Syntheses of p-phenylene- and p-biphenylylene-bridged methylated binuclear ferrocenes

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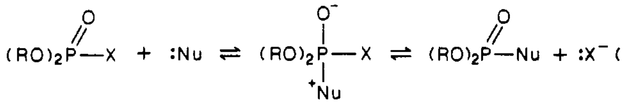

$$(RO)_2P(=O){-}X + {:}Nu \rightleftharpoons (RO)_2P(O^-)({-}X)({}^+Nu) \rightleftharpoons (RO)_2P(=O){-}Nu + {:}X^- \quad (6)$$

DPPC occurs in the organic phase. Moreover, the relatively high catalytic activity of **5** provides strong evidence for the importance of association or binding between the hydrophobic catalyst and DPPC prior to the first catalytic step. It is noteworthy that polysiloxanes, long recognized and utilized because of their inertness and hydrophobicity, are now shown to be important platforms for chemical catalysis even in water-containing media provided they are appropriately functionalized.

The importance of hydrophobic binding interactions in facilitating catalysis in enzyme reactions is well-known. The impact of this phenomenon in the action of synthetic polymer catalysts for reactions such as described above is significant. A full investigation of a variety of monomeric and polymeric catalysts with nucleophilic catalytic sites is currently underway. They are being used to study the effect of polymer structure and morphology on catalytic activity in transacylation reactions.

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Registry No. **2**, 108094-05-9; **6**, 17379-35-0; **7**, 111209-65-5; **8**, 694-59-7; **9**, 26715-00-4; diphenyl phosphorochloridate, 2524-64-3; benzoyl chloride, 98-88-4; benzoic acid, 65-85-0; benzoic anhydride, 93-97-0; 3-bromopyridine, 626-55-1.

Syntheses of *p*-Phenylene- and *p*-Biphenylene-Bridged Methylated Binuclear Ferrocenes

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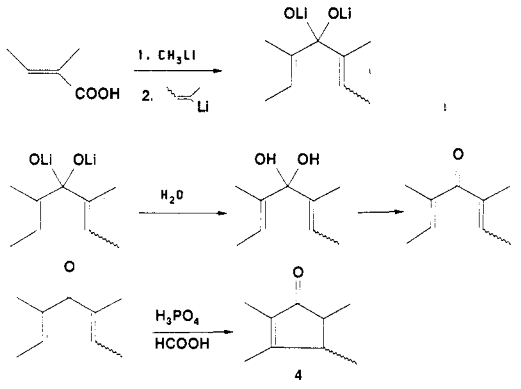
p-Phenylene and *p*-biphenylene-bridged methylated cyclopentadienyl rings were prepared. Reaction of the dilithio salts of the ligands with $(\eta^5\text{-}C_5Me_5)Fe(acac)$ provides cleanly ferrocenes bridged by *p*-phenylene and *p*-biphenylene groups. The electrochemistry of these compounds shows that a mixed-valence state is stabilized only in the $p\text{-}C_6H_4$-bridged species; if the bridge is extended to two aromatic rings, the individual ferrocenes do not interact. Methyl substitution on the ring increases the interaction between the metals centers as shown for $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5Me_4)C_6H_4(\eta^5\text{-}C_5Me_4)]Fe(\eta^5\text{-}C_5H_5)$, in which the mixed-valence state is less stable as compared with the analogous, fully methylated compound.

Introduction

Although bridged biferrocenes have been extensively investigated for their mixed-valence properties,[1] systematic variations in the bridging group, which could allow definition of the factors governing the Fe–Fe coupling, have generally not been used. We have recently adopted a general strategy for the synthesis of bridged biferrocenes different from the classical methods that involve the coupling of two ferrocene moieties.[2] Treatment of 2 equiv of $(\eta^5\text{-}C_5Me_5)Fe(acac)$ (acac = acetylacetonate) with the dilithium salt of a (cyclopentadienyl)–X–(cyclopentadienyl) linking ligand provides an efficient route to a variety of new biferrocenes joined by an unsaturated organic group X. We report herein the synthesis of new linked cyclopentadienyl ligands for which X = *p*-phenylene and *p*-biphenylene. These ligands were used to prepare biferrocenes, whose properties will also be discussed.

