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X-ray Crystal Structure of (η^5-Pentaphenylcyclopentadienyl){1-($\eta^{5/6}$-phenyl)-2,3,4,5-tetraphenylcyclopentadienyl}iron(II), $[Fe(\eta^5\text{-}C_5Ph_5)\{(\eta^{5/6}\text{-}C_6H_5)C_5Ph_4\}]$, a Linkage Isomer of Decaphenylferrocene

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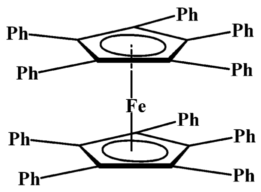
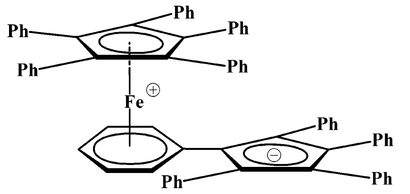
Very dark blue prismatic crystals of $[Fe(\eta^5\text{-}C_5Ph_5)\{(\eta^{5/6}\text{-}C_6H_5)(C_5Ph_4)\}]$, the linkage isomer of decaphenylferrocene, were grown from (3:1 v/v) hexane/ethyl acetate and characterized by single-crystal X-ray diffraction (space group $P2_1/n$, R1(F) 0.0404). The iron atom is coordinated to two C_5Ph_5 ligands: one with an η^5-C_5-configuration and the other with a coordinated arene configuration. The phenyl groups of the (η^5-C_5Ph_5) ligand are oriented in a "paddle-wheel" arrangement about the C_5 ring, with which four of them make an average angle of ~53°, the other, an angle of ~42°. The coordinated C_6H_5 ring of the other ligand is inclined at only ~5° to the uncoordinated C_5 ring, with which three of the other four phenyl rings make an average angle of ~64°, and the other (opposite the coordinated arene ring), an angle of 38°.

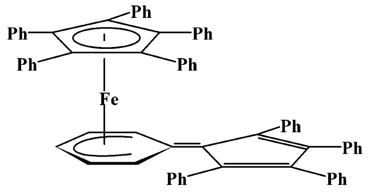
Despite the extensive range of substituted ferrocene derivatives,[1] and isolated claims of its synthesis,[2] decaphenylferrocene, $[Fe(C_5Ph_5)_2]$, remained elusive for some 30 years after early attempts at its preparation[3] until its authenticated synthesis in 1994.[4,5] Several authors had suggested that interligand steric pressures were too great to permit its isolation.[3,6,7] It is now clear that the compound of molecular formula $[Fe(C_5Ph_5)_2]$ exists in two isomeric forms: an insoluble pink solid with the conventional metallocene structure (**1**) and a soluble deep blue solid which was assigned the structure shown here as **2a**, a linkage isomer of decaphenylferrocene, on the basis of its ^{1}H and ^{13}C NMR spectra.[4,5,8,9] Heating the linkage isomer (**2**) as a solid or in xylene solution converts it to decaphenylferrocene (**1**).[9] The two isomers can also be interconverted by a series of redox and protonation/deprotonation steps.[10] It had been suggested that the linkage isomer (**2**) formed in preference to decaphenylferrocene (**1**), because the interligand distance expected



(**1**)



(**2a**)



(**2b**)

