Improved Synthesis of Pentabenzylcyclopentadiene and **Study of the Reaction between Pentabenzylcyclopentadiene and Iron Pentacarbonyl**

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An improved synthetic route to pentabenzylcyclopentadiene, C_5Bz_5H (1), has been developed, utilizing a larger amount of dicyclopentadiene, sodium, and excess benzyl alcohol as both reactant and solvent. Subsequent extraction and crystallization using hexane produced 1 in 62% yield. A reaction between 1 and iron pentacarbonyl in refluxing toluene led to the formation of $[(\eta^5-C_5Bz_5)Fe(CO)_2]_2$ (2) and $(\eta^4-C_5Bz_5H)Fe(CO)_3$ (3). Unlike the parent compound $(\eta^4-C_5H_6)Fe(CO)_3$, **3** exhibited exceptional air and thermal stability. A singlecrystal X-ray diffraction study of **3** has been undertaken and confirms the proposed structure.

Introduction

The η^5 -cyclopentadienyl group (η^5 -C₅H₅ or Cp), derived from cyclopentadiene, has become one of the most important and common ligands in organometallic chemistry. Compounds containing this ligand are known for virtually all the transition, main group, and f-block metals. The extensive series of known cyclopentadienylmetal derivatives has also created interest in the corresponding chemistry of other metal complexes in which the η^5 -cyclopentadienyl ring is completely substituted.1

Since the first definitive study on η^5 -pentamethylcyclopentadienyl derivatives of the metals in 1967,² the η^{5} -C₅Me₅ (or Cp^{*}) ligand has likewise played a major role in the development of organometallic chemistry. Replacement of all the hydrogen atoms by methyl substituents alters both the steric and electronic influence of the η^5 -cyclopentadienyl ring, resulting in differing reactivities and stabilities of $(\eta^5-C_5Me_5)$ -metal compounds relative to their $(\eta^5 - C_5 H_5)$ -metal counterparts.³⁻⁶

In 1986, we reported the first η^5 -pentabenzylcyclopentadienyl derivatives of the transition metals,⁷ and a series of perbenzylated metallocenes of the type (η^{5} -

 $C_5Bz_5)_2M$ (M = Ge, Sn, Pb)⁸ were also described at that time. Since then, studies on a variety of other η^{5} pentabenzylcyclopentadienyl derivatives of transition, lanthanide, and main group metals have been undertaken.^{9–21} Compared to η^{5} -C₅H₅ or even η^{5} -C₅Me₅, the η^5 -C₅Bz₅ ligand is very bulky and extremely sterically demanding, resulting in enhanced kinetic stabilization of corresponding (η^5 -pentabenzylcyclopentadienyl)metal compounds.²²

In this paper, we describe an improved synthetic route to pentabenzylcyclopentadiene (1) and its reaction with iron pentacarbonyl, leading to several new (η^5 -pentabenzylcyclopentadienyl)- and (η^4 -pentabenzylcyclopentadiene)iron compounds. In order to investigate steric

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effects in these bulky organic and organometallic compounds, a single-crystal X-ray diffraction study of one of the reaction products has been undertaken.

Results and Discussion

Synthetic Studies on 1. Pentabenzylcyclopentadiene (1) was first reported by Hirsch and Bailey²³ in 1978, as part of a program to study multiple alkylations of compounds containing cyclopentadiene rings by the action of alcohols in the presence of their corresponding alkoxides. Compound **1** was obtained in *ca.* 19% yield from a reaction between dicyclopentadiene and an excess of benzyl alcohol and sodium metal, using diisopropylbenzene as the solvent. The product was purified by vacuum distillation at ca. 250-275 °C/0.8 mmHg. Chambers et al. subsequently simplified the procedure by omitting the distillation step and utilizing trituration and crystallization from methanol as a means of purification. Unfortunately, this modified route to 1 still involved a high-boiling solvent that was tedious to remove, and the yields of **1** were often low and variable.