Scheme I



Results and Discussion

Synthesis and Characterization of *p*-Bis(3,4-dimethylcyclopentadienyl)phenylene (1), *p*-Bis(tetramethylcyclopentadienyl)phenylene (2), and *p*-Bis-

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[1] Cowan, D. O.; Le Vanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *1*, 1.

[2] (a) Rosenblum, M. *Chemistry of the Iron Group Metallocenes*; Wiley: New York, 1965. (b)Bublitz, D. E.; Rinehart, K. L., Jr. *Org. React.* **1969**, *17*, 1.

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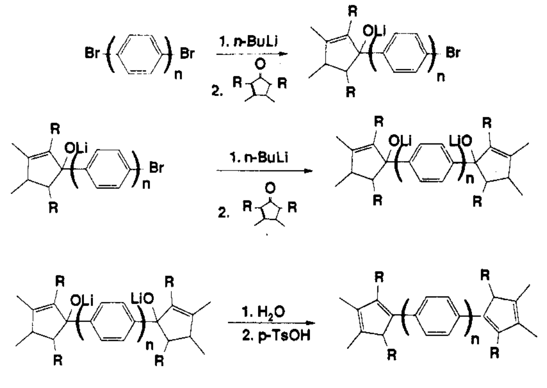
Scheme II

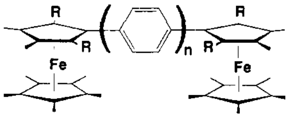


1 (n=1,R=H)
2 (n=1,R=Me)
3 (n=2,R=Me)

(tetramethylcyclopentadienyl)biphenylene (3). Key steps (vide infra) in the preparation of 1, 2 and 3 involve stepwise addition of a methyl-substituted cyclopent-2-en-1-one to an aryllithium. While 3,4-dimethylcyclopent-2-en-1-one is cleanly prepared (albeit in only 25% yield) by the method described by Conia,[3] 2,3,4,5-tetramethylcyclopent-2-en-1-one 2,3,4,5-tetramethylcyclopent-2-en-1-one (4) was heretofore available only by rather cumbersome procedures reported by de Vries,[4] Kohl,[5] or Whitesides.[6] A much more convenient synthesis involves treatment of lithium tiglate with 2-lithio-2-butene, hydrolysis of the resultant dilithium ketalate to di-*sec*-2-butenyl ketone, and closure to 4 using the method of De Vries[4] (Scheme I).

The synthesis of 1 and 2 is carried out as shown in Scheme II; isolation of intermediates is not required, so that the entire procedure may be performed in "one pot". The *p*-biphenylene-bridged derivative 3 is prepared in the same manner, except that *p,p'*-dibromobiphenyl is substituted for *p*-dibromobenzene. Mass spectral data and elemental analyses of these compounds support their formulation, and ^{1}H NMR spectra indicate a single double bond isomer in each case.

Synthesis of *p*-Phenylene- and *p*-Biphenylene-Bridged Ferrocenes. Preparation of ferrocenes 5, 6, and 7 proceeds straightforwardly by a previously reported route.[7] Thus, reaction of the dilithium salts of 1, 2, or 3 with (η^5-C$_5$Me$_5$)Fe(acac) affords the title compounds, which are easily separated from the Li(acac) byproduct. The air-stable orange crystalline compounds are obtained, analytically pure, in approximately 50% yield. Their structures were verified by ^{1}H NMR analysis.



