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# Pentasubstituted Ferrocene and Dirhodium(II) Tetracarboxylate as Building Blocks for Discrete Fullerene-Like and Extended Supramolecular Structures

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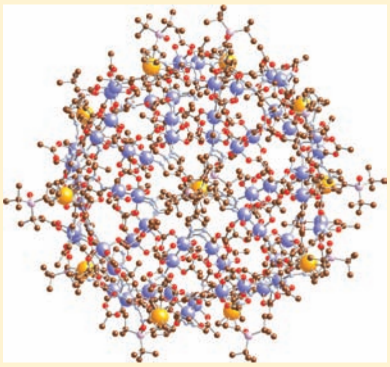
Supporting Information



**ABSTRACT:** The synthesis of a penta(1-methylpyrazole)ferrocenyl phosphine oxide ligand (**1**) $[Fe(C_5(C_3H_2N_2CH_3)_5)(C_5H_4PO(t\text{-}C_4H_9)_2)]$ is reported together with its X-ray crystal structure. Its self-assembly behavior with a dirhodium(II) tetraoctanoate linker (**2**) $[Rh_2(O_2CC_7H_{15})_4]$ was investigated for construction of fullerene-like assemblies of composition $[(\text{ligand})_{12}(\text{linker})_{30}]$. Reaction between **1** and **2** in acetonitrile resulted in the formation of a light purple precipitate (**3**). Evidence for the ligand-to-linker ratio of 1:2.5 expected for a fullerene-like structure $[Fe(C_5(C_3H_2N_2CH_3)_5)(C_5H_4PO(t\text{-}C_4H_9)_2)]_{12}[Rh_2(O_2CC_7H_{15})_4]_{30}$ was obtained from $^1H$ NMR and elemental analysis. IR and Raman studies confirmed the diaxially bound coordination environment of the dirhodium linker by comparing the stretching frequencies of the carboxylate group and the rhodium−rhodium bond with those in model compound (**5**), $[Rh_2(O_2CC_7H_{15})_4](C_3H_3N_2CH_3)_2$, the *bis*-adduct of linker **2** with 1-methylpyrazole. X-ray powder diffraction and molecular modeling studies provide additional support for the formation of a spherical molecule topologically identical to fullerene with a diameter of approximately 38 Å and a molecular formula of $[(\mathbf{1})_{12}(\mathbf{2})_{30}]$. Dissolution of **3** in tetrahydrofuran (THF) followed by layering with acetonitrile afforded purple crystals of $[(\mathbf{1})(\mathbf{2})_2]_\infty$ (**6**) $[Fe(C_5(C_3H_2N_2CH_3)_5)(C_5H_4PO(t\text{-}C_4H_9)_2)][Rh_2(O_2CC_7H_{15})_4]_2$ with a two-dimensional polymeric structure determined by X-ray crystallography. The dirhodium linkers link ferrocenyl units by coordination to the pyrazoles but only four of the five pyrazole moieties of the pentapyrazole ligand are coordinated. The ligand-to-linker ratio of 1:2 in **6** was confirmed by $^1H$ NMR spectroscopy and elemental analyis, while results from IR and Raman are in agreement with the diaxially coordinated environment of the linker observed in the solid state.

