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# Decacyclene as Complexation Manifold: Synthesis, Structure and Properties of Its $Fe_2$ and $Fe_4$ Slipped Triple-Decker Complexes

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*Dedicated to Professor Dr. mult. Günther Wilke on the occasion of his 80th birthday*

**Abstract:** Reaction of [($\eta^5$-$Me_4EtC_5$)$Fe^{II}$Cl(tmeda)] (tmeda = *N,N,N′N′*-tetramethylethylenediamine) with a polyanion solution of decacyclene (**1**) results in the formation of the triple-deckers [{($\eta^5$-$Me_4EtC_5$)Fe}$_2$-$\mu_2$-($\eta^6$:$\eta^6$-decacyclene)] (**3**) and [{($\eta^5$-$Me_4EtC_5$)Fe}$_4$-$\mu_4$-($\eta^6$:$\eta^6$:$\eta^6$:$\eta^6$-decacyclene)] (**4**). Metal complexation in **3** and **4** occurs on opposite faces of the π perimeter in an alternating mode. The decacyclene ring adopts a gently twisted molecular propeller geometry with twofold crystallographic symmetry ($C_2$). Complex **4** crystallizes in the chiral space group $C222_1$; the investigated crystal only contains decacyclene rings with *M* chirality. The handedness can be assigned unambiguously to the presence of the iron atoms. Cyclovoltammetric studies revealed quasireversible behavior of the redox events and a strong interaction of the Fe atoms in **3** and **4**, exemplified by potential differences $\Delta E$ of 660 and 770(780) mV between the first and the second individual oxidation processes. This corresponds to a high degree of metal–metal interaction for **3** and **4**. The sucesssful syntheses of **3** and **4** together with earlier results from our laboratory proves that all five- and six-membered π subunit sets of **1** are prone to metal complexation. A clear site preference in **1** towards the complexation of [$Cp^R$]iron, -cobalt, and -nickel fragments exists.

**Keywords:** arene ligands · coordination modes · electrochemistry · iron · sandwich complexes

## Introduction

Since the synthesis of the archetype of a triple-decker complex by Werner and Salzer, a variety of triple-decker,[1–3] tetra-decker,[4] penta-decker,[5] hexa-decker,[5] and large extended multidecker[6] π complexes have been synthesized. A variety of unusual bonding modes of π aromatic homo- and heteroaromatic middle decks to main group metals have been realized in these compounds so far. Introducing polycondensed aromatic hydrocarbons (PAHs) as bridging π perimeters opens up the possibility of multiple spatial arrangements and different coordination modes for transition metal/ligand fragments with these ligands. Recent examples in the area of transition-metal chemistry stem from the complexation of corannulene[7] and hemibuckminsterfullerene.[8] Stacked π complexes with redox-active metal centers in close proximity are model compounds for studying electron transfer across delocalized π perimeters. They may also serve as model compounds for studying haptotropic shifts of metal/ligand fragments over polycyclic surfaces.[9]

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## Results and Discussion

Herein we report on the synthesis, molecular structure, electrochemical characterization, and Mössbauer spectroscopy of a new type of triple-decker containing four iron atoms which decorate opposite faces of the PAH decacyclene $C_{36}H_{18}$ (**1**) in an alternate fashion. Decacyclene forms the middle deck of the triple-decker. It was chosen as bridging π-perimeter since it has three equivalent naphthalene units available for complexation to transition metals. Recently, we could show that the central six- and the neighboring five-membered rings of a decacyclene unit are able to coordinate to {(Cp$^R$)Ni} or {(Cp$^R$)Co} fragments in distinct coordination modes (Figure 1).[10,11] We have now explored the coordination properties of **1** towards substituted cyclopentadienyliron fragments and report here $Fe_2$ and $Fe_4$ slipped triple-decker complexes in which the naphthalene fragments forming the periphery of **1** are metal-coordinated. The results presented herein, together with our earlier studies on complexation of **1**,[10,11] prove that all π ring subsystems of the decacylene ligand are prone to complexation of metal/ligand entities. The PAH **1** is a rare case of a ligand which allows complexation of one to four metal atoms in up to three different positions with varying hapticity.

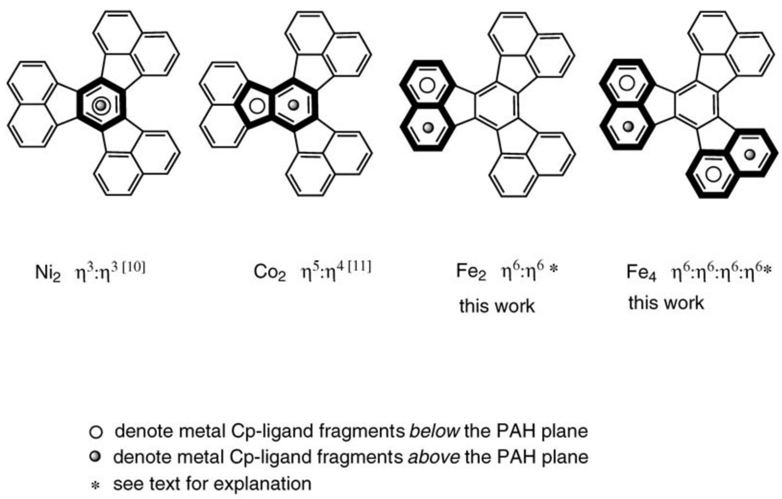
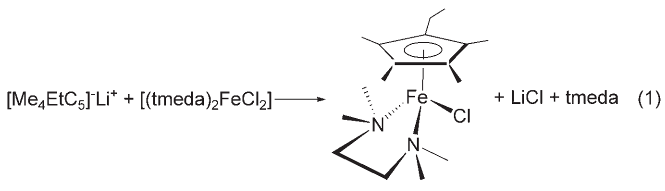


Figure 1. Experimentally realized coordination sites of decacyclene to iron, cobalt, and nickel.

As {($\eta^5$-Cp$^R$)Fe}-transfer agent we chose [($\eta^5$-$Me_4EtC_5$)Fe$^{II}$Cl(tmeda)][12] **2** [Eq. (1), tmeda = *N,N,N′N′*-tetramethyethylenediamine], which belongs to the rare class of half-sandwich complexes bearing no CO or phosphane ligands.[12] The structure of **2** was proven by X-ray crystallography (Figure 2),[13–15] which revealed a three-legged piano-stool geometry in which the tmeda ligand occupies two coordination sites (4e donor) resulting in a distorted tetrahedral coordination geometry around the Fe$^{II}$ center. Characteristic bond lengths and angles are given in the legend to Figure 2.



