member in the chemistry department at Michigan State University, and James Kenneth, 29, is a chemical engineer at Syntex, Boulder, CO.

Professor Stille's research accomplishments span a wide area of subjects, including mechanistic organometallic chemistry, catalysis, organic synthesis, and polymer chemistry. He carried out the seminal studies on the mechanism of oxidative-addition and reductive-elimination reactions of organic halides with palladium complexes, and his research in this area provides much of the current understanding of these processes. In addition, his careful studies on the stereochemistry of nucleophilic attack on palladium-complexed olefins, carbon monoxide insertion into metal-carbon bonds, and transmetalation were fundamental to the utilization of these processes in synthesis.

In the area of catalysis, he developed the efficient palladium(0)-catalyzed carbonylation of organic halides, the palladium(II)-catalyzed bis carboxylation of olefins, and the platinum-catalyzed asymmetric hydroformylation of olefins, with high enantiomeric excess *and* high branched to normal ratios. Perhaps his greatest contribution to catalysis was his development of the extremely general palladium-catalyzed coupling of organostannanes with organic halides and triflates. This mild C–C bond-forming process is broadly tolerant of normally reactive functional groups and is being widely used by others for the synthesis of complex organic compounds. Stille himself led the way in his utilization of this chemistry in the total synthesis of PGB_1, coriolic acid, Lipoxin A, $\Delta^{9(12)}$-capnellene, amphinedine, and jatrophone.

Professor Stille also directed an outstanding program in polymer chemistry, making major contributions in the areas of rigid-chain, thermally stable high-performance polymers including polyquinoxalines, polyphenylenes, and polyquinones. He carried out fundamental studies on the interaction of chain polymerization of vinyl monomers, through charge-transfer complexes, on Ziegler–Natta polymerization, and on the cross-linking of thermally stable aromatic polymers. He combined his interests in polymer chemistry and catalysis by tailor-making polymeric supports for transition-metal complex catalysts and was among the leaders in the field of polymer-supported catalysis.

Such were the accomplishments of John Stille, a fine scientist and a fine man. He will be sorely missed.

—Louis S. Hegedus

Communications

Synthesis and Structure of a [(1,2-Phenylenedioxy)boryl]iridium Hydride Complex: A Model System for Studying Catalytic Hydroboration[†]

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Received May 14, 1990

Summary: Oxidative addition of the B–H bond in (1,2-phenylenedioxy)borane to $Ir(COE)(PMe_3)_3Cl$ (COE = cyclooctene) produces *mer*-$Ir(H)(BO_2C_6H_4)(Cl)(PMe_3)_3$, **1**, which was characterized by single crystal X-ray diffraction. Compound **1** reacts with alkynes to form vinyliridium complexes and will catalyze the hydroboration of alkynes with (1,2-phenylenedioxy)borane.

Hydroboration as a general class of reactions has found a prominent place among synthetic organic methodologies.[1] While most hydroboration reactions do not require the use of metal catalysts, it has been shown that certain sluggish reactions may be accelerated by the use of a metal complex. Over the last several years, several examples of metal-promoted B–H addition across acetylenes and olefins have been reported.[2] It has been demonstrated that the use of a catalyst can direct the course of the hydroboration reaction toward a different regiochemistry than the uncatalyzed reaction.[3] The use of a catalyst to change

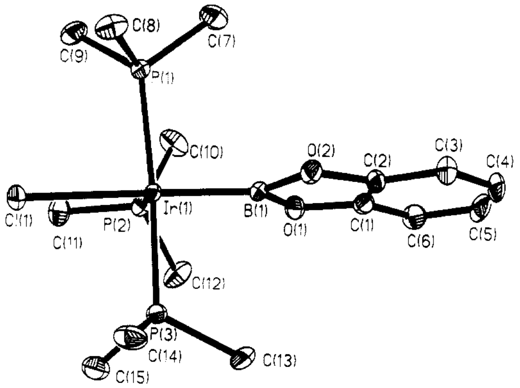


Figure 1. ORTEP plot of **1**. Important bond distances (Å): Ir(1)–P(1), 2.307 (2); Ir(1)–P(2), 2.351 (2); Ir(1)–P(3), 2.304 (2); Ir(1)–B(1), 2.023 (10); Ir(1)–Cl(1), 2.546 (2). Important bond angles (deg): P(1)–Ir(1)–P(2), 97.7 (1); P(1)–Ir(1)–P(3), 163.6 (1); P(2)–Ir(1)–P(3), 97.7 (1); P(1)–Ir(1)–Cl(1), 85.9 (1); P(2)–Ir(1)–Cl(1), 94.8 (1); P(3)–Ir(1)–Cl(1), 87.4 (1); P(1)–Ir(1)–B(1), 94.8 (3); P(2)–Ir(1)–B(1), 92.7 (3); P(3)–Ir(1)–B(1), 89.9 (3); Cl(1)–Ir(1)–B(1), 172.3 (3).

