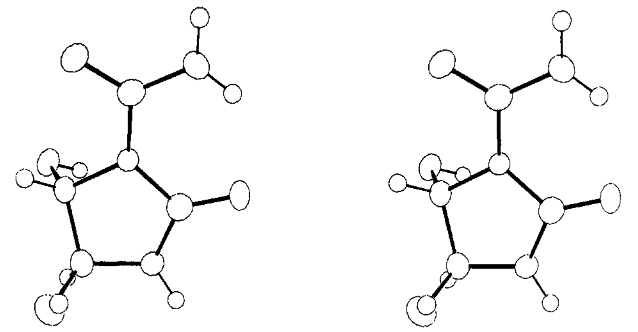

Figure 1. Stereodiagram of *trans*-1-carbamylimidazolidone-4,5-diol.

While irradiation of Cyt in aerated aqueous solutions has been studied,[10] no stable radiation product has previously been identified.[11] The high *g* value indicates that I and II are major radiolysis products of Cyt. Although the mechanism of formation remains obscure, I and II undoubtedly resulted from a facile rearrangement of an initial intermediate. With this structural elucidation, the possible importance of I and II in radiation chemistry and biology should be examined.

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[10] (a) B. Ekert and R. Monier, *Nature (London)*, **188**, 309 (1960); R. Latarjet, B. Ekert, S. Apelgot, and N. J. Rebeyrotte, *J. Chem. Phys.*, **58**, 1046 (1961); (b) M. N. Khattak and J. H. Green, *Int. J. Radiat. Biol.*, **11**, 131 (1966); (c) R. Teoule, J. Cadet, M. Poluerelli, and A. Cier, *Peaceful Uses At. Energy, Proc. Int. Conf., 4th, 1971*, in press; (d) R. Pletichia-Lansky and J. J. Weiss, *Anal. Biochem.*, **16**, 510 (1966).

[11] See review by E. Fahr, *Angew. Chem., Int. Ed. Engl.*, **8**, 578 (1969), and references therein.

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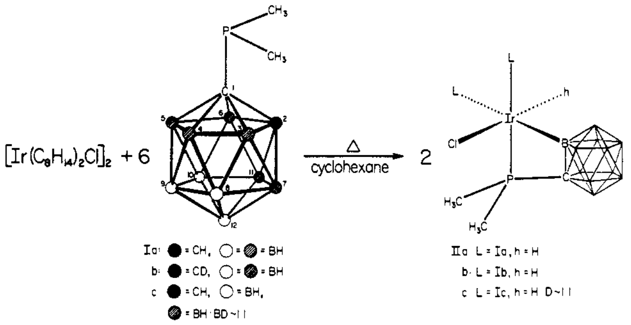
Intramolecular Oxidative Addition of Iridium to a Boron–Hydrogen Bond of a Complexed Carboranylphosphine

Sir:

Intramolecular oxidative addition of ortho carbon–hydrogen bonds in coordinated phenylphosphines to the central metal atom of transition metal complexes is a well known and much studied reaction.[1] We wish to report the first example of such an intramolecular oxidative addition involving an "ortho" boron–hydrogen bond. The phosphine is 1-dimethylphosphino-1,2-carborane.

When a suspension of yellow-orange $[Ir(C_8H_{14})_2Cl]_2$[2] is allowed to react in a nitrogen atmosphere at room temperature with excess 1-(Me_2P)-1,2-$C_2B_{10}H_{11}$ (Ia) in cyclohexane or petroleum ether, a yellow product is immediately formed. By analogy with the reactions of the iridium complex with a wide variety of phosphines,[3] this is believed to be the triphosphineiridium chloride. However, upon immediately collecting the yellow product, the ir spectrum shows that further reaction is occurring, signaled by the growth of a band at 2230 cm^{-1}, assigned to ν(IrH). Reflux of the suspension under nitrogen in cyclohexane for 2 hr yields a white, air stable powder (which exhibits ν(IrH) at 2230 cm^{-1} (Nujol mull)) in nearly quantitative yield. By analogy to the arylphosphine adducts of Bennett and Milner and as confirmed by analysis, molecular weight (829 ± 24 by osmometry in tetrahydrofuran), and 251-MHz proton nmr, this white product was determined to be $IrHCl[C_2B_{10}H_{10}P(CH_3)_2](C_2B_{10}H_{11}P(CH_3)_2)_2$ (IIa).