5 n = 1; R = H
6 n = 1; R = Me
7 n = 2; R = Me

Ligands 2 and 3 posses sufficient steric bulk to allow successful preparation of (acac)Fe[(η^5-C$_5$Me$_4$)C$_6$H$_4$(η^5-C$_5$Me$_4$)]Fe(acac) (8) and (acac)Fe[(η^5-C$_5$Me$_4$)C$_6$H$_4$C$_6$H$_4$-(η^5-C$_5$Me$_4$)]Fe(acac) (9) analogously to (η^5-C$_5$Me$_5$)Fe(acac). Although 8 and 9 are not isolated, treatment in situ with LiC$_5$Me$_5$ or NaC$_5$H$_5$ affords the respective biferrocenes (6, 7, and 10) in approximately 50% yield (Scheme III).

Scheme III

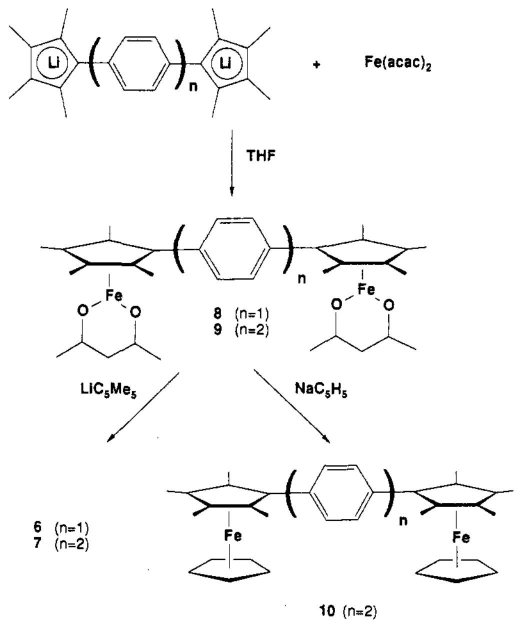


Table I. Cyclic Voltammetry Data[a]

compd	$E_{1/2}$[b]	$E_{1/2}$[c]	K_c[d]
5	0.084	0.208	124.8
6	−0.014	0.099	81.0
10	0.276	0.346	15.2

[a] Supporting electrolyte is 0.1 M NBu$_4$ClO$_4$. All potentials in V referenced to SCE. Temperature 20 °C. Sweep rate 20 mV/s. Solvent CH$_2$Cl$_2$. [b] For the process M(II)/M(II) → M(II)/M(III) + e$^-$. [c] For the process M(II)/M(III) → M(III)/M(III) + e$^-$. [d] Calculated according to ref 13.

All attempts to prepare symmetrical ferrocenes ([(η^5-C$_5$Me$_{4-x}$)(C$_6$H$_4$)$_n$(η^5-C$_5$Me$_{4-x}$)]$_2$Fe$_2$: x = 0, 2; n = 1, 2) by the reaction of the dilithio salts of ligand 1, 2, or 3 with FeCl$_2$–THF or Fe(acac)$_2$ were unsuccessful. Only amorphous, presumably oligomeric or polymeric materials were obtained.

Electrochemistry of *p*-Phenylene- and *p*-Biphenylene-Bridged Ferrocenes. Whereas compounds 5 and 6 exhibit two clearly reversible, one-electron oxidation peaks with ca. 120-mV separation (Table I), in compound 10 these two peaks are just barely resolved. Compound 7 exhibits only one reversible oxidation peak corresponds to the simultaneous transfer of two electrons per dimer. Although the previously noted increase in $\Delta E_{1/2}$ and hence K_c with increased methyl substitution on the cyclopentadienyl rings is observed here as well (compare 6 with 10), the reason for this effect is not yet clear. Moreover, the $\Delta E_{1/2}$ and K_c values for 5 and (η^5-C$_5$H$_5$)-Fe[(η^5-C$_5$H$_4$)C≡C (η^5-C$_5$H$_4$)]Fe(η^5-C$_5$H$_5$) (11)[12] are comparable, despite the fact that for 5 and especially for 6 the *p*-phenylene bridge is expected to be twisted out of direct resonance with the cyclopentadienyl π-orbitals, due to unfavorable nonbonding interactions between the ortho hydrogens and the cyclopentadienyl substituents. The similarity of the electrochemistry for these three compounds (5, 6, and 11) could well indicate a comparable degree of delocalization in the mixed-valent state. The $\Delta E_{1/2}$ value of zero for 7 indicates a reduced delocalization due to the increased distance between the iron centers.