## INTRODUCTION

The spontaneous association of molecular building blocks into well-defined discrete nanoscopic structures has attracted considerable interest over the past two decades.[1] The use of metal−ligand interactions[2−4] and hydrogen bonding[5] are among the most popular approaches for construction of self-organized molecular assemblies because of their strength and directionality which make them suitable to link building blocks. The synthesis of closed molecular cages is a particular challenge since it involves the formation of several bonds. Sargeson et al. used a metal ion template approach to prepare sepulchrate[6] and derivatives, but this approach is limited by the frequent impossibility of extracting the template after cyclization. Development of this field is encouraged by the increasing number of intriguing supramolecular phenomena observed within the cavities of a variety of elegantly designed molecular containers, from guest encapsulation[7,8] and catalysis[4,9] to creation of nanoscopic pseudosolution phases,[10] engineering discrete stacks of aromatic molecules[11] and initiating unusual reactivities of inert molecules,[3] as well as stabilization of molecular conformations[12] and reactive intermediates.[8,13] We have a particular interest in exploring the assembly of structures similar to fullerene.[14] Our previous approach to create a discrete spherical assembly made use of the coordination chemistry of a 5-fold symmetric ligand pentapyridylferrocenyl phosphine oxide ($L$) linked by tetraacetonitrile copper(I) hexafluorophosphate.[15] The rationale behind this approach was that pentagonal units cannot be joined together in a planar structure, and the resulting molecule must be curved, leading eventually to a closed spherical surface. $^1H$ NMR titration studies of the ligand with the copper(I) ion provided evidence for the formation of a species $[Cu_{2.5}(L)]$. The stoichiometry is consistent with that of a $[Cu_{30}(L)_{12}]^{30+}$ species, which is expected for a fullerene-type structure in which 12 pentagonal nodes are linked through each vertex by linear copper(I) ions. Further measurements obtained from $^1H$ DOSY NMR studies and dynamic light scattering measurements were consistent with the formation of the desired cage-like species of a size close to that expected from modeling studies. Other synthetic strategies

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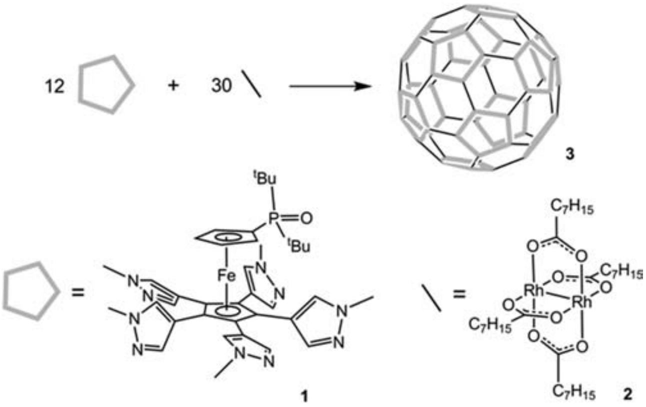


**Figure 1.** Metal-mediated self-assembly approach for construction of the fullerene-like cage **3** from the penta(1-methylpyrazole)-ferrocenyl phosphine oxide ligand **1** and the dirhodium(II) tetraoctanoate linker **2**.

to generate fullerene-like structures involving cluster chemistry have been reviewed recently.[16]

Coordination-driven self-assembly of discrete three-dimensional (3-D) structures relies on metal linkers bringing the organic ligands together in a predesigned and organized fashion. The most common approach involves the use of a single metal center for ligand coordination. An alternative to this is to employ dimetallic sources as linkers which may also show interesting electronic and redox properties because of the metal−metal interactions of the linker.[17] With two vacant axial sites readily available for coordination, dirhodium(II) tetracarboxylate can serve as a linear linker and indeed, it has recently been used in the preparation of one-dimensional (1-D)[15,18−20] and two-dimensional (2-D)[21] coordination polymers. To our knowledge, however, the use of dirhodium(II) tetracarboxylate as a bridging linker to obtain discrete metal−ligand coordination assemblies has not been reported.

In this paper, we wished to report an extension of our previous work[15] on the coordination-driven self-assembly of a fullerene-like supramolecular cage, by employing penta(1-methylpyrazole) ferrocenyl phosphine oxide (**1**) and dirhodium(II) tetraoctanoate (**2**) as the building blocks (Figure 1). Replacing the pyridine of our previous work by *N*-methyl pyrazole as the coordinating moiety has the result that the donor lone pair is no longer perpendicular to the radial vector but lies along the vector expected for the bond between two pentagons in the fullerene structure (Figure 2). The replacement of the Cu(I) and Ag(I) ions of our previous work by an electrically neutral dirhodium(II) tetracarboxylate allows metal-mediated assembly with no accompanying counteranions or cations. The dirhodium species has the advantage of being stable to air and humidity, and its diamagnetic nature allows characterization of the product by NMR spectroscopy. The carboxylate and Rh−Rh stretching frequencies may be used as spectroscopic handles to study coordination.

