

PHOTOLYTIC CARBONYL INSERTION AND SOLVOLYSIS OF 6-[(η^5 -C₅H₅)Fe(CO)₂]B₁₀H₁₃

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(Received July 26th, 1976)

Summary

The photolysis of 6-[(η^5 -C₅H₅)Fe(CO)₂]B₁₀H₁₃ in ethereal solvents leads to the formation of icosahedral metallocarboranes of the type (η^5 -C₅H₅)Fe-[(η^5 -B₁₀H₁₀C(Lewis base))], in which the Lewis base is either tetrahydrofuran (THF) or diethyl ether. This is believed to proceed via insertion of one of the carbonyl moieties into the boron cage framework and subsequent solvolysis.

Introduction

Previously it has been reported that Na[B₁₀H₁₃] reacted with M(CO)₆ (M = Cr, Mo, or W) under photochemical conditions to form [(OC)₄M(η^5 -B₁₀H₁₀COH)]⁻ derivatives [1]. We wish to report another example of photolytic carbonyl insertion into a borane fragment. In this particular case, 6-[(η^5 -C₅H₅)Fe(CO)₂]B₁₀H₁₃, a compound with an iron-boron single bond, is converted into the icosahedral metallocarborane (η^5 -C₅H₅)Fe[(η^5 -B₁₀H₁₀C(Lewis base))] in which the Lewis base is either tetrahydrofuran (THF) or diethyl ether.

Experimental

General comments

Boron (¹¹B) NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer, and were externally referenced to BF₃ · O(C₂H₅)₂. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York. IR spectra were obtained as KBr disks using a Perkin-Elmer 137G spectrometer. Low resolution mass spectra were obtained with an Atlas CH-7 instrument. Osmometer molecular weight measurements were made with a Mechrolab Vapor Pressure Osmometer 310A.

* Contribution No. 2881.

Starting material

The synthesis of 6-[(η^5 -C₅H₅)Fe(CO)₂]B₁₀H₁₃ was carried out according to the procedure described in the literature [2].

(η^5 -C₅H₅)Fe[η^5 -B₁₀H₁₀C(Lewis base)]

(Lewis base is THF for I and is O(C₂H₅)₂ for II).

A solution containing 0.35 g (1.17 mmol) 6-[(η^5 -C₅H₅)Fe(CO)₂]B₁₀H₁₃ in dry THF (for compound I) or in dry diethyl ether (for compound II) was placed in a Vycor Schlenk tube and photolyzed for 18 h, using a high pressure mercury lamp. The solvent was removed under vacuum and the residue was chromatographed

TABLE 1
CHEMICAL ANALYSES

Compound	Analysis found (calcd.) (%)	
	C	H
(η^5 -C ₅ H ₅)Fe[η^5 -B ₁₀ H ₁₀ C(THF)] (I)	36.53 (37.12)	6.99 (7.17)
(η^5 -C ₅ H ₅)Fe[η^5 -B ₁₀ H ₁₀ C(O(C ₂ H ₅) ₂)] (II)	37.33 (36.93)	7.41 (7.74)

TABLE 2
INFRARED SPECTRA ^a

Compound	Wavenumber (cm ⁻¹)
I	3131w, 2973(sh), 2938m, 2870w, 2545(sh), 2520s, 1988(sh), 1735vw, 1638vw, 1423w, 1354w
II	3116w, 2964m, 2929m, 2862m, 2532s, 1742w, 1642w, 1468w, 1456w, 1425w, 1387w

^a Obtained as KBr disk.

TABLE 3
¹¹B NMR Spectra ^a (70.6 MHz)

Compound	Chemical shift (ppm) (J (Hz))
I	-42.4 (127)
	-12.9 (107)
	12.2 ^b
	24.4 (122)
	41.7 (112)
II	95.3 (127)
	-58.8 (107)
	-18.1 (117)
	17.0 ^b
	27.7 (107)
	45.2 (107)
	206.5 (207)

^a C₅H₅ solvent. ^b Coupling constant could not be obtained.

on a silica gel column with CH_2Cl_2 as eluent. Following elution of a yellow band of $6\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{B}_{10}\text{H}_{13}$, a green band of the product was obtained. Dark-green feathery crystals of I or II were obtained in low yields (0.03–0.08 g, 1–3% yield) by crystallization from CH_2Cl_2 /hexanes. Elemental analyses, IR and ^{11}B NMR data are given in Tables 1–3.

Results and discussion

Unlike the photolytic reaction of the $\text{Na}[\text{B}_{10}\text{H}_{13}]$ and metal hexacarbonyls [1], irradiation of $6\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{B}_{10}\text{H}_{13}$ results in a final product in which a solvent molecule is coordinated to the cage carbon. The presence of the solvent moiety was first detected in the mass spectral data. In addition to the boron-containing parent ion fragments at the spectral cutoffs of m/e 322 (I) and m/e 324 (II), appeared non-boron-containing fragments at m/e 72 (I) and m/e 74 (II), which correspond to the ether fragments.

The molecular weight range suggested by the mass-spectrum was verified by an approximate osmometer molecular weight of 380 obtained in CH_2Cl_2 solution.