The nmr spectrum (in C_6D_6) shows the hydride as a quartet at δ −20.9 (from TMS) with J_{P-H} (apparent) = 12.3 Hz. This is consistent with three nearly equivalent cis phosphines but not with phosphines trans to the hydride.[3,4]

Examination of the ligand Ia reveals that there are five positions "ortho" to the carbon bearing the phosphine and therefore sterically allowed to participate in the reaction. However, there are only three chemically nonequivalent types of bonds: the carbon–hydrogen bond and the chemically equivalent pairs of boron–hydrogen bonds at positions 3,6 and 4,5.

To determine whether the reaction occurred at carbon or boron, the ligand Ib with deuterium at position 2 was prepared from 1,2-dideuterio-1,2-carborane. When used in the above reaction this ligand afforded complex IIb. The ir spectrum of this complex still shows ν(IrH) at 2230 cm^{-1} but no ν(IrD), expected at about 1600 cm^{-1}, thus proving that the carbon–hydrogen bond is not the source of hydride. To substantiate the supposition that a boron–hydrogen bond was involved, ligand Ic with approximately 50 atom % D at each of positions 3, 4, 5, 6, 7, and 11 was prepared *via* the carborane from μ,5,6,7,8,9,10-decadeuteriodecaborane[5] (~50 atom % D). When complex IIc was formed as before, it exhibited, as expected, ν(IrH) at 2250 cm^{-1} and ν(IrD) at 1610 cm^{-1} (ν(IrH)/ν(IrD) = 1.40, theoretical = 1.41) of approximately equal intensity.

Further labeling studies are underway to determine what, if any, preference iridium shows between the pairs of boron–hydrogen bonds at positions 3,6 and 4,5. It is expected that, in agreement with known patterns of electrophilic substitution on carborane substrates, the metal will prefer the more electronegative 4,5 positions.

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[1] G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

[2] A. van der Ent and A. L. Onderdelinden, *Inorg. Syn.*, submitted for publication.

[3] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

[4] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

[5] J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **84**, 1804 (1962).

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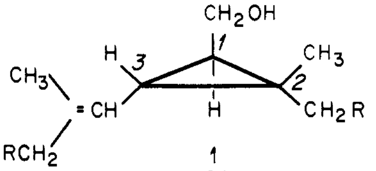
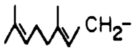
Absolute Configuration of Presqualene Alcohol[1]

Sir:

The structure of presqualene alcohol was shown to be that of a substituted cyclopropanecarbinol (**1a**)[2,3] and



1

a) R =  CH_2-

b) R = H

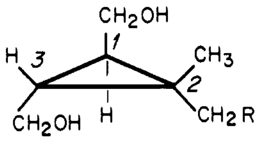
was confirmed by chemical synthesis.[4-6] Studies in our laboratory reduced the eight possible stereoisomers of this alcohol to one of two enantiomers: 1*R*,2*R*,3*R* or 1*S*,2*S*,3*S*.[3,7]

It was demonstrated first by Popják, *et al.*,[8] that presqualene pyrophosphate was optically active with a plain positive optical rotatory dispersion curve (ORD) as far as 280 nm; presqualene alcohol was shown to behave similarly.[3] Rilling, *et al.*,[9] made a correlation between the absolute configuration of presqualene alcohol and chrysanthemum alcohol (**1b**), prepared from natural chrysanthemum monocarboxylic acid, the absolute configuration of which is known to be 1*R*, 3*R*.[7,10] They have stated, without presentation of experimental data, that whereas both **1a** and **1b** were dextrorotatory, **1a** gave a "plain positive CD curve" and **1b** a "similar but negative curve." Hence, they concluded that the absolute configuration of presqualene alcohol was enantiomeric to that of chrysanthemum alcohol.

The correlation reported by Rilling, *et al.*,[9] is inconclusive because presqualene alcohol contains three asymmetric centers, whereas *trans*-(*R*)-chrysanthemum alcohol contains only two. Further, the effects of the two large branched-chain olefinic substituents in presqualene alcohol on the optical properties of the substance are not immediately predictable.