In order to develop a successful research program in (pentabenzycyclopentadienyl)metal chemistry, it was important to have available a sufficient supply of **1**. A study to improve the yield of **1** was therefore conducted. On the basis of a procedure suggested by Janiak,²⁴ an improved route to **1** has been developed, utilizing a larger amount of dicyclopentadiene and an excess of benzyl alcohol at reflux, without any diisopropylbenzene as in the earlier methods.

All previous methods used to prepare **1** have employed methanol as the crystallization solvent. However, subsequent reactions of **1** with *n*-butyllithium would be adversely affected by even trace amounts of this solvent. Therefore, as another modification, we found that **1** could be conveniently crystallized instead from hot hexane. Using these modifications, **1** (mp 72.5-73.5 °C) could be obtained in 62% yield.

Structural Studies on 1. Pentabenzylcyclopentadiene (1) has been the subject of two independent X-ray crystallographic investigations.^{25,26} Both studies confirm the original structural assignment proposed by Hirsch and Bailey.²³ The studies indicate that the cyclopentadiene ring is planar within standard deviations, and that C=C double bonds are located between C(1) and C(2) and between C(3) and C(4). Moreover, the orientation of the five benzyl groups indicates that **1** is a very sterically constrained molecule. Both ¹H and ¹³C NMR spectra for **1** have been obtained in the present study. Detailed spectral information including peak assignments is presented in the Experimental Section.

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Reaction between C₅**Bz**₅**H** (1) and **Fe**(**CO**)₅. A reaction between 1 and Fe(CO)₅ in refluxing toluene produced a purple solid which was chromatographed on a long alumina column using CH_2Cl_2 -hexane (30/70) as the eluent. A yellow band and a red band developed and were collected separately.

The second band after removal of the solvent and recrystallization produced a red crystalline solid, mp 166.5–167.0 °C. On the basis of the IR and NMR spectral data as well as microanalysis, the red product can be assigned as $[(\eta^5-C_5Bz_5)Fe(CO)_2]_2$ (2), having a



trans-centrosymmetric structure with two bridging and two terminal carbonyl groups. The structure of **2** is thus analogous to that found for $[(\eta^5-C_5Me_5)Fe(CO)_2]_2$.²⁷ The initial yellow band after solvent removal and recrystallization afforded a yellow crystalline solid, mp 204-205 °C. The IR spectrum of the product exhibited three strong terminal carbonyl bands at 1947, 1972, and 2034 cm⁻¹. On the basis of the similarity of these data to IR spectral data for $(\eta^4$ -C₅H₆)Fe(CO)₃ [IR (hexane): ν_{CO} 1974, 1981, 2048 cm⁻¹]²⁸ and on microanalytical data, the second reaction product was tentatively assigned the structure (η^4 -C₅Bz₅H)Fe(CO)₃ (**3**). Both the ¹H and ¹³C NMR spectra of the yellow product were likewise consistent with its formulation as **3**. The mass spectrum of the product exhibited a molecular ion peak for **3** as well as fragmentation peaks resulting from losses of each of the three CO ligands.

Compound **3**, $(\eta^4-C_5Bz_5H)Fe(CO)_3$, exhibited unexpected stability. The cyclopentadiene analog, $(\eta^4-C_5H_6)-Fe(CO)_3$, is very reactive and converts thermally to the corresponding dimer, $[(\eta^5-C_5H_5)Fe(CO)_2]_2$, even under argon.²⁸ In addition to its thermal instability, $(\eta^4-C_5H_6)-Fe(CO)_3$ has been reported to decompose to its dimer upon exposure to air in solution at room temperature. Compound **3**, however, proved to be air-stable in the crystalline state, and upon heating of a solution of **3** in xylene to 135 °C, no significant decomposition was observed.

