establish that two isomers **7a** and **7b** equilibrate in solution. At −30°, the ^{13}C spectrum of the carbonyl ligands consists of two unequal sets of resonances, each set having two signals in 2:1 ratio. As the temperature is raised, all resonances collapse and at 25°, a single 2:1 pattern emerges. Similarly the variable temperature ^1H spectrum shows the appropriate changes in both the olefinic and benzylic resonances. The equilibration **7a** ⇌ **7b** is thus not accompanied by interchange of the olefin with an axial carbonyl ligand since this could necessarily cause axial–equatorial carbonyl site equilibration.[21] Exchange of the olefin with the axial isocyanide ligand can also be ruled out by studies on **9**. Isomers **9a** and **9b** are seen to interconvert at 0°, but again no equilibration of axial and equatorial isocyanide ligands is observed during this process. It is noteworthy that this latter process can be observed at higher temperatures (>60°) in this case.

9a   **9b**
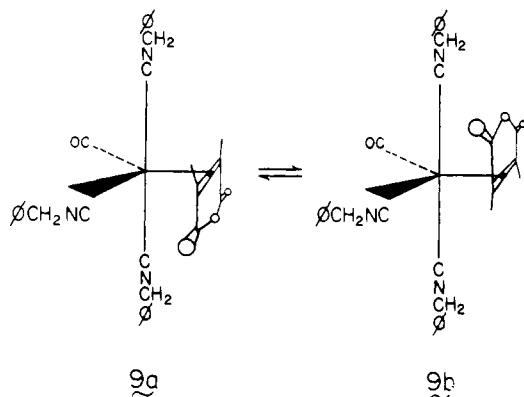
The observations on **7**, **8**, and **9** could be simply explained by rotation about the metal–olefin bond without accompanying motion about the metal center. However, we have seen that this cannot be so with the closely analogous $Fe(CO)_4$(olefin) complexes **1** and **2**. Hence, a preferable description for the observed behavior (including **7**, **8**, and **9**) involves a concerted process involving the coupling of the olefin rotation with Berry pseudorotation about iron. In **7**, **8**, and **9**, the accompanying motion about the metal cannot be observed in the nmr experiment. However, a nonconcerted mechanism is an attractive alternative, in which the square pyramidal **7c** is not a transition state but an intermediate of sufficient lifetime during which rate determining olefin rotation can occur. Olefin rotation in such an intermediate would be expected to be of lower energy than in the ground TBP states **7a** and **7b**.

(21) Note that although the preference[7] for the equatorial site is olefin > CO > RNC (a) the interchange between carbonyl and isocyanide ligands in $Fe(CO)_4(C_6H_5CH_2NC)$ is very fast at −80° in CD_2Cl_2 and (b) use of a bulkier isocyanide, e.g., t-BuNC may cause the stability sequence above to be altered.

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Isolation and Thermolysis of 4,5-Benzotetracyclo[4.4.0.0²,¹⁰.0³,⁹]deca-4,7-diene, a New $(CH)_{10}$ Derivative

Sir:

It has been reported that photolysis of **1** results in an apparent 1,3-carbon shift to afford an isomer **2** which rearranges to **3** when irradiated under similar conditions.[1] We have reexamined this reaction and find that **2** is not formed photochemically. The major photoproduct is **4**, a substance having a hitherto unknown $(CH)_{10}$ skeleton.

We have used nmr spectroscopy to follow photolysis of **1** at room temperature in ether or acetone solution (Pyrex filter). The nmr signals due to starting material disappear, and a new substance, **4**, appears together with a small amount of phenanthrene as the only other significant product.[2] Neither **2** nor **3** can be detected by nmr in the final photolysis mixture.

