

(η^5 -Pentaphenylcyclopentadienyl){1-(η^6 -phenyl)-2,3,4,5-tetraphenylcyclopentadienyl} iron(II), [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{C}_5\text{Ph}_4\}$], a Linkage Isomer of Decaphenylferrocene

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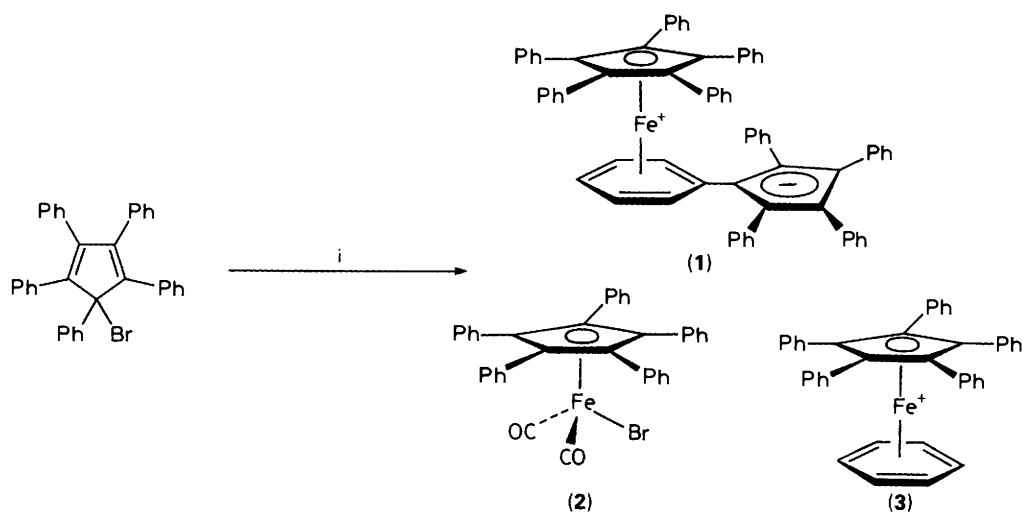
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Reaction between $[\text{Fe}(\text{CO})_5]$, zinc dust, and bromopentaphenylcyclopentadiene in refluxing benzene under argon affords (η^5 -pentaphenylcyclopentadienyl){1-(η^6 -phenyl)-2,3,4,5-tetraphenylcyclopentadienyl}iron(II), [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{C}_5\text{Ph}_4\}$], a linkage isomer of decaphenylferrocene, with a novel, zwitterionic structure; the compound is readily protonated to give [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{HC}_5\text{Ph}_4\}$] $^+\text{X}^-$.

Substituted cyclopentadienyl ligands have been shown to be of considerable utility in organometallic chemistry. Pentaphenylcyclopentadiene, although isolated over fifty years ago,¹ has received surprisingly little attention as a ligand precursor,² although it can be readily synthesised as an air-stable crystalline compound.^{3–6} The syntheses of a number of decaphenylmetallocenes have been claimed,^{4,7} but only the tin,⁵ germanium,⁸ lead,⁸ nickel,⁹ and possibly molybdenum^{10,11} derivatives have been satisfactorily characterised, and only decaphenylstannocene has been structurally characterised.⁵ Surprisingly, decaphenylferrocene has defied isolation. We describe here the preparation and characterization of (η^5 -pentaphenylcyclopent-

adienyl){1-(η^6 -C₆H₅)-2,3,4,5-tetraphenylcyclopentadienyl}-iron(II), [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{C}_5\text{Ph}_4\}$] (1) a linkage isomer of decaphenylferrocene, with a novel, zwitterionic structure.

Pentacarbonyliron(0) (one equiv.), zinc dust (two equivs.), and bromopentaphenylcyclopentadiene (two equivs.) were refluxed in benzene (100 ml g⁻¹ C₅Ph₅Br) under argon for 40 h. The product was purified by chromatography on alumina using ethyl acetate as eluent, or on silica (230–400 mesh) using 25 vol% ethyl acetate in n-hexane as eluent. [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{C}_5\text{Ph}_4\}$] is obtained in 53% yield, based on [$\text{Fe}(\text{CO})_5$], and melts with decomposition at 255–257 °C. The complexes [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$] (2) and [$\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^6\text{-$



Scheme 1. Reagents and conditions: i, $\text{Fe}(\text{CO})_5/\text{Zn}$, benzene, reflux.