[†] This paper is dedicated to the memory of John K. Stille.

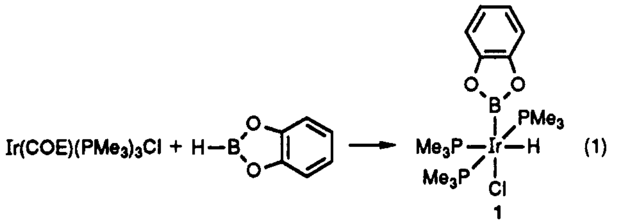
[1] (a) Cragg, G. M. L. *Organoboranes in Organic Synthesis*; Marcel Dekker: New York, 1973. (b) Brown, H. C. *Tetrahedron* **1981**, *37*, 3547.

[2] (a) Herves, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757. (b) Sneddon, L. G. *Pure Appl. Chem.* **1987**, *59*, 837 and references therein.

0276-7333/90/2309-3008$02.50/0

the direction of the hydroboration reaction has been most elegantly demonstrated in asymmetric hydroboration.[4] We recently described an iridium complex capable of C–H bond cleavage followed by further reactions of the resulting iridium hydride with unsaturated organic compounds.[5] It seemed to us that a similar iridium/B–H addition system would allow us to study the individual steps in a metal-catalyzed hydroboration sequence and to model metal-catalyzed hydroboration in general. In this communication, we report our results on such a system.

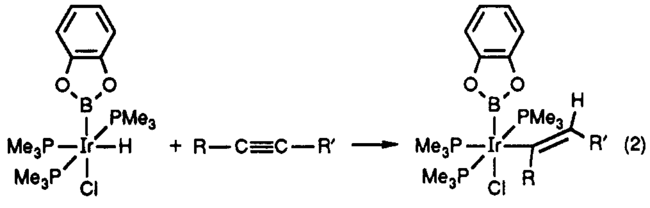
Reaction between (1,2-phenylenedioxy)borane and $Ir(COE)(PMe_3)_3Cl$ (COE = cyclooctene) leads to the production of $Ir(H)(Cl)(BO_2C_6H_4)(PMe_3)_3$ (**1**) in fair yield[6] (eq 1).



1

Compound **1** was fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopies as well as by single crystal X-ray diffraction.[7] The ORTEP plot of **1** is shown in Figure 1, and the structure consists of an octahedral arrangement of ligands with the three PMe_3 groups in a meridional arrangement with the (1,2-phenylenedioxy)boryl and chloro groups mutually trans. The Ir–B bond distance of 2.023 (10) Å is reasonable for an Ir–B bond length based on covalent radii and in keeping with other structurally characterized Ir–B compounds.[8]

The reaction depicted in eq 1 can be thought of as the first step in a potential catalytic hydroboration cycle. We investigated the reaction chemistry of **1** with various unsaturated organic compounds in order to detect other intermediates in the hydroboration scheme, and the most striking results were obtained with alkynes. In our previous work with C–H addition, we found that the hydridochlorophenyliridium complex formed was unreactive toward alkynes but could be induced to react via chemical removal of Cl^- by Tl^+.[5] **1** reacts with dimethylacetylene dicarboxylate directly without the need for chloride removal to form the vinyl complex **2a** via the formal insertion of the alkyne into the Ir–H bond (eq 2).[9] NMR spectroscopy (^1H, ^{31}P, ^{13}C) indicates that there are two isomers of **2a** in solution, a surprising occurrence for a symmetrically disubstituted alkyne. We attribute the existence of the isomers to hindered rotation about the Ir–C bond, resulting in two conformations of the vinyl group—one with the vinyl group "up" toward the boryl group, and the second with the vinyl group "down" toward the chlorine.[10]



2a: R′ = R = C(O)OCH$_3$
b: R′ = H; R = Si(CH$_3$)$_3$
c: R′ = H; R = C$_6$H$_5$
d: R′ = H; R = C(CH$_3$)$_3$

A striking feature of the ^1H NMR spectra of the vinyliridium compounds observed in this study is long-range 4-bond coupling between the phosphine ligands (both cis and trans to the vinyl group) and the proton on the vinyl cis to the iridium across the double bond. A similar observation was recently made for an iridium ethyl compound, but for only the usually larger *trans*-P–H complex.[11]

1 also reacts with other acetylenes such as those shown in eq 2 to yield vinyl compounds **2b**–**2d**. However, when the vinyl group does not contain strong electron-withdrawing groups as in **2a**, reductive elimination of the boryl and vinyl ligands occurs readily in $CHCl_3$ solution to form vinyl(1,2-phenylenedioxy)boranes. Compounds **2b**–**2d** were not isolated but were observed in solution via ^1H NMR spectroscopy.[12]

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(3) Männing, D.; Nöth, H. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 878.

