

photolysis and to purify the products in the initial study.¹ Under our glpc conditions (heated injection block, 240°) rearrangement is instantaneous, and **1** and **2** are formed in a 2:1 ratio.

Thermal reversion of **4** to **1**, presumably by a non-concerted process, is anticipated from the analogous behavior of other strained cyclobutanes.⁵ However, the competing rearrangement to **2** requires a more elaborate rationale. Any reasonable pathway to **2** must assume the formal Cope rearrangement product **5** as an intermediate. The latter can then undergo a well-precedented retro-Diels-Alder reaction⁶ which restores the benzene ring to a happy aromatic state and results in formation of **2**. The activation energy (29.2 kcal) is consistent with such a pathway and corresponds reasonably to the estimated loss of resonance energy in the nonaromatic polyene **5** compared to **4**. No previous example of Cope rearrangement involving an aromatic double bond has been observed under simple thermal conditions.^{7,8}

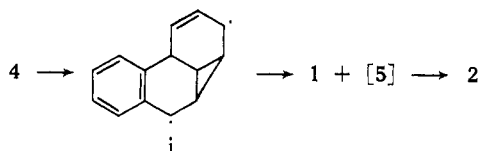
Finally, we note that the apparently simple $2\pi + 2\pi$ cycloaddition **1** \rightarrow **4** can also be viewed as a $4\pi + 4\pi$ cycloaddition to give **5**, followed by a highly favorable Cope rearrangement. There is no rigorous way to exclude the latter possibility at present but neither is it possible to decide whether the well-established¹²

(5) M. R. Willcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 25 (1972), and references therein.

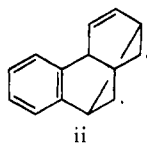
(6) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968); R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970).

(7) There are two examples in the literature of reactions speculated to involve analogous Cope rearrangement followed by H shifts: E. N. Marvell and C. Lin, *Tetrahedron Lett.*, 2679 (1973); L. A. Paquette and S. Maiorana, *Chem. Commun.*, 313 (1971).

(8) A referee has suggested a common diradical intermediate, *i*, as a precursor to both **1** and **2**. We do not wish to imply that such a species can be ruled out. However, molecular models show that the σ -orbital at C₇-C₈ is nearly orthogonal to the adjacent π -orbitals in **4**. Also, the benzyl and allyl π systems in *i* cannot simultaneously adopt coplanar geometries required for normal delocalization. Therefore, incipient diradical stabilization in the transition state should be less effective than for the model compound *trans*-1,2-divinylcyclobutane ($E_a = 35$ kcal/mol),⁹ and concerted rearrangement of **4** to **5** seems more consistent



with the low activation energy. A second diradical, *ii*, must be con-



sidered as a potential intermediate between **4** and **1**. Simple bicyclopentanes undergo central bond cleavage with $E_a = 33$ –39 kcal/mol,¹⁰ or $E_a = 29$ kcal/mol for an unusually strained system, bicyclo[2.1.0]pentane-5-spirocyclopropane.¹¹ The strain in **4** is not known, and we cannot distinguish between the possible routes from **4** to **1**.

(9) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

(10) J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); M. J. Jorgenson, T. J. Clark, and J. Corn, *ibid.*, **90**, 7020 (1968); for qualitative studies, see J. E. Baldwin and J. Ollerenshaw, *Tetrahedron Lett.*, 3757 (1972); M. C. Flowers, H. M. Frey, and H. Hopf, *J. Chem. Soc., Chem. Commun.*, 1284 (1972); L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 4922 (1971).

(11) W. R. Roth and K. Enderer, *Justus Liebigs Ann. Chem.*, **730**, 82 (1969).

(12) S. Masamune and N. Darby, *Accounts Chem. Res.*, **5**, 272 (1972), and references therein.

photolytic conversion of **7** to **8** at -70° is a $4\pi + 4\pi$ process or occurs by initial $2\pi + 2\pi$ cycloaddition to **9** with subsequent rapid Cope rearrangement. We anticipate negligible activation energy for the process **9** \rightarrow **8**, based on the difference between $E_a = 29.2$ kcal and the energy required to disrupt the aromatic ring (*ca.* 30 kcal/mol?) for the reaction **4** \rightarrow **5**. There is no comparable barrier to overcome for the parent hydrocarbon **9**, and the Cope rearrangement should be exceptionally facile.¹³

(13) The most facile Cope rearrangement known (semibullvalene) is immeasurably fast at -70° : H. E. Zimmerman and G. L. Gruenwald, *J. Amer. Chem. Soc.*, **88**, 183 (1966).

(14) Alfred P. Sloan Fellow, 1971–1973.

