Preparation and Characterization of Iron Complexes of the Penta-*p*-tolylcyclopentadienyl and *o*-Tolyltetraphenylcyclopentadienyl Ligands

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The synthesis and characterization of the compounds $C_5(p\text{-tolyl})_5X$ (X = OH (**3**), Br (**4**)) and $C_5(o\text{-tolyl})Ph_4X$ (X = OH (**8**), Br (**9**)), which are precursors to the bulky ligands $[C_5(p\text{-tolyl})_5]^-$ and $[C_5(o\text{-tolyl})Ph_4]^-$, are described. The iron complexes $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(CO)_2Br]$ (**10**), $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^6\text{-}C_6H_6)][BPh_4]$ (**12**), $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^6\text{-}CH_3C_6H_6)][X]$ (**13**) (X = Br^- or a complex haloanion), and $[Fe(\eta^5\text{-}C_5(o\text{-tolyl})_5)(CO)_2Br]$ (**11**) can be prepared from these precursors. $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(CO)_2Br]$ (**10**) reacts with NaC_5H_5 to yield $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^1\text{-}C_5H_5)(CO)_2]$ (**14**), which was converted to $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^5\text{-}C_5H_5)]$ (**15**). The dimer $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(CO)_2]_2$ (**16**) was produced by reduction of $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(CO)_2Br]$ (**10**). The crystal and molecular structure of *sym*-penta-*p*-tolylferrocene, $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^5\text{-}C_5H_5)]$ (**15**), was determined by single-crystal X-ray diffraction. $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^5\text{-}C_5H_5)]$ (**15**) crystallizes in the orthorhombic space group $R\bar{3}$, with a = 37.540 (9) Å and D_{calcd} = 1.177 g cm^{-3} for Z = 18. The C_5 rings are parallel and eclipsed. The average Fe–C distances are 2.044_5 Å (C_5H_5) and 2.046_5 Å ($C_5(p\text{-tolyl})_5$). The Fe–C_5 centroid distances are 1.660 Å (C_5H_5) and 1.645 Å ($C_5(p\text{-tolyl})_5$). The *p*-tolyl ipso carbon atoms are displaced by 0.08–0.14 Å away from the iron atom.

Introduction

The pentaphenylcyclopentadienyl ligand has considerable versatility, and complexes with a variety of transition metals in a variety of coordination modes have been reported.[1] The ligand confers unique steric, electronic, and stability properties upon some complexes. Thus, for example, whereas the red oil $[(\eta^5\text{-}C_5H_5)PdNO]$ is reported to be unstable at room temperature under an argon atmosphere,[2,3] the pentaphenylcyclopentadienyl analogue, $[\eta^5\text{-}C_5Ph_5)PdNO]$, is a purple solid, indefinitely stable at room temperature under dinitrogen.[4] The be s of stannocene[5] and decamethylstannocene[6] are in r rast to the two parallel C_5 rings of decaphenylst and diamagnetic decaphenylnickelocene[8] contrasts wi letic nickelocene.[9]

However, from the first report of complexes of the pentaphenylcyclopentadienyl ligand, the insolubility of some of its metal complexes has been a recurrent problem.[6,10,11] For example, decaphenylmolybdenocene, which has no cyclopentadienyl analogue, has remained inaccessible to synthetic exploitation because of its insolubility.[11,12] Similarly, the insolubility of decaphenylferrocene has resulted in some considerable confusion over its characterization.[10,13,14] In fact, "$[Fe(C_5Ph_5)_2]$" is more readily isolated as its linkage isomer, $[Fe(\eta^6\text{-}C_6H_5)C_5Ph_4(\eta^5\text{-}C_5Ph_5)]$, the η^6-ligand of which is easily protonated to give $[Fe(\eta^6\text{-}C_6H_5)C_5Ph_4H(\eta^5\text{-}C_5Ph_5)]^+$.[13] Although the pentaphenylcyclopentadienyl ligand may have the steric and/or electronic properties necessary to stabilize desirable reactive organometallics, such compounds are paradoxically too insoluble to find widespread application. In particular, the dimer $[Fe(C_5H_5)(CO)_2]_2$ can be dissociated to form the highly reactive monomer radical $[Fe(C_5H_5)(CO)_2]$. However, the rate of recombination of the radical is so great (10^9 M^{-1} s^{-1}) that it is accessible only in matrix isolation experiments and has not yet been synthetically exploited.[15] Several reports have hinted at the existence of the pentaphenyl analogue, $[Fe(C_5Ph_5)(CO)_2]_2$, but this species has so far evaded isolation and it is reported to be so reactive as to "...react with any solvent in which it is soluble..." or as "...too insoluble and unstable to permit full purification, analysis, or molecular-weight determination...".[16,17] Thus the synthetic potential of $[Fe(C_5Ph_5)(CO)_2]_2$ is frustrated by the compound's low solubility.

Considerably enhanced solubilities of pentaarylcyclopentadienyl complexes can be achieved by the introduction of solubilizing alkyl substituents on one of the phenyl rings of the ligand. Monoalkylation is readily achieved in high yield by treating commercially available tetracyclone with a substituted aryl–Grignard reagent.[18] While the introduction of a substituent has the desired effect of increasing the solubility of the resultant metal complexes, the consequent asymmetry can result in the formation of a large number of positional isomers.

Substitution on all five phenyl rings eliminates the problem of positional isomers and the penta-*p*-tolylcyclopentadienyl ligand is a desirable target. Pentaarylcyclopentadienyl ligand precursors with methyl substituents on any combination of the phenyl rings are available by base-catalyzed condensation of the appropriate disubstituted 1,3-diphenylacetone and disubstituted benzil.[18]

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(1) For a recent review see: Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291.
(2) Fischer, E. O.; Vogler, A. *Z. Naturforsch., B* **1963**, *18*, 771.
(3) Fischer, E. O.; Schuster-Woldan, H. *Z. Naturforsch., B* **1964**, *19*, 766.
(4) Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707.
(5) Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 925.
(6) Jutzi, P.; Kohl, F.; Hofmann, P.; Kruger, C.; Tsay, Y. H. *Chem. Ber.* **1980**, *113*, 757.
(7) Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259.
(8) Schott, A.; Schott, H.; Wilke, G.; Brandt, J.; Hoberg, H.; Hoffmann, E. G. *Liebigs Ann. Chem.* **1973**, 508.
(9) (a) Wilkinson, G.; Pauson, P. L.; Cotton, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1970. (b) Barnett, K. W. *J. Organomet. Chem.* **1974**, *78*, 139.
(10) Lindall, C. M. Ph.D. Thesis, University of Sydney, 1992.
(11) Huebel, W.; Merenyi, R. *J. Organomet. Chem.* **1964**, *2*, 213.
(12) Hiltzapple, G. M.; Woon, P. S.; Farona, M. F. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 623.
(13) Brown, K. N.; Field, L. D.; Lay, P. A.; Lindall, C. M.; Masters, A. F. *J. Chem. Soc., Chem. Commun.* **1990**, 408.
(14) Slocum, D. W.; Duraj, S.; Matusz, M.; Cmarik, J. L.; Simpson, K. M.; Owen, D. A. In *Metal Containing Polymeric Systems*; Sheats, J. E., Carraher, C. A., Jr., Pittman, C. V., Eds.; Plenum: New York, 1985.
(15) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7794.
(16) McVey, S.; Pauson, P. L. *J. Chem. Soc.* **1965**, 4312.
(17) Connelly, N. G.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1989**, 283.
(18) Field, L. D.; Ho, K. M.; Lindall, C. M.; Masters, A. F.; Webb, A. G. *Aust. J. Chem.* **1990**, *43*, 281.

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We report here a high yielding route to the ligand precursors $[C_5(p\text{-tolyl})_5X]$ (X = OH, Br, H), their characterization, and the preparation and characterization of several complexes of the $[C_5(p\text{-tolyl})_5]^-$ ligand. The synthetic scheme is in principle suitable for the introduction of a range of substituents to the $[C_5Ph_5]^-$ framework.