The presence of the solvent moiety was confirmed by elemental analyses and by a single-crystal X-ray structure determination which has been completed for II [3]. The structure of this new type of carborane complex is presented in Fig. 1. The known compound $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(1,2\text{-B}_9\text{C}_2\text{H}_{11})$ is isoelectronic with the

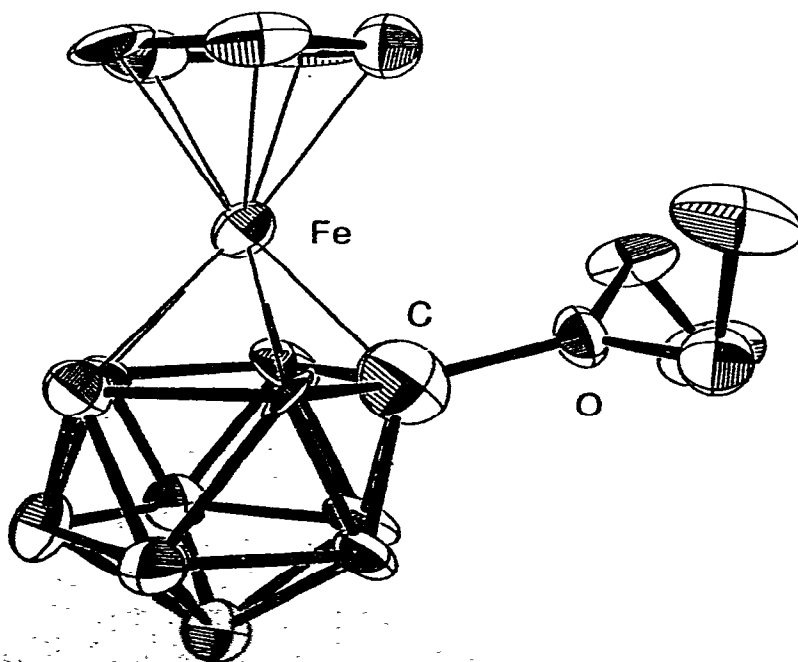


Fig. 1. The structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-B}_{10}\text{H}_{10}\text{CO}(\text{C}_2\text{H}_5)_2]$. All hydrogen atoms have been omitted for clarity.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^+$ ion. The monocarbon carborane anion $\text{B}_{10}\text{H}_{10}\text{CN}(\text{CH}_3)_3^-$ generated by proton abstraction from $\text{B}_{10}\text{H}_{12}\text{CN}(\text{CH}_3)_3$ [4] is isoelectronic with the 1,2- $\text{B}_9\text{C}_2\text{H}_{11}^-$ ion. We view the $\text{B}_{10}\text{H}_{10}\text{C}$ (Lewis base) ligand generated in these photochemical reactions as being isoelectronic with the $\text{B}_{10}\text{H}_{10}\text{CN}(\text{CH}_3)_3^-$ ion.

The spread of chemical shifts in the ^{11}B NMR spectra over 150 ppm indicates a contact shift as a result of the paramagnetic nature of the compound. According to the crystal structure, six resonances are expected for II: four of relative area 2 and two of relative area 1. Similar results are expected for I since the structures should be analogous, and indeed, the observed spectra are nearly identical. In both cases, the number of resonances actually seen is in accord with the expected number, but the relative areas observed do not agree with those expected. Reading upfield, the resonances were found to have relative areas of approximately 2 : 2 : 1.5 : 1.5 : 1.5 : 1. Integration of the peaks is hindered somewhat by baseline roll present in the spectra.

The IR spectra are in agreement with the structures of I and II. Near 2500 cm^{-1} , strong bands are observed due to B-H stretching modes. The other bands observed may be assigned to the C-H stretching frequencies of the cyclopentadienyl and ether ligands. No bands are observed in the terminal or bridging carbonyl region.

We assume that the reaction proceeds through initial formation of an intermediate such as $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\eta^5\text{-B}_{10}\text{H}_{10}\text{C}(\text{OH}_2)]$ which would be analogous to the class 1 compounds reported by Wegner and coworkers [1]. We suspect that the original oxygen ligand attached to the carborane carbon is subsequently displaced by the Lewis base ether. Further studies with other Lewis base solvents are underway which hopefully will lead to a better understanding of this interesting reaction sequence.

Acknowledgements

The authors thank Mr. William Wright for obtaining the ^{11}B NMR spectra and Mr. Robert Eckardt for the osmometer study.

References

- 1 P.A. Wegner, L.J. Guggenberger and E.L. Muetterties, *J. Amer. Chem. Soc.*, **92** (1970) 3473.
- 2 F. Sato, T. Yamamoto, J.R. Wilkinson and L.J. Todd, *J. Organometallic Chem.*, **86** (1975) 243.
- 3 W. Johnson and J. Huffman, to be submitted for publication.
- 4 D.E. Hyatt, J.L. Little, J.T. Moran, F.R. Schoier and L.J. Todd, *J. Amer. Chem. Soc.*, **89** (1967) 3342.