**2**

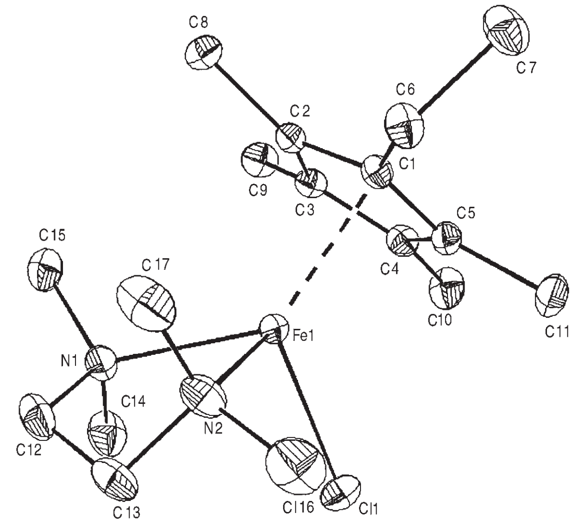
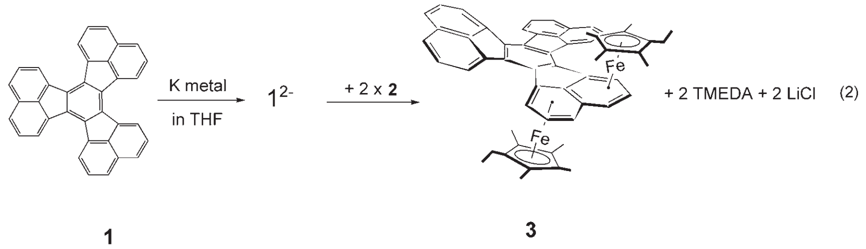


Figure 2. Molecular structure of **2** as determined by single-crystal X-ray analysis. Anisotropic displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1−N1 2.312(2), Fe1−N2 2.236(2), Fe1−Cl1 2.340(1), Fe1−C1–5 2.312–2.430(2); N1-Fe1-N2 78.57(6), N1-Fe1-Cl1 96.80(4), N2-Fe1-Cl1 94.68(5), Fe1-N1-C12 108.10(12), Fe1-N2-C13 103.01(12), N1-C12-C13 110.97(17), N2-C13-C12 110.76(18); Fe1−Cp$_{Centroid}$ 2.045(2), Cl1-Fe1-Cp$_{Centroid}$ 119.20, N1-Fe1-Cp$_{Centroid}$ 131.30(6), N2-Fe2-Cp$_{Centroid}$ 125.20(6).

**Synthesis of 3**: The reaction of **2** with $\mathbf{1}^{2-}$, prepared in situ from **1** and potassium metal in THF in a 1:2 molar ratio, yielded the dinuclear complex [{($\eta^5$-$Me_4EtC_5$)Fe}$_2$-$\mu_2$-(decacyclene)] (**3**) as main product, to which we assigned a triple-decker structure with a bridging decacyclene unit [Eq. (2)].

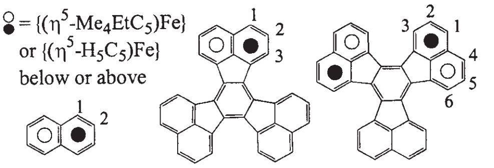
The NMR data of **3** are in agreement with twofold complexation of a single naphthalene unit of decacyclene with two {($\eta^5$-$Me_4EtC_5$)Fe} fragments. The individual $^1$H NMR signals of dinuclear **3** ($C_2$ symmetry) can be assigned to three AMX spin systems corresponding to the protons of three naphthalene units and giving rise to nine signal multiplets. The $^1$H NMR resonances of the protons of one naph-



thalene unit ($\delta = 2.12$, 5.56, 7.82 ppm) are significantly shifted to high field due to twofold metal coordination. Their coordination shifts are well in accord with the protons of the dinuclear naphthalene iron complexes **7** and **8** reported by Jonas et al.[16–18] as well as the mononuclear cobalt complex [{($\eta^5$-Me$_4$EtC$_5$)Co}($\eta^4$-decacyclene)] reported by us.[11] The $\eta^4$-complexed diene part of **3** shows the typical, significantly larger high-field chemical shift of the *ortho* proton at C1 compared to the protons at C2 and C3 of the naphthalene diene fragments (see Table 1 for shifts and numbering). A comparable gradation of the chemical shifts is found for protons H1 and H2 of the diene fragment of the iron naphthalene complexes **7** and **8** as well as for a variety of other iron-coordinated dienes (see Table 1).[19–21]

Table 1. $^1$H NMR data for the metal-complexed naphthalene parts of complexes **3** and **4** together with $^1$H NMR data of dinuclear complexes **7** and **8** and free naphthalene and decacyclene (**1**) for comparison.

● = {($\eta^5$-Me$_4$EtC$_5$)Fe} or {($\eta^5$-H$_5$C$_5$)Fe} below or above



| | H$_{Pos}$ | $\delta$ [ppm] | $\Delta\delta$[a] [ppm] |
|---|---|---|---|
| **3** | 1 | 2.12 (d, 2H, $^3J = 5.4$ Hz) | −5.58 |
| | 2 | 5.56 (t, 2H, $^3J = 5.4$ Hz) | −1.96 |
| | 3 | 7.82 (d, 2H, $^3J = 5.4$ Hz) | −0.91 |
| **4** | 1 | 2.19 (d, 2H, $^3J = 5.3$ Hz) | −5.51 |
| | 2 | 5.67 (t, 2H, $^3J = 5.3$ Hz) | −1.85 |
| | 3 | 7.96 (d, 2H, $^3J = 5.3$ Hz) | −0.77 |
| | 4 | 2.53 (d, 2H, $^3J = 5.4$ Hz) | −5.17 |
| | 5 | 5.59 (t, 2H, $^3J = 5.4$ Hz) | −1.93 |
| | 6 | 7.77 (d, 2H, $^3J = 5.4$ Hz) | −0.96 |
| **7** | 1 | 1.57 (m) | −6.09 |
| | 2 | 5.68 (m) | −1.62 |
| **8** | 1 | 2.06 (m) | −5.60 |
| | 2 | 6.55 (m) | −0.75 |
| **1** | 1 | 7.70 (d, 6H, $^3J = 7.6$ Hz) | |
| | 2 | 7.52 (t, 6H, $^3J = 7.6$ Hz) | |
| | 3 | 8.73 (d, 6H, $^3J = 7.6$ Hz) | |
| naphthalene | 1 | 7.66 (m) | |
| | 2 | 7.30 (m) | |

[a] $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$.