Nakanishi and his colleagues[11] have exploited successfully the Cotton effect of benzoates for the determination of the absolute configuration of cyclic secondary alcohols and glycols. Harada and Nakanishi stated in a footnote to one of their papers that benzoates of asymmetric primary alcohols exhibit also the characteristic Cotton effect "provided the optical center is not too far removed from the hydroxyl group."[12] Thus, it seemed likely that a comparison of the optical properties of the benzoates of presqualene and *trans*-(*R*)-chrysanthemum alcohol and of their degradation products would provide further evidence as to the absolute configuration of presqualene alcohol.

We have prepared, therefore, the benzoates of **1a** and **1b**[13] and the benzoates of their ozonolysis products, **2a** and **2b**, which correspond to the "triacetate" and the "diacetate"[14] ozonolysis products of **1a** and **1b**, respectively, and reported previously.[3] We record here briefly some of the optical properties of these benzoates. Figure 1A shows the CD curves of the benzoates of **1a** and **1b** and Figure 1B the similar curves given by the tribenzoate of **2a** and the dibenzoate of **2b**. All four substances gave negative CD curves with minima in the range of 230–237 nm indicating that they belong to the same optical series. The correlation between the benzoates of **2a** and **2b** is particularly significant. We have found previously that the triacetate of **2a** was optically active;[3] hence its two asymmetric centers must have the same absolute configuration, either *R* or *S*. Since the absolute configuration of the two asymmetric centers in **2b** is *R*, it follows from the identical CD curves of the benzoates of **2a** and **2b** that their absolute configuration is also identical. These correlations imply that the absolute configuration of presqualene alcohol at positions 1 and 3 in **1a** is the same as in natural chrysanthemumic acid, *i.e.*, *R*,*R*. Since the position of the methyl group on the cyclopropane ring in **1a** was deduced to be syn to the carbinol carbon,[3] it also follows that the absolute configuration of **1a** at its third asymmetric center is also *R*.



2

a) R: $-CH_2CH_2OH$

b) R: H

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[1] This research was supported by United States Public Health Service Research Grant HE-12745 from the National Heart and Lung Institute.

[2] W. W. Epstein and H. C. Rilling, *J. Biol. Chem.*, **245**, 4597 (1970).

[3] J. Edmond, G. Popják, S. M. Wong, and V. P. Williams, *J. Biol. Chem.*, **246**, 6254 (1971).

[4] R. V. M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, 218 (1971).

[5] L. J. Altman, D. C. Kowerski, and H. C. Rilling, *J. Amer. Chem. Soc.*, **93**, 1782 (1971).

[6] R. M. Coates and W. H. Robinson, *J. Amer. Chem. Soc.*, **93**, 1785 (1971).

[7] The numbering of positions follows the numbering of the cyclopropane ring in formula **1**.

[8] G. Popják, J. Edmond, K. Clifford, and V. Williams, *J. Biol. Chem.*, **244**, 1897 (1969).

[9] H. C. Rilling, C. D. Poulter, W. W. Epstein, and B. Larsen, *J. Amer. Chem. Soc.*, **93**, 1783 (1971).

[10] L. Crombie and M. Elliott, *Fortschr. Chem. Org. Naturst.*, **19**, 120 (1961).

[11] N. Harada and K. Nakanishi, *Accounts Chem. Res.*, **5**, 257 (1972), and references cited therein.

[12] N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **90**, 7351 (1968); *cf.* footnote 8.

[13] The *trans*-(*R*)-chrysanthemum alcohol (**1b**) was made by the reduction with $LiAlH_4$ of methyl *trans*-(*R*)-chrysanthemum monocarboxylate prepared from a specimen of a concentrate of natural pyrethrins. The pmr and mass spectra of this optically active alcohol ($[\alpha]_{500}$ +71°, max $[\alpha]_{210}$ +10,800°) were indistinguishable from the reported[3] spectra of the racemic *trans*-chrysanthemum alcohol.

[14] We propose naming the product of the "reductive" ozonolysis of **1b**, *i.e.*, the product obtained by the reduction of the ozonide of **1b** with $LiAlH_4$, *trans*-(*R*)-caronic alcohol, in analogy with caronic acid which is the product of the oxidative cleavage of the ozonide of chrysanthemumic acid.