Since $(\eta^4$ -C₅H₆)Fe(CO)₃ has been suggested to be an intermediate to $[(\eta^5$ -C₅H₅)Fe(CO)₂]₂,²⁹ an attempt was made to convert **3** to **2**. However, when a xylene solution containing both **2** and **3** was heated to reflux in air over a 40 min period, the intensities of the carbonyl frequencies for **2** and not for **3** gradually decreased while the solution was being heated. At 135 °C, absorption bands for **2** had completely disappeared, while those for **3** had not changed. These results suggest that the pentabenzylcyclopentadiene complex **3** is more oxidatively stable in solution than is the dimer **2**.

X-ray Crystallographic Studies. In order to further examine steric effects resulting from the coordina-

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Figure 1. Molecular structure and atom-labeling scheme for $(\eta^4-C_5Bz_5H)Fe(CO)_3$ (3).

tion of **1** to an Fe(CO)₃ moiety, an X-ray crystallographic study of **3** was undertaken. The study demonstrates that crystals of **3** consist of discrete molecules of (η^{5} -C₅Bz₅H)Fe(CO)₃ separated by normal van der Waals distances. Figure 1 shows the molecular structure and atom-labeling scheme for **3**. A complete table of bond lengths and angles is given in the Supporting Information.

From Figure 1, it is clear that the pentabenzylcyclopentadiene ligand in 3 is bonded to the iron atom in an η^4 -manner. In order to minimize steric repulsions, C(8) is out of the ring plane and bent away from the iron atom. The benzyl group that is attached to C(8) also points away from the iron center. Methylene carbons C(9), C(16), C(23), and C(30) are basically coplanar with the ring. The benzyl groups attached to the ring carbons C(5) and C(6) are bent away from the iron atom. Unlike (η^5 -pentabenzylcyclopentadienyl)metal compounds, the benzyl groups which are attached to ring carbons C(4) and C(7) do not bend up or down but are oriented horizontally away from the other benzyl groups. The two benzyl groups attached to C(5) and C(6) are bent away from the iron atom. On the basis of the bond lengths between the iron atom and the ring carbon atoms (see Table S1 of the Supporting Information), the Fe–Cent vector is not perpendicular to the η^4 -plane. The bond lengths Fe-C(5) (2.067(5) Å) and Fe-C(6) (2.062(6) Å) are shorter than Fe-C(4) (2.130(5) Å) or Fe-C(7) (2.105(5) Å).

Experimental Section

All operations were carried out under an argon atmosphere using Schlenk techniques except where specified. The argon was deoxygenated with BTS catalyst and dried with molecular sieves and magnesium perchlorate. IR spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer Model 1310 or a Perkin-Elmer FTIR Model 1600 infrared spectrometer, whereas NMR spectra were recorded in $CDCl_3$ solution on either Varian XL-200 or XL-300 spectrometers. ¹H and ¹³C NMR chemical shifts are reported relative to Me₄Si, all referencing done internally. Melting points were determined in air and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts. Chromatography columns were packed under argon, using 5% deactivated and deoxy-

Table 1. Crystal Data a	and Summary of Intensity
Data Collection and S	tructure Refinement for
$(\eta^4 - C_5 Bz_5 H) Fe(CO)_3$	

(./ °J==J==)=	0(00)3
compd	$(\eta^4-C_5Bz_5H)Fe(CO)_3$
color/shape	yellow/cube
fw	656.60
space group	$P\overline{1}$
temp, °C	21
cell consts ^a	
<i>a</i> , Å	10.513(3)
<i>b</i> , Å	10.725(3)
<i>c</i> , Å	16.349(9)
α, deg	79.26(3)
β , deg	73.45(3)
γ , deg	78.89(2)
cell vol, Å ³	1716.9
formula units/unit cell	2
$D_{\rm calc}, { m g}{ m cm}^{-3}$	1.27
$\mu_{\text{calc}}, \text{cm}^{-1}$	4.93
diffractometer/scan	Enraf-Nonius CAD-4/ ω -2 θ
radiation, graphite monochromator	Mo K α ($\lambda = 0.710$ 73)
max cryst dimens, mm	0.30 imes 0.33 imes 0.33
scan width	$0.80 \pm 0.35 \tan \theta$
std reflns	400, 020, 006
decay of stds	$\pm 2\%$
no. of reflns measd	5953
2θ range, deg	$2 \le 2 heta \le 50$
range of h,k,l	$+12,\pm12,\pm19$
no. of reflns obsd $[F_0 \ge 5\sigma(F_0)]$	3518
computer program	SHELX
struct solution	SHELXS
no. of params varied	424
weights	$[\sigma(F_0)^2]^{-1}$
GOF	1.43
$R = \sum F_0 - F_c / \sum F_0 $	0.055
R _w	0.062
largest feature final diff map, e/Å ⁻³	0.3