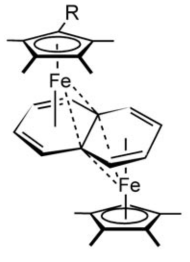
Metal coordination comparable to that in **3** in which opposite sides of the decacyclene ligand are complexed by two metal/ligand fragments was found for Ni$_2$ decacylene complex **5**[10] and Co$_2$ decacylene complex **6**.[11]

◎ = {($\eta^5$-Me$_4$EtC$_5$)Ni} above and below

**5**[10]

{($\eta^5$-Me$_5$C$_5$)Co}
● = above
○ = below

**6**[11]



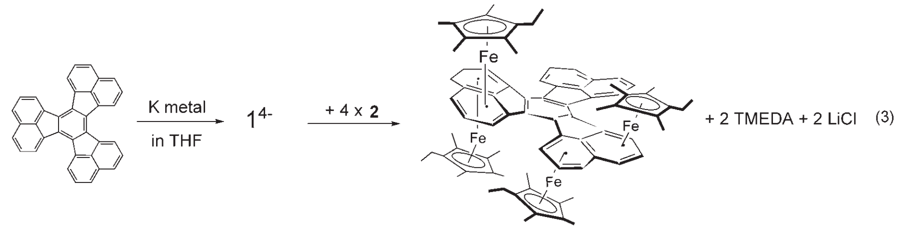
**7**[18] (R = Me)
**8**[17] (R = H)

Interestingly, crystal batches obtained from reaction (2) gave low yields of crystals of the larger, tetranuclear aggregate **4** in addition to the dinuclear main product **3**. One may assume that tetranuclear **4** is formed in a stepwise manner from **3** followed by a subsequent further reduction/complexation sequence. An alternative route may first involve reduction of **1** by four electrons, after which four consecutive complexation steps yield **4**. However, the second route has no precedent in transition metal hydrocarbon chemistry so far. Nevertheless, reports on the formation and characterization of multiple anions in the area of hydrocarbon chemistry are known. To the best of our knowledge, the rubrene tetraanion,[22] and the tetraanion of decacyclene,[23] obtained by alkali metal reduction in dme, are the only PAH tetraanions which have been unambiguously characterized by single-crystal structure analysis. In the case of decacyclene it is even known that multiple reversible reductions up to $\mathbf{1}^{6-}$ can be carried out by electrochemical means.[24] Moreover, there are reports by Scott, Baumgarten et al. in which the tetraanion of the PAH corannulene has been studied and fully characterized in solution.[25,26]

These reports encouraged us to study the synthesis of **4** by a direct reduction route.

**Selective synthesis of 4**: Reaction of **2** with a brown THF solution of $\mathbf{1}^{4-}$, prepared from **1** and four equivalents of potassium at room temperature, gave dark crystals of **4** after workup [Eq. (3)]. In **4**, four {($\eta^5$-Me$_4$EtC$_5$)Fe} fragments are coordinated to the $\pi$ perimeter of **1**.

The $^1$H NMR spectrum of **4** exhibits three distinct sets of resonances for the protons of the complexed decacyclene ligand. Two of these are shifted to higher field and one to



**1**

**4**

lower field compared to free decacyclene (**1**). This is in accord with a twofold {($\eta^5$-$Me_4EtC_5$)Fe} coordination on two of the three naphthalene subsets of the decacylene $\pi$ perimeter. The two high-field sets of naphthalene signals have twice the intensity as the low-field set. Table 1 compares $^1H$ NMR resonances and coordination shifts of **4** to those of the related complexes **3**, **7**,[16,17] and **8**,[18] free ligand **1**, and free naphthalene. The unambiguous assignment of the separate multiplets in **3** and **4** is based on $^1H$,$^{13}C$ double-resonance experiments. The two high-field-shifted proton multiplets show a strong splitting characteristic of the coordinated diene positions of the naphthalene subunits, as observed for **3**. Signals forH1 and H4 are shifted about 5–6 ppm to higher field, while those for H2, H3 and H5, H6 are shifted only by 1–2 ppm. The $^{13}C$ NMR spectrum yielded similar results. Here positions C1 and C4 are shifted to high field by about 20 ppm compared to C2, C3, C5, and C6, in full agreement with other $\eta^4$-naphthalene iron complexes.[19,20] Their signals are found in the same characteristic shift region for complexed versus uncomplexed carbon positions. Consistent with the twofold complexation of two of the three naphthalene subunits of **4** is also the agreement with data reported for the closely related [($\eta^5$-$Cp^RFe)_2(\mu_2$-naphthalene)] (R = $H_5$, $Me_5$) complexes **7**[16,17] and **8**[18] (Table 1).

**Attempts to produce decacyclene complexes with nuclearity greater than 4**: Treating a concentrated THF solution of tetranuclear **4** in an NMR tube with a solid potassium mirror (metal excess) at ambient temperature results in a color change of the solution from green to brown after 1 h and disappearance of the remaining proton signals of the decacyclene ligand, while at the same time the $Me_4EtC_5$ proton signals became broadened. No precipitation occurred and the NMR spectrum was still unchanged after several hours. This finding indeed indicates the possibility of a further electron transfer to the decacylide $\pi$ perimeter in **4** and prompted us to attempt the synthesis of the hexanuclear complex [{($Me_4EtC_5$)Fe}$_6$($\mu_6$-$\eta^6$:$\eta^6\eta^6$:$\eta^6\eta^6$:$\eta^6$-decacyclene)]. However, $^1H$ NMR spectroscopy on the material isolated from such a preparation showed a mixture of isomers which could not be assigned individually. Nevertheless, the ratio of the proton signals of the {($\eta^5$-$Me_4EtC_5$)Fe} fragments and the coordinated naphthalene units of the decacyclene ligand gives evidence of a {($\eta^5$-$Me_4EtC_5$)Fe}/decacylene ratio of 6/1, that is, complete complexation of the naphthalene subunits of **1**. So far we have not been able to isolate pure hexanuclear [{($\eta^5$-$Me_4EtC_5$)Fe}$_6$($\mu_6$-$\eta^6$:$\eta^6\eta^6$:$\eta^6\eta^6$:$\eta^6$-decacyclene)].

