

the rearrangement occurring at platinum centres subsequent to the formation of the Me_3NOSO_2 adduct.

A route by which either 2 or 3 may be converted to 1 is shown in Scheme II. Addition of Me_3NO to a solution of 2 under an atmosphere of CO leads to the regeneration

of 1. Addition of Me_3NO to 2 yields the previously discussed mixture of 1 and 3, while the presence of the CO atmosphere converts 3 back to 2 and more 1. In this manner, the cycle is repeated until complete conversion of 2 or 3 to 1 has been affected. The absence of reaction between 3 and a 10-fold excess of Me_3NO under N_2 after 4 days indicates that abstraction of SO_2 from the system occurs exclusively from 2. This lies in contrast to the work of Mingos and Hallam,⁸ who reported the conversion of $\text{Pt}_3(\mu\text{-CO})_2(\mu\text{-SO}_2)(\text{PCy}_3)_3$ to the PCy_3 analogue of 1, in high yield, using Me_3NO .

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada for operating and equipment grants.

Registry No. 1, 62931-81-1; 2, 97703-27-0; 3, 97719-79-4; 4, 97689-48-0; 5, 118714-49-1; 6[I], 118714-50-4; 6[BF_4], 118714-52-6; 7, 118722-42-2; MCPBA, 937-14-4; $\text{Pt}(\text{P-}t\text{-Bu}_2\text{Ph})(\text{C}_2\text{H}_4)_2$, 79503-49-4; $\text{PtI}_2(\text{CO})(\text{P-}t\text{-Bu}_2\text{Ph})$, 19618-88-3; Me_3NO , 1184-78-7; S^2 , 18496-25-8.

Synthetic and X-ray Structural Studies on Pentabenzylcyclopentadienyl Derivatives of Manganese, Rhenium, and Iron

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Received August 31, 1988

(η^5 -Pentabenzylcyclopentadienyl)tricarbonylmanganese (3) and -rhenium (4) have been prepared in low yields from reactions between pentabenzylcyclopentadiene and dimanganese or dirhenium decacarbonyl in refluxing aromatic solvents. A reaction between pentabenzylcyclopentadienyllithium and anhydrous iron(II) chloride has afforded decabenzylferrocene (5) in 34% yield. The mixed-ring metallocenes pentamethylpentabenzylferrocene (6) and 1,2,3,4,5-pentabenzylferrocene (7) have been obtained via reactions of $(\text{C}_5\text{R}_5)\text{Fe}(\text{acac})$ ($\text{R} = \text{Me}, \text{Bz}$; $\text{acac} = \text{acetylacetonate}$) intermediates. The crystal structures of 3 and 5 have been determined via single-crystal X-ray diffraction. ($\eta^5\text{-C}_5\text{Bz}_5$) $\text{Mn}(\text{CO})_3$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.908$ (4) Å, $b = 14.907$ (3) Å, $c = 18.575$ (8) Å, $\beta = 108.21$ (4)°, and $D_{\text{calcd}} = 1.28 \text{ g cm}^{-3}$ for $Z = 4$. The manganese center is pseudotetrahedral with $\text{Mn-C}(\eta^5) = 2.14$ (1) Å, $\text{Mn-Cent} = 1.77$ Å, and $\text{Mn-CO} = 1.772$ (6) Å. ($\eta^5\text{-C}_5\text{Bz}_5$) $2\text{Fe}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.871$ (6) Å, $b = 22.135$ (8) Å, $c = 23.700$ (9) Å, $\beta = 103.47$ (5)°, and $D_{\text{calcd}} = 1.19 \text{ g cm}^{-3}$ for $Z = 4$. The substituted cyclopentadienyl rings are parallel ($\text{Cent-Fe-Cent} = 179.6^\circ$) and are staggered. The average Fe-C and Fe-Cent distances are 2.058 (7) and 1.65 Å, respectively. In 3, four of the phenyl rings are oriented up and away from the manganese center, with the fifth down toward the tripod ligands. Unexpectedly, in 5 all five phenyl rings in each ligand are oriented away from the metal center.

Introduction

The η^5 -pentamethylcyclopentadienyl ligand has played an extremely significant role in organometallic chemistry during the past 20 years, due to both steric and electronic influences imparted by the methyl substituents on the corresponding (η^5 -pentamethylcyclopentadienyl)metal compounds. More recently, studies on related η^5 -penta-phenyl- and η^5 -pentabenzylcyclopentadienyl derivatives of metals have been undertaken.¹⁻⁴ The $\eta^5\text{-C}_5\text{Bz}_5$ ($\text{Bz} =$

benzyl) ligand is of special interest, since a variety of conformational features and shielding effects can be expected for organometallic compounds that contain this very bulky organic moiety.

We have recently described the first η^5 -pentabenzylcyclopentadienyl derivatives of the transition metals,

(2) Schumann, H.; Janiak, C.; Hahn, E.; Kolax, C.; Loebel, J.; Rausch, M. D.; Zuckerman, J. J.; Heeg, M. *J. Chem. Ber.* **1986**, *119*, 2656.

(3) Schumann, H.; Janiak, C.; Khani, H. *J. Organomet. Chem.* **1987**, *330*, 347.

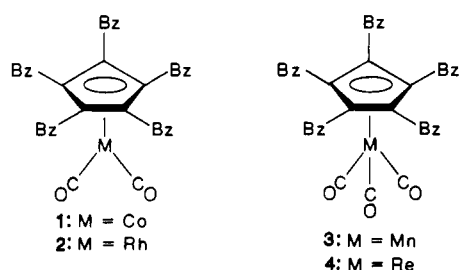
(4) Schumann, H.; Janiak, C.; Pickardt, J.; Börner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789.

(1) Chambers, J. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L.; Rausch, M. D. *Organometallics* **1986**, *5*, 1635. See also references cited therein.