 a Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 19^\circ.$

genated CAMAG neutral grade alumina. Hexane, tetrahydrofuran (THF), and toluene were distilled under argon from sodium-potassium alloy before use. Benzyl alcohol was used as received from Fisher Scientific Co., whereas dicyclopentadiene and iron pentacarbonyl were purchased from Aldrich Chemical Co.

Synthesis of Pentabenzylcyclopentadiene (1). A 500mL three-necked flask equipped with a mechanical stirrer and a Dean-Stark receiver attached to a reflux condenser was charged with 450 g (4.16 mol) of benzyl alcohol. After the flask was evacuated and back-flushed with argon three times, 11.5 g (0.50 mol) of sodium was added and the mixture was heated with stirring by means of a heating mantle at 120 °C until all the sodium was consumed. The temperature was then raised to 160-170 °C, and 23 g (0.17 mol) of dicyclopentadiene was added dropwise into the solution over 4 h. The mixture was stirred for another 15 h at reflux. The mechanical stirrer was then removed and refluxing was continued for another 24-48 h. A white semisolid was formed during the reaction, and about 30 mL of H₂O was collected in the Dean-Stark receiver.³⁰ Most of the benzyl alcohol was then removed in vacuo with heating. The residue was treated in air with 5% hydrochloric acid until all the solid dissolved. The organic layer was collected, and the remaining benzyl alcohol was removed in vacuo at ca. 100 °C. The resulting oily yellow residue was allowed to cool to room temperature and was repeatedly extracted (ca. 4 times using ca. 250 mL portions) with hot hexane. The combined hexane extract was stored at -20 °C overnight, resulting in the formation of an oily layer. The hexane solution was decanted into another flask and stored at -20 °C for another 3 d, producing a white crystalline

⁽³⁰⁾ The reaction should be monitored carefully after *ca*. two-thirds of the solution turns to solid. If the resulting white semisolid material coating the bottom of the flask turns light yellow, continued heating can result in extensive decomposition.

solid. This crystallization procedure was repeated 4–5 times for the oily layer until no more white solid was formed after hexane extraction and cooling. All the precipitated white solids were then combined and dried under vacuum overnight, yielding 109.5 g (0.21 mol, 62%) of pentabenzylcyclopentadiene (1). The product was further purified by redissolving it in hot hexane and storage at room temperature for 2 d, producing **1** as a white crystalline solid, mp 72.5–73.5 °C (lit.²³ mp 69.2– 75.5 °C; lit.⁷ mp 68–70 °C). Anal. Calcd for C₄₀H₃₆: C, 92.98; H, 7.02. Found: C, 93.10; H, 6.89. ¹H NMR (CDCl₃): δ 3.10 (d, 2 H, CH₂C₆H₅), 3.21 (t, 1 H, CH), 3.45 (s, 4 H, CH₂C₆H₅), 3.5–3.9 (2 d, 4 H, CH₂C₆H₅), 6.65–7.28 (m, 25 H, C₆H₅). ¹³C NMR (assignments confirmed by APT): δ 31.65, 33.25, 34.13 (CH₂C₆H₅), 52.55 (CH), 125.4–142.8 (C₆H₅ + C=C). MS: *m/e* 516 (M+), 425 (M – Bz)⁺, 334 (M – 2Bz)⁺, 243 (M – 3Bz)⁺.