**Molecular structure of 4**: Single-crystal structural analysis of **4** confirmed the proposed molecular structure with four {($\eta^5$-$Me_4EtC_5$)Fe} ligand fragments bound to two of the three peripheral naphthalene units in an antarafacial geometry (Figure 3). The molecule has twofold crystallographic symmetry with the $C_2$ axis positioned along the bond C1a–C1b, which bisects the uncoordinated naphthalene unit of the decacyclene ring. The decacyclene ring adopts a gently twisted molecular propeller geometry, which has been found for free decacyclene (**1**)[27] and an $Ni_2$ complex.[10]

Since **4** crystallizes in the chiral space group $C222_1$ the investigated crystal only contains decacyclene rings with M chirality. In contrast to the crystal structure of free decacyclene, which crystallizes in the same space group, the handedness can be assigned unambiguously as due to the presence of the iron atoms. However, the CD spectrum of a dissolved single crystal shows no optical activity. Unlike the crystal structure of free decacyclene there is no indication for twinning, which would be responsible for the optical inactivity, but rapid racemization of **4** in solution is assumed. Similarly, the absence of any diastereomers, formally obtainable by interchanging the antarafacial positions of the iron atoms, follows directly from the racemization.

Both iron atoms display, at first glance, similar coordination geometries. The distances between the ring carbon atoms of the $Me_4EtC_5$ ligand and the iron atoms range between 2.051(5) and 2.097(5) Å, which is a significant deviation from equidistant positions. For Fe1 these distances can be divided into one group of three distances averaging 2.056(5) Å and two longer distances averaging 2.088(13) Å. For Fe2 there are three longer Fe–C distances with an average of 2.084(4) Å and two shorter distances of 2.063(5) and 2.069(4) Å. The distances between the iron atoms and the decacyclene ring atoms cover an even larger range. As expected, the longest distances are found between the iron atoms and the bridging carbon atoms C6a and C6b. Approximately 0.2 Å shorter distances are observed between the metal atoms and C4a and C9a, which link the naphthalene ring to the central benzene ring. Even shorter distances, within the range of distances between the iron atoms and the carbon atoms of the cyclopentadienyl rings, are found to the unsubstituted carbon atoms on the perimeter of the naphthalene rings. A closer comparison of the distances involving pairwise chemically equivalent atoms reveals that all distances formed by Fe1 and the unsubstituted carbon atoms are systematically shorter, while the distances to the bridging atoms are significantly longer than those of Fe2. The biggest absolute and relative differences are found be-

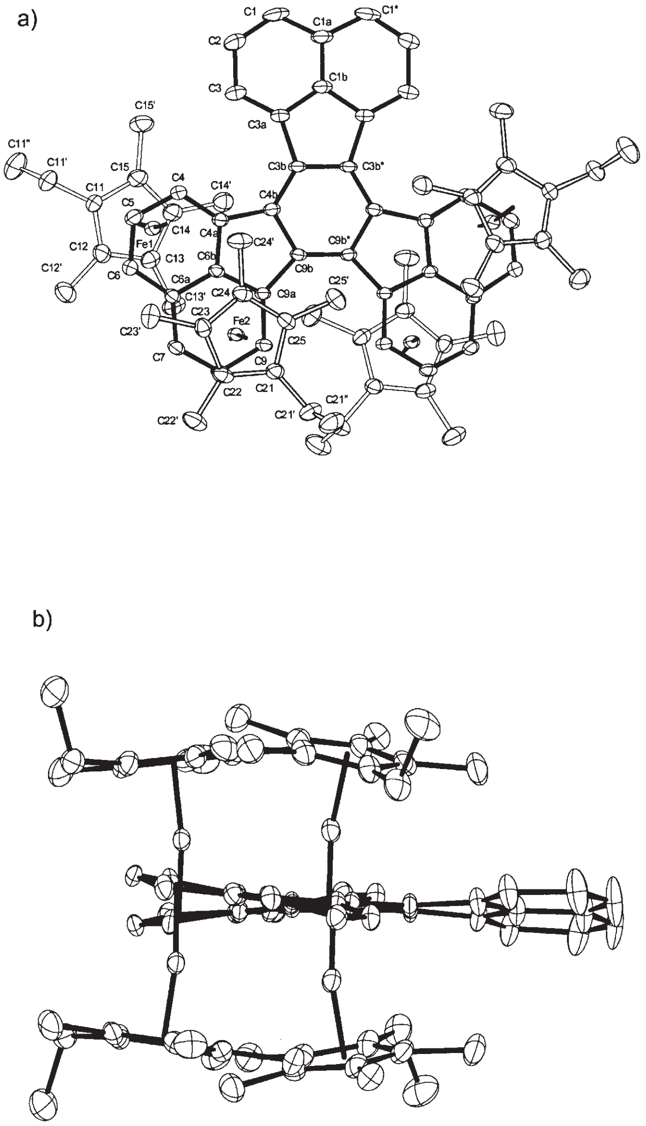


Figure 3. Molecular structure of **4** as determined by single-crystal X-ray analysis. Anisotropic displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1−C4a 2.200(4), Fe1−C4 2.036(4), Fe1−C5 2.016(6), Fe1−C6 2.097(5), Fe1−C6a 2.445(4), Fe1−C6b 2.435(4), Fe1−C11 2.060(4), Fe2−C6b 2.374(4), Fe2−C6a 2.395(4), Fe2−C7 2.112(4), Fe2−C8 2.035(4), Fe2−C9 2.053(5), Fe2−C9a 2.176(4), Fe2−C21 2.088(4), C4a−C4 1.439(6), C4−C5 1.425(6), C5−C6 1.435(5), C6−C6a 1.420(6), C6a−C6b 1.413(6), C4a−C6b 1.434(5); C4a-C4-C5 119.0(3), C4-C5-C6 119.6(4), C5-C6-C6a 121.1(4), C6-C6a-C6b 116.4(3), C6a-C6b-C4a 123.6(4), C6b-C4a-C4 117.8(4), C6-C6a-C7 128.4(4), C4a-C6b-C9a 112.2(3), C4a-C4b-C9b 108.7(3). a) Top view of **4** with atom-numbering scheme. b) Side view of the molecular structure of **4** showing the propeller-like ligand twist and the arrangement of the $\{(\eta^5\text{-}Me_4EtC_5)Fe\}$ fragments in a double triple-decker fashion.

tween the metal atoms and C6a/C6b, which amount to 0.050(4) and 0.061(4) Å. Together with the distance pattern found for the two cyclopentadienyl rings, there is an overall balance of shorter and longer distances for either iron atom. This observation is also reflected by the sum of all Fe1−C distances of 23.573(5) Å, while the equivalent sum for Fe2 is 23.529(4) Å.