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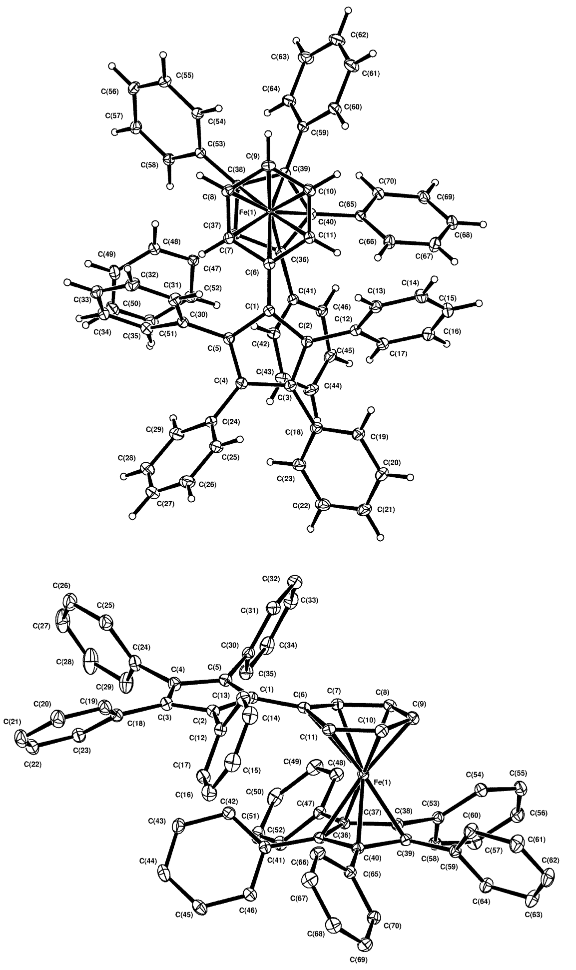

Figure 1. ORTEP[11a] illustrations (thermal ellipsoids at the 20% level) of the structure of a molecule of **2** [Fe(η^5-C_5Ph_5){$\eta^{5/6}$-C_6H_5)C_5Ph_4}].

in a substituted ferrocene (ca. 3.3 Å) was too small to accommodate the interligand steric interactions. Although decaphenylferrocene has been subsequently isolated and structurally characterized,[4] the structural data are not of sufficient precision to allow useful determinations of interatomic distances and angles.

We report here the crystal structure of the linkage isomer (**2**), which confirms our earlier assignment based on spectroscopic data.

Very dark blue prismatic crystals of **2** were grown by slow evaporation of a hexane (75% v/v)/ethyl acetate (25%) solution of **2**, obtained by elution from a silica column.[32] The crystals rapidly lost solvate molecules on removal from the mother liquor, and accordingly, X-ray diffraction data were collected at −100 °C.[33]

The unit cell contains two independent, nearly identical, linkage isomer molecules, **2*** and **2****. The structure of molecule **2*** is illustrated in Figure 1. As predicted from spectroscopic data,[8] the iron atom is coordinated in an η^5 fashion to the C_5 ring of one C_5Ph_5 ligand and to one of the phenyl rings of the other ligand. There are some noteworthy intermolecular contacts between the differently coordinated ligands. There is a canted T-type π stacking interaction between a phenyl residue of complex **2**** and the noncoordinated cyclopentadienyl residue of complex **2***, and there is a similar interaction between a phenyl residue of complex **2**** and the coordinated phenyl residue of complex **2***. The dihedral angles between the interacting planes are 60.1(1)° and −54.4(1)°, respectively. The phenyl C(133) of complex **2**** is 3.518(2) Å above the least squares plane of the noncoordinated cyclopentadienyl residue of complex **2***, and the phenyl C(127) of complex **2**** is 3.443(3) Å above the coordinated phenyl residue of complex **2***. The C(30)−C(35) phenyl residue of complex **2*** forms a dihedral angle of 70.0(1)° with the coordinated cyclopentadienyl residue of complex **2****, and C(32) is 3.664(2) Å from the coordinated cyclopentadienyl plane.

The rings coordinated to the iron atom are almost parallel: they are oriented at approximately 1° to each other in both molecules. The orientations and dimensions of the η^5-C_5 coordinated C_5Ph_5 ligand are typical of this ligand in many transition metal complexes. The C_5 ring is planar, with C−C distances averaging 1.440 Å in both molecules.