We also report the preparation and molecular structure of a pentaarylferrocene, *sym*-penta-*p*-tolylferrocene. Not only does this compound provide the only structural data on the new $[C_5(p\text{-tolyl})_5]^-$ ligand, it is also of significance in providing structural data on the chemistry of bulky cyclopentadienyl ligands.[1,19,20] *sym*-Pentaphenylferrocene has been isolated previously in high yield from the thermolysis of $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2(\eta^1\text{-}C_5H_5)]$ and in 55% yield from the reaction between $[Fe(\eta^5\text{-}C_5H_5)(CO)_2I]$ and $Li(C_5Ph_5)$.[14,16]

In penta-*p*-tolylcyclopentadienyl ligands, the solubilizing substituents have been introduced at the para position of the phenyl rings. To assess the steric effects of substituents at the ortho position of the phenyl ring, we also report the synthesis and characterization of precursors to the *o*-tolyltetraphenylcyclopentadienyl ligand and of bromodicarbonyl(*o*-tolyltetraphenylcyclopentadienyl)iron(II), $[Fe(\eta^5\text{-}(o\text{-tolyl})C_5Ph_4)(CO)_2Br]$.

Experimental Section

General Methods. All procedures were carried out at atmospheric pressure using standard inert-atmosphere techniques.[21] All solvents were dried over an appropriate drying agent for at least 24 h and then distilled and degassed under nitrogen prior to use. Benzene and diethyl ether were distilled from sodium wire and benzophenone ketyl. Hexane, heptane, and xylenes were distilled from sodium. Methanol, ethanol, and propanol were distilled from magnesium alkoxide and iodine. Dichloromethane was distilled from calcium hydride. Ethyl acetate was distilled from phosphorus pentoxide. Acetone was distilled from potassium carbonate.

p-Bromotoluene, α-bromo-*p*-xylene, 4,4′-dimethylbenzil, iron pentacarbonyl, tetracyclone, *o*-bromotoluene, and tetrabutylammonium bromide (Aldrich) and sodium tetraphenylborate (Merck) were used as received. 2,3,4,5-Tetra-*p*-tolylcyclopenta-2,4-dien-1-one (**2**) was synthesized by following the method of Field et al.[18] Deuterated solvents $CDCl_3$ (Merck and Aldrich), CD_2Cl_2 (Merck), and CD_3OD (Merck), for NMR studies were used as received. KBr (Aldrich) for solid infrared absorption studies was used as received. Solution infrared studies were conducted using a sodium chloride solution cell with an optical path length of 0.2 mm.

The 200-MHz ^1H and 50-MHz ^{13}C NMR spectra were recorded on a Bruker AC 200F NMR spectrometer. The spectra were referenced internally to TMS or to residual solvent resonances ($CDCl_3$, ^1H, δ 7.27 ppm, ^{13}C, δ 77.0 ppm; CD_2Cl_2, ^1H, δ 5.30 ppm, ^{13}C, δ 54.20 ppm). Mass spectra were obtained using a Kratos MS 902 analyzer with a direct insertion probe, a 200 °C source temperature (variations as required), 70 eV ionization voltage and 8 kV acceleration voltage. Infrared spectra were recorded on a Digilab 20/80 FTS infrared spectrophotometer. Melting points were determined in air on a Branson melting point apparatus and are uncorrected.

Ligand Syntheses. Preparation of 1,3-Di-*p*-tolylpropanone (1). 1,3-Di-*p*-tolylpropanone (**1**) was prepared following the general procedure of Kimura et al.[22] for the preparation of diarylacetones. A solution of tetrabutylammonium bromide (5.2 g, 16.2 mmol) and α-bromo-*p*-xylene (14.4 g, 0.135 mol) in benzene (350 mL) was added to a stirred solution of sodium hydroxide in water (50%, 250 mL). Iron pentacarbonyl (26.4 g, 0.135 mol) was added via syringe, and the color of the upper benzene layer changed to pale yellow. Over the space of a few minutes, the color of the benzene layer changed to dark brown, and stirring was continued for 14 h at room temperature. A solution of iodine (34.3 g, 0.135 mol) in benzene (250 mL) was added and stirring continued for 4 h. The organic layer was washed successively with a saturated sodium thiosulfate solution (3 × 250 mL), 10% HCl (3 × 200 mL), and water (3 × 200 mL). The organic phase was separated, the solvent was removed in vacuo and the brown precipitate redissolved in a minimum quantity of methanol. The solution was filtered through silica (200 mL) and the silica was eluted with methanol until the washings were colorless. The solvent was removed from the filtrate to give crude 1,3-di-*p*-tolylpropanone, (15.9 g, 67 mmol, 99%), mp 30–32 °C, which was used without further purification. ^1H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.2–7.0 (q, 8H, Ar-H), 3.65 (s, 4H, CH_2), 2.35 (s, 6H, CH_3).

Preparation of 1,2,3,4,5-Penta-*p*-tolylcyclopenta-2,4-dien-1-ol (3). A solution of *p*-bromotoluene (1.9 g, 11 mmol) in diethyl ether (50 mL) was added over a period of 30 min at 0 °C to magnesium turnings (0.36 g, 15 mmol) which had been activated with a crystal of iodine under vacuum. The mixture was stirred at room temperature for 2 h and the resultant Grignard reagent was added over 30 min to a solution of 2,3,4,5-tetra-*p*-tolylcyclopenta-2,4-dien-1-one (**2**) (2.8 g, 6.4 mmol) in diethyl ether (75 mL). By the end of the addition the color of the solution had changed from purple to orange. Stirring was continued for 14 h, and the solution was poured onto a mixture of ice (50 mL) and 2 M HCl (50 mL). The fractions were separated and the aqueous layer extracted with ether (50 mL). The combined ether fractions were washed with dilute aqueous sodium carbonate (2 × 100 mL) and water (2 × 100 mL) and then dried over anhydrous sodium sulfate. The solvent was removed in vacuo to leave an oily residue which was triturated with heptane to yield a gray precipitate. The crude product was washed with cold heptane to give 1,2,3,4,5-penta-*p*-tolyl-2,4-cyclopentadien-1-ol (**3**) as a pale yellow solid (2.5 g, 4.6 mmol, 72%), mp 200–204 °C (lit.[23] 206–208 °C). ^1H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.5–6.8 (m, 20H, Ar-H), 2.4 (bs, 1H, OH), 2.3–2.1 (m, 15H, CH_3). MS: *m/e* 532 (M^+, 100%), 516 (80%), 428 (65%), 309 (35%), 206 (35%), 119 (55%).

Preparation of 1-Bromo-1,2,3,4,5-penta-*p*-tolylcyclopenta-2,4-diene (4). 1,2,3,4,5-Penta-*p*-tolylcyclopenta-2,4-dien-1-ol (**3**) (2.0 g, 3.7 mmol) was dissolved in glacial acetic acid (50 mL) at 50 °C. A solution of hydrobromic acid (48%, 5 mL) and glacial acetic acid (20 mL) was added over 30 min and the resultant solution heated at 90–100 °C for 2 h. Stirring was continued at room temperature for 14 h. The precipitated yellow product was collected by suction filtration, washed with acetic acid, recrystallized from benzene/heptane, and dried under high vacuum over sodium hydroxide. 1-Bromo-1,2,3,4,5-penta-*p*-tolylcyclopenta-2,4-diene was obtained as a yellow powder (1.5 g, 2.6 mmol, 70%), mp 221–225 °C (lit.[23] 217–219 °C). ^1H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.5–6.8 (m, 20H, Ar-H), 2.4–2.1 (m, 15H, $-CH_3$). MS: *m/e* 596 (M^+ (^{81}Br), ~1%), 594 (M^+ (^{79}Br), ~1%), 518 (20%), 517 (70%), 516 (100%), 515 (80%), 423 (20%), 348 (20%), 195 (20%).