Finally, closer inspection of the decacyclene moiety and comparison with the geometry of the decacyclene moieties in the Ni and Co complexes,[11] as well as in the tetrakis(alkali metal) salts[23] and free decacyclene,[27] seems to be warranted. The two independent dihedral angles of **4** formed between the naphthalene units and the essentially planar central benzene ring are 8.87° for the Fe-complexed naphthalene unit and 6.53° for the uncomplexed part. The corresponding angles in free decacyclene are 9.30 and 7.75°, while in the Ni complex these values are 13.92, 14.33, and 4.71°. In the case of the decacyclene tetraanions, only the potassium salt has a reported crystal structure. The decacyclene moiety also exhibits two twisted napthalene units with dihedral angles of 9.40 and 13.47°, while the third naphthalene ring is twisted by only 3.80°. 2,8,14-Trichlorodecacyclene[28] is even more twisted towards a propeller-shaped geometry. The single, symmetry-independent dihedral angle is 18.52°.[1] While this propeller shape seems to be preserved for decacyclenes in general and has been explained by repulsion between the hydrogen atoms or substituents in positions 3–4, 9–10, and 15–16, a different geometry was found for 1,6,7,12,13,18-hexa-*tert*-butyldecacyclene,[29] which can be described as bowl-shaped. A similar shape was found for the Co complex.[11] Since the central benzene ring adopts a boat conformation, one naphthalene ring is deflected out of the molecular plane, while the other two show a butterflylike arrangement and thus minimize repulsion between the hydrogen atoms in the fjord regions.

The naphthalene units in **4** are themselves slightly distorted from planarity, with rms derivatives of 0.21 and 0.08 Å for the complexed and the uncomplexed rings, respectively. Compared to free decacyclene, which exhibits significant bond-length alternation between the *endo* and *exo* bonds of the central benzene ring, this effect is less pronounced in **4**.

According to the structural parameters all carbons atoms of the two complexed naphthalene fragments are coordinated to iron. The finding that the Fe−C distances to the naphthalene bridgehead carbons atoms C6a and C6b are significantly longer than those to C4, C5, C6, and C4a seems to indicate unsymmetrical $\eta^6$ coordination, which can be described as an $\eta^4+\eta^2$ coordination mode of the naphthalene fragments of **1** to each of the Fe centers. Each naphthalene subunit contributes as a 10e-donating ligand fragment to the overall valence electron count. This results in an 18e configuration of each iron center and 36 valence electrons for each "isolated" $Fe_2$ triple-decker unit in **4**.

Due to the large distance between the iron centers in **4** (4.611 Å) their direct electronic interaction is unlikely. However, mediation of such a interaction by the bridging polycondensed decacyclene ligand seems possible and can indeed be proven experimentally for **3** and **4** by cyclic voltammetry (see below).

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[1] The molecular least-squares planes of the naphthalene units were defined to encompass all ten atoms formally belonging to this unit. The same approach holds for the central benzene ring.

**Electrochemistry of 3 and 4**: The cyclic voltammograms (CVs) of **3** and **4** recorded at ambient temperature in THF, are shown in Figures 4 and 5. The corresponding data are given in Tables 2 and 3.

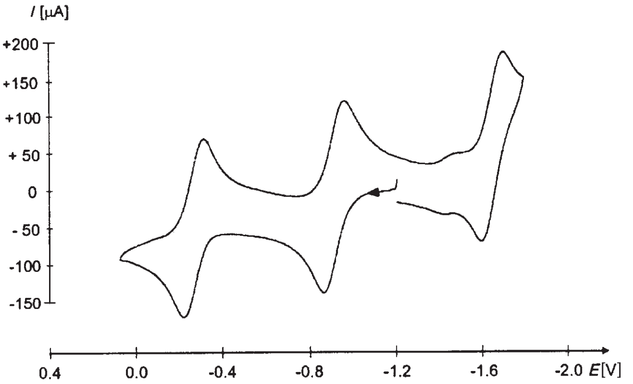


Figure 4. Cyclic voltammogram of **3** in THF under ambient conditions.

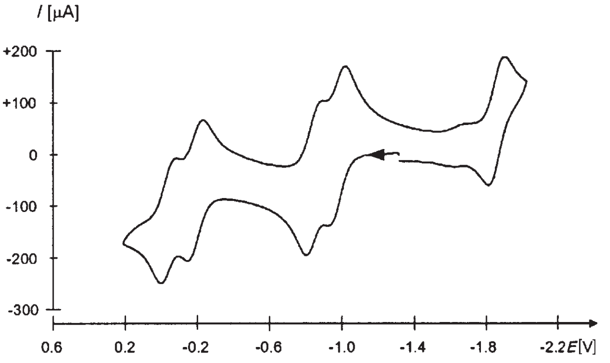


Figure 5. Cyclic voltammogram of **4** under ambient conditions.

Table 2. Cyclovoltammetric data for **3**.

| $E_{1/2}$ [V] vs SCE[a] | $E_{1/2}$ [V] vs Fc/Fc$^+$ | $\Delta E_p$[b] | $\Delta E^{(1+/2+)}$ [V] | $K_{\text{comp}}$[c] |
|---|---|---|---|---|
| −0.25 | −0.77 | 88(5) | | |
| −0.91 | −1.43 | 91(4) | 0.66 | $1.4\times10^{11}$ |
| −1.65 | −2.17 | 99(1) | | |

[a] In THF/$n$Bu$_4$NClO$_4$, at 25 °C, Pt electrode, scan rate = 100 mV s$^{-1}$, Fc/Fc$^+$ complex: $E_{1/2}=0.52$ V versus SCE. [b] Peak-to-peak difference of reduction and oxidation waves; $\Delta E_p=|E_p(\text{cathodic})-E_p(\text{anodic})|$. [c] lg $K_{\text{comp}}=16.9\,\Delta E^{(1+/2+)}$.