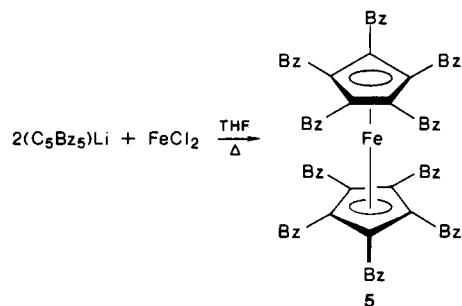
(η^5 -C₅Bz₅)Co(CO)₂ (1) and (η^5 -C₅Bz₅)Rh(CO)₂ (2), and the molecular structure of the former compound was elucidated by an X-ray structural analysis.¹ We now report on the synthesis and molecular structures of η^5 -pentabenzylcyclopentadienyl compounds of manganese, rhenium, and iron.

Results and Discussion

Reactions between pentabenzylcyclopentadiene and either dimanganese decacarbonyl or dirhenium decacarbonyl in refluxing aromatic solvents have produced (η^5 -C₅Bz₅)Mn(CO)₃ (3) and (η^5 -C₅Bz₅)Re(CO)₃ (4), respectively, in low yields. An attempt to prepare 3 via reactions of (pentabenzylcyclopentadienyl)lithium and Mn(CO)₅Br in either refluxing THF or benzene led primarily to Mn₂(CO)₁₀ and not 3.⁵ Both 3 and 4 have been fully characterized by means of their ¹H NMR, ¹³C NMR, and IR spectra, as well as by elemental analyses. Both compounds are air-stable in the solid state.



Since ferrocene represents the prototype (η^5 -cyclopentadienyl)metal compound, it was of interest to examine the effects of perbenzylation in this system as well. Decabenzylferrocene (5) was readily prepared from a reaction between 2 equiv of (pentabenzylcyclopentadienyl)lithium and anhydrous iron(II) chloride in THF solution. Com-



ound 5 is likewise an air-stable solid, mp 295–296 °C dec. Organic solutions of 5 are also stable in air, in contrast to decamethylferrocene which is reported to undergo spontaneous oxidation when dissolved in organic solvents in air.⁶ Perhaps the most noteworthy feature of 5 is its unique molecular structure in the solid state (vide infra).⁷

Using the elegant procedure developed recently by Manriquez and co-workers,⁸ we have now obtained the first mixed-ring metallocenes that contain the η^5 -pentabenzylcyclopentadienyl ligand. Thus, a reaction between (η^5 -C₅Me₅)Fe(acac) (acac = acetylacetonate) and (penta-

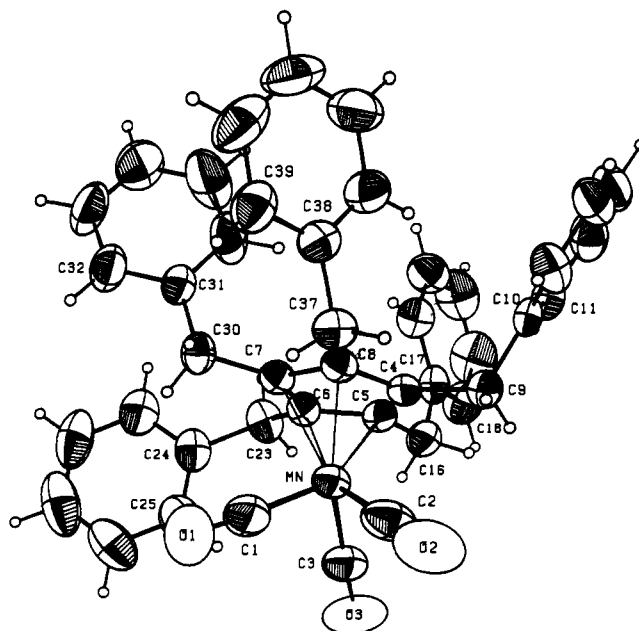
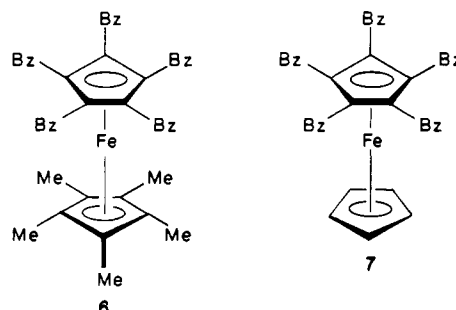


Figure 1. Molecular structure and atom-labeling scheme for (η^5 -C₅Bz₅)Mn(CO)₃ (3).

benzylcyclopentadienyl)lithium in THF solution has afforded (η^5 -C₅Me₅)(η^5 -C₅Bz₅) (6) in 25% yield. More sig-



nificantly, a reaction between equivalent amounts of pentabenzylcyclopentadienyllithium and Fe(acac)₂ in THF at -78 °C followed by subsequent treatment with (η^5 -cyclopentadienyl)thallium at -78 °C and warming to room temperature has led to 1,2,3,4,5-pentabenzylferrocene (7) in 35% yield. (η^5 -C₅Bz₅)Fe(acac) is presumed to be formed in this sequence, based on related studies.⁸ (η^5 -C₅Bz₅)M(acac) compounds may also therefore prove to be valuable intermediates in pentabenzylcyclopentadienyl-transition-metal chemistry.

Previous structural studies on compounds containing the η^5 -pentabenzylcyclopentadienyl ligand are limited to (C₅Bz₅)₂Tl,⁴ (η^5 -C₅Bz₅)Co(CO)₂ (1),¹ and the series (η^5 -C₅Bz₅)₂M (M = Ge, Sn, Pb).² In each case, packing effects appear to control the orientation of the benzyl substituents, with one or more phenyl groups directed toward the bonded metal atom. In 1, only one of the five phenyl groups is directed toward the cobalt center. In the compounds (η^5 -C₅Bz₅)₂M, one ring is oriented as in 1, while the other ring has two benzyl groups toward the metal. A third orientation is noted for (C₅Bz₅)Tl, in which three phenyl groups are arranged toward the thallium atom. In the compounds reported here, 3 and 5, we observed two different orientations: four up, one down in 3 and the unique five up found for 5.

