the low yield of I was presumably due to the strength of the Ir–P bond, which inhibits dissociation of a phosphine.[2,6] Thus, it was found that $(PPh_3)_2IrCl$, formed *in situ* from $[Ir(C_8H_{14})_2Cl]_2$ and 2 equiv of PPh_3 in benzene,[6] reacted readily with a slight excess of 1,2-$C_2B_{10}H_{12}$ when heated at reflux for a few minutes. I was isolated in 84% yield upon addition of hexane to the cooled solution. The same product was formed in over 90% yields upon heating at reflux stoichiometric mixtures of $[Ir(C_8H_{14})_2Cl]_2$, PPh_3, and 1,2-$C_2B_{10}H_{12}$ (1:4:2) in cyclohexane for 1 hr or in hexane for 18 hr (eq 1). Similar

$$\tfrac{1}{2}[Ir(C_8H_{14})_2Cl]_2 + 2PPh_3 + 1,2\text{-}C_2B_{10}H_{12} \longrightarrow \underset{\text{I}}{3\text{-}[(PPh_3)_2IrHCl]\text{-}1,2\text{-}C_2B_{10}H_{11}} \quad (1)$$

complexes have been obtained from 1,7-$C_2B_{10}H_{12}$ and 1,12-$C_2B_{10}H_{12}$ (complexes II and III, respectively), but mixtures with species formed by successive oxidative addition reactions with the same carborane cage are obtained with these carboranes unless a large excess of the carborane is employed. I, II, and III are all yellow crystalline solids. They are stable to air in the solid state, but solutions slowly decompose upon exposure to air.

The reaction of $(PPh_3)_2IrCl$ with 1,2-$C_2H_2B_{10}D_{10}$ yielded a complex with ν_{IrD} at 1580 and 1570 cm^{-1} (ν_{IrH}/ν_{IrD} = 1.40, theoretical = 1.41), which confirmed that the product arises from oxidative addition of a carboranyl B–H bond to the metal atom. When carborane with deuterium only at the B(3,6) sites (>80% at B(3,6), <5% elsewhere by ^{11}B nmr[1]) was used, the product had an ir spectrum with much stronger ν_{IrD} bands than ν_{IrH}, proving that the position of substitution was indeed the B(3,6) sites. This type of oxidative addition has previously been observed as an intramolecular reaction in an iridium complex with a carboranyl phosphine,[7] and a similar reaction has very recently been reported between $(PMe_3)_2(CO)IrCl$ and pentaborane(9).[8]

That the *B*-σ-metallocarboranes are good models for intermediates in the transition metal catalyzed exchange reactions was shown by use of II as a deuterium exchange catalyst for excess 1,7-$C_2B_{10}H_{12}$. With 0.05 mmol of II, 1.0 mmol of 1,7-$C_2B_{10}H_{12}$ was completely deuterated at boron (>95%) in less than 20 hr at 65° (in 20 ml of toluene with a D_2 flow rate of *ca.* 3 ml/min). This is considerably faster than the most active previously known catalyst for this reaction, 2,2-$(PPh_3)_2$-2-H-2,1,7-$IrC_2B_9H_{11}$, which produced carborane with only about 60% exchange under the same conditions.[9]

I reacted rapidly with excess CO in benzene solution at room temperature to yield *trans*-$(PPh_3)_2(CO)IrCl$ (IV) and 1,2-$C_2B_{10}H_{12}$ (eq 2). Even upon prolonged

$$3\text{-}[(PPh_3)_2IrHCl]\text{-}1,2\text{-}C_2B_{10}H_{11} + CO \longrightarrow \textit{trans}\text{-}(PPh_3)_2(CO)IrCl + 1,2\text{-}C_2B_{10}H_{12} \quad (2)$$

heating of IV in toluene solutions with 1,2-$C_2B_{10}H_{12}$, no stable σ-metallocarboranes were formed. However, IV is an active deuteration catalyst for 1,2-$C_2B_{10}H_{12}$,[9] implying that the carborane does undergo oxidative addition to the complex, but that the product is not thermodynamically favored. Similarly unfavorable thermodynamics may account for the failure to isolate a stable σ-metalloborane from the reaction of IV with pentaborane(9).[8]