Preparation of 1,2,3,4,5-Penta-*p*-tolylcyclopenta-2,4-diene (5). 1,2,3,4,5-Penta-*p*-tolylcyclopenta-2,4-dien-1-ol (**3**) (1.5 g, 2.8 mmol) was dissolved in glacial acetic acid (50 mL) at 50 °C. A solution of hydrobromic acid (48%, 3 mL) and glacial acetic acid (7 mL) was added over 30 min and the resultant solution heated at 90–100 °C for 1 h. Zinc (0.78 g, 12.0 mmol) was added slowly (as a solid) and heating was continued for 1 h. The reaction mixture was cooled to room temperature and filtered and the precipitated white product washed with acetic acid. The precipitate was extracted with diethyl ether (50 mL) and the extract washed with saturated aqueous sodium carbonate (3 × 50 mL) and water (3 × 50 mL). Removal of the solvent and recrystallization of the crude product from methanol afforded 1,2,3,4,5-penta-*p*-tolyl-1,3-cyclopenta-2,4-diene (**5**) as a pale white solid (1.14 g, 2.2 mmol, 78%), mp 243–245 °C. Anal. Calcd for $C_{40}H_{36}$: C, 92.98; H, 7.02. Found: C, 92.6; H, 7.4. ^1H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.2–6.7 (m, 20H, Ar-H), 5.0 (s, 1H, Cp-H), 2.3 (s, 6H, 2 × CH_3), 2.2 (s, 3H, 1 × CH_3), 2.15 (s, 6H, 2 × CH_3). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 145.9, 143.4 (2 × s, sp^2-C_5), 135.9–128.4 (m, Ar-C), 62.0 (s, sp^3-C_5), 21.2 (s, CH_3). MS: *m/e* 517 (M^+ + 1, 45%), 516 (M^+, 100%), 428 (10%). UV/vis: λ_{max} = 346 nm, ε = 2.37 × 10^4 mol^{-1} dm^3 cm^{-1}.

Preparation of 1,2,3,4,5-Penta-*p*-tolylcyclopent-1-ene (6). 1,2,3,4,5-Penta-*p*-tolylcyclopenta-2,4-dien-1-ol (**3**) (1.5 g, 2.8 mmol) was dissolved in glacial acetic acid (50 mL) at 50 °C. Hydriodic acid (57%, 1.5 mL) was added dropwise, and the solution was heated to reflux. After 10 min, hypophosphorous acid (50%, 1.5 mL) was added dropwise and reflux continued for 2 h more. The solution was cooled to room temperature, and the solvent was removed in vacuo. The brown residue was taken up in glacial acetic acid and filtered and the solvent again removed. This procedure was repeated twice more until a white residue remained. The residue was taken up in diethyl ether (50 mL) and washed with saturated

(19) Schumann, H. *Pure Appl. Chem.* **1991**, *63*, 813.
(20) Okuda, J. In *Topics in Current Chemistry*; Herrmann, W. A., Ed.; Springer-Verlag: Berlin, 1992, Vol. 160, p 97.
(21) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.
(22) Kimura, Y.; Tomita, Y.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1979**, 321.
(23) Tuzun, C. *Commun. Fac. Sci. Univ. Ankara Ser. B.* **1966**, 53.

aqueous sodium carbonate (3 × 50 mL) and water (3 × 50 mL). Removal of the solvent and recrystallization from hexane/methanol gave 1,2,3,4,5-penta-*p*-tolylcyclopent-1-ene (**6**) as a white powder (1.2 g, 2.3 mmol, 82%), mp 156–158 °C. Anal. Calcd for $C_{40}H_{38}$: C, 92.62; H, 7.38. Found: C, 92.5; H, 7.4. ^{1}H NMR (ppm, 600 MHz, $CDCl_3$): δ 7.1–6.8 (m, 20H, Ar-H), 4.4 (d, 2H, 2 × Cp-H), 3.3 (t, 1H, 1 × Cp-H), 2.3 (s, 3H, 1 × CH_3), 2.25 (s, 6H, 2 × CH_3), 2.2 (s, 6H, 2 × CH_3). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 142.0–134.6 (m, quaternary Cp-C and Ar-C), 129.1–127.4 (m, tertiary Ar-C), 64.1 (s, 2 × tertiary Cp-C), 63.5 (s, 1 × tertiary Cp-C), 21.14, 21.07 (2 × s, CH_3). MS: *m/e* 519 (M^+ + 1, 45%), 518 (M^+, 100%), 426 (45%), 413 (40%), 323 (45%), 219 (25%), 195 (35%), 105 (25%).

Preparation of Li(C_5(*p*-tolyl)$_5$) (7). Butyllithium (2.08 M in hexane, 0.45 mL, 0.9 mmol) was added dropwise to a solution of 1,2,3,4,5-penta-*p*-tolylcyclopenta-2,4-diene (**5**) (0.4 g, 0.78 mmol) in tetrahydrofuran (25 mL), and the brown solution was stirred for 2 h. The solvent was removed in vacuo, and the resultant solid was dried under high vacuum for 1 h.

Preparation of 2,3,4,5-Tetraphenyl-1-*o*-tolylcyclopenta-2,4-dien-1-ol (8). A solution of *o*-tolylmagnesium bromide, produced from *o*-bromotoluene (8.3 mL, 41 mmol) and magnesium turnings (1.0 g, 41 mmol) in dry ether (25 mL), was added slowly to a well-stirred solution of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (10 g, 26 mmol) in dry benzene (50 mL). The dark purple color of the solution changed to a translucent orange after the addition was complete. Stirring was continued for 1 h at room temperature and the solution left to stand for 16 h. The solution was transferred to a separating funnel and washed with sulfuric acid (1 M, 50 mL) and water (4 × 50 mL). The solution was concentrated under vacuum until solid began to precipitate, and the remaining product was precipitated by the addition of *n*-heptane (30 mL) and cooling. The product was collected by filtration, washed with *n*-heptane until the washings were colorless, and dried under vacuum. The crude material was purified by column chromatography on flash silica with hexane/dichloromethane (30:70) as eluent. The crude product was recrystallized from dichloromethane/*n*-heptane (1:2 v/v) to give 2,3,4,5-tetraphenyl-1-*o*-tolylcyclopenta-2,4-dien-1-ol (**8**) as a yellow crystalline solid (8.4 g, 17.6 mmol, 67%), mp 165–166 °C. Anal. Calcd for $C_{36}H_{28}O$: C, 90.72; H, 5.92. Found: C, 90.7; H, 6.0. ^{1}H NMR (ppm, 200 MHz, $CDCl_3$): δ 2.29 (s, 3H, CH_3), 2.41 (bs, 1H, OH), 6.88–7.07 (m, 24H, Ar-H). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 145.4, 143.6, 135.3, 134.2, 133.0, 131.4, 131.1, 129.7, 129.6, 129.4, 128.8, 128.7, 128.2, 128.1, 127.9, 126.5, 126.2, 125.5, 124.7, 124.5 (quaternary Cp-C and Ar-C), 90.1 (C-OH), 20.86 (CH_3). MS: *m/e* 476 (M^+, 100%), 399 (18%), 384 (80%), 356 (34%), 291 (36%), 279 (33%), 202 (22%), 178 (38%), 105 (13%), 84 (64%), 57 (13%), 49 (88%).

Preparation of Bromotetraphenyl-*o*-tolylcyclopentadiene (9) (Mixture of Isomers). 2,3,4,5-Tetraphenyl-1-*o*-tolylcyclopenta-2,4-dien-1-ol (**8**) (5 g, 10.5 mmol) was suspended in glacial acetic acid (80 mL) in a round-bottom flask fitted with a reflux condenser, drying tube, and dropping funnel. The stirred solution was heated to approximately 80 °C, and a solution of hydriodic acid (48%, 6 mL) in glacial acetic acid (8 mL) was added dropwise over a period of 45 min. The color of the solution immediately changed from yellow to a dark orange/red. After the addition was complete, stirring was continued for 2 h at 70 °C before the solution was cooled to room temperature and left to stand for 16 h. The precipitated product was collected by filtration and dried under vacuum over potassium hydroxide. The product was purified by chromatography on a flash silica column with hexane/dichloromethane (30:70) as eluent. The crude product was recrystallized from dichloromethane/hexane (1:3 v/v) to give 1-bromotetraphenyl-*o*-tolylcyclopenta-2,4-diene (mixture of isomers) as an orange crystalline solid (5.7 g, 10.7 mmol, 85%), mp 76–78 °C. Anal. Calcd for $C_{36}H_{27}Br$: C, 80.15; H, 5.04. Found: C, 80.3; H, 5.2. ^{1}H NMR (ppm, 200 MHz, $CDCl_3$): δ 2.05, 2.06 (2 × s, 3H, CH_3), 6.83–7.18 (m, 24H, Ar-H). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 135.2, 134.2, 130.7, 130.5, 130.1, 130.0, 129.9, 129.7, 129.4, 129.3, 129.1, 128.5, 128.4, 127.8, 127.7, 127.4, 127.0, 125.7 (Cp-C and Ar-C), 20.4, 19.7 (CH_3). MS: *m/e* 538 (M^+, <1%), 459 (100%), 381 (50%), 368 (38%), 367 (33%), 366 (15%), 365 (16%), 303 (42%), 289 (27%), 267 (22%), 183 (17%), 182 (15%), 181 (10%), 167 (53%), 165 (9%), 91 (30%).