The crystal structure of 3 (Figure 1) reveals an identical conformation to that observed for (η^5 -C₅Bz₅)Co(CO)₂ (1)—one of the phenyl groups is bent down toward the Mn(CO)₃ tripod. The Mn-C separations average 2.14 (1)

(5) Singh, P.; Rausch, M. D., unpublished studies.

(6) Nesmeyanov, A. N.; Materikova, R. B.; Lyatifov, I. R.; Kurbanov, T. Kh.; Kochetkova, N. S. *J. Organomet. Chem.* 1978, 145, 241.

(7) The NMR spectra of 5 and various other (η^5 -C₅Bz₅)M (M = metal) compounds exhibit dynamic behavior in solution, suggesting restricted rotation of the benzyl substituents. Variable-temperature NMR studies are in progress and will be reported later.

(8) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* 1985, 4, 1680.

Table I. Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-C}_5\text{Bz}_2)\text{Mn}(\text{CO})_3$ (3)

Bond Distances			
Mn-C(1)	1.767 (5)	Mn-C(2)	1.769 (4)
Mn-C(3)	1.781 (4)	Mn-C(4)	2.129 (3)
Mn-C(5)	2.146 (4)	Mn-C(6)	2.152 (3)
Mn-C(7)	2.159 (3)	Mn-C(8)	2.130 (3)
O(1)-C(1)	1.146 (7)	O(2)-C(2)	1.148 (6)
O(3)-C(3)	1.146 (5)	Cent-Mn	1.77
Bond Angles			
C(1)-Mn-C(2)	91.0 (2)	C(1)-Mn-C(3)	93.4 (2)
C(2)-Mn-C(3)	88.6 (2)	Mn-C(1)-O(1)	177.2 (4)
Mn-C(2)-O(2)	178.3 (4)	Mn-C(3)-O(3)	178.3 (3)
Cent-Mn-C(1)	123.4	Cent-Mn-C(2)	123.9
Cent-Mn-C(3)	126.4		

Table II. Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-C}_5\text{Bz}_5)_2\text{Fe}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (5)

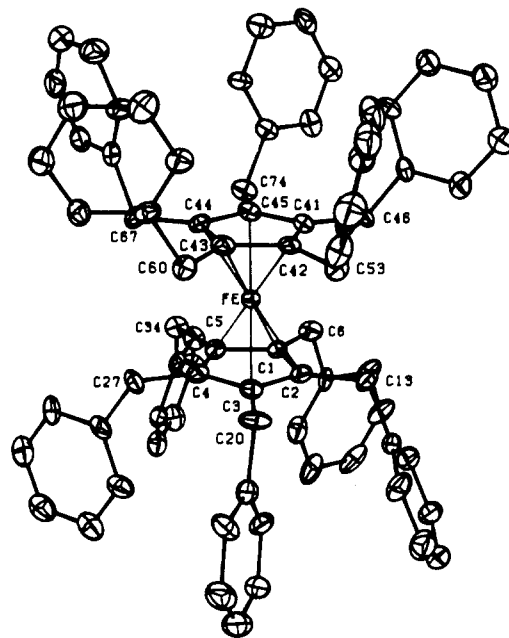
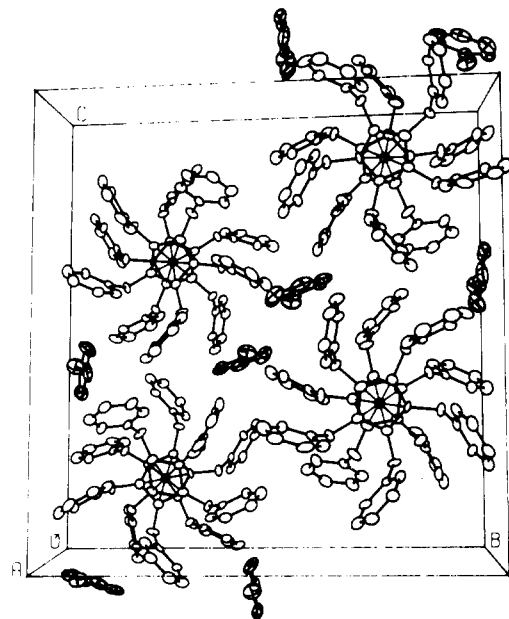
Bond Distances			
Fe-C(1)	2.053 (8)	Fe-C(2)	2.057 (8)
Fe-C(3)	2.057 (9)	Fe-C(4)	2.067 (9)
Fe-C(5)	2.064 (9)		
Fe-C(41)	2.056 (9)	Fe-C(42)	2.068 (9)
Fe-C(43)	2.057 (8)	Fe-C(44)	2.057 (7)
Fe-C(45)	2.044 (8)		
Cent1-Fe	1.65	Cent2-Fe	1.65
Bond Angles			
Cent1-Fe-Cent2	179.6		

Å (Table I). The C_5 ring is planar to within 0.009 Å, and an interesting variation in out-of-plane bending by the benzyl carbon atoms is observed. C(9) and C(37) are bent toward manganese by an average 0.03 Å, while the remainder are bent away from the metal an average of 0.14 Å. C(23) and not C(9) carries the phenyl group bent down toward the metal. Preliminary unit cell data have been used to determine that $(\eta^5\text{-C}_5\text{Bz}_5)\text{Re}(\text{CO})_3$ (4) is isostructural with 3.

Unlike the bent decabenzylgermanocene, -stannocene, and -plumbocene, decabenzylferrocene (5) (Figure 2) exhibits parallel, staggered cyclopentadienyl rings as expected: Cent-Fe-Cent = 179.6° (Table II). In addition, all 10 benzyl groups are directed away from the metal center. Despite this apparent steric effect, the Fe-C distances [2.958 (7) Å] and Fe-Cent separations (1.65 Å) are close to those observed for ferrocene and decamethylferrocene.^{9,10}

The benzyl carbon atoms do not show any consistent trend in bending out of the cyclopentadienyl ring plane. All five benzyl carbon atoms attached to the ring comprised of C(41)-C(45) bend out of the plane toward the iron atom an average of 0.04 Å. Only three of the benzyl carbon atoms attached to ring C(1)-C(5) bend toward the metal [C(13), C(27), and C(34) an average of 0.03 Å], while two [C(6) and C(20)] bend away from the metal an average of 0.05 Å. All 10 phenyl groups are arranged propeller fashion around the metal center as clearly seen in the cell packing diagram (Figure 3). The Cent-Fe-Cent axis is directed along unit cell axis *a*, and the toluene molecules fit between decabenzylferrocene units in the *b* and *c* directions.