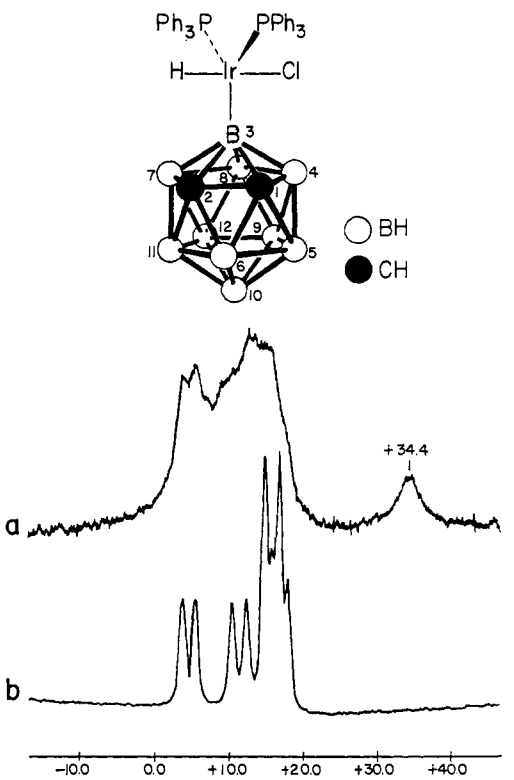

Figure 1. The proposed structure of I, 3-$[(PPh_3)_2IrHCl]$-1,2-$C_2B_{10}H_{11}$, and the 80.53-MHz ^{11}B nmr spectra of I (a) and 1,2-$C_2B_{10}H_{12}$ (b).

Further members in the series of *B*-σ-metallocarboranes have been prepared and characterized. The synthesis and chemistry of these species will be described elsewhere.

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(9) The details of an extensive study of transition metal catalyzed deuterium exchange will appear elsewhere.

Violacene, a Polyhalogenated Monocyclic Monoterpene from the Red Alga *Plocamium violaceum*

Sir:

We have previously reported the occurrence of two polyhalogenated monoterpenes, 3,7-dimethyl-1,8,8-tribromo-3,4,7-trichloro-1,5-octadiene (**1**)[1] and 7-chloro-

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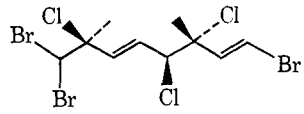
3,7-dimethyl-1,4,6-tribromo-1-octen-3-ol (**2**)[2] in extracts from the digestive gland of the sea hare *Aplysia californica*. Subsequent investigations[3] revealed that both monoterpenes were obtained from the red alga *Plocamium pacificum*,[4] an important constituent in the sea hare's diet. *Plocamium pacificum* was shown to be a source of a further nine additional highly halogenated monoterpenes,[5] all having the basic geraniol skeleton, while a related alga, *Plocamium violaceum*, was found to contain an array of ten polyhalogenated monoterpenes. The major constituent of the nonpolar fraction of *P. violaceum* has been shown to possess a previously unknown monoterpene skeleton.



