(6)[16] gives products whose spectra contain absorption characteristic of $\equiv$C—H (3320 cm^{-1}) and $\equiv$C—D (2585 cm^{-1}) stretches.[12a] At even low photoconversions, the spectrum of products from the irradiation of 5 is virtually identical with the spectrum of products from 6. A most significant point is that the isotopic species 7 and 8 are formed in the same ratio from the irradiation of either 5 or 6.

Under the conditions of the photolysis, 4- and 5-deuteriothiadiazole are not interconvertible, and, hence, this potential isomerization is not responsible for the production of the mixture of ethynyl-d_1 mercaptans 7 and 8.[17] Photolysis of parent 1, embedded in an acetylene-d_2 host, leads to thioketene-d_0 2 (C=C str, 1760 cm^{-1}), lacking detectable amounts of thioketene-d_2 (C=C str, 1735 cm^{-1}). Thus, a hypothetical pathway involving trapping of sulfur atoms by acetylene to give products can be eliminated.[18] The most economical tentative interpretation of our observations with parent and labeled 1 involves the intervention of a symmetrical species, most likely thiirene, from which 7 and 8 are derived.

(16) R. S. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *J. Amer. Chem. Soc.*, **88**, 4265 (1966).

(17) (a) Products 2 and 4 do not interconvert under our experimental conditions. (b) 1,3,4-Thiadiazole is stable to our photochemical conditions, but with λ >220 nm gives hydrogen cyanide as a major product.

(18) We have also established that photolysis of ethylene sulfide in carbon monoxide matrices leads to carbonyl sulfide, suggesting that solid carbon monoxide can act as a trap for sulfur atoms. Photodecomposition of 1 to 2 and 4 in a matrix of carbon monoxide (M/R ∼ 200) is not accompanied by carbonyl sulfide.[19] This result gives support to our contention that sulfur atoms are not being formed from 1.

(19) Nor is the formyl radical [D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **51**, 277 (1969)] formed, which indicates that hydrogen atoms are not playing a detectable role in our system.

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Preparation of B-σ-Metallocarboranes by Oxidative Addition. Model Intermediates for Transition Metal Catalyzed Hydrogen–Deuterium Exchange in Boron–Hydrogen Containing Species

Sir:

The recent report of transition metal catalyzed exchange of deuterium gas with hydrogen at terminal B–H bonds in a wide variety of boron compounds[1] postulated intermediates formed by oxidative addition of the B–H bonds to a transition metal complex. Stable B-σ-metallocarboranes have now been prepared in this manner which presage the existence of a new area in metallocarborane chemistry.

Slow addition of hexane to a cooled solution prepared by heating (PPh$_3$)$_3$IrCl with a threefold excess of 1,2-C$_2$B$_{10}$H$_{12}$ in toluene at the reflux temperature produced a small quantity (∼5%) of yellow crystals, I. Further addition of hexane precipitated the major

(1) E. L. Hoel and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 4676 (1974).

product, Ir(PPh$_3$)$_2$[(o-C$_6$H$_4$)PPh$_2$]HCl, the result of intramolecular ortho metalation in (PPh$_3$)$_3$IrCl.[2] The infrared spectrum (Nujol mull) of I exhibited a strong band at 2560 cm^{-1} assigned to ν_{BH} and a pair of sharp, medium intensity bands at 2209 and 2199 cm^{-1} assigned to ν_{IrH}. The 251-MHz ^{1}H nmr spectrum (in CD$_2$Cl$_2$) consisted of resonances in the τ 2.0–2.8 region assigned to coordinated PPh$_3$, a typically broad carboranyl C–H singlet at τ 7.29, and a 1:2:1 triplet at τ 28.08 (J_{PIrH} = 14.3 Hz), assigned to the hydride. The 80.53-MHz ^{11}B nmr spectrum (Figure 1a) consisted of an unresolved set of broad, overlapping resonances between 0.0 and +20.0 ppm (from BF$_3$·O(C$_2$H$_5$)$_2$) of relative area 9.1 and a broad singlet (width at half-height *ca.* 300 Hz) at +34.4 ppm of relative area 0.9.

On the basis of the spectral data, I was formulated as a five-coordinate complex of iridium(III) bonded to two triphenylphosphine ligands, a hydride, a chloride, and a carboranyl moiety σ-bonded through a boron atom. Chemical analysis confirmed the empirical formula. The stereochemistry about iridium was posulated to be a trigonal bipyramid with the bulky triphenylphosphine and carboranyl ligands in the trigonal plane. Support for this assignment is provided by both the ir and ^{1}H nmr spectra. The symmetrical hydride triplet is consistent with two equivalent phosphines cis to the hydride, and the chemical shift and position of ν_{IrH} are consistent with chloride trans to the hydride.[3] Although a square pyramidal structure with an axial hydride would also have phosphines cis to the hydride, Shaw and coworkers have shown that such species exhibit ν_{IrH} at about 2000 cm^{-1} and the hydride resonance at about τ 60.[4]

