the field, bringing with them fresh ideas and expertise spawned in other areas of research.

REFERENCES

1. von Dechend, F., and Wichelhaus, H., *Chem. Ber.* **8,** 1609 (1875).
2. McCleland, N. P., and Whitworth, J. B., *J. Chem. Soc.* 2753 (1927); see also Chatt, J., and Mann, F. G., *J. Chem. Soc.* 1184 (1940).
3. Weinberg, K. G., and Whipple, E. B., *J. Am. Chem. Soc.* **93,** 1801 (1971); Weinberg, K. G., *J. Org. Chem.* **40,** 3586 (1975); U.S. Patents 3,557,204 (1971) and 3,651,147 (1972).
4. Woodard, C. M., Hughes, G., and Massey, A. G., *J. Organomet. Chem.* **112,** 9 (1976).
5. Mistry, T. K., and Massey, A. G., *J. Organomet. Chem.* **209,** 45 (1981).
6. Al-Jabar, N. A. A., and Massey, A. G., *J. Organomet. Chem.* **276,** 331 (1984).
7. Al-Jabar, N. A. A., Massey, A. G., and Mistry, T. K., *Organomet. Synth.* **3,** 630 (1986).
8. Massey, A. G., unpublished work.
9. Humphries, R. E., Al-Jabar, N. A. A., Bowen, D., Massey, A. G., and Deacon, G. B., *J. Organomet. Chem.* **319,** 59 (1987).

10. Al-Jabar, N. A. A., Bowen, D., and Massey, A. G., *J. Organomet. Chem.* **295,** 29 (1985).

11. Brown, D. S., Mistry, T. K., and Massey, A. G., *J. Fluorine Chem.* **16,** 483 (1980).

12. Cohen, S. C., Reddy, M. L. N., and Massey, A. G., *J. Organomet. Chem.* **11,** 563 (1968).

13. Cullen, W. R., and Wu, A. W., *J. Fluorine Chem.* **8,** 183 (1976).

14. Wittig, G., and Bickelhaupt, F., *Chem. Ber.* **91,** 883 (1958); Winkler, H. J. S., and Wittig, G., *J. Org. Chem.* **28,** 1733 (1963).

15. Al-Jabar, N. A. A., and Massey, A. G., *J. Organomet. Chem.* **275,** 9 (1984).

16. Al-Jabar, N. A. A., and Massey, A. G., *J. Organomet. Chem.* **287,** 57 (1985).

17. Al-Jabar, N. A. A., and Massey, A. G., *J. Organomet. Chem.* **288,** 145 (1985).

18. Wittig, G., and Steinhoff, G., *Justus Liebigs Ann. Chem.* **676,** 21 (1964).

19. Early, R. A., and Gallagher, M. J., *J. Chem. Soc. C* 158 (1970); *Org. Mass Spectrom.* **3,** 1283 (1970).

20. Hellwinkel, D., and Schenk, W., *Angew. Chem., Int. Ed. Engl.* **8,** 987 (1969).

21. Baker, T. N., Doherty, W. P., Kelley, W. S., Newmeyer, W., Rogers, J. E., Spalding, R. E., and Walter, R. I., *J. Org. Chem.* **30,** 3714 (1965).

22. Hellwinkel, D., Schenk, W., and Blaicher, W., *Chem. Ber.* **111,** 1798 (1978).

23. Gilman, H., and Brown, G. E., *J. Am. Chem. Soc.* **62,** 3209, (1940).

24. van Rooyen-Reiss, C., and Stam, C. H., *Acta Crystallogr., Sect. B* **B36,** 1252 (1980).

25. Freijee, F. J. M., and Stam, C. H., *Acta Crystallogr., Sect. B* **B36,** 1247 (1980).

26. van der Putten, N., and Stam, C. H., *Acta Crystallogr., Sect. B* **B36,** 1250 (1980).

27. Schomburg, D., and Sheldrick, W. S., *Acta Crystallogr., Sect. B* **B31,** 2427 (1975).

28. Fawcett, J. K., and Trotter, J., *Acta Crystallogr.* **20,** 87 (1966); Bowen Jones, J., Brown, D. S., Massey, A. G., and Slater, P. J., *J. Fluorine Chem.* **31,** 75 (1986).

29. Schomburg, D., and Sheldrick, W. S., *Acta Crystallogr., Sect. B* **B32,** 1021 (1976).

30. Hellwinkel, D., Blaicher, W., Krapp, W., and Sheldrick, W. S., *Chem. Ber.* **113,** 1406 (1980).

31. Smit, F., and Stam, C. H., *Acta Crystallogr., Sect. B* **B36,** 1254 (1980).

32. Allen, D. W., Coppola, J. C., Kennard, O., Mann, F. G., Motherwell, D. S., and Watson, D. G., *J. Chem. Soc. C* 810 (1970).

33. Miller, J. M., Nye, J. W., private communication; Nye, J. W., M.Sc. Thesis, Brock University, Ontario, Canada, 1986.

34. Vande Griend, L. J., Verkade, J. G., Jongsma, C., and Bickelhaupt, F., *Phosphorus* **6,** 131 (1976).

35. Sorensen, S., and Jakobsen, H. J., *Org. Magn. Reson.* **9,** 101 (1977).

36. Abraham, R. J., "The Analysis of High Resolution NMR Spectra." Elsevier, Amsterdam, 1971; Abraham, R. J., Macdonald, D. B., and Pepper, E. S., *J. Am. Chem. Soc.* **90,** 147 (1968).

37. Bartlett, P. D., and Greene, F. D., *J. Am. Chem. Soc.* **76,** 1088 (1954).

38. Mann, F. G., and Baker, F. C., *J. Chem. Soc.* 4142 (1952).