## ■ EXPERIMENTAL SECTION

**General Procedures.** All reactions were carried out using standard Schlenk line techniques under an atmosphere of dinitrogen; workups were performed in air unless otherwise stated. $[Fe(C_5H_4\{(t\text{-}C_4H_9)_2\}(C_5H_5)]BF_4$ was prepared following the literature procedures.[15] All other chemicals were obtained from Aldrich and Strem and were used without further purification. Silica gel (70−230 mesh) for flash-column chromatography was purchased from Aldrich. Preparative TLC plates (Silica Gel GF, 1000 μm, 20 × 20 cm) were purchased from Analtech. All $^1H$ and $^{13}C\{1H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer ($^1H$, 400 MHz and $^{13}C$, 101 MHz) at room temperature. Chemical shifts are given with respect to tetramethylsilane. Electrospray mass spectra were obtained by the Mass Spectrometry Laboratory, University of Geneva. High resolution spectra were obtained on a QSTAR XL (AB/MSD Sciex) instrument on an Electrospray Ionization (ESI) positive mode. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer on solid samples using a Golden Gate ATR accessory. Raman spectra were obtained at room temperature on powder samples (contained in melting point capillaries) in backscattering geometry using a Kaiser Holospec monochromator in conjunction with a liquid nitrogen cooled CCD camera. The spectra were excited using 488 nm radiation with an intensity of 50 mW for the commercial sample, and 5 mW for the other samples. Exposure times were 100 s with 50mW and 1000 to 3000 s with 5mW irradiation. The spectral resolution is about 3 $cm^{-1}$. Microanalyses were performed at the Microchemical Laboratory of the University of Geneva.

**X-ray Crystallographic Procedures.** A summary of crystal data, intensity measurements, and structure refinements for ligand **1**, and $[(\mathbf{1})(\mathbf{2})_2]_\infty$ (**6**) is given in Table 1. All crystals were mounted on quartz fibers with protective oil. Cell dimensions and intensities were measured at 150 K on a Stoe IPDS diffractometer with graphite-monochromated Mo[$K_\alpha$] radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods (SIR97);[22] all other calculations were performed with ShelX97[23] systems and ORTEP[24] programs.

*Comments on the Crystal Structure of* ***1***. The low measured diffraction fraction (93%) is due to the highly anisotropic shape of the crystal and the impossibility of collecting the data with another crystal orientation (only $\varphi$-scans available). All non H atoms were refined anisotropically. One solvent $CHCl_3$ molecule showed some disorder (rotation along C−H axis), as shown by the rather high refined $U_{aniso}$. Attempts to model this disorder with two partially occupied molecules did not improve the refinement.

*Comments on the Crystal Structure of* ***6***. Numerous attempts to get single crystals of **3** yielded some fragile small purple crystals of polymeric complex **6**, from which only data of limited quality could be obtained with small intensities for high-angle reflexions despite long exposure times (10 min) and attempts to increase the image plate-crystal distance = 190 mm to improve resolution at the cost of limiting the angular domain ($2\theta_{max} = 40.92°$). Only rhodium, iron, and phosphorus atoms were refined anisotropically. All other atoms were refined isotropically. All hydrogen atoms bound to observed atoms were calculated and refined with constraints. Atoms of the pyrazole groups were refined with constraints on bond lengths. The aliphatic chains were highly disordered and were only partially seen in the electron density map, leading to large accessible voids in the crystal structure. The SQUEEZE routine[25] was used to take these contributions into account in the final refinement. In view of the low quality of this crystal structure, we do not intend to deposit the structure in the CCDC file, but considering its importance for confirming the formation of a polymeric structure we have given the .cif file in the Supporting Information.