The results presented here underscore the importance of further crystallographic studies of the pentabenzylcyclopentadienyl ligand and its metal complexes. Detailed structural analyses of complexes such as 3 and 5 should provide important information concerning the nature of

**Figure 2. Molecular structure and atom-labeling scheme for $(\eta^5\text{-C}_5\text{Bz}_5)_2\text{Fe}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (5).****Figure 3. Cell packing diagram for $(\eta^5\text{-C}_5\text{Bz}_5)_2\text{Fe}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (5).**

the effects responsible for the variation in the benzyl group positions.

Experimental Section

All operations were carried out under an argon atmosphere by using Schlenk tube techniques except where specified. The argon was deoxygenated with BTS catalyst and dried with molecular sieves (4 Å) and magnesium perchlorate. Infrared spectra were recorded on a Perkin-Elmer Model 1310 infrared spectrometer, whereas NMR spectra were recorded on either a Varian XL-200 or XL-300 spectrometer. Melting points were determined in air and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA 01003. Chromatography columns were packed dry under argon, using 5% deactivated and deoxygenated CAMAG neutral grade alumina. Hexane, tetrahydrofuran (THF), and toluene were distilled under argon from sodium/potassium alloy before use. Xylene and mesitylene were dried over sodium metal and calcium hydride, respectively, before use. Pentabenzylcyclopentadiene,¹ $\text{Fe}(\text{acac})_2$,¹¹ $\text{C}_5\text{Me}_5\text{Li}$,¹² and $\text{C}_5\text{H}_5\text{Ti}$ ¹³ were

(9) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* 1979, 101, 892.

(10) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* 1979, 35, 1068, 2020.

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	3	5
color/shape	brown/ parallelepiped	yellow/ parallelepiped
fw	654.7	1271.6
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
temp, °C	20	-150
cell constants ^a		
<i>a</i> , Å	12.908 (4)	13.871 (6)
<i>b</i> , Å	14.907 (3)	22.135 (8)
<i>c</i> , Å	18.575 (8)	23.700 (9)
β, deg	108.21 (4)	103.47 (5)
cell vol, Å ³	3395.2	7076.5
formula units/unit cell	4	4
<i>D</i> _{calcd} , g cm ⁻³	1.28	1.19
<i>μ</i> _{calcd} , cm ⁻¹	3.83	2.23
diffractometer/scan	Enraf-Nonius CAD-4/θ-2θ	
range of rel transm factors, %	96/100	
radiatn, graphite monochromator	Mo Kα (λ = 0.71073)	
max cryst dimens, mm	0.25 × 0.35 × 0.45	0.15 × 0.30 × 0.40
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflctns	800; 0,0,10; 0,10,0	700; 0,12,0; 408
decay of stds, %	±1	±2
reflctns measd	6475	9283
2θ range, deg	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 44
range of <i>h,k,l</i>	+15,+17,±22	+14,+23,±24
reflections obsd	3357	5186
[<i>F</i> _o ≥ 5σ(<i>F</i> _o)] ^b		
computer programs ^c	SHELX ¹⁴	
structure solution	heavy-atom techniques	MULTAN ¹⁶
no. of parameters varied	424	856
weights	[σ(<i>F</i> _o) ² + 0.0002 <i>F</i> _o ²] ⁻¹	UNIT
GOF	0.70	5.0
<i>R</i> = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o	0.041	0.081
<i>R</i> _w	0.044	0.091
largest feature final diff map, e/Å ³	1.0	0.7

^aLeast-squares refinement of ((sin θ)/λ)² values for 25 reflections (θ > 20°). ^bCorrections: Lorentz-polarization and absorption (empirical, psi scan, 3 only). ^cNeutral scattering factors and anomalous dispersion corrections from ref 15.

prepared by literature methods. Mn₂(CO)₁₀ and Re₂(CO)₁₀ were obtained from Pressure Chemical Co. and Strem Chemicals, respectively.

(η^5 -Pentabenzylcyclopentadienyl)tricarbonylmanganese (3). In a 250-mL three-necked flask equipped with gas inlet tube, magnetic stirrer, and reflux condenser were placed 2.00 g (5.13 mmol) of Mn₂(CO)₁₀, 5.29 g (10.3 mmol) of pentabenzylcyclopentadiene, and 150 mL of xylene. The reaction was stirred at reflux for 48 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, 100 mL of hot hexane was added, and