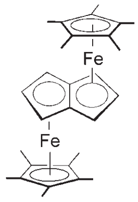
Table 3. Cyclovoltammetric data for **4**.

| $E_{1/2}$ [V] vs SCE[a] | $E_{1/2}$ [V] vs Fc/Fc$^+$ | $\Delta E_p$[b] | $\Delta E^{(1+/2+)}$ [V] | $K_{\text{comp}}$[c] |
|---|---|---|---|---|
| −0.06 | −0.58 | 94(16) | | |
| −0.19 | −0.71 | 89(5) | | |
| −0.84 | −1.36 | 94(6) | 0.78 | $1.5\times10^{13}$ |
| −0.96 | −1.48 | 90(6) | 0.77 | $1.0\times10^{13}$ |
| −1.83 | −2.35 | 94(5) | | |

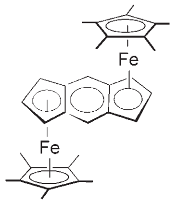
[a] In THF/$n$Bu$_4$NClO$_4$, at 25 °C, Pt electrode, scan rate = 100 mV s$^{-1}$, Fc/Fc$^+$ complex: $E_{1/2}=0.52$ V versus SCE. [b] Peak-to-peak difference of reduction and oxidation waves; $\Delta E_p=|E_p(\text{cathodic})-E_p(\text{anodic})|$. [c] lg $K_{\text{comp}}=16.9\,\Delta E^{(1+/2+)}$.

The CVs of **3** and **4** show three and five quasireversible redox processes, respectively. Compared to ferrocene (0.52 V) and decamethylferrocene (−0.05 V) the first oxidation of **3** and **4** occurs at significantly lower potentials (Table 2). This is indicative of the ease of oxidation of **3** and **4** compared to these parent sandwich compounds; however, one must keep in mind that different Fe oxidation states are involved in these processes for ferrocene and decamethylferrocene.

The first two oxidation peaks in the CV of **3** can be assigned to two successive one-electron transfer steps. In bimetallic complexes that contain two metal centers, the separation between two redox events can be indicative of the degree of electronic interaction.[30–37]The large potential separation $\Delta E$ of 660 mV between the two successive electrochemical events in **3** is characteristic of a strong electronic interaction between the two Fe centers and extensive electronic delocalization in the mixed-valent form **3**$^+$. The potential separation $\Delta E$ of **3** compares well with that of bis(iron)-µ-pentalene **9** ($\Delta E=850$ mV[33]) and bis(iron)-µ-indacene **10** ($\Delta E=820$ mV[33]) which are known to be highly delocalized species in their mixed-valent forms.[32,33] The bonding situation in pentalene complex **9** and indacene complex **10** is related to those in **3** and **4** in that the two metal ions in the latter complexes share the same ligand orbitals.



9[33]



10[32,33]

The cyclic voltammetric data of tetranuclear **4** fit nicely into the line of dinuclear Fe$_2$ complex **3**. Compared to **3** two additional quasireversible oxidation events occur in the cyclic voltammogram of **4**. The separation of redox potentials of the one-electron oxidation steps Fe$_{\text{I–IV}}^{1+/2+}$ and Fe$_{\text{I–IV}}^{2+/3+}$ is at an almost identical potential $E_{1/2}$, which indicates chemically equivalent metal/ligand centers ($\Delta E_{1/2}^{0/1+}=0.13$ and $\Delta E_{1/2}^{0/1+}=0.12$ V). The potential differences $\Delta E$ between the first and second individual oxidation events are 780 and 770 mV, and this underlines the high degree of possible metal interaction in the mixed-valent states of **4**. However, Geiger et. al showed that care must be taken when estimating electronic interactions from $\Delta E$ data due to their strong dependence on solvent and counterion.[34] Nevertheless, even if $\Delta E$ for **3** and **4** is assumed to be solvent-dependent and thus might be influenced significantly by changing the solvent, the strongly coupled situation between the metal centers will not be eliminated by the solvent alone.

In addition to the two (for **3**) or four oxidation events (for **4**) a quasireversible redox event occurs for **3** (−1.65 V) and

**4** (−1.82 V). Decacyclene itself undergoes four reversible single-electron transfers at $E_{1/2}^{\mathrm{red\,I}} = -2.05$, $E_{1/2}^{\mathrm{red\,II}} = -2.46$ V, $E_{1/2}^{\mathrm{red\,III}} = -2.88$ V, and $E_{1/2}^{\mathrm{red\,IV}} = -3.35$ V.[24a] The assignment of the two most anodic waves in the CV of **3** and **4** to the first ligand reduction of complexed decacylene seems reasonable, because successive metal/ligand complexation of **1** with {($\eta^5$-$Me_4EtC_5$)Fe} fragments as in **3** and **4** should enhance the ease of reduction and therefore lower the first reduction potential of the metal-complexed decacyclene ligand substantially.

**Mössbauer spectroscopy of 4**: Owing to the unusual coordination mode of **4** determined by X-ray crystallography and NMR spectroscopy, we studied **4** by Mössbauer spectroscopy at 273 and 78 K. The Mössbauer resonance spectra of **4** consist of well-resolved doublets (Figure 6). Two additional well-resolved doublet components, with about 7 % overall spectral intensity, have Mössbauer parameters clearly characteristic for $Fe^{II}$. We assign this minor component to an oxidized contaminant. Since **4** is highly air sensitive (see Experimental Section) this minor component might be due to an $Fe^{II}$ contaminant formed by oxidation of **4**, which contains formally $Fe^{I}$. The overall observed characteristic isomer shifts (IS), related to the electron density around the metal nucleus, and quadrupole splittings (QS), related to the symmetry of the charge distribution around the metal atom, determined for **4** are given in Table 4, together with the same data on the parent sandwich compounds ferrocene, its permethylated derivative, the dinuclear naphthalene iron compound **8**, and a couple of other organoiron compounds containing $\eta^4$-coordinated ligands. Complex **4** shows a symmetrical doublet indicative of symmetry-equivalent iron centers. For **4** and the structurally related dinuclear naphthalene complex **8**, the observed IS and QS values are in the same range. The IS for **4** and **8** are significantly higher than those of ferrocene and its permethylated derivative, as well as the pentalene and *s*-indacene complexes **9** and **10**.[33] (all formally $Fe^{II}$; see Table 4). Interestingly, the IS values for **4** and **8** are in between those of these four $Fe^{II}$ complexes and the homoleptic iron complexes [{($\eta^6$-toluene)Fe}$_2$-($\mu_2$-$\eta^3$:$\eta^3$-toluene)][39] and [{($\eta^6$-benzene)Fe($\eta^4$-benzene)}],[40] both of which contain formally $Fe^0$ metal centers.