After purification by chromatography, **4** is obtained as a colorless oil, $\lambda_{max}^{C_2H_5OH}$ 273 (ϵ 800) and 266 nm (ϵ 870), m/e 180. The nmr spectrum ($CDCl_3$) contains four aromatic protons, δ 6.7–7.1 (m), H_7 at δ 6.22 (d of d with partly resolved fine coupling, $J_{7,8} = 8$ Hz, $J_{6,7} = 7$ Hz), H_8 at δ 5.40 ppm (d of d, $J_{7,8} = 8$ Hz, $J_{8,9} = 7$ Hz), H_6 at δ 3.70 (br t, $J_{6,7} = J_{1,6} = 7$ Hz), H_3 and H_9 at δ 3.2–3.5 (m), and cyclopropyl protons H_1, H_2, and H_{10} at δ 1.46–1.90 ppm (m). Of the possible benzo $(CH)_{10}$ structures,[4] only **4** and **6** are consistent with the chemical shifts in the spectrum. A final decision in favor of **4** is based on extensive spin decoupling experiments which show that neither vinyl proton is coupled to cyclopropyl protons ($J < 1$ Hz).
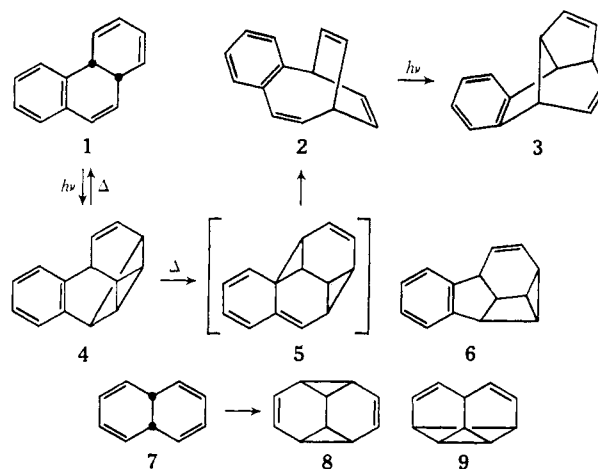
The new hydrocarbon is thermally labile and rearranges to a 6:5 mixture of **1** and **2** in the temperature range 71–83° ($E_a = 29.2 \pm 0.6$ kcal/mol, log $A = 14.2 \pm 0.4$). This finding provides an obvious explanation for the contrast between our results and those reported previously, since glpc analysis was used to monitor the

(1) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Amer. Chem. Soc.*, **94**, 4902 (1972).

(2) Phenanthrene is also formed from **1** by disproportionation,[1] but control experiments indicate that this is a much slower reaction than the photolytic process. According to nmr analysis, the relative yield of phenanthrene formed photolytically is ca. 15%. At least four unidentified minor products are also present by glpc, 5% relative yield. Two of these correspond by glpc retention time to 2,3- and 5,6-benzotricyclo[5.3.0.0⁴,¹⁰]deca-2,5,8-trienes.[1,3]

(3) E. Vedejs, R. A. Shepherd, and R. P. Steiner, *J. Amer. Chem. Soc.*, **92**, 2158 (1970).

(4) A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

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 reaction[6] 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** → **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-established[12]

(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 C_3–C_9 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

4 → → 1 + [5] → 2

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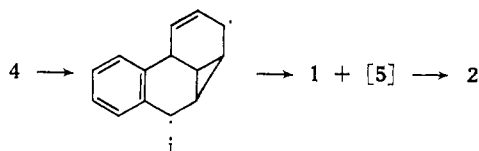
with the low activation energy. A second diradical, ii, must be con-

ii
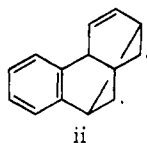
sidered as a potential intermediate between **4** and **1**. Simple bicyclopentanes undergo central bond cleavage with $E_a = 33$–39 kcal/mol,[10] or $E_a = 29$ kcal/mol for an unusually strained system, bicyclo[2.1.0]-pentane-5-spirocyclopropane.[11] The strain in **4** is not known, and we cannot distinguish 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** → **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** → **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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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 noted[2] 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} nmr[3] (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 C₇H₂₆B₅Br₂-IrOP₂: 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**.