Preparation of [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$Br] (10). Iron pentacarbonyl (0.46 g, 2.35 mmol) was added via syringe to a solution of 1-bromo-1,2,3,4,5-penta-*p*-tolylcyclopenta-2,4-diene (**4**) (1.4 g, 2.35 mmol) in benzene (75 mL) and the green solution was heated to reflux. The color of the solution changed to purple and finally green as the reaction progressed. The solution was heated under reflux for 1.5 h and then cooled and stirred for 16 h at room temperature. The solvent was removed in vacuo and the residue recrystallized from dichloromethane/hexane (80/20 v/v) to give bromodicarbonylpenta-*p*-tolylcyclopentadienyliron(II) (**10**) as a red-brown powder (1.27 g, 1.79 mmol, 76%), mp 263 °C. Anal. Calcd for $C_{42}H_{35}FeO_2Br$: C, 71.30; H, 4.99. Found: C, 71.1; H, 5.2. ^{1}H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.1–6.8 (q, 20H, Ar-H), 2.3 (s, 15H, CH_3). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 138.0, 132.1, 128.4, 126.9 (4 × s, Ar-C), 100.9 (s, η^5-C_5), 21.3 (s, CH_3). IR, ν_{max} (cm^{-1}, KBr): 2029, 1989, 1515, 1432, 1188, 805, 727. MS: *m/e* 517 (55%), 516 (100%), 428 (15%).

Preparation of [Fe(η^5-C_5Ph_4(*o*-tolyl))(CO)$_2$Br] (11). Iron pentacarbonyl (0.3 g, 1.5 mmol) was added to a solution of 1-bromotetraphenyl-*o*-tolylcyclopenta-2,4-diene isomers (**9**) (0.63 g, 1.2 mmol) in benzene (75 mL), and the solution was heated under reflux for 2 h. The solvent was removed in vacuo and the residue taken up in dichloromethane (30 mL). *n*-Hexane (15 mL) was added to precipitate unreacted 1-bromotetraphenyl-*o*-tolylcyclopenta-2,4-diene, the mixture was filtered and the solid residue was washed with *n*-hexane. The filtrate and *n*-hexane washings were combined and allowed to stand overnight. [Fe(η^5-C_5Ph_4(*o*-tolyl))(CO)$_2$Br] (**11**) precipitated as a red crystalline solid (0.49 g, 0.75 mmol, 63%), mp 187–188 °C. Anal. Calcd for $C_{38}H_{27}BrFeO_2$: C, 70.07; H, 4.18. Found: C, 70.1; H, 4.2. ^{1}H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.07–6.85 (m, 24H, Ar-H), 2.51, 2.42 (2 × s, 3H, CH_3). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 213.1, 211.2 (CO), 145.9, 144.2, 138.6, 135.9, 134.7, 133.4, 131.7, 131.5, 130.0, 129.8, 129.3, 128.6, 128.3, 127.4, 126.8, 126.6, 126.1, 125.5, 125.0, 124.9 (Ar-C), 94.5, 90.3 (s, η^5-C_5), 21.1, 18.6 (CH_3). IR, ν_{max} (cm^{-1}, KBr): 2031, 1977. MS: *m/e* 650 (M^+ <1%), 462 (40%), 461 (68%), 460 (100%), 459 (38%), 458 (50%), 386 (40%), 291 (53%), 289 (43%), 265 (31%), 191 (50%), 179 (31%), 178 (31%), 167 (38%).

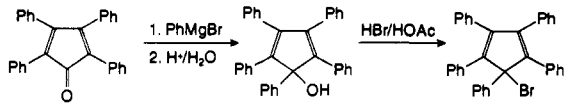
Preparation of [(η^6-C_6H_6)Fe(η^5-C_5(*p*-tolyl)$_5$)][BPh$_4$] (12). Iron pentacarbonyl (0.15 g, 0.76 mmol) was injected via syringe into a stirred mixture of 1-bromo-1,2,3,4,5-penta-*p*-tolylcyclopenta-2,4-diene (**4**) (0.9 g, 1.5 mmol) and zinc (0.1 g, 1.5 mmol) in benzene (50 mL). The initially green solution was heated to reflux where the color changed to deep purple and finally to red/brown. The reaction mixture was heated for 24 h until a red precipitate formed. The precipitate was collected by filtration and recrystallized from dichloromethane/hexane. Reprecipitation from methanol containing sodium tetraphenylborate afforded [(η^6-C_6H_6)Fe(η^5-C_5(*p*-tolyl)$_5$)][BPh$_4$] (**12**) as a deep orange microcrystalline solid (0.33 g, 0.34 mmol, 45%), mp >265 °C. Anal. Calcd for $C_{70}H_{61}FeB$: C, 86.78; H, 6.35. Found: C, 86.7; H, 6.4. ^{1}H NMR (ppm, 200 MHz, $CDCl_3$): δ 7.1–6.8 (q, 20H, Ar-H of C_5(*p*-tolyl)$_5$), 6.3 (s, 6H, Ar-H of C_6H_6), 2.3 (s, 15H, CH_3). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 138.9, 131.7, 129.1, 126.4 (Ar-C of C_5(*p*-tolyl)$_5$Me$_5$), 93.1 (η^5-C_5), 92.5 (η^6-C_6), 21.4 (CH_3). IR, ν_{max} (cm^{-1}, KBr): 3021, 2954, 2918, 2861, 1606, 1513, 1507, 1447, 1398, 1261, 1185, 1109, 1098, 1036, 1018, 815, 806, 750, 725.

Preparation of [(η^6-$C_6H_5CH_3$)Fe(η^5-C_5(*p*-tolyl)$_5$)][X] (13). Iron pentacarbonyl (0.15 g, 0.76 mmol) was injected via syringe into a stirred mixture of 1-bromo-1,2,3,4,5-penta-*p*-tolylcyclopenta-2,4-diene (**4**) (0.9 g, 1.5 mmol) and zinc (0.1 g, 1.5 mmol) in toluene (50 mL). The initially green solution was heated to approximately 90 °C where the color changed to deep purple and finally to light brown. The mixture was stirred at 90 °C for 36 h until a red precipitate formed. The precipitate was collected by filtration and recrystallized from dichloromethane/hexane to give [(η^6-$C_6H_5CH_3$)Fe(η^5-C_5(*p*-$C_6H_5CH_3$)$_5$)][X] (where X is Br^- or a complex halo anion) as an orange solid.

Preparation of [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^1-C_5H_5)(CO)$_2$] (14). Freshly cracked cyclopentadiene (approximately 4 mmol) was added dropwise over 30 min to a stirred suspension of sodium pieces (50 mg, 2.1 mmol) in tetrahydrofuran (30 mL). The reaction mixture was stirred for 2 h when all of the sodium had reacted and the resulting solution of Na^+Cp^- was added dropwise over 30 min to a stirred solution of bromodicarbonylpenta-*p*-tolylcyclopentadienyliron(II) (**10**) (0.5 g, 0.71 mmol) in tetrahydrofuran (30 mL). After the addition was complete, stirring was continued for 2 h, the solvent was removed in vacuo and the residue was recrystallized from dichloromethane to give [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^1-C_5H_5)(CO)$_2$] as a deep red air-stable solid (0.30 g, 0.43 mmol, 61%). ^{1}H NMR (ppm, 200 MHz, $CDCl_3$): δ 6.9 (broad s, 20H, Ar-H), 6.1 (s, 4H, uncoordinated C–H of η^1-C_5H_5), 4.1 (s, 1H, coordinated C–H of η^1-C_5H_5), 2.2 (s, 15H, CH_3). IR, ν_{max} (cm^{-1}, KBr) 2003, 1956, 1648, 1612, 1518, 1446.