**X-ray Powder Diffraction Procedures.** The synchrotron powder diffraction experiments were carried out at the Swiss−Norwegian Beamlines at the European Synchrotron Radiation Facility. The data were collected on the 0.5 or 0.8-mm glass capillaries filled with the sample, using a Kuma CCD camera at a sample-to-detector distance of 360 mm, $\lambda = 0.690581$ Å. The data were integrated using the Fit2D program (Dr. A. Hammersley, ESRF) and a calibration measurement of a NIST LaB6 standard sample. Powder pattern of empty capillaries were measured in exactly the same conditions.

*Synthesis of* $[Fe(C_5H_4PO(t\text{-}C_4H_9)_2)][C_5(C_3H_2N_2CH_3)_5)]$ *(**1**).* In a two-necked flask, a mixture of $[Fe(C_5H_4P(t\text{-}C_4H_9)_2)(C_5H_5)]BF_4$ (0.150 g,

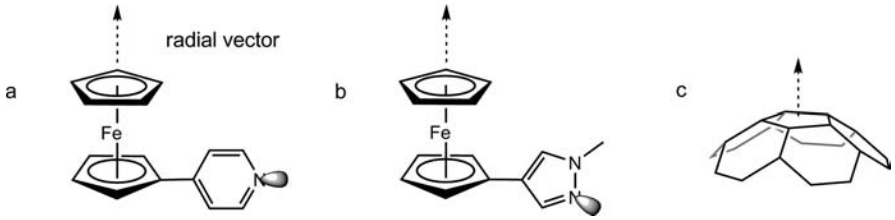


**Figure 2.** Use of *N*-methylpyrazole substituted ferrocene ligand as building block for construction of fullerene-like self-assembly: (a) with pyridine as the coordinating moiety the donor lone pair is perpendicular to the radial vector; (b) the lone pair of pyrazole nitrogen lies at an angle with respect to the radial vector in the present study; (c) section of the fullerene showing the edge between two hexagons in the spherical structure.

**Table 1. Selected Crystallographic Data and Structural Refinement Parameters for 1 and 6**

| | 1 | 6 |
|---|---|---|
| molecular formula | $C_{38}H_{47}FeN_{10}OP$ $\cdot CHCl_3$ | $C_{59}H_{57}FeN_{10}O_{17}PRh_4$ $\cdot C_2H_3N$ |
| molecular weight | 866.04 | 1717.66 |
| color | red prism | purple prism |
| crystal size/mm | 0.26 × 0.22 × 0.08 | 0.25 × 0.15 × 0.08 |
| crystal system | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/n$ |
| $a$/Å | 9.0221(8) | 19.152(2) |
| $b$/Å | 10.4690(9) | 30.145(4) |
| $c$/Å | 22.543(2) | 22.918(3) |
| α/deg | 94.647(11) | 90 |
| $\beta$/deg | 98.548(11) | 92.807(10) |
| $\gamma$/deg | 96.760(11) | 90 |
| $V$/Å$^3$ | 2080.4(3) | 13215(3) |
| $Z$ | 2 | 4 |
| density/mg m$^{-3}$ | 1.382 | 0.863[a] |
| $\mu$ /mm$^{-1}$ | 0.64 | 0.65 |
| reflections collected | 16393 | 47024 |
| unique data measured | 7511 | 12866 |
| observed data with $I \geq 2\sigma(I)$ | 4423 | 3706 |
| no. of parameters | 507 | 385 |
| $R1$ | 0.047 | 0.126 |
| w$R$(all data) | 0.109 | 0.337 |

[a] Density calculated for the atoms observed and refined.