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Received July 25, 1973

Oxidative Addition of Pentaborane(9) and Bromopentaborane(9). The Crystal Structure of 2-[IrBr₂(CO)(PMe₃)₂]B₅H₈

Sir:

Oxidative addition of boron-halide^{1a} and boron-hydrogen^{1b} bonds is a potentially convenient route to σ -metalloboranes. We wish to report addition of bromopentaborane(9) and pentaborane(9) to *trans*-IrCl(CO)(PMe₃)₂ (**1**). In all cases the iridium atom is linked to B(2), regardless of the stereochemistry of the starting borane. Such behavior has previously been noted² in nucleophilic displacement reactions of NaMn(CO)₅ with 1- or 2-ClB₅H₈.

Treatment of **1** with excess 1- or 2-BrB₅H₈ (40°, neat), followed by removal of volatile components *in vacuo*, chromatography on acetylated polyamide (toluene eluent), and recrystallization from toluene-hexane afforded colorless crystals of 2-[IrBr₂(CO)(PMe₃)₂]B₅H₈ (**2**): ir (Kel-F and Nujol mulls) 2573 (m, ν_{BH}), 2554 (m, ν_{BH}), 2024 (s, ν_{CO}), and 945 cm⁻¹ (s, δ apical BH); mp 148° dec; ¹H {¹¹B} nmr³ (CD₂Cl₂) 1.4 (s, 2, μ_{BH}), 0.0 (s, 2, μ_{BH}), -1.4 (s, 1, B(1)H), and -2.6 (t, 18, PCH₃, J_{PCH} = 4.2 Hz); ³¹P {¹H} nmr (CH₂Cl₂) 7.0 (s); ¹¹B {¹H} nmr (CH₂Cl₂) 11.3 (B(2)), 14.4 (B(3,5)), 17.3 (B(4)), and 50.2 (B(1)). Anal. Calcd for C₇H₂₆B₅Br₂IrOP₂: C, 14.15; H, 4.42; B, 9.09; Br, 26.89; Ir, 32.34; P, 10.42. Found: C, 14.09; H, 4.39; B, 8.84; Br, 26.88; Ir, 35.45; P, 10.50. **2** is remarkably stable for a substituted pentaborane and is not oxidized upon exposure to air for several days.

In an attempt to observe an intermediate 1-metalated isomer, we monitored the reaction of **1** with 1-BrB₅H₈ in CH₂Cl₂ at 0° *via* ir spectroscopy. The solution decolorized in seconds indicating rapid formation of an Ir(III) species. In addition to **2** an iridium carbonyl

(1) (a) G. Schmid, W. Petz, W. Arloth, and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, **6**, 696 (1967); (b) E. L. Hoel and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 2712 (1973).

(2) D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, **7**, 1041 (1968).

(3) (a) Chemical shifts for H, P, and B are referenced to external TMS, 85% H₃PO₄, and BF₃·Et₂O, respectively, and are in ppm. A nucleus more shielded than that in the reference is assigned a positive shift. (b) A comparison of the ¹H with the ¹H {¹¹B} nmr spectrum shows that the basal terminal B-H resonances occur together with the PCH₃ resonances. Different power levels were used for B-H *vs.* C-H resonances; integration was against an internal trace of benzene for **2** and against Ir-H for **3**.

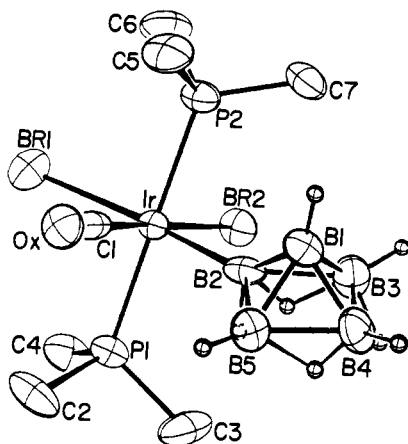


Figure 1. Stereochemistry of the 2-[IrBr₂(CO)(PMe₃)₂]B₅H₉ molecule. [ORTEP diagram, 50% ellipsoids for non-hydrogen atoms and artificial 0.1 Å radius spheres for pentaboranyl hydrogen atoms.]

hydride ($\nu_{\text{CO}} = 2085$, $\nu_{\text{IrH}} = 1985 \text{ cm}^{-1}$) was observed,⁴ which slowly decayed to **2**. The observation of the intermediate IrClH(CO)(PMe₃)₂(BrB₅H₇) (*vide infra*) of undetermined stereochemistry shed no light on the formation of only the 2-metalated isomer of **2**. It did, however, suggest that oxidative addition of BH may be a facile, reversible process.