Preparation of Penta-*p*-tolylferrocene (15). [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^1-C_5H_5)(CO)$_2$] (**14**) (0.10 g, 0.15 mmol) was heated to 165 °C as a solid under high vacuum for 1.5 h. Recrystallization of the resulting solid from

Scheme I



dichloromethane gave 1,2,3,4,5-penta-*p*-tolylferrocene, a red crystalline solid, (0.02 g, 0.03 mmol, 20%). A crystal suitable for X-ray diffraction was obtained by slow evaporation of a $CDCl_3$ solution. ^1H NMR (ppm, 200 MHz, $CDCl_3$): δ 6.9 (q, 20H, Ar-H), 4.1 (s, 5H, C_5H_5), 2.2 (s, 15H, CH_3). ^{13}C NMR (ppm, 50 MHz, $CDCl_3$): δ 135.2, 133.2 (quaternary Cp-C and Ar-C), 132.1–127.7 (tertiary Ar-*C*), 87.2 (C_5 of $C_5(p\text{-tolyl})_5$), 75.0 (C_5 of C_5H_5), 21.2 (CH_3). IR, ν_{max} (cm^{-1}, KBr) 2354, 1730, 1645, 1588, 1501, 1418.

Preparation of $[Fe(C_5(p\text{-tolyl})_5)(CO)_2]_2$ (16). Tetrahydrofuran (50 mL) was added to a mixture of bromodicarbonylpenta-*p*-tolylcyclopentadienyliron(II) (**10**) (0.5 g, 0.71 mmol) and zinc (0.4 g, 6.1 mmol) and the solution stirred vigorously for 1.5 h. The solution was filtered and recrystallization (tetrahydrofuran) of the green precipitate afforded $[Fe(C_5(p\text{-tolyl})_5(CO)_2]_2$ as a green air-sensitive solid (crude yield: 0.4 g, 90%). A sample was recrystallized again for analytical purposes: mp >300 °C. Anal. Calcd for $C_{84}H_{70}Fe_2O_4$: C, 80.38; H, 5.62. Found: C, 80.1; H, 5.9. IR, ν_{max} (cm^{-1}, Nujol): 1953 (strong), 1778 (strong), 1519 (weak). IR, ν_{max} (cm^{-1}, KBr): 2040 (w), 1988 (w), 1952 (s), 1918 (w), 1781 (s), 1609 (w), 1519 (w). MS: *m/e* 927 (4%), 926 (5%), 532 (10%), 517 (45%), 516 (100%), 515 (45%), 428 (55%), 393 (10%), 320 (10%), 189 (20%), 178 (30%), 119 (40%), 91 (40%), 65 (20%), 44 (45%). ^1H NMR (ppm, 200 MHz, THF-d_8): δ 7.2–6.7 (m, 4H), 2.7 (bs, 1H), 2.3–2.1 (m, 3H). ^{13}C NMR (ppm, 50 MHz, THF-d_8): δ 148–128 (m), 62.6 (s), 30.5 (s), 20.9 (s).

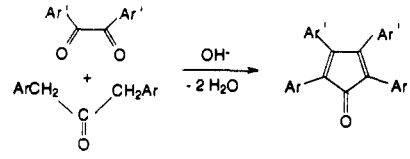
Structure Solution and Refinement. Cell constants were determined by a least squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD-4 diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarization and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package.[24] The structure was solved by direct methods within the SHELXS-86 program.[25] Non-H atoms were refined anisotropically and H atoms were included at calculated sites (C–H 0.97 Å) with group isotropic thermal parameters. Blocked-matrix least-squares refinement was carried out using program SHELX-76.[26] Scattering factors and anomalous dispersion corrections for Fe were taken from ref 27, and for all others the values supplied in SHELX-76 were used. Full tables of bond lengths and angles and listings of hydrogen atom coordinates, thermal parameters, and details of least-squares planes calculations have been deposited. Figures were drawn using the program ORTEP.[28]

Results and Discussion

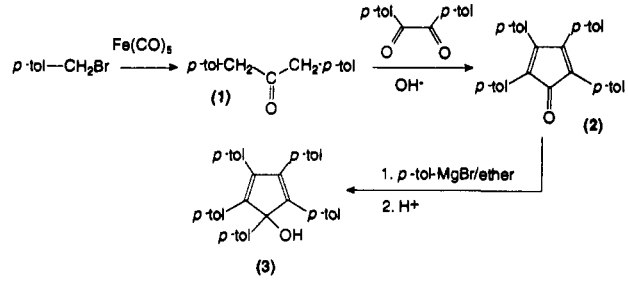
Syntheses of Ligand Precursors. Pentaphenylcyclopentadiene can be prepared in good yield by reduction of 1-hydroxy-1,2,3,4,5-pentaphenyl-2,4-cyclopentadiene or 1-bromo-1,2,3,4,5-pentaphenyl-2,4-cyclopentadiene. The alcohol and bromide precursors are obtained in good yield by addition of a Grignard reagent to tetracyclone (Scheme I).[29,30] A substituent on one of the phenyl rings is readily introduced by the use of the appropriately substituted aryl–Grignard reagent.[18] The monomethylated ligand precursor, 1-bromo-1-*o*-tolyl-2,3,4,5-tetraphenylcyclopentadiene (**9**), is smoothly prepared by this route as a mixture of isomers.

The incorporation of substituents on additional phenyl rings requires the synthesis of substituted tetraphenylcyclopentadienone

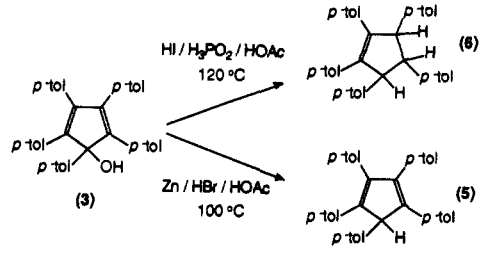
Scheme II



Scheme III



Scheme IV



derivatives, which are generally prepared by condensation of a substituted benzil with substituted dibenzylketones (Scheme II).[18]

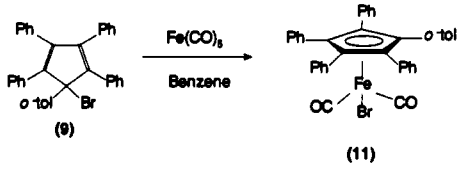
Substituted dibenzylketones have been obtained in three steps from substituted α-bromotoluenes,[18] however they can be synthesized (generally in higher yield) by reaction of substituted benzyl bromides with iron pentacarbonyl in a phase transfer reaction.[22] Tetra-*p*-tolylcyclopentadienone was synthesized in high yield from α-bromo-*p*-xylene. Reaction of α-bromo-*p*-xylene with iron pentacarbonyl afforded 1,3-di-*p*-tolylpropanone (**1**) which was condensed with 4,4′-dimethylbenzil to give tetra-*p*-tolylcyclopentadienone (**2**). The ketone (**2**) is only sparingly soluble in ethanol, and filtration separates it cleanly from other biproducts. Addition of *p*-tolylmagnesium bromide to **2** in ether affords 1-hydroxy-1,2,3,4,5-penta-*p*-tolyl-2,4-cyclopentadiene (**3**),[23] which can be converted to the corresponding bromo compound (**4**) with hydrobromic acid in acetic acid (Scheme III). The conversion of alcohol to bromide requires more forcing conditions (90–100 °C for at least 2 h) than those required for related bromopentaphenylcyclopentadiene derivatives.[18] The preparation of bromopenta-*p*-tolylcyclopentadiene from tetra-*p*-tolylcyclopentadienone has been reported previously.[23]

The method of choice to form pentaarylcyclopentadienes is via reduction of pentaarenecyclopentadienols with HI and H_3PO_2 in refluxing acetic acid.[14,18,29–31] However, reaction of 1-hydroxy-1,2,3,4,5-penta-*p*-tolyl-2,4-cyclopentadiene (**3**) with HI and H_3PO_2 in refluxing acetic acid produced the reduced product 1,2,3,4,5-penta-*p*-tolylcyclopent-1-ene (**6**) in high yield with no detectable penta-*p*-tolylcyclopentadiene (**5**). Reduction of the alcohol with HBr and zinc in acetic acid at 100 °C afforded the required penta-*p*-tolylcyclopentadiene (**5**) (Scheme IV).