Experimental Section

All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of dinitrogen. Fe(acac)$_2$,[7] C$_5$Me$_5$H,[8] 3,4-dimethylcyclopent-2-

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[3] Conia, J. M.; Lerivenend, M. L. *Bull. Soc. Chim. Fr.* **1978**, 2981.
[4] de Vries, L. *J. Org. Chem.* **1960**, *25*, 1838.
[5] Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119.
[6] Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466.
[7] Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

en-1-one,[3] p,p'-dibromobiphenyl,[9] tiglic acid,[10] and *cis,trans*-2-bromo-2-butene[11] were prepared according to published procedures. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Elemental analyses and mass spectra were recorded by Larry A. Henling at the analytical facility of the California Institute of Technology. NMR spectra were recorded by using a Varian EM 390 or JEOL GX 400 spectrometer. Cyclic voltammetry was performed with a PARC Model 370 electrochemistry system.

2,3,4,5-Tetramethylcyclopent-2-en-1-one (4). To 50 g (500 mmol) of tiglic acid dissolved in 500 mL of anhydrous diethyl ether was added dropwise 312.5 mL (500 mmol) of a 1.6 M solution of methyllithium in diethyl ether. (*Caution*: reaction is exothermic and methane is liberated). The resulting white slurry was stirred for 1 h. A solution of *cis*- and *trans*-2-lithio-2-butene prepared from *cis*- and *trans*-2-bromo-2-butene (67.5 g, 500 mmol) and lithium wire (7 g, 1 mol) in 500 mL of ether was added dropwise to the lithium tiglate suspension. The mixture was refluxed for 2 h after the addition was completed. It was quenched with aqueous saturated ammonium chloride. The aqueous phase was extracted twice with 100 mL of ether. The combined ether solutions were dried with magnesium sulfate. After removal of solvent, the product was purified by vacuum transfer. The product was cyclized according to the method of de Vries:[3] yield 27.7 g (40%); bp 70 °C (5 mmHg) (lit.[3] bp 70 °C (10 mmHg)); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (d, $J = 7.1$ Hz, 3 H), 1.00 (d, $J = 7.3$ Hz, 3 H), 1.54 (s, 3 H), 1.60 (s, 3 H), 1.62 (m, 1 H), 1.86 (m, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz) δ 11.2, 14.5, 15.0, 17.9, 46.2, 48.5, 134.5, 169.7, 208.5; IR (neat) 1650 ($\nu_{C=C}$), 1700 cm^{-1} ($\nu_{C=O}$).

***p*-Bis(3,4-dimethylcyclopentadienyl)benzene (1).** To 9.8 g (41.5 mmol) of *p*-dibromobenzene dissolved in 150 mL of anhydrous diethyl ether was added dropwise 26 mL (41.6 mmol) of 1.6 M *n*-butyllithium in hexanes. After the solution was stirred for 20 min, a solution of 3,4-dimethylcyclopent-2-en-1-one (4.5 g, 41.3 mmol) in 10 mL of diethyl ether was added. The mixture was then refluxed for 1 h. The reaction was cooled to room temperature, and 26 mL of *n*-butyllithium was added. A white precipitate formed in the first 5 min of the reaction. The mixture was stirred for 1 h. A solution of 4.5 g of 3,4-dimethylcyclopent-2-en-1-one dissolved in 10 mL of ether was then added dropwise, causing the precipitate to dissolve instantaneously. Stirring was continued for 1 h. The ethereal solution was quenched with aqueous saturated ammonium chloride, the layers were separated, and the aqueous phase was extracted twice with 30 mL of ether. The solution was concentrated to ca. 30 mL, and 2 g of *p*-toluenesulfonic acid dihydrate was added. After 10 min of stirring a precipitate formed. The solid was filtered, washed with water and then with methanol, and finally dried. The crude product (4.3 g) was recrystallized from 100 mL of hot chloroform to afford 3.9 g (35.6% yield) of yellow crystals. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.47; H, 8.55. ^{1}H NMR ($CDCl_3$, 90 MHz); δ 1.80 (s, 3 H); 1.90 (s, 3 H), 3.20 (s, 2 H), 6.57 (s, 1 H), 7.30 (s, 2 H). MS: *m/e* 262.