Table IV. Final Fractional Coordinates for (η^5 -C₅Bz₅)Mn(CO)₃ (3)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eqv), ^a Å ²
Mn	0.18030 (4)	0.64356 (3)	0.52782 (3)	2.65
O(1)	-0.0051 (3)	0.7082 (2)	0.5707 (3)	9.03
O(2)	0.2311 (3)	0.5056 (2)	0.6450 (2)	7.08
O(3)	0.0540 (3)	0.5081 (2)	0.4226 (2)	5.68
C(1)	0.0670 (4)	0.6806 (3)	0.5539 (3)	4.88
C(2)	0.2101 (3)	0.5605 (3)	0.5995 (2)	4.29
C(3)	0.1026 (3)	0.5621 (2)	0.4631 (2)	3.50
C(4)	0.3494 (2)	0.6632 (2)	0.5436 (2)	2.39
C(5)	0.2919 (2)	0.6665 (2)	0.4650 (2)	2.40
C(6)	0.2152 (2)	0.7390 (2)	0.4515 (2)	2.34
C(7)	0.2275 (2)	0.7816 (2)	0.5217 (2)	2.39
C(8)	0.3094 (2)	0.7345 (2)	0.5793 (2)	2.39
C(9)	0.4352 (3)	0.5954 (2)	0.5833 (2)	2.89
C(10)	0.5526 (3)	0.6220 (2)	0.5967 (2)	2.67
C(11)	0.5972 (3)	0.6250 (2)	0.5384 (2)	3.22
C(12)	0.7062 (3)	0.6455 (3)	0.5520 (2)	4.15
C(13)	0.7713 (3)	0.6645 (3)	0.6245 (3)	4.35
C(14)	0.7279 (3)	0.6626 (3)	0.6821 (2)	4.02
C(15)	0.6199 (3)	0.6410 (3)	0.6689 (2)	3.64
C(16)	0.3112 (3)	0.6102 (2)	0.4035 (2)	2.98
C(17)	0.3796 (3)	0.6551 (2)	0.3608 (2)	2.76
C(18)	0.3910 (3)	0.6144 (3)	0.2973 (2)	4.22
C(19)	0.4554 (4)	0.6512 (4)	0.2592 (3)	6.00
C(20)	0.5097 (4)	0.7300 (4)	0.2824 (3)	5.54
C(21)	0.4988 (3)	0.7718 (3)	0.3445 (2)	4.25
C(22)	0.4332 (3)	0.7351 (2)	0.3831 (2)	3.45
C(23)	0.1495 (3)	0.7709 (3)	0.3732 (2)	3.33
C(24)	0.0366 (3)	0.8076 (3)	0.3615 (2)	3.15
C(25)	-0.0473 (3)	0.7536 (3)	0.3674 (2)	3.94
C(26)	-0.1511 (4)	0.7881 (4)	0.3543 (3)	5.23
C(27)	-0.1720 (4)	0.8758 (4)	0.3341 (3)	6.06
C(28)	-0.0906 (5)	0.9283 (5)	0.3261 (3)	5.45
C(29)	0.0128 (3)	0.8954 (3)	0.3402 (2)	3.94
C(30)	0.1719 (3)	0.8659 (2)	0.5333 (2)	2.82
C(31)	0.2164 (3)	0.9499 (2)	0.5088 (2)	2.76
C(32)	0.1567 (4)	1.0268 (2)	0.4941 (2)	4.42
C(33)	0.1942 (4)	1.1048 (3)	0.4719 (3)	5.32
C(34)	0.2929 (4)	1.1074 (3)	0.4640 (3)	5.92
C(35)	0.3542 (4)	1.0317 (3)	0.4771 (3)	7.68
C(36)	0.3161 (3)	0.9539 (3)	0.4994 (3)	5.18
C(37)	0.3450 (3)	0.7581 (2)	0.6628 (2)	2.89
C(38)	0.4137 (3)	0.8414 (2)	0.6834 (2)	2.82
C(39)	0.3840 (4)	0.9105 (3)	0.7224 (2)	3.97
C(40)	0.4488 (5)	0.9851 (3)	0.7442 (3)	5.34
C(41)	0.5444 (5)	0.9920 (3)	0.7294 (3)	5.46
C(42)	0.5755 (4)	0.9251 (3)	0.6914 (3)	4.96
C(43)	0.5097 (3)	0.8504 (3)	0.6674 (2)	3.85

^a*B*(eqv) = 1/3[*a*²*b*(11) + *b*²*b*(22) + *c*²*b*(33) + *ab*(cos γ)*b*(12) + *ac*(cos β)*b*(13) + *bc*(cos α)*b*(23)].

the resulting solution was filtered while hot. The filtrate was concentrated to about one-third volume and cooled, producing 0.85 g of 3 as yellow crystals. Concentration of the mother liquor afforded an additional 0.12 g for a total yield of 0.97 g (15%): mp 137-138 °C; IR (CH₂Cl₂) ν_{CO} 2008 (vs), 1924 (vs) cm⁻¹; ¹H NMR (CDCl₃) δ 3.63 (s, 10 H, CH₂), 6.83 (m, 10 H, Ph), 7.06 (m, 15 H, Ph); ¹³C NMR (CDCl₃) δ 31.43 (CH₂), 100.8 (Cp), 126.2, 128.2, 128.5, 138.9 (Ph), 225.5 (CO). Anal. Calcd for C₄₃H₃₅MnO₃: C, 78.89; H, 5.39. Found: C, 78.75; H, 5.58.

(η^5 -Pentabenzylcyclopentadienyl)tricarbonylrhenium (4). Re₂(CO)₁₀ (0.500 g, 0.767 mmol), pentabenzylcyclopentadiene (1.00 g, 1.94 mmol), and 100 mL of solvent (xylene/mesitylene, 1:1) were stirred at reflux for 72 h as described above. The resulting solution was allowed to cool and filtered through an alumina plug. The solvent was removed from the filtrate, 30 mL of hexane was added, and the solution was placed in a freezer at -20 °C for 48 h. White crystals of pentabenzylcyclopentadiene separated first during the cooling procedure. The remaining solution was decanted into another flask and was concentrated until about 10 mL remained. After the solution was left standing at -20 °C for another 48 h, 0.150 g (13%) of 4 was obtained as yellow crystals: mp 140-141 °C; IR (CH₂Cl₂) ν_{CO} 2015 (vs), 1931 (vs) cm⁻¹; ¹H NMR δ 3.73 (s, 10 H, CH₂), 6.89 (m, 10 H, Ph), 7.11 (m, 15 H, Ph); ¹³C NMR (CDCl₃) δ 31.45 (CH₂), 104.5 (Cp), 126.4, 128.3,