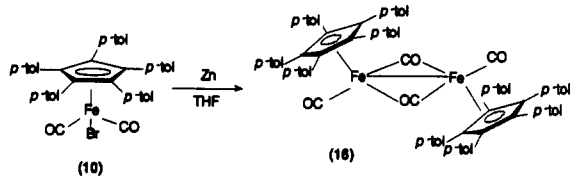
Deprotonation of $[C_5(p\text{-tolyl})_5H]$ with butyllithium smoothly forms $Li[C_5(p\text{-tolyl})_5]$ in high yield. The salt, although air sensitive, can be handled in air for short periods. The synthetic route can in principle be extended to the preparation of a wide

(24) Enraf Nonius Structure Determination Package, Enraf Nonius, Delft, 1985.
(25) Sheldrick, G. M. SHELXS-86. In *Crystallographic Computing, 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; p 175.
(26) Sheldrick, G. M. *SHELX-76, A Program for X-ray Structure Determination*; University of Cambridge: Cambridge, England, 1976.
(27) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynock Press: Birmingham, England, 1974; Vol. IV.
(28) Johnson, C. K. *ORTEP, a Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratories: Oak Ridge, TN, 1965.
(29) Ziegler, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1925**, *445*, 266.
(30) Chambers, J. W.; Baskar, A. J.; Bott, S. G.; Atwood, J. L.; Rausch, M. D. *Organometallics* **1986**, *5*, 1635.
(31) Schumann, H.; Janiak, C.; Zuckerman, J. J. *Chem. Ber.* **1988**, *121*, 207.
(32) Field, L. D.; Hambley, T. W.; Lay, P. L.; Lindall, C. M.; Masters, A. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1499.

Scheme V



Scheme VI



range of symmetrically and asymmetrically substituted pentaphenylcyclopentadienyl derivatives.

In developing the chemistry of bulky ligands, the significance of any interactions of ligand substituents with the metal needs to be established. In order to assess the likelihood of interactions of ortho substituents on the phenyl rings of perarylcyclopentadienyl ligands with the coordinated metal, we have prepared [(*o*-tolyl)C_5Ph_4)X] ([(*o*-tolyl)C_5Ph_4)X], (X = OH, (**8**), Br (**9**)) and complexes of the [(*o*-tolyl)C_5Ph_4]$^-$ ligand. The reaction of tetracyclone with *o*-tolylmagnesium bromide proceeds in high yield to give [(*o*-tolyl)C_5Ph_4OH] (**8**), which is readily converted to the bromide [(*o*-tolyl)C_5Ph_4Br] (**9**) by treatment with HBr.

Syntheses of Metal Complexes. The coordinating abilities of the [C_5(*p*-tolyl)$_5$]$^-$ and [(*o*-tolyl)C_5Ph_4]$^-$ ligands were assessed via the preparation of the complexes [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$Br], [Fe(η^5-(*o*-tolyl)C_5Ph_4)(CO)$_2$Br], and [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^6-arene)]$^+$Y$^-$. The steric demands of the ortho substituents on the aryl rings could be gauged using the (η^5-(*o*-tolyl)C_5Ph_4)$^-$ ligand and the solubilizing and stabilizing effects of the (η^5-C_5(*p*-tolyl)$_5$)$^-$ ligand might be assessed by attempting to prepare compounds such as [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^5-C_5H_5)] and [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$]$_2$, respectively.

The reaction of equimolar amounts of [C_5(*p*-tolyl)$_5$Br] (**4**) or [(*o*-tolyl)C_5Ph_4Br] (**9**) and iron pentacarbonyl in benzene results in formation of the open sandwich compounds [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$Br] (**10**) and [Fe(η^5-(*o*-tolyl)C_5Ph_4)(CO)$_2$Br] (**11**) in high yield (Scheme V). The analogous synthesis is well established for the unsubstituted pentaphenylcyclopentadienyl ligand.[16,18,33] The room-temperature ^{1}H NMR spectrum of [Fe(η^5-(*o*-tolyl)C_5Ph_4)(CO)$_2$Br] (**11**) exhibits two resonances for the methyl substituent (at δ 2.42 and 2.51 ppm) in the ratio 7:4, consistent with the presence of isomers with the *o*-methyl substituent oriented on the same and opposite sides of the C_5 ring with respect to the Fe(CO)$_2$Br moiety. Thus substituents of at least the size of a methyl group can be accommodated at the ortho position in these open sandwich compounds.

The reaction of 2 equiv of [C_5Ph_5Br] with iron pentacarbonyl under reducing conditions (zinc) in refluxing benzene results in a moderate yield of the linkage isomer of decaphenylferrocene, [Fe(η^5-C_5Ph_5)((η^6-C_6H_6)C_5Ph_4)].[13] The open sandwich compound, [Fe(η^5-C_5Ph_5)(CO)$_2$Br], and the arene cation, [Fe(η^5-C_5Ph_5)(η^6-C_6H_6)]$^+$, are minor products.[13] By contrast, [C_5(*p*-tolyl)$_5$Br] reacts under the same conditions to give moderate yields of the arene cation, [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^6-C_6H_6)]$^+$ (**12**), and no detectable amount of the corresponding linkage isomer. An infrared spectrum of the reaction solution established that the open sandwich compound [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$Br] (**10**) was also produced. Further, when the reaction is performed in toluene at 90 °C, only the arene complex [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^6-C_6H_5-Me)]$^+$ (**13**) was isolated. It is possible that the [C_5(*p*-tolyl)$_5$]$^-$ ligand is too bulky to accommodate the η^6-coordination of the aryl ring to form the linkage isomer [Fe(η^5-C_5(*p*-tolyl)$_5$)(η^6-*p*-tolyl)C_5(*p*-tolyl)$_4$] in the presence of excess arene.

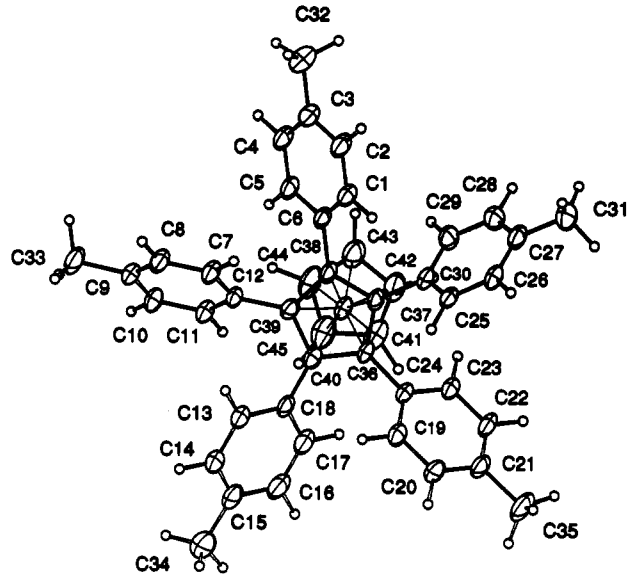


Figure 1. ORTEP (30% probability) plot of *sym*-penta-*p*-tolylferrocene (**15**) viewed along the normal to the C_5 plane.

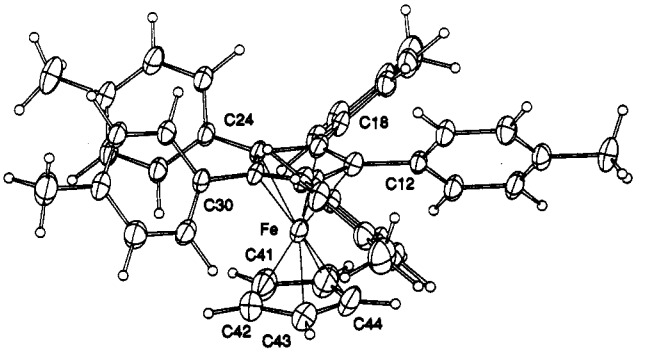


Figure 2. ORTEP (30% probability) plot of *sym*-penta-*p*-tolylferrocene (**15**) viewed perpendicular to the normal to the C_5 plane.