$\text{C}_6\text{H}_6)^+ (3)$ were obtained from the reaction mixture as minor products (Scheme 1) and identified by comparison with authentic samples prepared by alternative methods.^{2,12}

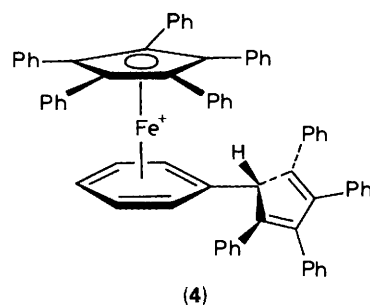
$(\eta^5\text{-Pentaphenylcyclopentadienyl})\{1-(\eta^6\text{-C}_6\text{H}_5)\text{-}2,3,4,5\text{-tetraphenylcyclopentadienyl}\}\text{iron(II)}$ is an intensely blue crystalline solid,^{†‡} soluble in tetrahydrofuran (THF), chloro-

[†] Compound (1) gave satisfactory elemental analysis and spectroscopic data in accord with its structure.

[‡] Selected spectroscopic data for $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{C}_5\text{Ph}_4\}]$ (1): ¹H NMR ($[\text{D}_2\text{H}_8]\text{THF}$) δ 5.2 (m, 2H, $\eta^6\text{-C}_6\text{H}_5$ ring), 5.6 (t, 1H), 6.4 (d, 2H), 6.7–7.4 (m, 45H, uncomplexed C_6H_5 rings); ¹³C NMR ($[\text{D}_2\text{H}_8]\text{THF}$) δ 73.3, 88.8 ($\eta^6\text{-C}_6\text{H}_5$ ring, *o*- and *m*-CH), 82.6 ($\eta^6\text{-C}_6\text{H}_5$ ring, *p*-CH), 93.1 ($\eta^5\text{-C}_5$ ring, 5 \times C-Ph), 115.3 ($\eta^6\text{-C}_6\text{H}_5$ ring, *ipso*-C), 125.6, 126.8, 128.2, 128.9, 129.3, 129.6 (C-H), 133.1 (5 \times *ipso*-C of C_6H_5 rings on $\eta^5\text{-C}_5$ ring), 133.2, 133.6, 133.9 (C-H); 134.8, 136.9 (*ipso*-C of 2- and 3- C_6H_5 rings on uncomplexed C_5 ring), 139.6, 141.5, 144.4 (ring carbons of uncomplexed C_5 ring); *m/z* (70 eV) 946 (M^+ , 100%), 891 (11%), 501 (24%), 446 (31%), 289 (11%), 207 (15%); λ_{max} (THF, nm) (log ϵ) 595 (3.90), 530 (3.81), 412 (4.20), 322 (4.30); IR ν_{max} (KBr, cm^{-1}) 3056w, 3023w, 2965w, 1594m, 1572w, 1532w, 1487m, 1443m, 1261s, 1097s, 1072s, 1025s, 931w, 907w, 800s, 768w, 694s.

$[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^6\text{-C}_6\text{H}_6)]^+ (3)$: ¹H NMR (CD_3OD) δ 6.77 (s, 6H, $\eta^6\text{-C}_6\text{H}_6$), 7.57–7.32 (m, 25H, C_6H_5); ¹³C NMR (CD_3OD) δ 94.0 ($\eta^6\text{-C}_6\text{H}_6$ ring, 6 \times C-H), 95.5 ($\eta^5\text{-C}_5$ ring, 5 \times C), 129.6, 133.6 (C_6H_5 rings, *o/m*-CH), 130.3 (C_6H_5 rings, *p*-CH), 131.4 (C_6H_5 rings, *ipso*-C); *m/z* (70 eV) 502 (M^+ , 1%), 446 (100%); IR ν_{max} (KBr, cm^{-1}) 3056m, 1501w, 1444m, 1408w, 1078w, 1025w, 801w, 784w, 740m, 709s, 700s.