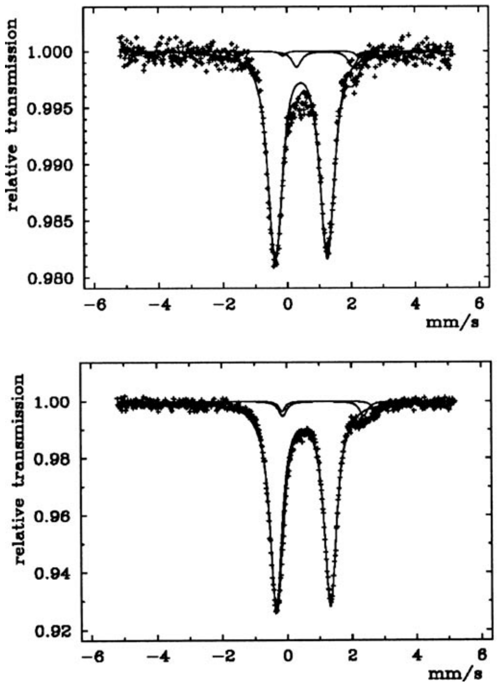


Figure 6. Mössbauer spectra of **4** at 273 and 78 K.

Table 4. Mössbauer data for the diiron complexes **4** and **8**, ferrocene, decamethylferrocene, and related iron π complexes.

| Compound | $T$ [K] | IS $\delta$ [mm s$^{-1}$] | QS [mm s$^{-1}$] |
|---|---|---|---|
| ferrocene[38] | 90 | 0.531(3) | 2.491(1) |
| [($C_5Me_5$)$_2$Fe][38] | 90 | 0.492(3) | 2.473(17) |
| [($C_5H_5$)$_2$Fe]$^+$[38] | 90 | 0.4 | 0.1–0.6 |
| **4** (this work) | 78 | 0.60 | 1.68 |
|  | 273 | 0.55 | 1.63 |
| **8**[16,17] | 273 | 0.543 | 1.555 |
| **9**[33] | 293 | 0.48 | 2.49 |
| **10**[33] | 77 | 0.49 | 2.40 |
| [{($\eta^6$-toluene)Fe}$_2$-($\mu_2$-$\eta^3$:$\eta^3$-toluene)][39] | 80 | 0.66 | 0.23 |
| [($\eta^6$-benzene)Fe($\eta^4$-benzene)][40] | 7 | 0.64 | 1.04 |
| [($\eta^6$-benzene)Fe($\eta^4$-cyclohexadiene)][40] | 77 | 0.49 | 0.92 |

A plausible explanation for the significantly reduced QS values for **4** and **8** compared to the ferrocenes and dinuclear $Fe_2$ complexes **9** and **10** might be a high degree of metal/ligand orbital mixing due to the unique ligand bonding situation for **4** and **8** (see above), which produces a somewhat symmetrical valence electron distribution around the iron centers.

In conclusion, synthesis of the new iron complexes **3** and **4** underpins the ability of decacyclene to act as a versatile and unique ligand towards transition metal fragments. Alternating metal complexation on opposite faces of **1** was observed, with coordination of two or four iron/ligand fragments. To the best of our knowledge the latter coordination was characterized for the first time in transition metal chemistry. The iron centers are strongly coupled across the bridging decacyclene ligand, as can be judged from electrochemical measurements.

## Experimental Section

All manipulations were done in Schlenk tubes under argon using dried solvents. [($\eta^5$-$Me_4EtCp$)FeCl(tmeda)] was prepared according to a procedure developed by Jonas et al.[12] NMR measurements were performed on a Bruker WM 300 instrument in vacuum-sealed tubes with the residual proton signals of the deuterated solvent as standard. The appropriate deuterated solvent was vacuum-transferred onto the solid sample. Electrochemical experiments were carried out on a PAR Model 270 Research Electrochemistry Software controlled Potentiostat/Galvanostat Model 273 A with the electrochemical cell placed in a glovebox. The experiments were performed on 1–2 mM THF solutions containing 0.6 M $(Bu_4N)ClO_4$ as supporting electrolyte; a higher than normal electrolyte concentration was applied to minimize solution resistance. All potentials were measured vs an SCE reference electrode at 25 °C. The potentials were not corrected for junction potentials. A Pt foil electrode was employed as working electrode. Under these conditions the potential for the ferrocene/ferrocenium ion couple was 0.52 V versus SCE.

Mössbauer spectroscopy was carried out on a conventional spectrometer equipped with a cryostat unit CF 500 (Oxford Instruments, England). Calibration of the Doppler velocity of the Mössbauer source (ca. 10 mCi $^{57}$Co in Rh) was performed using the hyperfine splitting of metallic iron. The isomer shift values are quoted relative to α-Fe.

**3**: Decacylene (**1**, Aldrich, 250 mg, 0.56 mmol, sublimed prior to use) was suspended in THF (50 mL) and transferred into a flask in which a thin mirror of potassium metal (60 mg, 1.54 mmol) had been prepared. After three days about 90 % of the metal had dissolved, and a deep red-brown solution containing varying small amounts of precipitate had formed. After the mixture had been cooled to −78 °C, solid **2** (450 mg, 1.26 mmol) was added to this solution in one batch with stirring, and the resulting mixture allowed to warm to room temperature over 5 h. After removal of all volatile substances, the residue was dissolved in diethyl ether and crystallized from that solvent at −30 °C to give black microcrystals of **3** (260 mg, 0.30 mmol, 54 %). A further crop (90 mg, 0.07 mmol, 13 %) of **4** could be isolated from the mother liquor.