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Table V. Final Fractional Coordinates for $(\eta^5\text{-C}_5\text{Bz}_5)_2\text{Fe} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eq), Å ²	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eq), Å ²
Fe	0.06033 (8)	0.24264 (5)	0.16230 (5)	0.99	C(48)	-0.1772 (6)	0.2793 (4)	0.3011 (4)	1.43
C(1)	0.1952 (6)	0.2820 (4)	0.1968 (3)	1.16	C(49)	-0.2444 (6)	0.2625 (4)	0.3339 (4)	1.85
C(2)	0.1988 (6)	0.2176 (4)	0.2091 (4)	1.40	C(50)	-0.2190 (7)	0.2208 (4)	0.3787 (4)	1.93
C(3)	0.1749 (6)	0.1868 (4)	0.1542 (3)	1.27	C(51)	-0.1242 (7)	0.1938 (4)	0.3911 (4)	1.85
C(4)	0.1566 (6)	0.2309 (4)	0.1084 (3)	1.25	C(52)	-0.0577 (6)	0.2103 (4)	0.3578 (3)	1.57
C(5)	0.1690 (6)	0.2899 (4)	0.1346 (3)	1.25	C(53)	-0.0306 (6)	0.1371 (4)	0.2234 (3)	1.36
C(6)	0.2188 (6)	0.3318 (4)	0.2409 (4)	1.53	C(54)	-0.1245 (6)	0.1009 (4)	0.2219 (3)	1.23
C(7)	0.3307 (6)	0.3448 (4)	0.2609 (3)	1.19	C(55)	-0.1278 (7)	0.0407 (4)	0.2037 (4)	1.79
C(8)	0.3979 (6)	0.3270 (4)	0.2283 (4)	1.98	C(56)	-0.2099 (7)	0.0043 (5)	0.2038 (4)	2.44
C(9)	0.4978 (7)	0.3420 (5)	0.2479 (4)	2.40	C(57)	-0.2900 (7)	0.0291 (5)	0.2223 (4)	2.36
C(10)	0.5304 (7)	0.3721 (4)	0.3006 (4)	2.41	C(58)	-0.2892 (7)	0.0897 (5)	0.2398 (4)	2.35
C(11)	0.4651 (7)	0.3878 (4)	0.3338 (4)	2.23	C(59)	-0.2037 (6)	0.1247 (4)	0.2400 (4)	1.73
C(12)	0.3637 (7)	0.3738 (4)	0.3145 (4)	1.74	C(60)	-0.0909 (6)	0.1508 (4)	0.0846 (3)	1.30
C(13)	0.2209 (6)	0.1899 (4)	0.2689 (4)	1.79	C(61)	-0.1980 (6)	0.1466 (4)	0.0506 (3)	1.30
C(14)	0.3284 (6)	0.1677 (4)	0.2907 (3)	1.35	C(62)	-0.2212 (6)	0.1564 (4)	-0.0098 (3)	1.47
C(15)	0.3521 (7)	0.1074 (4)	0.2844 (4)	2.08	C(63)	-0.3189 (7)	0.1534 (4)	-0.0420 (4)	1.94
C(16)	0.4496 (8)	0.0872 (5)	0.3052 (4)	2.53	C(64)	-0.3951 (7)	0.1394 (4)	-0.0142 (4)	1.93
C(17)	0.5242 (7)	0.1270 (5)	0.3328 (4)	2.23	C(65)	-0.3720 (7)	0.1281 (4)	0.0461 (4)	1.94
C(18)	0.4983 (7)	0.1870 (4)	0.3393 (4)	2.04	C(66)	-0.2737 (6)	0.1317 (4)	0.0776 (4)	1.47
C(19)	0.4024 (6)	0.2076 (4)	0.3188 (4)	1.77	C(67)	-0.1007 (6)	0.2941 (4)	0.0553 (3)	1.29
C(20)	0.1732 (6)	0.1192 (4)	0.1465 (4)	1.71	C(68)	-0.2016 (6)	0.3238 (4)	0.0367 (3)	1.33
C(21)	0.2696 (6)	0.0935 (4)	0.1356 (4)	1.54	C(69)	-0.2888 (6)	0.2939 (4)	0.0423 (4)	1.57
C(22)	0.2655 (7)	0.0380 (4)	0.1064 (4)	1.96	C(70)	-0.3807 (7)	0.3212 (5)	0.0215 (4)	2.20
C(23)	0.3525 (8)	0.0095 (5)	0.0984 (4)	2.59	C(71)	-0.3882 (7)	0.3784 (5)	-0.0053 (4)	2.36
C(24)	0.4438 (8)	0.0397 (5)	0.1186 (4)	2.86	C(72)	-0.3020 (8)	0.4077 (5)	-0.0105 (4)	2.62
C(25)	0.4482 (7)	0.0961 (5)	0.1473 (4)	2.51	C(73)	-0.2089 (7)	0.3813 (4)	0.0110 (4)	1.77
C(26)	0.3612 (6)	0.1223 (4)	0.1548 (4)	1.78	C(74)	-0.0493 (6)	0.3665 (4)	0.1752 (4)	1.54
C(27)	0.1278 (6)	0.2167 (4)	0.0443 (3)	1.57	C(75)	-0.1290 (6)	0.3943 (4)	0.2023 (4)	1.41
C(28)	0.2078 (6)	0.2354 (4)	0.0129 (3)	1.47	C(76)	-0.0995 (7)	0.4262 (4)	0.2545 (4)	1.74
C(29)	0.3021 (6)	0.2094 (4)	0.0287 (4)	1.90	C(77)	-0.1722 (7)	0.4541 (4)	0.2793 (4)	2.09
C(30)	0.3754 (7)	0.2262 (4)	-0.0001 (4)	2.21	C(78)	-0.2713 (7)	0.4498 (4)	0.2513 (4)	2.21
C(31)	0.3541 (7)	0.2688 (5)	-0.0451 (4)	2.35	C(79)	-0.3001 (7)	0.4182 (4)	0.1987 (4)	2.03
C(32)	0.2606 (7)	0.2945 (5)	-0.0616 (4)	2.28	C(80)	-0.2294 (6)	0.3907 (4)	0.1740 (4)	1.57
C(33)	0.1863 (7)	0.2775 (4)	-0.0322 (3)	1.61	C(81)	0.3166 (8)	0.0540 (6)	-0.0516 (5)	3.78
C(34)	0.1542 (6)	0.3493 (4)	0.1030 (4)	1.37	C(82)	0.2058 (8)	0.0633 (4)	-0.0624 (4)	2.38
C(35)	0.2501 (6)	0.3861 (4)	0.1082 (3)	1.26	C(83)	0.1612 (9)	0.1188 (4)	-0.0819 (4)	2.60
C(36)	0.3272 (6)	0.3641 (4)	0.0855 (3)	1.46	C(84)	0.059 (1)	0.1262 (6)	-0.0912 (4)	3.52
C(37)	0.4107 (6)	0.3995 (4)	0.0879 (4)	1.86	C(85)	-0.0008 (9)	0.0794 (7)	-0.0803 (5)	3.80
C(38)	0.4188 (7)	0.4584 (4)	0.1142 (4)	2.24	C(86)	0.0423 (9)	0.0230 (6)	-0.0611 (5)	3.61
C(39)	0.3413 (7)	0.4787 (4)	0.1373 (4)	2.33	C(87)	0.143 (1)	0.0157 (5)	-0.0524 (4)	3.17
C(40)	0.2572 (7)	0.4428 (4)	0.1345 (4)	1.68	C(88)	0.3154 (9)	0.4587 (6)	-0.0770 (5)	4.10
C(41)	-0.0360 (5)	0.2555 (4)	0.2153 (3)	1.25	C(89)	0.2027 (9)	0.4573 (4)	-0.0827 (4)	2.82
C(42)	-0.0482 (6)	0.1953 (4)	0.1904 (3)	1.17	C(90)	0.1637 (9)	0.4486 (5)	-0.0338 (4)	3.04
C(43)	-0.0742 (6)	0.2025 (4)	0.1279 (4)	1.41	C(91)	0.0616 (9)	0.4482 (5)	-0.0364 (5)	3.64
C(44)	-0.0782 (6)	0.2666 (4)	0.1150 (3)	1.20	C(92)	-0.006 (1)	0.4558 (5)	-0.0919 (7)	4.53
C(45)	-0.0542 (6)	0.2981 (3)	0.1691 (3)	1.03	C(93)	0.035 (1)	0.4642 (5)	-0.1404 (6)	4.10
C(46)	-0.0057 (5)	0.2709 (4)	0.2797 (3)	1.22	C(94)	0.138 (1)	0.4640 (5)	-0.1358 (5)	3.65
C(47)	-0.0820 (6)	0.2530 (4)	0.3134 (3)	1.14					