0.36 mmol), Pd(OAc)$_2$ (0.007 g, 0.03 mmol), PPh$_3$ (0.043 g, 0.16 mmol), 4-bromo-1-methyl-1*H*-pyrazole (0.45 mL, 4.4 mmol), and *t*-C$_4$H$_9$OK (0.444 g, 4.0 mmol) was placed in toluene (20 mL) and heated at reflux overnight. The solution was filtered through Celite, and the solvent was removed. The solid was purified by preparative TLC using CHCl$_3$/EtOH (90:10) as the eluent. A mixture of [Fe(C$_5$H$_4$PO(*t*-C$_4$H$_9$)$_2$)(C$_5$H(C$_3$H$_2$N$_2$CH$_3$)$_4$)] and [Fe(C$_5$H$_4$PO($^t$Bu)$_2$)(C$_5$(C$_3$H$_2$N$_2$CH$_3$)$_5$)] (0.03 g) was isolated as pink solid. The mixture was treated with 4-methylmorpholine *N*-oxide monohydrate (0.013 g, 0.09 mmol) in tetrahydrofuran (THF, 5 mL) and heated under reflux overnight. After cooling, the solvent was removed under vacuum and replaced by CH$_2$Cl$_2$. The solution was washed with water (3 × 10 mL), dried over Na$_2$SO$_4$, and filtered. The reaction mixture was purified by preparative TLC using CHCl$_3$/EtOH (85:15) as the eluent. The title compound was isolated as a dark red solid in 6% yield (0.015 g, 0.02 mmol). Recrystallization was achieved by diffusion of hexane into solutions of chloroform at room temperature. $^1$H NMR (400 MHz, CDCl$_3$): 7.36 (s, 5H, Ar*H*), 7.22 (s, 5H, Ar*H*), 4.35 (br s, 2H, Cp*H*), 4.00 (br s, 2H, Cp*H*), 3.80 (s, 15H, NC*H*$_3$), 0.92 (d, $J$ = 13.8 Hz, 18H, C(C*H*$_3$)$_2$); $^{13}$C{$^1$H} NMR (CDCl$_3$):140.45, 131.33, 115.64, 78.32, 75.69, 74.84, 39.00, 36.49, 35.87, 26.87; $^{31}$P{$^1$H} NMR (CDCl$_3$) 61.9 ppm; ES-HRMS: $m/z$ calcd: 747.3094; found: 747.3074 [M+H]$^+$; UV−vis (CHCl$_3$)/nm 498 (log [$\varepsilon$/M$^{-1}$ cm$^{-1}$] 466); IR (selected): $\nu$ = 3389, 3100, 2927, 1455, 1277, 1127 cm$^{-1}$. Anal. Calcd for C$_{38}$H$_{47}$FeN$_{10}$OP·CHCl$_3$: C, 54.09; H, 5.59; N, 16.17%. Found: C, 54.13; H, 5.59; N, 16.20%.