Subsequently, we found that excess B₅H₉ reacted with **1** (but not with *trans*-IrCl(CO)(PPh₃)₂) in hexane at -45° , yielding colorless 2-[IrClH(CO)(PMe₃)₂]B₅H₉ (**3**) in 80% yield: ir (Kel-F and Nujol mulls) 2573 (m, ν_{BH}), 2555 (m, ν_{BH}), 2082 (s, ν_{CO}), 1978 (s, ν_{IrH}), and 945 cm^{-1} (s, δ apical BH); mp 64° dec (rapid heat); ¹H {¹¹B} nmr³ (-30° , CD₂Cl₂) 6.9 (t, 1, IrH, $J_{\text{PIrH}} = 20$ Hz), 1.4 (s, 2, μ_{BH}), -0.1 (s, 2, μ_{BH}), -1.4 (s, 1, B(1)H), -2.8 (t, 18, PCH₃, $J_{\text{PCH}} = 4.2$ Hz); ³¹P {¹H} nmr (-70° , CH₂Cl₂) 4.0 (s). **3** slowly decomposes at 25° , but may be kept indefinitely at -20° . The reaction is at least partially reversible, since pyrolysis of **3** at 150° gave a 38% yield of B₅H₉.

The molecular stereochemistry of **2** has been determined unambiguously *via* a three-dimensional X-ray structural analysis.

The species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (no. 14; C_{2h}^5) with $a = 13.824$ (4) Å, $b = 10.661$ (3) Å, $c = 13.611$ (3) Å, $\beta = 104.90$ (2) Å, $\rho_{\text{obsd}} = 2.01$ (1) g cm^{-3} , $\rho_{\text{calcd}} = 2.036$ g cm^{-3} for $Z = 4$, and molecular weight = 594.305. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer, using Mo K α radiation and a θ - 2θ scan technique. All data were corrected for absorption ($\mu = 118.16 \text{ cm}^{-1}$). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the final discrepancy indices being $R_{\text{F}} = 4.64\%$ and $R_{\text{wF}} = 4.25\%$ for the 2546 independent reflections representing data complete to $2\theta = 45^\circ$. All atoms other than the methyl hydrogens have been located, the determined molecular stereochemistry being shown in Figure 1.

The crystal consists of an ordered racemic array of 2-[IrBr₂(CO)(PMe₃)₂]B₅H₉ molecules in which the iridium atom is in a fairly regular octahedral coordination environment. (Angles between mutually cis ligands

(4) This hydride could also be detected *via* ¹H nmr (*cf.* ref 3b).

range from 86.1 (1) to 93.5 (4) $^\circ$, while angles between trans ligands vary from 172.2 (1) to 177.8 (4) $^\circ$.)

The iridium-phosphorus distances are equivalent, with Ir-P(1) = 2.362 (3) and Ir-P(2) = 2.361 (3) Å. Iridium-bromine distances are, however, decidedly non-equivalent, with Ir-Br(1) = 2.638 (1) and Ir-Br(2) = 2.516 (1) Å. (Note that the pentaboranyl ligand exerts a stronger trans-lengthening influence than does the carbonyl ligand!) Other distances within the iridium(III) coordination sphere are Ir-CO = 1.95 (2) and Ir-B(2) = 2.07 (1) Å.

The pentaboranyl ligand is bonded to iridium *via* its basal (2-) position. B(1)-B(basal) distances range from 1.64 (2) to 1.69 (2) Å, while B(basal)-B(basal) distances vary from 1.80 (2) to 1.91 (2) Å. The eight hydrogen atoms of the 2-pentaboranyl ligand have been located and refined, resulting distances being B(1)-H(1) = 1.08 (8), B(basal)-H(terminal) = 1.08 (11)-1.55 and B(basal)-H(bridging) = 1.03 (10)-1.45 (10) Å.

It is of note that the strong trans influence⁵ of the borane ligand, color⁶ of the adducts, and carbonyl stretching frequencies⁶ of the same indicate that a σ -bound pentaborane (9) unit is electronically similar to a σ -alkyl ligand.

Acknowledgment. We are grateful to Professor J. A. Osborn for a helpful discussion concerning the synthesis of the iridium precursor (**1**), and to Professor W. N. Lipscomb for a gift of B₅H₉. This work was made possible by a generous allocation of computer time on the IBM 370/158 computer of the Computer Center, University of Illinois at Chicago Circle, and by financial support from the National Science Foundation through Grants GP-33018 and GP-42724X (to M. R. C.) and GP-37334X (to A. D.).

(5) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1971); see especially Section X.A., pp 151-152.

(6) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972).

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Received March 18, 1974

Organolanthanides and Organoactinides. X. Synthesis of a New Type of σ -Bonded Organolanthanide Complex: $(\eta^5\text{-C}_5\text{H}_5)_2\text{LnC}\equiv\text{CPh}$

Sir:

In the past several years, there has been a revival of interest in the organometallic chemistry of the actinides. One area which has received active interest has been the preparation of σ -bonded derivatives.¹⁻⁴ However, the lanthanides seem to have escaped investigation of this type. Their chemistry consists mainly of derivatives containing ionic π -bonded cyclopenta-

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(2) T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Amer. Chem. Soc.*, **95**, 5529 (1973).

(3) G. Brandi, M. Brunelli, G. Lugli, and A. Mazzei, *Inorg. Chim. Acta*, **7**, 319 (1973).

(4) M. Tsutsui and N. Ely, submitted for publication.