**3**: $^{1}$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 0.70$ (t, 6 H), 1.12 (s, 6 H), 1.13 (s, 6 H), 1.21 (s, 6 H), 1.25 (s, 6 H), 1.74 (q, 4 H), 2.12 (d, 2 H, $^{3}J = 5.4$ Hz), 5.56 (t, 2 H, $^{3}J = 5.4$ Hz), 7.44 (t, 2 H, $^{3}J = 7.9$ Hz), 7.65 (t, 2 H, $^{3}J = 7.3$ Hz), 7.66 (d, 2 H, $^{3}J = 7.9$ Hz), 7.73 (d, 2 H, $^{3}J = 7.9$ Hz), 7.82 (d, 2 H, $^{3}J = 5.4$ Hz), 8.77 (d, 2 H, $^{3}J = 7.3$ Hz), 9.19 ppm (d, 2 H, $^{3}J = 7.3$ Hz); $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 9.0$, 9.1, 9.2, 14.7, 18.3, 53.3, 69.6, 75.7, 77.4, 79.2, 79.9, 80.9, 81.8, 82.5, 86.6, 94.1, 122.7, 122.8, 125.9, 126.0, 131.0, 131.3, 134.0, 134.3, 136.3, 139.5, 139.9 ppm; MS (EI): *m/z* (%): 860 (1) [$M^+$], 450 (42) [decacyclene], 354 (49) [$(Me_4EtC_5)_2Fe$], 150 (50) [$Me_4EtC_5$]; elemental analysis (%) for $C_{58}H_{52}Fe_2$ (860.75 g mol$^{-1}$): calcd: C 80.93, H 6.09; found: C 79.23, H 7.01.

**4**: Decacylene (**1**, 360 mg, 0.8 mmol) was suspended in THF (50 mL) and transferred into a flask in which a thin mirror of potassium metal (140 mg, 3.6 mmol) had been prepared. After 3 h the deep red-brown solution was cooled to −78 °C. **2** (1140 mg, 3.2 mmol) was added to this solution in one batch with stirring, and the resulting mixture allowed to warm to room temperature over 5 h. After removal of all volatile substances, the residue was dissolved in diethyl ether, and **4** (660 mg, 0.52 mmol, 65 %) was obtained as shimmering black crystals from that solvent at −30 °C.

**4**: $^{1}$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 0.82$ (t, 6 H), 0.97 (t, 6 H), 1.29 (s, 6 H), 1.32 (s, 6 H), 1.35 (s, 6 H), 1.38 (s, 6 H), 1.47 (s, 6 H), 1.48 (s, 6 H), 1.51 (s, 6 H), 1.52 (s, 6 H), 1.92 (q, 4 H), 2.02 (q, 4 H), 2.19 (d, 2 H, $^{3}J = 5.3$ Hz), 2.53 (d, 2 H, $^{3}J = 5.4$ Hz), 5.59 (t, 2 H, $^{3}J = 5.4$ Hz), 5.67 (t, 2 H, $^{3}J = 5.3$ Hz), 7.61 (t, 2 H, $^{3}J = 7.5$ Hz), 7.74 (d, 2 H, $^{3}J = 7.5$ Hz), 7.77 (d, 2 H, $^{3}J = 5.4$ Hz), 7.96 (d, 2 H, $^{3}J = 5.3$ Hz), 9.25 ppm (d, 2 H, $^{3}J = 7.5$ Hz); $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 9.79$, 9.80, 9.87, 9.91, 9.93, 9.98, 10.0, 15.0, 18.8, 52.1, 56.6, 67.0, 72.9, 75.2, 76.4, 76.5, 77.1, 79.1, 79.9, 80.0, 80.2, 80.8, 80.9, 81.6, 82.4, 86.5, 86.9, 87.1, 95.9, 123.0, 125.1, 130.7, 130.8, 133.8, 134.1, 135.2, 140.7 ppm; elemental analysis (%) for $C_{80}H_{86}Fe_4$ (1270.96 g mol$^{-1}$): calcd: C 75.60, H 6.82; found: C 78.64, H 6.43.

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[13] Crystal data of **2**: $C_{17}H_{33}FeClN_2$, $M_r = 356.75$ g mol$^{-1}$, $a = 10.3095(5)$, $b = 14.5272(7)$, $c = 12.4882(6)$ Å, $\beta = 90.610(3)°$, $V = 1870.23(16)$ Å$^3$, $T = 133(2)$ K, monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$, $\rho_{calcd} = 1.267$ g m$^{-3}$, $\mu = 0.946$ mm$^{-1}$, $\lambda = 0.71073$ Å, empirical absorption correction (SADABS), 24638 reflections collected, 4196 independent and 3908 reflections $[I \geq 2\sigma(I)]$, 199 parameters, $R = 0.0391$, $wR_2 = 0.0850$, largest diff. peak/hole = 0.3/−0.5 e Å$^{-3}$. SHELXL-97 weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 1.53P]$; $P = \mathrm{max.}(F_o^2, 0) + 2F_c^2/3$. Crystal data of **4**: $C_{80}H_{86}Fe_4$, $M_r = 1270.89$ g mol$^{-1}$, black, crystal size 0.30 × 0.09 × 0.05 mm, $a = 12.416(3)$, $b = 30.133(6)$, $c = 16.338(3)$ Å, $V = 6113(2)$ Å$^3$, $T = 100$ K, orthorhombic, $C222_1$ (No. 20), $Z = 4$, $\rho_{calcd} = 1.381$ g m$^{-3}$, $\mu = 0.977$ mm$^{-1}$, $\lambda = 0.71073$ Å, Gaussian absorption correction ($_{\mathrm{min./max.}}$ 0.60/0.78), 33997 reflections collected, 11578 independent reflections, 6202 reflections with $I > 2\sigma(I)$, $\theta_{max} = 33.90°$, 380 refined parameters, $R = 0.059$, $wR_2 = 0.163$, $S = 0.933$, largest diff. peak/hole = 1.8/−3.0 e Å$^{-3}$. SHELXL-97 weighting scheme: $w_{calcd} = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. CCDC-254760 (**2**) and CCDC-260690 (**4**) contain the supplementary crystallographic data for this paper. These data

can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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