$[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{(\eta^6\text{-C}_6\text{H}_5)\text{C}_5\text{Ph}_4\text{H}\}]^+[\text{BF}_4]^- (4)$: ¹H NMR (CDCl_3) δ 4.38 (s, 1H, CH of uncomplexed C_5 ring), 5.69 (d, 1H, H-2 of $\eta^6\text{-C}_6\text{H}_5$ ring), 5.97 (t, 1H, H-3 of $\eta^6\text{-C}_6\text{H}_5$ ring), 6.11 (d, 1H, H-6 of $\eta^6\text{-C}_6\text{H}_5$ ring), 6.20 (t, 1H, H-4 of $\eta^6\text{-C}_6\text{H}_5$ ring), 6.48 (t, 1H, H-5 of $\eta^6\text{-C}_6\text{H}_5$ ring), 6.63–7.53 (m, 45H, uncomplexed C_6H_5 rings); ¹³C NMR (CDCl_3) δ 61.7 [$\text{CH}-(\eta^6\text{-C}_6\text{H}_5)$ on uncomplexed C_5 ring], 86.8, 87.6, 91.5, 93.0 (C-2, C-3, C-5, C-6 on $\eta^6\text{-C}_6\text{H}_5$ ring), 90.7 (C-4 on $\eta^6\text{-C}_6\text{H}_5$ ring), 93.7 (ring C on $\eta^5\text{-C}_5$ ring), 105.6 (*ipso*-C on $\eta^6\text{-C}_6\text{H}_5$ ring), 128.1 (5 \times *p*-CH on rings on $\eta^5\text{-C}_5$ ring), 128.4, 128.7 (*p*-CH on C_6H_5 rings on uncomplexed C_5 ring), 129.1, 132.4 (*o*- and *m*-CH of rings on $\eta^5\text{-C}_5$ ring), 129.3, 129.8, 130.5, 130.8 (*o*- and *m*-CH of C_6H_5 rings on uncomplexed C_5 ring), 130.1 (5 \times *ipso*-C of C_6H_5 rings on $\eta^5\text{-C}_5$ ring), 133.8, 134.4 (*ipso*-C of C_6H_5 rings on uncomplexed C_5 ring), 135.3, 136.1, 137.2, 143.3 (C-2, C-3, C-4, C-5 on uncomplexed C_5 ring); *m/z* (70 eV) 946 (M^+ , 36%), 501 (11%), 446 (45%), 242 (15%), 164 (35%), 154 (16%), 78 (60%), 69 (12%), 44 (100%); IR ν_{max} (KBr, cm^{-1}) 3048s, 3024s, 1598m, 1547m, 1528w, 1499m, 1478m, 1444m, 1406m, 1329w, 1181w, 1076w, 1028w, 849w, 799w, 766w, 739m, 696s, 674m.



form, dichloromethane, acetone, acetonitrile, dimethyl sulphoxide, dimethylformamide (DMF), and dry methanol, and insoluble in petroleum spirit and *n*-pentane. The solid is stable in air and in dry solutions of the above solvents. The mass spectrum exhibits a molecular ion (*m/z* 946) and fragments due to the protonated ligand, $[\text{C}_5\text{Ph}_5\text{H}]^+$ (*m/z* 446), and to $[\text{Fe}(\text{C}_5\text{Ph}_5)]^+$ (*m/z* 501).

The ¹H NMR spectrum of (1) shows the presence of one unique monosubstituted phenyl ring, the ¹H NMR resonances of which are significantly shielded, consistent with an $\eta^6\text{-C}_6\text{H}_5$ co-ordination.¹³ Similarly, the ¹³C NMR spectrum shows the four aromatic carbon resonances of the $\eta^6\text{-C}_6\text{H}_5$ ring at characteristically high field (δ 73–115), with the resonances of the uncomplexed cyclopentadienyl ring carbons well into the aromatic region (δ 139–145). Both ¹H and ¹³C NMR spectra of (1) indicate that in solution the $\eta^6\text{-C}_6\text{H}_5\text{-C}_5\text{Ph}_4^-$ ligand adopts a geometry with the η^6 -ring coplanar with the five carbon atoms of the attached cyclopentadienyl ring, such that the ligand has mirror symmetry. This conformation permits the $\eta^6\text{-C}_6\text{H}_5\text{-C}_5\text{Ph}_4^-$ fragment to maximise π -overlap and delocalise charge over the Ph_4C_5^- and co-ordinated $\eta^6\text{-C}_6\text{H}_5$ ring.