The phenyl rings are planar, with average C−C distances of 1.390 (in molecule **2***) and 1.388 Å (in molecule **2****) and are oriented in a "paddle wheel" arrangement at an average of 51.07° (**2***) and 49.32° (**2****) to the C_5 ring. The iron atom is 1.6933(10) (**2***) and 1.6988(10) Å (**2****) from the plane of the C_5 ring, similar to the Fe−C_5Ar_5 centroid distances in the Fe(II) derivatives, [Fe(η^5-C_5Ph_5)(η^5-C_5H_5)] (1.652 Å), [Fe(η^5-C_5Ph_5)(η^6-$C_6H_5CH_3$)]$^+$ (1.70 Å), [Fe(η^5-C_5Ph_5)(CO)$_2$Br] (1.74 Å), and [Fe{η^5-C_5(p-tol)$_5$}(η^5-C_5H_5)] (1.645 Å),[12−15] and, as expected, shorter than the corresponding distances in the Fe(III) derivatives [Fe(η^5-C_5Ph_5)$_2$]X (1.81 Å, X = Br_3^-; 1.79 Å, X = BF_4^-).[4,16] The Fe−C(C_5 ring) distances are typical of those in iron(II) cyclopentadienyl derivatives. The arene coordinated C_5Ph_5 ligand is, as far as we are aware, unique in structurally characterized complexes of this type. Five of the coordinated phenyl ring carbon atoms are coplanar. The average Fe−C distance involving these five carbon atoms is 2.09 Å, which is similar to the corresponding Fe−C distances in many iron(II) η^6-arene and pseudocyclopentadienyl complexes. The iron atom is 1.5715 (10) (**2***) and 1.5792 (10) Å (**2****) from the plane of the five coplanar carbon atoms of the coordinated phenyl ring, a distance similar to the analogous distance in the [Fe(η^5-C_5Ph_5)(η^6-$C_6H_5CH_3$)]$^+$ cation.[13] The sixth carbon atom, the *ipso* carbon atom, is displaced from the iron atom and is 0.2480(22) (**2***) and 0.2111(23) Å (**2****) out of the plane

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defined by the other five carbon atoms. A similar displacement of an *ipso* carbon atom is observed in the $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C}_5\mathrm{Ph}_5)(\eta^6\text{-}\mathrm{C}_6\mathrm{H}_5\mathrm{CH}_3)]^+$ cation. The Fe−C(*ipso*) distance is 2.4045(14) (**2***) and 2.3792(16) Å (**2****), considerably longer than the average of the other five Fe−(arene-C) distances (2.094 (**2***) and 2.101 Å (**2****)) and longer than the Fe−C(toluene *ipso*-C) distance of 2.184 Å in the $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C}_5\mathrm{Ph}_5)(\eta^6\text{-}\mathrm{C}_6\mathrm{H}_5\mathrm{CH}_3)]^+$ cation. This distortion is significant and could arise from intramolecular interligand close contacts between the noncoordinated cyclopentadienyl residue and a phenyl group attached to the coordinated cyclopentadienyl moiety. The phenyl ring is directly over and inclined with respect to the noncoordinated cyclopentadienyl residue, with the least squares planes of the two rings forming a dihedral angle of 48.3(1)° in complex **2*** and 36.8(1)° in complex **2****. In complex **2***, the phenyl atoms C(42) and C(43) are, respectively, 3.204(2) and 3.500(2) Å from the cyclopentadienyl C(1)−C(5) plane, and in complex **2****, C(112) and C(113) are 3.194(2) and 3.441(2) Å from the cyclopentadienyl C(71)−C(75) plane.

An alternative description of the structure is to consider the coordinated arene ring to be η^5-coordinated, as in pseudoferrocenes and η^5-cyclohexadienyl complexes of iron. The compound exhibits some distortion consistent with this description. Thus, the Fe-*ipso*-C distance in the coordinated phenyl ring (2.40 Å) is significantly greater than the average Fe−C distance over the other five carbon atoms of this phenyl ring (2.09 Å). However, this distance is also considerably shorter than the Fe−(sp^3)C distances in a range of iron(II) cyclohexadienyl and pseudoferrocene complexes (∼2.66 Å)[17−30] (although it is close to that in (μ_2,η^6-biphenyl)bis(η^5-pentamethylcyclopentadienyl)diiron (2.47 Å)[31]).[34] Accordingly, the description of the coordinated arene ring as η^5-coordinated (**2b**) may also be appropriate. In this case, the zwitterionic structure (**2a**) would represent one of several (differently weighted) resonance structures.