***p*-Bis(2,3,4,5-tetramethylcyclopentadienyl)benzene (2).** The procedure for 1 was followed except 2,3,4,5-tetramethylcyclopent-2-en-1-one was substituted for 3,4-dimethylcyclopent-2-en-1-one. 2 was obtained as yellow crystals in 18% yield. Anal. Calcd for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.70; H, 9.70. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.01 (d, $J = 8$ Hz, 3 H), 1.92 (b s, 6 H), 2.06 (s, 3 H), 3.32 (q, $J = 8$ Hz, 1 H), 7.20 (s, 2 H). MS: *m/e* 318.

***p*-Bis(2,3,4,5-tetramethylcyclopentadienyl)biphenylene (3).** The procedure for 2 was followed except p,p'-dibromobiphenyl was substituted for *p*-dibromobenzene. 3 was obtained as yellow crystals in 20% yield. Anal. Calcd for $C_{30}H_{34}$: C, 91.31; H, 8.69. Found: C, 91.05; H, 8.73. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.97 (d, $J = 7.5$ Hz, 3 H), 1.83 (s, 3 H), 1.90 (s, 3 H), 2.05 (s, 3 H), 3.16 (q, $J = 7.5$ Hz, 1 H), 7.20, 7.30, 7.50, 7.60 (AA′BB′, 4 H). MS: *m/e* 394.

$(\eta^5\text{-}C_5Me_5)Fe[(\eta^5\text{-}C_5H_2Me_2)C_6H_4(\eta^5\text{-}C_5H_2Me_2)]Fe(\eta^5\text{-}C_5Me_5)$ (5). A suspension of LiC_5Me_5 in THF (prepared from 2.75 g (20 mmol) of C_5Me_5H and 12.6 (20 mmol) of 1.6 M *n*-butyllithium in 50 mL of THF) was added slowly to a THF solution (100 mL) of $Fe(acac)_2$ (5 g, 20 mmol) cooled to −78 °C. The reaction mixture was warmed to room temperature. After 1 h the deep red solution was recooled to −78 °C, and a suspension of the dilithio salt of ligand 1 (prepared from 1 (2.63 g, 10 mmol) and 1.6 M *n*-butyllithium (12.6 mL, 20 mmol) in 30 mL of THF) was added. The mixture was warmed to room temperature and stirred for 1 h. The volatiles were removed under reduced pressure, and the residue was suspended in 20 mL of methanol and filtered. The solid was washed with two portions of methanol (20-mL each) and recrystallized from hot toluene to afford 1.67 g (50%) of 5 as orange. Anal. Calcd for $C_{40}H_{50}Fe_2$: C, 74.77; H, 7.84. Found: C, 74.86; H, 8.14. ^{1}H NMR (C_6D6, 90 MHz): δ 1.72 (s, 15 H), 1.80 (s, 6 H), 3.92 (s, 2 H), 7.30 (s, 2 H).