(4) (a) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917. (b) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. (c) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 395. (d) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5857. (e) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 586. (f) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.

(5) Merola, J. S. *Organometallics* **1989**, *8*, 2975.

(6) In a typical reaction, 2.0 g (2.23 mmol) of $[Ir(COE)_2Cl]_2$ was dissolved in 70 mL of tetrahydrofuran and stirred while adding (1.39 mL, 13.39 mmol) PMe_3. The solvent was stripped off under reduced pressure to remove liberated cyclooctene and any excess PMe_3. The red residue was redissolved in 50 mL of tetrahydrofuran, 4.46 mL of 1 M (1,2-phenylenedioxy)borane in THF was added dropwise, and the reaction mixture was stirred at room temperature. The solvent was removed at reduced pressure, and the crude product was recrystallized from THF to yield 0.99 g (1.72 mmol) of $Ir(H)(Cl)(BO_2C_6H_4)(PMe_3)_3$, **1**. Anal. Calcd (Found) for $C_{15}H_{32}BClIrO_2P_3$: C, 31.29 (31.21); H, 5.60 (5.59). ^1H NMR (270 MHz, 20 °C in $CDCl_3$): δ −9.69 (dt, $J_{P\text{-}H}$ = 136.3, 21.1 Hz, 1 H, Ir–H), 1.64 (t, $J_{P\text{-}H}$ = 3.5 Hz, 18 H, *trans*-PMe_3), 1.58 (d, $J_{P\text{-}H}$ = 5.1 Hz, 9 H, *cis*-PMe_3), 6.95 ppm (AA′BB′, 4 H, $BO_2C_6H_4$). $^{31}P\{^1H\}$ NMR (81 MHz, 20 °C in C_6D_6): δ −39.61 (d, $J_{P\text{-}P}$ = 21 Hz, *trans*-PMe_3), −46.35 ppm (t, $J_{P\text{-}P}$ = 20 Hz, *cis*-PMe_3). $^{13}C\{^1H\}$ NMR (50 MHz, 20 °C in C_6D_6): δ 18.49 (d, $J_{P\text{-}C}$ = 27 Hz, *cis*-PMe_3) 20.42 (t, $J_{P\text{-}C}$ = 19 Hz, *trans*-PMe_3), 110.81, 121.20, 150.97 ppm ($BO_2C_6H_4$). ^{11}B NMR (64.2 MHz, 20 °C in C_6D_6): δ 32.8 ppm (br s) with $BF_3{\cdot}Et_2O$ as reference at 0 ppm.

(7) Crystal structure data for **1**, $C_{15}H_{32}BO_2P_3ClIr$. Crystals were grown by slow diffusion of pentane into a chloroform solution of **1**. The crystals belong to the orthorhombic space group $P2_12_12_1$ (No. 19) with a = 11.316 (3) Å, b = 13.348 (3) Å, c = 14.889 (4) Å, V = 2248.9 (9) Å^3 and d_{calcd} = 1.698 g m^{-3} for $Z = 4$. Data was collected at 298 K on a Nicolet R3m/V diffractometer with Mo Kα radiation (λ = 0.71073 Å) using the ω scan technique. A total of 2926 reflections were collected with 2776 being independent and observed ($F > 3.0\sigma(F)$). A semiemperical adsorption correction was applied to the data (μ = 6.249 mm^{-1}) based on a series of ψ scans. The structure was solved by using Patterson methods and refined by using full-matrix least-squares procedures employing the SHELXTL-PLUS software as supplied by Nicolet Corporation. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the ligands were added at calculated positions. The solution was refined with the final residuals R = 0.0353 and R_w = 0.0464.

(8) Churchill, M. R.; Hackbanth, J. *J. Inorg. Chem.* **1975**, *14*, 2047.