The red dimer [Fe(η^5-C_5H_5)(CO)$_2$]$_2$, which exists as a mixture of cis and trans isomers, is one of the most useful synthetic entry points to the chemistry of iron cyclopentadienyl compounds.[34] The permethylated analogue, [Fe(η^5-C_5Me_5)(CO)$_2$]$_2$, exists exclusively as the trans isomer and has also been exploited synthetically.[35] It has not been possible to prepare well-characterized samples of the corresponding pentaphenyl derivative, [Fe(η^5-C_5Ph_5)(CO)$_2$]$_2$. Reduction of [Fe(η^5-C_5Ph_5)(CO)$_2$Br] has been reported to yield an unstable green solid with the infrared spectral absorptions expected for *trans*-[Fe(η^5-C_5Ph_5)(CO)$_2$]$_2$; however, the compound was too unstable to be purified. We have confirmed the formation and high reactivity of this green solid. The solid has characteristic infrared spectral absorptions at 1953 and 1773 cm^{-1}.[10,16,17] The (C_5(*p*-tolyl)$_5$)$^-$ ligand, however, confers sufficient stability on the dimer, [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$]$_2$, that it can be isolated, purified and characterized. The reduction of [Fe(η^5-C_5(*p*-tolyl)$_5$)(CO)$_2$Br] with zinc powder yields a green solid, which was purified by recrystallization from tetrahydrofuran. This complex has the composition $C_{84}H_{70}Fe_2O_4$ and exhibits strong carbonyl absorptions at 1953 and 1778 cm^{-1} in the infrared spectrum—its structure is assigned as *trans*-[Fe(η^5-C_5(*p*-tolyl)$_5$(CO)$_2$]$_2$ (**16**) (Scheme VI). The complex is stable indefinitely as a solid under nitrogen

(33) Field, L. D.; Hambley, T. W.; Lindall, C. M.; Masters, A. F. *Polyhedron* **1989**, *8*, 2425.

(34) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(35) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

Table I. Crystal Data for *sym*-Penta-*p*-tolylferrocene (**15**)

space group	$R\bar{3}$	Z	18
a, Å	37.540 (9)	abs coeff, cm^{-1}	4.2
c, Å	13.244 (5)	temp, °C	21
V, Å^3	16163 (4)	λ, Å	0.710 69
fw	636.66	$R(F_o)^a$	0.058
D_{calcd}, g cm^{-3}	1.177	$R_w{}^b$	0.058
empirical formula	$C_{45}H_{40}Fe$		

^{a} $R(F_o) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w(F_o) = \Sigma w^{1/2}(|F_o| - |F_c|)/\Sigma w^{1/2}|F_o|$.

Table II. Positional Parameters (×10^4) for *sym*-Penta-*p*-tolylferrocene (**15**)

	x	y	z
Fe	576 (1)	8772 (1)	3426 (1)
C(1)	711 (2)	7751 (2)	4421 (5)
C(2)	560 (2)	7414 (2)	5049 (6)
C(3)	154 (3)	7206 (2)	5337 (6)
C(4)	-93 (2)	7348 (2)	4965 (6)
C(5)	54 (2)	7686 (2)	4340 (5)
C(6)	467 (2)	7900 (2)	4052 (5)
C(7)	-25 (2)	7580 (2)	1896 (5)
C(8)	-395 (2)	7272 (2)	1502 (6)
C(9)	-703 (2)	7353 (2)	1235 (5)
C(10)	-630 (2)	7749 (2)	1352 (5)
C(11)	-259 (2)	8057 (2)	1742 (5)
C(12)	48 (2)	7975 (2)	2027 (5)
C(13)	503 (2)	8586 (2)	187 (5)
C(14)	434 (2)	8731 (3)	-713 (6)
C(15)	523 (2)	9124 (3)	-836 (6)
C(16)	694 (2)	9386 (3)	-22 (7)
C(17)	759 (2)	9249 (2)	889 (6)
C(18)	662 (2)	8844 (2)	1015 (5)
C(19)	1669 (2)	9348 (2)	1494 (5)
C(20)	2044 (2)	9702 (2)	1320 (6)
C(21)	2231 (2)	9997 (2)	2055 (6)
C(22)	2031 (2)	9932 (2)	2970 (6)
C(23)	1659 (2)	9582 (2)	3150 (5)
C(24)	1470 (2)	9282 (2)	2413 (5)
C(25)	1720 (2)	8752 (2)	3930 (5)
C(26)	2018 (2)	8793 (2)	4613 (6)
C(27)	1953 (2)	8795 (2)	5641 (6)
C(28)	1581 (2)	8749 (3)	5957 (6)
C(29)	1281 (2)	8700 (2)	5277 (5)
C(30)	1348 (2)	8701 (2)	4248 (5)
C(31)	2288 (3)	8853 (3)	6382 (6)
C(32)	-16 (3)	6838 (3)	6044 (7)
C(33)	-1112 (2)	7012 (3)	819 (7)
C(34)	441 (3)	9270 (3)	-1835 (7)
C(35)	2647 (3)	10387 (3)	1872 (8)
C(36)	1088 (2)	8889 (2)	2619 (5)
C(37)	1032 (2)	8626 (2)	3466 (5)
C(38)	637 (2)	8259 (2)	3368 (5)
C(39)	4967 (2)	1182 (2)	886 (5)
C(40)	2022 (2)	4626 (2)	4681 (5)
C(41)	617 (3)	9321 (3)	3799 (8)
C(42)	633 (3)	9121 (3)	4679 (7)
C(43)	267 (3)	8746 (3)	4718 (7)
C(44)	32 (3)	8715 (3)	3860 (8)
C(45)	249 (3)	9071 (3)	3282 (8)
C(1′)	255 (4)	410 (4)	5256 (9)
C(2′)	0 (1)	0 (1)	3235 (15)

Table III. Selected Core Bond Lengths (Å) for *sym*-Penta-*p*-tolylferrocene (**15**)

C(36)–Fe(1)	2.047 (7)	C(37)–Fe(1)	2.045 (9)
C(38)–Fe(1)	2.055 (9)	C(41)–Fe(1)	2.048 (11)
C(42)–Fe(1)	2.057 (10)	C(43)–Fe(1)	2.041 (10)
C(44)–Fe(1)	2.027 (11)	C(45)–Fe(1)	2.044 (14)
C(37)–C(30)	1.491 (10)	C(38)–C(6)	1.478 (9)
C(37)–C(36)	1.438 (10)	C(38)–C(37)	1.440 (7)
C(24)–C(36)	1.484 (10)	C(42)–C(41)	1.404 (14)
C(45)–C(41)	1.401 (12)	C(43)–C(42)	1.393 (11)
C(44)–C(43)	1.407 (14)	C(45)–C(44)	1.396 (14)

Table IV. Selected Bond Angles (deg) for *sym*-Penta-*p*-tolylferrocene (**15**)