Precedent exists for the slipped-sandwich zwitterionic type of structure amongst ferrocene derivatives. These include the dark green $[\text{Fe}^{\text{II}+}\text{cp}(\text{fluorenyl}^-)]$ complex (cp = cyclopentadienyl),¹⁴ the red-black $[\text{Fe}^{\text{II}+}\text{cp}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2^-)]$,¹⁵ a variety of zwitterionic species derived by deprotonation of α -carbon substituents of suitable η^6 -arene- η^5 -cyclopentadienyliron cations,¹⁶ and several zwitterionic complexes such as $[\text{Fe}^{\text{II}+}\text{cp}(\eta^6\text{-C}_6\text{H}_5)\text{Ph}_3\text{B}^-]$.¹⁷ The fluorenyl complex, $[\text{Fe}^{\text{II}+}\text{cp}(\text{fluorenyl}^-)]$ has been shown to exist as a zwitterionic structure with an η^6 -arene ring, a positively charged metal centre, and the negative charge localised primarily on C(9) of the fluorenyl ligand.¹⁴

The isolation of the byproducts (2) and (3) suggests that reaction proceeds by loss of CO and oxidative addition of the unsaturated metal to bromopentaphenylcyclopentadiene to form (2). Following further loss of CO, (2) can competitively accept C₆H₆ (reaction solvent) to form (3) or one of the phenyl rings of the Ph₅C₅Br substrate eventually giving (1).§ The complex, (1), is readily protonated in protic solvents or by an aqueous acetone solution of HBF₄ in air to give a red solid, with protonation at C-1 of the C₅ ring of the η⁶-ligand. Both the ¹³C and ¹H NMR spectra of this cation, [Fe(η⁵-C₅Ph₅){(η⁶-C₆H₅)HC₅Ph₄}]⁺ (4) indicate that the molecule no longer has the symmetry of (1), but that the η⁶-(C₆H₅)C₅HPh₄ fragment is locked in a skewed conformation where all carbons of the cyclopentadienyl ring are non-equivalent.

The complex, [Fe(η⁵-C₅Ph₅){(η⁶-C₆H₅)C₅Ph₄}] (1), undergoes a reversible, one electron oxidation on the cyclic voltammetric time scale.¶ The E_{1/2} value for this oxidation varies from -65 mV (ΔE_p 108 mV) vs. the ferricenium/ferrocene couple (Fc⁺⁰) in dimethyl sulphoxide (DMSO) to -152 mV vs. Fc⁺⁰ in dichloromethane (ΔE_p 55 mV). Although the oxidation of (1) is reversible on the cyclic voltammetric time-scale, electrogenerated (1⁺) undergoes a further chemical reaction(s). Thus, the coulometric one-electron oxidation of (1) in THF produces a red solution, the cyclic voltammogram of which shows no response at the oxidation potential of (1). These data are consistent with [Fe(η⁵-C₅Ph₅){(η⁶-C₆H₅)C₅Ph₄}] undergoing a reversible oxidation on the cyclic voltammetric time scale to produce [Fe(η⁵-C₅Ph₅){(η⁶-C₆H₅)C₅Ph₄}]⁺, which on the coulometric time scale reacts further. By comparison, the cation, [Fe(η⁵-C₅Ph₅)(η⁶-C₆H₆)]⁺ (3), which also has an η⁶-arene ligand, exhibits an irreversible oxidation at E_p 840 mV vs. Fc⁺⁰ at 100 mV s⁻¹, and a quasi-reversible cyclic voltammetric reduction at E_{1/2} -1417 mV (ΔE_p 74 mV) in THF at a glassy carbon electrode.

§ The synthesis of (3) from (2) and benzene in the presence of AlCl₃ has been reported previously.²

¶ Electrochemical measurements were made at room temperature as described previously, with tetrabutylammonium tetrafluoroborate as supporting electrolyte.¹⁸ All potentials are quoted relative to the Fc⁺⁰ couple taken as 0.00 V. A platinum disc working electrode was used unless otherwise stated. Full iR compensation was employed.

We thank the Australian Research Council for financial support, and Professor Didier Astruc for valuable discussions. C. M. L. thanks the Commonwealth of Australia for a Commonwealth Postgraduate Research Award.

Received, 20th November 1989; Com. 9/04952E

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