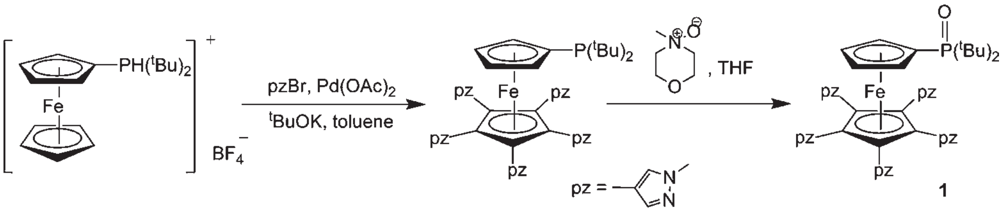
*Synthesis of [Fe(C$_5$(C$_3$H$_2$N$_2$CH$_3$)$_5$)(C$_5$H$_4$PO(t-C$_4$H$_9$)$_2$)]$_{12}$[Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$]$_{30}$ (**3**).* [Fe(C$_5$H$_4$PO(*t*-C$_4$H$_9$)$_2$)(C$_5$(C$_3$H$_2$N$_2$CH$_3$)$_5$)] (0.03 g, 0.045 mmol) in acetonitrile (3 mL) was added dropwise to a solution of dirhodium(II) tetraoctanoate (0.14 g, 0.18 mmol) in acetonitrile (6 mL). The mixture was stirred at room temperature for 0.5 h. The precipitate was filtered, washed with acetonitrile (3 × 5 mL) and ether (3 × 5 mL), and dried in vacuum at 60 °C overnight, giving a light-purple powder. Yield: 0.07 g (64%). IR (selected): $\nu$(CO$_2$)$_{asym}$ = 1587 cm$^{-1}$, $\nu$(CO$_2$)$_{sym}$ = 1410 cm$^{-1}$; Anal. Calcd for C$_{1416}$H$_{2364}$N$_{120}$P$_{12}$O$_{252}$Fe$_{12}$Rh$_{60}$: C, 52.60; H, 7.38; N, 5.20; Fe, 2.07%. Found: C, 52.56; H, 7.32; N, 5.55; Fe 2.34%.

*Synthesis of [Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$(C$_4$H$_6$N$_2$)] (**4**).* To dirhodium(II) tetraoctanoate (0.035 g, 0.045 mmol) in chloroform (5 mL) was added 75 $\mu$L (0.045 mmol) of a 0.6 M solution of 1-methylpyrazole in chloroform. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to afford the *mono*-adduct in quantitative yield. $^1$H NMR (400 MHz, CDCl$_3$): 8.03 (d, $J$ = 2.2 Hz, 1H, pz*H*), 7.68 (d, $J$ = 2.2 Hz, 1H, pz*H*), 6.60 (t, $J$ = 2.3 Hz, 1H, pz*H*), 4.32 (s, 3H, NC*H*$_3$), 2.16 (t, $J$ = 7.4 Hz, 8H, CO$_2$(C*H*$_2$)(CH$_2$)$_5$CH$_3$), 1.54−1.38 (m, 8H, CO$_2$(CH$_2$)(C*H*$_2$)(CH$_2$)$_4$CH$_3$), 1.32−1.04 (m, 32H, CO$_2$(CH$_2$)$_2$(C*H*$_2$)$_4$CH$_3$), 0.85 (t, 12H, $J$ = 7.0 Hz, CO$_2$(CH$_2$)$_6$C*H*$_3$); UV−vis (CHCl$_3$)/nm 435, 581 (log [$\varepsilon$/M$^{-1}$ cm$^{-1}$] 136, 258; IR (selected): $\nu$(CO$_2$)$_{asym}$ = 1577 cm$^{-1}$, $\nu$(CO$_2$)$_{sym}$ = 1411 cm$^{-1}$; Anal. Calcd for C$_{36}$H$_{66}$N$_2$O$_8$Rh$_2$: C, 50.23; H, 7.73; N, 3.25%. Found: C, 50.11; H, 7.65; N, 3.31%.