$(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5Me_4)C_6H_4(\eta^5\text{-}C_5Me_4)Fe(\eta^5\text{-}C_5Me_5)$ (6). The procedure for 5 was followed except 2 was substituted for 1. 6 was obtained as orange crystals from hot methylcyclohexane; yield 1.45 g (48%). Anal. Calcd for $C_{44}H_{58}Fe_2$: C, 75.65; H, 8.37. Found: C, 75.69, H, 8.60. ^{1}H NMR (C_6D_6, 90 MHz): δ 1.69 (s, 15 H), 1.73 (s, 6 H), 1.93 (s, 6 H), 7.66 (s, 2 H).

$(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5Me_4)(C_6H_4)_2(\eta^5\text{-}C_5Me_4)Fe(\eta^5\text{-}C_5Me_5)$ (7). The procedure for 5 was followed except 3 was substituted for 1. 7 was obtained as yellow crystals from hot toluene, yield 2.53 g (33.3%). Anal. Calcd for $C_{50}H_{62}Fe_2$: C, 77.52; H, 8.07. Found: C, 77.37; H, 8.36. ^{1}H NMR (C_6D_6, 90 MHz): δ 1.66 (s, 15 H), 1.72 (s, 6 H), 1.88 (s, 6 H), 7.72 (b s, 4 H).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5Me_4)C_6H_4(\eta^5\text{-}C_5Me_4)Fe(\eta^5\text{-}C_5H_5)$ (10). A suspension of the dilithio salt of 2 (prepared from 2.5 g (7.85 mmol) of 2 and 9.7 mL (15.5 mmol) of 1.6 M *n*-butyllithium in 70 mL of THF) was added to a solution of 3.93 g (15.5 mmol) of $Fe(acac)_2$ in 100 mL of THF cooled to −78 °C. The mixture was allowed to warm to room temperature, and stirring was continued for 1 h. The solution was recooled to −78 °C, and 6 mL (15.5 mmol) of 2.6 M NaC_5H_5 in THF was added. The reaction mixture was warmed to room temperature and stirred for 1 h. The THF was removed under vacuum. 10 was isolated as described for 5. The crude product was recrystallized from hot toluene, affording 1.86 g (48%) as orange plates. Anal. Calcd for $C_{34}H_{38}Fe_2$: C, 73.14; H, 6.85. Found: C, 73.29; H, 6.87. ^{1}H NMR (C_6D_6, 90 MHz): δ 1.86 (s, 6 H), 2.00 (s, 6 H), 3.74 (s, 5 H), 7.67 (s, 2 H).

Electrochemical Procedures. Cyclic voltammetric data were obtained in a specially designed, three-electrode glass cell. The working electrode was a carbon glassy electrode, the counter electrode was a platinum wire, and the reference electrode was an aqueous saturated calomel electrode (SCE) connected to the working cell through a Luggin capillary placed ca. 1 mm from the working electrode. Measurements were made on 10^{-3} M solutions of the compounds in CH_2Cl_2 with a 0.1 M concentration of tetrabutylammonium perchlorate used as supporting electrolyte. All measurements were performed in an argon atmosphere, and the $E_{1/2}$ values reported were determined at the first cyclic voltammogram.

Acknowledgment. We thank Professor John E. Bercaw for helpful discussions and Pamela J. Shapiro for her help in the writing of this manuscript.

Registry No. 1, 111690-90-5; 2, 82734-26-7; 3, 82734-27-8; 4 (isomer 1), 111690-89-2; 4 (isomer 2), 34103-90-7; 5, 111717-96-5; 6, 111742-37-1; 7, 111717-97-6; 10, 111717-98-7; $Fe(acac)_2$, 14024-17-0; C_5Me_5H, 41539-64-4; tiglic acid, 80-59-1; *cis*-2-bromo-2-butene, 3017-68-3; *trans*-2-bromo-2-butene, 3017-71-8; *p*-dibromobenzene, 106-37-6; 3,4-dimethylcyclopent-2-en-1-one, 30434-64-1; p,p'-dibromodiphenyl, 92-86-4.

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