C(37)–Fe(1)–C(36)	41.2 (3)	C(38)–Fe(1)–C(36)	69.3 (3)
C(38)–Fe(1)–C(37)	41.1 (2)	C(41)–Fe(1)–C(36)	108.7 (3)
C(41)–Fe(1)–C(37)	127.7 (3)	C(41)–Fe(1)–C(38)	165.0 (3)
C(42)–Fe(1)–C(36)	119.9 (3)	C(42)–Fe(1)–C(37)	108.4 (4)
C(42)–Fe(1)–C(38)	127.1 (4)	C(42)–Fe(1)–C(41)	40.0 (4)
C(43)–Fe(1)–C(36)	154.0 (3)	C(43)–Fe(1)–C(37)	119.8 (4)
C(43)–Fe(1)–C(38)	108.3 (4)	C(43)–Fe(1)–C(41)	66.6 (4)
C(43)–Fe(1)–C(42)	39.7 (3)	C(44)–Fe(1)–C(36)	163.7 (4)
C(44)–Fe(1)–C(37)	154.1 (4)	C(44)–Fe(1)–C(38)	119.4 (4)
C(44)–Fe(1)–C(41)	66.6 (4)	C(44)–Fe(1)–C(42)	67.5 (4)
C(44)–Fe(1)–C(43)	40.5 (4)	C(45)–Fe(1)–C(36)	126.3 (3)
C(45)–Fe(1)–C(37)	164.5 (3)	C(45)–Fe(1)–C(38)	153.0 (3)
C(45)–Fe(1)–C(41)	40.0 (4)	C(45)–Fe(1)–C(42)	68.0 (4)
C(45)–Fe(1)–C(43)	67.8 (4)	C(45)–Fe(1)–C(44)	40.1 (4)
C(38)–C(6)–C(1)	121.0 (6)	C(38)–C(6)–C(5)	122.7 (8)
C(36)–C(24)–C(19)	120.4 (6)	C(36)–C(24)–C(23)	121.8 (6)
C(37)–C(30)–C(25)	118.0 (6)	C(37)–C(30)–C(29)	123.9 (7)
C(24)–C(36)–Fe(1)	130.3 (6)	C(37)–C(36)–Fe(1)	69.3 (4)
C(37)–C(36)–C(24)	124.2 (6)	C(30)–C(37)–Fe(1)	131.4 (6)
C(36)–C(37)–Fe(1)	69.5 (5)	C(36)–C(37)–C(30)	125.6 (5)
C(38)–C(37)–Fe(1)	69.8 (5)	C(38)–C(37)–C(30)	125.8 (6)
C(38)–C(37)–C(36)	108.2 (6)	C(6)–C(38)–Fe(1)	129.3 (6)
C(37)–C(38)–Fe(1)	69.1 (5)	C(37)–C(38)–C(6)	125.8 (6)
C(42)–C(41)–Fe(1)	70.3 (6)	C(45)–C(41)–Fe(1)	69.8 (7)
C(45)–C(41)–C(42)	109.8 (7)	C(41)–C(42)–Fe(1)	69.7 (6)
C(43)–C(42)–Fe(1)	69.5 (6)	C(43)–C(42)–C(41)	106.8 (8)
C(42)–C(43)–Fe(1)	70.7 (6)	C(44)–C(43)–Fe(1)	69.2 (6)
C(44)–C(43)–C(42)	108.3 (8)	C(43)–C(44)–Fe(1)	70.3 (6)
C(45)–C(44)–Fe(1)	70.6 (7)	C(45)–C(44)–C(43)	108.8 (7)
C(41)–C(45)–Fe(1)	70.1 (7)	C(44)–C(45)–Fe(1)	69.3 (8)
C(44)–C(45)–C(41)	106.4 (9)		

or (hours) in tetrahydrofuran solution under nitrogen in the presence of zinc, but like the putative $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2]_2$, the complex decomposes rapidly (minutes) at room temperature in the absence of zinc. *trans*-$[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5(CO)_2]_2$ reacts with KBr in the solid state to form the open sandwich compound $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(CO)_2Br]$, as determined by infrared spectroscopy. The further reaction chemistry and electrochemistry of *trans*-$[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5(CO)_2]_2$ will be reported separately.[36]

$[Fe(C_5Ph_5)(CO)_2Br]$ reacts with $Na[C_5H_5]$ to produce a deep red solid in moderate yield. This compound is formulated as $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^1\text{-}C_5H_5)(CO)_2]$ on the basis of its ^{1}H NMR and infrared spectra and its subsequent reaction chemistry. Infrared absorptions at 2003 and 1953 cm^{-1} are consistent with those reported for the analogous $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^1\text{-}C_5H_5)(CO)_2]$ (2010, 1961 cm^{-1})[16] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2]$ (2013 vs, 1965 vs cm^{-1}).[34] Similarly, the ^{1}H NMR resonances at δ 6.1 and 4.1 ppm can be assigned to the protons on the olefinic and metal-bound carbons of the η^1-C_5H_5 ligand respectively (*cf.* δ 6.6 ppm for the η^1-C_5H_5 ligand of $[Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2]$).[34] $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^1\text{-}C_5H_5)(CO)_2]$ was not characterized further, but was heated as a solid to produce penta-*p*-tolylferrocene, $[Fe(\eta^5\text{-}C_5(p\text{-tolyl})_5)(\eta^5\text{-}C_5H_5)]$. Although the synthesis of pentaphenylferrocene has been reported, no structural data are available and the material has been incompletely characterized.[14,16] In order to fully characterize penta-*p*-tolylferrocene and because of the current interest in bulky cyclopentadienyl ligands and decaarylferrocenes in particular,[1,19,20] the structure of penta-*p*-tolylferrocene was determined by single-crystal X-ray diffraction.

Molecular Structure of *sym*-Penta-*p*-tolylferrocene. Penta-*p*-tolylferrocene crystallized from $CDCl_3$ as its $CDCl_3$ solvate. Penta-*p*-tolylferrocene exists as discrete monomers in the solid state with the nearest intermolecular contacts being 1.976 Å between methyl hydrogen atoms of adjacent molecules. The structure of penta(*p*-tolyl)ferrocene is illustrated in Figures 1 and 2. The atom numbering is illustrated in Figure 1. The crystal data, final atomic positional coordinates, with estimated standard deviations, and selected bond distances and angles are given in Tables I–IV.

(36) Field, L. D.; Latimer, D. R.; Lay, P. A.; Lindall, C. M.; Masters, A. F. Unpublished results.

The C_5 rings of **15** are almost rigorously planar (maximum deviation of the C_5C atoms from the C_5R_5 rings: 0.001 Å, R = *p*-tolyl; 0.004 Å, R = H). The two rings are almost parallel (angle between the normals to the rings is 1°) and are eclipsed in the solid state. The *p*-tolyl ipso carbon atoms are displaced by 0.08–0.14 Å to the opposite side of the ligand from the iron. All C–C bond distances are normal. The Fe–(ring centroid) distances are 1.660 Å (C_5H_5) and 1.645 Å ($C_5(p\text{-tolyl})_5$) with the average Fe–C distances being 2.044_5 Å (C_5H_5) and 2.046_5 Å ($C_5(p\text{-tolyl})_5$). Thus, the separation between the ligand planes is 3.305 Å. This compares with values of 3.308 Å in $[Fe(C_5H_5)_2]$,[37] 3.324 Å in $[Fe(C_5Me_5)_2]$,[38] 3.390 (2) Å in $[Fe(C_5Ph_4H)_2]$,[39] and 3.313 (2) Å in $[Fe(C_5Bz_5)_2]$,[40,41] respectively, and a value of 3.304 (9) Å in pentamethylferrocene $[Fe(C_5Me_5)(C_5H_5)]$.[42,43] The Fe–(C_5H_5 centroid) distance (1.660 (9) Å) is similar to that in ferrocene (1.654 Å)[37] and pentamethylferrocene (1.663 Å).[42] However, the Fe–($(C_5(p\text{-tolyl})_5$ centroid) distance is shorter than the Fe–(C_5H_5 centroid) distance. Thus, the very bulky $C_5(p\text{-tolyl})_5$ ligand is closer to the iron than is the C_5H_5 ligand in both this compound and in ferrocene. A similar effect is observed for the C_5Me_5 ring in pentamethylferrocene (Fe–(C_5Me_5 centroid) of $[Fe(C_5Me_5)(C_5H_5)]$ 1.641 Å).[42] This effect is probably electronic in origin and may indicate alkyl-like (electron-donating) rather than aryl-like (electron-withdrawing) character of the $C_5(aryl)_5$ aryl substituents as a consequence of their lack of coplanarity with the C_5 ring of the $C_5(aryl)_5$ ligand.

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Supplementary Material Available: Listings of bond lengths, bond angles, hydrogen atom coordinates and thermal parameters, anisotropic thermal parameters, and details of least-squares planes calculations (11 pages). Ordering information is given on any current masthead page.

(37) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1979**, *35*, 1068.
(38) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892.
(39) Castellani, M. P.; Wright, J. M.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1986**, *5*, 1116.
(40) Schumann, H.; Janiak, C.; Köhn, R. D.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *365*, 137.
(41) Rausch, M. D.; Tsai, W.-M.; Chambers, J. W.; Rogers, R.; Alt, H. G. *Organometallics* **1989**, *8*, 816.
(42) Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans.* **1988**, 1383.
(43) Struchkov, Yu. T.; Andrianov, V. G.; Sal'nikova, T. N.; Lyatifov, I. R.; Materikova, R. B. *J. Organomet. Chem.* **1978**, *145*, 213.