$$^{\circ}B(\text{eqv}) = \frac{4}{3}[a^2b(11) + b^2b(22) + c^2b(33) + ab(\cos \gamma)b(12) + ac(\cos \beta)b(13) + bc(\cos \alpha)b(23)].$$

128.4, 139.5 (Ph), 197.5 (CO). Anal. Calcd for $\text{C}_{43}\text{H}_{35}\text{O}_3\text{Re}$: C, 65.71; H, 4.49. Found: C, 65.91; H, 4.72.

Decabenzylferrocene (5). Into a 250-mL three-necked flask equipped with a gas inlet tube, magnetic stirrer, and reflux condenser were added 6.00 g (11.6 mmol) of pentabenzylcyclopentadiene and 150 mL of THF. The solution was cooled in an ice bath, and 5.20 mL (11.6 mmol) of 2.22 M *n*-butyllithium in hexane was added with stirring under argon. The reaction mixture turned dark red-purple immediately and was stirred for an additional 30 min. Anhydrous FeCl_2 (0.75 g, 5.92 mmol) was added, and the mixture was heated at reflux for 48 h. The solvent was removed under vacuum, 150 mL of hot toluene was added, and the mixture was filtered through an alumina plug while hot. The filtrate was concentrated to about one-third volume and allowed to stand at room temperature for 48 h, affording to 2.15 g (34%) of **5** as bright yellow crystals: $^1\text{H NMR}$ (CDCl_3) δ 4.13 (s, 20 H, CH_2), 6.43 (d, 20 H, Ph), 6.88 (m, 30 H, Ph); $^{13}\text{C NMR}$ (CDCl_3) δ 32.50 (CH_2), 84.64 (Cp), 125.6, 127.9, 129.0, 139.2 (Ph); MS, *m/e* 1086 (M^+), 571 ($\text{M} - \text{C}_{40}\text{H}_{35}$)⁺, 516 ($\text{C}_{40}\text{H}_{36}$)⁺. Anal. Calcd for $\text{C}_{80}\text{H}_{70}\text{Fe}$: C, 88.37; H, 6.49. Found: C, 88.43; H, 6.49.

1,2,3,4,5-Pentamethyl-1',2',3',4',5'-pentabenzylferrocene (6). Into a 100-mL Schlenk flask was added 50 mL of THF, 0.28 g (1.93 mmol) of $\text{C}_6\text{Me}_5\text{Li}$, and 0.500 g (1.93 mmol) of $\text{Fe}(\text{acac})_2$. The mixture was stirred at -78°C for 15 min, allowed to warm to room temperature, and stirred for an additional 1 h (the color

changed to dark red). $\text{C}_5\text{Bz}_5\text{Li}$ (1.93 mmol) in THF, prepared from 1.00 g of pentabenzylcyclopentadiene and 0.78 mL of 2.5 M *n*-butyllithium in hexane, was added to the above solution at -78°C . The mixture was allowed to warm at room temperature and stirred for 1 h. The solvent was removed in vacuo, and 50 mL of methanol was added to the residue. The solid was filtered and washed with two 15-mL portions of methanol, leaving a yellow solid. Recrystallization of the product from hot hexane yielded 0.34 g (25%) of **6** as yellow crystals: mp 222–223 $^\circ\text{C}$ dec; $^1\text{H NMR}$ (CDCl_3) δ 1.95 (s, 15 H, Me), 3.82 (s, 10 H, CH_2), 6.37 (d, 10 H, Ph), 6.75 (t, 10 H, Ph), 6.85 (t, 5 H, Ph). Anal. Calcd for $\text{C}_{50}\text{H}_{50}\text{Fe}$: C, 84.97; H, 7.13. Found: C, 84.76; H, 7.08.