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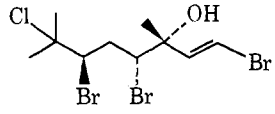

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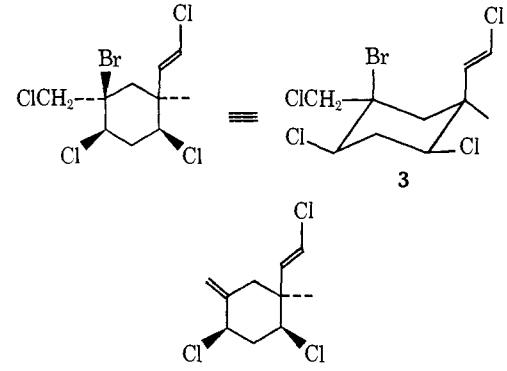
Repeated alumina chromatography of the pentane extracts of air-dried *P. violaceum* yielded crystalline violacene (**3**), mp 71.0–71.5° (0.07% yield). The molecular formula, $C_{10}H_{13}BrCl_4$, was established by high resolution mass spectrometry. A single trans olefinic bond was indicated by an AB quartet at δ 6.02 and 6.44 ppm (J = 13.5 Hz) in the pmr spectrum and by signals at 119.2 and 135.4 ppm in the cmr spectrum; violacene (**3**) was therefore monocyclic. The remaining pmr signals indicated the presence of a methyl group at δ 1.29 ppm, a methylene group at 2.16 and 2.32 ppm (AB quartet, J = 15 Hz), a halomethyl group at 3.48 and 3.85 ppm (AB quartet, J = 10.5 Hz), and a four-signal pattern at 4.29 (dd, J = 4, 12 Hz), 3.64 (dd, J = 4, 12 Hz), 2.64 (dt, J = 12, 12, 14 Hz) and 2.44 ppm (dt, J = 4, 4, 14 Hz), indicative of a partial structure –CHX–CH_2–CHX– contained within a six-membered ring. The cmr spectrum was completely compatible with these assignments and showed the presence of two additional tetrasubstituted carbon atoms with signals at 42.1 and 71.3 ppm. Treatment of **3** with chromous sulfate in aqueous dimethylformamide yielded a trichloride **4**, which contained an exocyclic methylene group (nmr, broad singlets at δ 5.40 and 4.98 ppm). Since the mass spectrum of **3** contained a [M^+–CH_2Cl] cluster but no [M^+–CH_2Br] cluster, one of the tetrasubstituted ring carbons must bear a bromine and a chloromethyl group. The methyl group and the chlorovinyl group of violacene (**3**) were therefore attached to the remaining carbon atom.

The stereochemistry of violacene (**3**) was established by careful analysis of the nmr spectra of violacene and its derivatives. The coupling constants (see above) of the two protons on ring carbon atoms bearing chlorine indicated that the chlorine atoms were equatorial on a cyclohexane ring in the chair conformation. Ozonolysis of **3**, followed by reductive work-up, yielded an aldehyde **5** whose nmr spectrum showed the presence of a small long-range W coupling (J = 1 Hz) between an axial methylene proton (δ 2.29 ppm) and the



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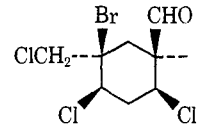
4

aldehyde proton (δ 10.11 ppm); thus, the vinyl chloride group in violacene (**3**) must be axial.[6] Reduction of the aldehyde **5** with sodium borohydride in ethanol, followed by acetylation with acetic anhydride in pyridine, yielded an acetate **6**. Analysis of the Eu(fod)$_3$ induced shifts for the nmr signals of the six ring protons of the acetate **6** followed an assignment of the location of the europium atom in the complex.[7] The magnitudes of the induced shifts for the two chloromethyl protons indicated that the chloromethyl group must be equatorial and the bromine atom axial.[8]



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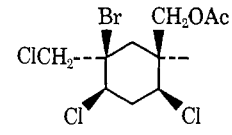

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The carbon skeleton of violacene (**3**) has not been found previously among naturally occurring monoterpenes. The biosynthesis of this interesting compound can be rationalized as resulting from cyclization of an acyclic monoterpene *via* a bromonium ion, a process which can be invoked to explain the biosynthesis of many brominated marine natural products.

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Supplementary Material Available. A listing of Eu(fod)$_3$ induced shift data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6771.

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(8) See paragraph at end of paper regarding supplementary material.

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