The position of substitution on the carborane cage is not readily apparent from the ^{11}B nmr spectrum. The singlet at +34.4 ppm clearly represents the boron atom to which the metal is bonded, but the remainder of the spectrum cannot be readily assigned, except to note the general similarity to the spectrum of 1,2-C$_2$B$_{10}$H$_{12}$ (Figure 1b), allowing for small shifts and extensive line broadening.[5] However, the existence of only one carboranyl C–H resonance in the ^{1}H nmr spectrum requires the metal to be substituted on the plane of symmetry between the carbon atoms, *i.e.*, at either B(3,6) or B(8,10). On the basis of the results of transition metal catalyzed deuterium exchange on 1,2-C$_2$B$_{10}$H$_{12}$, which indicated that the order of deuterium incorporation follows the nucleophilic substitution pattern B(3,6) > B(4,5,7,11) > B(8,10) > B(9,12),[1] the position of substitution would be expected to be B(3,6). This was later confirmed (*vide infra*). The proposed structure of I, 3-[(PPh$_3$)$_2$IrHCl]-1,2-C$_2$B$_{10}$H$_{11}$ is shown in Figure 1.

It seemed probable that I was formed either by oxidative addition of 1,2-C$_2$B$_{10}$H$_{12}$ to (PPh$_3$)$_3$IrCl followed by loss of PPh$_3$ or by prior dissociation of PPh$_3$ followed by oxidative addition to (PPh$_3$)$_2$IrCl. In either case,
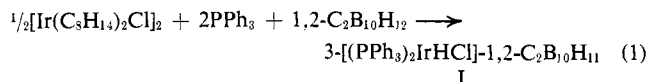
(2) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

(3) E. L. Muetterties, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971.

(4) C. Masters, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Dalton Trans.*, 664 (1972).

(5) The nature of the relaxation phenomena responsible for the broadening is not known but is probably not due to paramagnetic impurities since the spectra are reproducible and the ^{1}H nmr spectra are not affected. Similar broadening was observed for II, III, and triphenylarsine analogs.

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 $1,2\text{-}C_2B_{10}H_{12}$ 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 $1,2\text{-}C_2B_{10}H_{12}$ (1:4:2) in cyclohexane for 1 hr or in hexane for 18 hr (eq 1). Similar
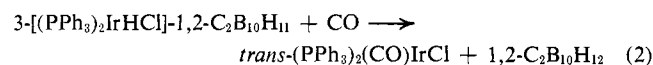
$$\tfrac{1}{2}[Ir(C_8H_{14})_2Cl]_2 + 2PPh_3 + 1,2\text{-}C_2B_{10}H_{12} \longrightarrow$$
$$3\text{-}[(PPh_3)_2IrHCl]\text{-}1,2\text{-}C_2B_{10}H_{11} \quad (1)$$
$$\mathbf{I}$$

complexes have been obtained from $1,7\text{-}C_2B_{10}H_{12}$ and $1,12\text{-}C_2B_{10}H_{12}$ (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 $1,2\text{-}C_2H_2B_{10}D_{10}$ yielded a complex with ν_{IrD} at 1580 and 1570 cm^{-1} ($\nu_{IrH}/\nu_{IrD} = 1.40$, 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 $B\text{-}\sigma$-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 $1,7\text{-}C_2B_{10}H_{12}$. With 0.05 mmol of II, 1.0 mmol of $1,7\text{-}C_2B_{10}H_{12}$ 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, $2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1,7\text{-}IrC_2B_9H_{11}$, 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 $trans\text{-}(PPh_3)_2(CO)IrCl$ (IV) and $1,2\text{-}C_2B_{10}H_{12}$ (eq 2). Even upon prolonged

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

heating of IV in toluene solutions with $1,2\text{-}C_2B_{10}H_{12}$, no stable σ-metallocarboranes were formed. However, IV is an active deuteration catalyst for $1,2\text{-}C_2B_{10}$-

(6) H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, Chem. Commun., 1694 (1970).

(7) E. L. Hoel and M. F. Hawthorne, J. Amer. Chem. Soc., 95, 2712 (1973).

(8) M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, and S. S. Wreford, J. Amer. Chem. Soc., 96, 4041 (1974).

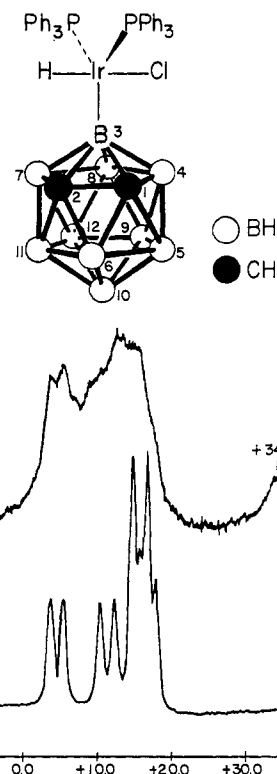(9) The details of an extensive study of transition metal catalyzed deuterium exchange will appear elsewhere.

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

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]

Further members in the series of $B\text{-}\sigma$-metallocarboranes have been prepared and characterized. The synthesis and chemistry of these species will be described elsewhere.

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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-

(1) D. J. Faulkner, M. O. Stallard, J. Fayos, and J. Clardy, J. Amer. Chem. Soc., 95, 3413 (1973).