(9) Analytical information for **2d**. Anal. Calcd (Found) for $C_{21}H_{38}BClIrO_6P_3$: C, 35.13 (35.18); H, 5.34 (5.31). Major isomer: ^1H NMR (C_6D_6): δ 1.11 (d, $J_{P\text{-}H}$ = 8.7 Hz, 9 H, *cis*-PMe_3), 1.53–1.59 (v br, 18 H, *trans*-PMe_3), 3.33 (s, 3 H, COOMe), 3.99 (s, 3 H, COOMe), 6.08 (dt, $J_{P\text{-}H}$ = 8.0, 2.6 Hz, 1 H, C=C(H)), 6.88 ppm (AA′BB′, 4 H, $BO_2C_6H_4$). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta 1$ = −41.70, $\delta 2$ = −43.07, $\delta 3$ = 49.00 ppm, J_{12} = −507, J_{13} = 21.2, J_{23} = 23.2 Hz. These ^{31}P NMR data show the *trans*-PMe_3 groups are inequivalent and was modeled as an ABX spin system to get the above data. Minor isomer: ^1H NMR (C_6D_6): δ 1.15 (d, $J_{P\text{-}H}$ = 8.6 Hz, 9 H, PMe_3), 1.46 (t, $J_{P\text{-}H}$ = 4.0 Hz, 18 H, PMe_3), 3.47 (s, 3 H, COOMe), 3.61 (s, 3 H, COOMe), 6.90 (AA′BB′, 4 H, $BO_2C_6H_4$) 7.64 ppm (dt, $J_{P\text{-}H}$ = 7.4, 2.6 Hz, 1 H, C=C(H)). $^{31}P\{^1H\}$ NMR: δ −48.86 (t, $J_{P\text{-}P}$ = 20 Hz, 1 P, PMe_3), −43.09 ppm (d, $J_{P\text{-}P}$ = 20 Hz, 2 P, PMe_3).

(10) Modeling with chem-X (developed and distributed by Chemical Design Ltd., Oxford, England) shows that steric interactions between the vinyl group and the PMe_3 ligands cis to it account for a very high barrier to rotation, but due to the unavailability of parameters for P or Ir, the exact values can't be determined. We cannot rule out at this time that the two isomers may be *cis*- and *trans*-vinyl compounds. However, this would imply a free-radical mechanism for the insertion reaction, which we find less likely given our current state of knowledge of these $Ir(PMe_3)_3$ compounds.

(11) Deutsch, P. P.; Eisenberg, R. *R. J. Am. Chem. Soc.* **1990**, *112*, 714.

The reductive elimination of vinyl(1,2-phenylenedioxy)borane from the vinyliridium complexes suggested that this might be a true catalytic hydroboration system. We have found that this is indeed the case, following the system through greater than 6 turnovers.[13] The "resting state" of the catalyst under these conditions appears to be the vinyliridium complex. When the (1,2-phenylenedioxy)borane and alkyne have been depleted, the $Ir(PMe_3)_3Cl$ presumably formed reacts with chloroform solvent to form as an as-yet uncharacterized iridium(III) complex.

While this manuscript was in review, Evans reported on the mechanism of the rhodium-catalyzed hydroboration of olefins where the investigation involved careful deuterium labeling studies for a number of olefins.[14] Our isolation of complexes 1 and 2 and the observation of catalytic (albeit slow) hydroboration show that this is a useful system for modeling catalytic hydroboration. Through a combination of studies such as those of Evans and those contained in this report, the details of the mechanism(s) of metal-catalyzed hydroboration will be unraveled. We plan to continue our investigations into this system to further understand the nature of the unsaturate/metal interaction step and the role that ligand dissociation (both Cl^- and PMe_3) play in this system.

Acknowledgment. We acknowlege support for this work from the Jeffress Trust, Exxon Education Foundation, and the Corporation for Innovative Technology, as well as a generous loan of iridium from Engelhard and Johnson-Matthey. We also thank Drs. T. B. Marder and R. T. K. Baker for sharing of data prior to publication.

Supplementary Material Available: Tables I–IV, listings of final atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for 1 (2 pages); a table of observed and calculated structure factors for 1 (11 pages). Ordering information is given on any current masthead page.