*Synthesis of [Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$(C$_4$H$_6$N$_2$)$_2$] (**5**).* To dirhodium tetraoctanoate (0.10 g, 0.13 mmol) in chloroform (5 mL) was added 0.43 mL (0.26 mmol) of a 0.6 M solution of 1-methylpyrazole in chloroform. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to afford the *bis*-adduct in quantitative yield. $^1$H NMR (400 MHz, CDCl$_3$): 8.10 (d, $J$ = 2.1 Hz, 2H, pz*H*), 7.68 (d, $J$ = 2.1 Hz, 2H, pz*H*), 6.58 (t, $J$ = 2.2 Hz, 2H, pz*H*), 4.35 (s, 6H, NC*H*$_3$), 2.13 (t, $J$ = 7.4 Hz, 8H, CO$_2$(C*H*$_2$)(CH$_2$)$_5$CH$_3$), 1.49−1.39 (m, 8H, CO$_2$(CH$_2$)(C*H*$_2$)(CH$_2$)$_4$CH$_3$), 1.31−1.05 (m, 32H, CO$_2$(CH$_2$)$_2$(C*H*$_2$)$_4$CH$_3$), 0.85 (t, $J$ = 7.0 Hz, 12H, CO$_2$(CH$_2$)$_6$C*H*$_3$); UV−vis (CHCl$_3$)/nm 442, 554 (log [$\varepsilon$/M$^{-1}$ cm$^{-1}$] 128, 228); IR (selected): $\nu$(CO$_2$)$_{asym}$ = 1587 cm$^{-1}$, $\nu$(CO$_2$)$_{sym}$ = 1412 cm$^{-1}$; Anal. Calcd for C$_{40}$H$_{72}$N$_4$O$_8$Rh$_2$: C, 50.96; H, 7.70; N, 5.94%. Found: C, 50.79; H, 7.70; N, 5.26%.

*Synthesis of [Fe(C$_5$(C$_3$H$_2$N$_2$CH$_3$)$_5$)(C$_5$H$_4$PO(t-C$_4$H$_9$)$_2$)][Rh$_2$(O$_2$C-C$_7$H$_{15}$)$_4$]$_2$ (**6**).* The precipitate **3** (0.013 g, 0.40 $\mu$mol) was dissolved in THF and layered with acetonitrile. The solution was left in the dark to afford purple crystals, which were separated by filtration and washed with several portions of acetonitrile (3 × 5 mL) and hexane (3 × 5 mL). The product was then dried under vacuum overnight at 60 °C,

**Scheme 1. Synthesis of Penta(1-methylpyrazole)ferrocenyl Phosphine Oxide Ligand 1**



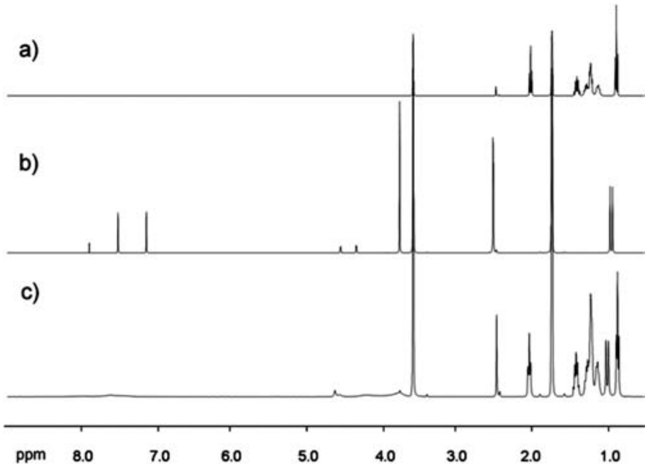


**Figure 3.** $^1$H NMR (400 MHz, $d^8$-THF) spectra of the (a) dirhodium tetraoctanoate, **2**, (b) penta(1-methylpyrazole)ferrocenyl phosphine oxide ligand **1**, and (c) precipitate **3**.

giving a red powder. Yield: 0.008 g (70%). IR (selected): $\nu(CO_2)_{asym}$ = 1588 cm$^{-1}$, $\nu(CO_2)_{sym}$ = 1410 cm$^{-1}$; Anal. Calcd: $C_{102}H_{167}N_{10}PO_{17}FeRh_4$: C, 53.16; H, 7.31; N, 6.08%. Found: C, 52.97; H, 7.27; N, 6.05%.