1,2,3,4,5-Pentabenzylferrocene (7). A 100-mL Schlenk flask was charged with 1.00 (1.93 mmol) of pentabenzylcyclopentadiene and 50 mL of THF. *n*-Butyllithium (0.78 mL, 2.5 M, 1.93 mmol) in hexane was then added dropwise to the solution at 0°C . The deep purple solution was stirred for 30 min and then cooled to -78°C . $\text{Fe}(\text{acac})_2$ (0.500 g, 1.93 mmol) was added to the $\text{C}_5\text{Bz}_5\text{Li}$ /THF solution at -78°C . The reaction mixture was stirred for 1.5 h and the color changed to brown. $\text{C}_5\text{H}_5\text{Ti}$ (0.52 g, 1.93 mmol) was added at -78°C , and the mixture was allowed to warm to room temperature and stirred overnight at 40°C . After the solution had cooled to room temperature, it was filtered, and a yellow filtrate was collected. The solvent was removed, and the residue was recrystallized from hot methanol. The solvent was

then decanted and the solid dried in vacuo, giving 0.43 g (35%) of **7** as yellow crystals: mp 142.5–143 °C; $^1\text{H NMR}$ (CDCl_3) δ 3.79 (s, 5 H, Cp), 3.89 (s, 10 H, CH_2), 6.63–6.92 (m, 25 H, Ph); $^{13}\text{C NMR}$ (CDCl_3) δ 33.29 (CH_2), 72.11 (C_5H_5), 85.62 (C_5Bz_5), 125.4, 127.8, 128.6, 140.9 (Ph). Anal. Calcd for $\text{C}_{46}\text{H}_{40}\text{Fe}$: C, 84.90; H, 6.33. Found: C, 84.64; H, 6.51.

X-ray Data Collection, Structure Determination, and Refinement. Single crystals of the title complexes were mounted on pins and transferred to the goniometer. The crystal of **5** was cooled to -150 °C during data collection, using a stream of cold nitrogen gas. The space groups were uniquely determined from the systematic absences. A summary of data collection parameters is given in Table III.

The geometrically constrained hydrogen atoms in **3** 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 found in Table III. The final values of

the positional parameters are given in Tables IV (3) and V (5).

Acknowledgment is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research to M.D.R. The National Science Foundation Chemical Instrumentation Program provided funds used to purchase the diffractometer (N.I.U.).

Registry No. **3**, 118631-25-7; **4**, 118631-26-8; **5**, 118631-28-0; **6**, 118631-29-1; **7**, 118631-30-4; pentabenzylcyclopentadiene, 67209-29-4.

Supplementary Material Available: Full tables of bond distances and angles, H-atom coordinates, thermal parameters, and least-squares plane results (21 pages); listings of structure factors (17 pages). Ordering information is given on any current masthead page.

Asymmetric Catalysis. 44.¹ Enantioselective Monophenylation of Diols with $\text{Cu}(\text{OAc})_2$ /Pyridinyloxazoline Catalysts

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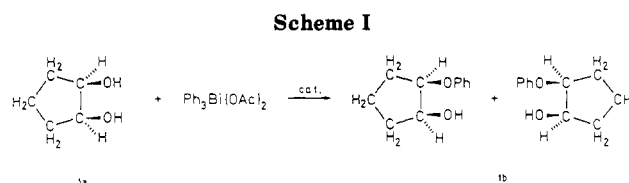
Received September 9, 1988

The $\text{Cu}(\text{OAc})_2$ -catalyzed monophenylation of meso diols with $\text{Ph}_3\text{Bi}(\text{OAc})_2$ was rendered enantioselective by using optically active pyridinyloxazoline ligands as cocatalysts. Screening of 12 meso diols and 14 optically active pyridinyloxazolines gave enantioselectivities in the middle range up to 50.4% ee. *trans*-Cyclohexane-1,2-diol was submitted to a kinetic resolution.

Introduction

For several years organobismuth compounds^{2–4} have been increasingly used in organic synthesis. Bi(V) compounds are reagents for the oxidation of alcohols, thiols, and hydrazones, and the cleavage of 1,2-diols under mild conditions.⁵ Arylated Bi(V) reagents may transfer the aryl group to organic substrates such as phenols⁶ or ketones.⁷ Alcohols can be phenylated with triphenylbismuth diacetate in a copper-catalyzed reaction without oxidation.⁸

A special case is the monophenylation of diols with triphenylbismuth diacetate. In refluxing CH_2Cl_2 , 1,*n*-diols ($n = 2$ –6) are converted into the corresponding monophenyl ethers in good yields.^{9–11} The chemoselectivity of



this reaction is very high. Diphenylated byproducts have never been observed. Typical for this reaction is an induction period of about 2 h and a remarkable solvent dependence. In solvents other than CH_2Cl_2 the yield drops drastically.¹² Recently, Barton et al. discovered that the monophenylation of diols is catalyzed by copper(II) acetate.¹² In the presence of small amounts of $\text{Cu}(\text{OAc})_2$ there is no induction period, the reaction now proceeds at room temperature, and the yields are higher than in the uncatalyzed reaction. Additionally, the Cu-catalyzed reaction is not confined to CH_2Cl_2 as a solvent.¹²

With the use of prochiral substrates and optically active copper catalysts, we tried to make this monophenylation reaction enantioselective. A typical example is the monophenylation of meso-cyclopentane-1,2-diol (**1a**) with $\text{Ph}_3\text{Bi}(\text{OAc})_2$ to give the two enantiomers of 1-phenoxy-2-hydroxycyclopentane (**1b**) (Scheme I). A short account of part of this work has already been published.¹³ In this paper we describe our results on the enantioselective monophenylation of diols **1a**–**13a** with $\text{Ph}_3\text{Bi}(\text{OAc})_2$, ex-

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