Consistent with this description, some localization of bonds (as a diene) is apparent in the uncoordinated C_5 rings. This interpretation of the uncoordinated C_5 rings as dienes could have the negative charge also localized on the uncoordinated C_5 rings, consistent with our earlier suggestion of a zwitterionic structure of the molecule, or, alternatively, on the coordinated phenyl ring, producing an η^5-cyclohexadienylidene ligand. The coordinated phenyl ring is approximately 5° from coplanarity with the uncoordinated C_5 ring in both molecules: an orientation not previously observed in the structures of pentaphenylcyclopentadienyl complexes. The remaining phenyl rings of this ligand have regular dimensions (average C−C 1.390 (**2***) and 1.391 Å (**2****)) and are oriented with respect to the C_5 ring at somewhat smaller (38.1° (**2***) and 37.8° (**2****)) and somewhat larger (62.2°, 63.5°, and 65.4° (**2***) and 65.9°, 68.4°, and 70.6° (**2****)) angles than observed in other structures.

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(32) The unit cell formula corresponds to $[\mathrm{C}_{70}\mathrm{H}_{50}\mathrm{Fe}]\cdot\mathrm{C}_2\mathrm{H}_4\mathrm{O}$. The residual $\mathrm{C}_2\mathrm{H}_4\mathrm{O}$ is likely to arise from the ethyl acetate eluant.

(33) X-ray diffraction data were collected with a Bruker SMART 1000 CCD diffractometer equipped with an Oxford Cryosystems Cryostream. Structure solved with SIR97[11b] and refined with SHELXL97.[11c] Crystal data for $\mathrm{C}_{72}\mathrm{H}_{54}\mathrm{FeO}$: $M = 991.00$, monoclinic, space group $P2_1/n$ (No. 14), $a = 20.095(1)$ Å, $b = 17.675(1)$ Å, $c = 30.584(2)$ Å, $\beta = 104.287(1)°$, $V = 10526.8(11)$ Å^3, $D_c = 1.251$ g cm^{-3}, $Z = 8$, crystal size 0.412 × 0.286 × 0.201 mm^3, color deep blue, habit irregular prism, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.333 mm^{-1}, $T(\mathrm{SADABS}^{11d})_{\mathrm{min,max}} = 0.856, 1.000$, $2\theta_{\max} = 56.06$, *hkl* range −26 to 25, −23 to 23, −40 to 40, $N = 111759$, $N_{\mathrm{ind}} = 25004$ ($R_{\mathrm{merge}} = 0.0266$), $N_{\mathrm{obsd}} = 20169$ ($I > 2\sigma(I)$), $N_{\mathrm{var}} = 1333$, residuals *R1(F) = 0.0404, wR2(F^2) = 0.1186, GOF(all) = 0.967, $\Delta\rho_{\mathrm{min,max}} = -0.369, 0.458$ e^{-1} Å^{-3}. (*$\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; $\mathrm{wR2} = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 6.7404P]$ where $P = (F_o^2 + 2F_c^2)/3$). Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallography Data Centre, deposition number CCDC 150277. We have also obtained crystals of a C-centered monoclinic phase ($C2/c$ $a = 31.383(5)$ Å, $b = 22.903(3)$ Å, $c = 23.321(4)$ Å, $\beta = 116.86\ (1)°$, $V = 14954(4)$ Å^3) with one complex molecule in the asymmetric unit. The current structure solution for this sample is not of publication quality. ^{1}H NMR (400 MHz, d_8-thf): 5.05−5.06, 5.23−5.26 (2 × m, 2 × 2H, η^6-C_6H_5); 5.76 (t, 1H, η^6-C_6H_5); 6.44−6.46, 6.71−6.81, 6.99−7.18 (3 × m, 45H, Ar-*H*). IR (KBr) $\nu_{\max}$ (cm^{-1}): 3053w, 3023w, 2981vw, 1743w, 1734vw, 1596w, 1573vw, 1533s, 1507s, 1496m, 1476m, 1446m, 1410w, 1388m, 1350s, 1242m, 1168m, 1132m, 1074w, 1049w, 1028w, 932m, 785w, 777w, 744m, 717m, 708s, 700vs, 670w, 633m, 614w, 568m, 557m, 552m, 544m, 457w.

(34) Note that both this and the present compounds are intensely blue, in contrast to the red/orange colors of the $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C}_5\mathrm{Ph}_5)(\eta^6\text{-arene})]^+$ cations and the pale yellows of their cyclopentadienyl analogues.