Preparation of Bis[$(\eta^5$ -pentabenzylcyclopentadienyl)dicarbonyliron] (2) and (η^4 -Pentabenzylcyclopentadiene)tricarbonyliron (3). In a 250-mL three-necked flask equipped with a gas inlet tube, magnetic stirrer, and reflux consenser were placed 5.00 g (25.5 mmol) of Fe(CO)₅, 10.0 g (19.3 mmol) of pentabenzylcyclopentadiene, and 150 mL of toluene. The reaction mixture was stirred at reflux for 24 h, during which time the reaction progress was monitored by IR spectroscopy. The resulting solution was then filtered through a plug of alumina under argon, the solvent was removed from the filtrate, and 100 mL of methylene chloride was added. After the solution was again filtered through a plug of alumina, the filtrate was concentrated to ca. 50 mL, hexane (ca. 75 mL) was added, and the solvent was removed slowly in vacuo. During this solvent removal process, the more volatile methylene chloride is removed in preference to the less volatile hexane, causing a purple precipitate which is almost insoluble in hexane to crystallize from solution. The resulting crystals were filtered out, washed with pentane, and dried under vacuum. The purple solid obtained in this manner was chromatographed on an alumina column (2×45 cm) packed using hexane and was eluted with CH₂Cl₂-hexane (30/70). A yellow and a red band developed and were collected separately. After removal of the solvents, both were recrystallized from CH₂Cl₂-hexane. Red crystals of $[(\eta^5-C_5Bz_5)Fe(CO)_2]_2$ (2) (4.6 g, 8%), mp 166.5–167.0 °C, and yellow crystals of (η^4 -C₅Bz₅H)-Fe(CO)₃ (3) (3.2 g, 25%), mp 204–205 °C, were obtained in this manner.

[(η^{5} -C₅Bz₅)Fe(CO)₂]₂ (2). Anal. Calcd for C₈₄H₇₀Fe₂O₄: C, 80.38; H, 5.62. Found: C, 80.12; H, 5.56. IR (CH₂Cl₂): ν(CO) 1750, 1935 cm⁻¹. ¹H NMR (CDCl₃): δ 3.61 (s, 10 H, CH₂C₆H₅), 6.60–7.25 (m, 25 H, C₆H₅). ¹³C NMR (CDCl₃): δ 30.38 (CH₂C₆H₅), 102.7 (C₅Bz₅), 126.1, 128.0, 129.1, 138.5 (C₆H₅), 200.3 (CO).

(η⁴-C₅Bz₅H)Fe(CO)₃ (3). Anal. Calcd for C₄₃H₃₆FeO₂: C, 78.66; H, 5.53. Found: C, 78.58; H, 5.59. IR (CH₂Cl₂): ν(CO) 1947, 1972, 2034 cm⁻¹. ¹H NMR (CDCl₃): δ 2.33 (d, 2 H, CH₂C₆H₅), 2.72 (t, 1 H, CH), 2.74–3.11 (2 d, 4 H, CH₂C₆H₅), 3.94–4.28 (2 d, 4 H, CH₂C₆H₅), 6.62–7.30 (m, 25 H, C₆H₅). ¹³C NMR (CDCl₃): δ 73.46, 35.50, 46.18 (CH₂C₆H₅), 60.60 (CH), 79.76, 103.6 (C=C), 126.3–140.0 (C₆H₅), 211.3 (CO).

X-ray Data Collection, Structure Determination, and Refinement for (η^4 -C₅Bz₅H)**Fe**(CO)₃ (3). A yellow single crystal of the title compound was mounted in a thin-walled glass capillary under argon and transferred to the goniometer. The space group was determined to be either the centric $P\overline{1}$ or acentric P1. The subsequent solution and successful refinement of the structure was carried out in the centric space group $P\overline{1}$. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to R = 0.118. The hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å². Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.055 and $R_w = 0.062$.

Supporting Information Available: Tables of bond distances and angles, atomic coordinates, fractional coordinates for hydrogen atoms, thermal parameters, and least-squares results for compound **3** (14 pages). Ordering information is given on any current masthead page.

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