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[12] **2b**, ^1H NMR ($CDCl_3$): δ −0.04 (s, 9 H, $SiMe_3$), 1.49 (t, $J_{P-H} = 3.7$ Hz, 18 H, *trans*-PMe_3), 1.57 (d, $J_{P-H} = 8.1$ Hz, 9 H, *cis*-PMe_3), 6.72 (ddt, $J_{H-H} = 20.2$, $J_{P-H} = 11.2$, 3 Hz, IrC(H)═C(*H*)), 6.99 (AA′BB′, 4 H, $BO_2C_6H_4$), 8.23 ppm (ddt, $J_{H-H} = 20.2$, $J_{P-H} = 5.9$, 3.8 Hz, 1 H, IrC(*H*)═C(H)). **2c**; ^1H NMR ($CDCl_3$): δ 1.51 (t, $J_{P-H} = 3.7$ Hz, 18 H, PMe_3), 1.63 (d, $J_{P-H} = 8.2$ Hz, 9 H, PMe_3), 7.03 (AA′BB′, 4 H, $BO_2C_6H_4$) 7.19–7.36 (m, 5 H, phenyl), 8.17 ppm (ddt, $J_{H-H} = 17.4$, $J_{P-H} = 3.0$, 3.5 Hz, IrC(*H*)═C(H)). IrC(H)═C(*H*) obscured. **2d**, ^1H NMR ($CDCl_3$): δ 0.94 (s, 9 H, CMe_3), 1.50 (t, $J_{P-H} = 3.7$ Hz, 18 H, PMe_3), 1.57 (d, $J_{P-H} = 8.2$ Hz, 9 H, PMe_3), 5.84 (ddt, $J_{H-H} = 17.0$, $J_{P-H} = 7.0$, 3 Hz, 1 H, IrC(H)═C(*H*)), 6.66 (ddt, $J_{H-H} = 17.0$, $J_{P-H} = 3.5$, 3.5 Hz, 1 H, IrC(*H*)═C(H)), 6.96 ppm (AA′BB′, 4 H, $BO_2C_6H_4$).

[13] At room temperature, 6 turnovers require approximately 2 days. Control experiments show that this is faster than the rate of uncatalyzed hydroboration with (1,2-phenylenedioxy)borane under these conditions.

[14] Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280.

Dyotropic Rearrangement in Homochiral Organoiron Complexes Resulting in Inversion at Two Adjacent Carbon Centers

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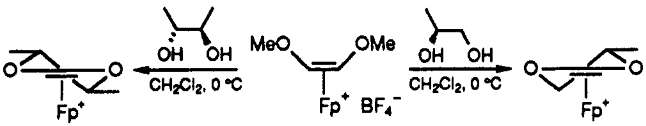
Summary: The kinetic products derived from addition of phthalimide, *N*-methyltoluenesulfonamide, or benzenethiol to homochiral Fp(dioxene)BF_4 salts **2** and **3** [Fp = $CpFe(CO)_2$] undergo unimolecular dyotropic rearrangement, resulting in inversion of the two initially formed asymmetric centers.

Transition-metal complexes are now widely used in organic synthesis, and many of these have in recent years found increasing use in asymmetric synthesis as reagents, catalysts, or auxiliaries.[1] As part of a program directed toward the use of the homochiral $Fp(\eta^2\text{-olefin})^+BF_4^-$ complexes in organic synthesis [Fp = $CpFe(CO)_2$], we have prepared a number of these salts, among them 2 and 3, by exchange etherification of 1[2] with (*S*)-(+)-1,2-propanediol[3] and (*R*,*R*)-butane-2,3-diol, respectively (absolute configurations are shown throughout). These cations undergo regioselective nucleophilic addition with both carbon and heteroatomic nucleophiles to give the neutral complexes 4 and 5,[2] respectively, which may be further transformed to optically active α,β-disubstituted carboxylic acids.[4]



3 1 2

We wish now to report that several of these neutral homochiral organoiron complexes undergo facile rear-

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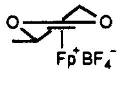
[1] *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5. Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187. Noyori, R.; Suga, S.; Kawai, K.; Okads, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597. Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937 and references therein. Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 463. Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 13. Hayashi, T. *Ibid.* **1988**, *60*, 7. Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. Bandara, M. M. R.; Birch, A. J.; Kelley, L. F. *J. Org. Chem.* **1984**, *49*, 2496. Tamao, K.; Kumada, M. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Ed.; Wiley: New York, 1987; p 820. *J. Organomet. Chem.* **1989**, *370*, 1–407 (Brunner, H., Ed.).

[2] Turnbull, M. M.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 200.

[3] Complex 2 is obtained as a mixture with its diastereomer 2′



but these are readily separated by preferential precipitation of the less soluble 2 from methylene chloride solutions of the mixtures. Since 2 and 2′ equilibrate in solution through reversible complexation, ratios of 2:2′ as high as 3:1 can be achieved. In practice, it is unnecessary to separate these diastereomers, since the adducts derived by nucleophilic addition have the same absolute configurations at all centers on the dioxane ring.

[4] Unpublished work with K.-H. Chu.

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