## RESULTS AND DISCUSSION

**Synthesis and Crystal Structure of Penta(1-methylpyrazole)ferrocenyl Phosphine Oxide Ligand.** The synthetic strategy for the new pentasubstituted ferrocenyl phosphine oxide ligand **1** is shown in Scheme 1. The two-step approach was adapted from our previous report on the preparation of a similar pentapyridyl ferrocenyl ligand with minor modifications.[15] Attempts to obtain exclusive formation of the pentapyrazole ferrocenyl phosphine intermediate failed, and the palladium-catalyzed coupling of phosphonium salt of di-*tert*-butyl-ferrocene with 4-bromo-1-methyl-1*H*-pyrazole was always observed to give a mixture of differently substituted compounds which inevitably lowered the yield of the fully substituted product. Characterization of the phosphine intermediate was not possible because of its susceptibility to aerial oxidation. Complete oxidation of the pentapyrazole ferrocenyl phosphine to the corresponding phosphine oxide was achieved by reaction with 4-methylmorpholine *N*-oxide monohydrate in THF. The ligand **1** was obtained with an overall yield of 6% after separation by preparative TLC.

**1** was fully characterized by NMR spectroscopy ($^1$H, $^{13}$C, and $^{31}$P NMR), IR, UV−vis, high resolution mass spectrometry and elemental analysis. The $^1$H NMR spectrum of **1** in deuterated THF consists of a doublet for the *tert*-butyl groups ($\delta$ = 0.94 ppm), and a singlet at 3.76 ppm is assignable to the *N*-methyl groups of the pyrazole ring (Figure 3). Two broad singlets at 4.34 and 4.55 ppm are attributed to the four protons of the cyclopentadienyl ring with the phosphine oxide, and the two remaining singlets ($\delta$ = 7.14 and 7.52 ppm) correspond to the two different types of aromatic pyrazole protons. The simplicity of the spectrum suggests that both radial rotation of the pyrazole groups with respect to the cyclopentadienyl (Cp) rings, and the axial rotation of the two Cp rings about the Cp−Fe−Cp axis are rapid on the $^1$H NMR time scale. Similar fast rotations were observed in the pentapyridyl analogue.[15]

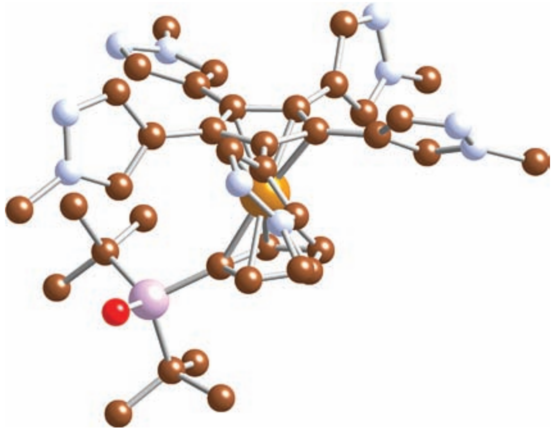


**Figure 4.** Crystal structure of the penta(1-methylpyrazole)ferrocenyl phosphine oxide ligand **1**. Hydrogen atoms and the solvate chloroform molecules have been omitted for clarity. Color code: iron, orange; phosphorus, violet, oxygen, red, nitrogen, light blue, carbon, brown.

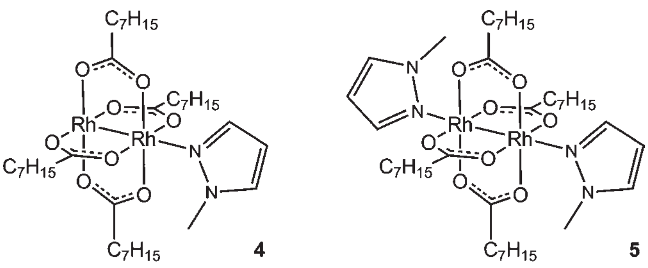
The molecular structure of **1** was established by single crystal X-ray diffraction analysis (Figure 4). X-ray quality crystals were obtained by slow diffusion of hexane into the chloroform solution of the ligand. The compound crystallizes in the triclinic space group $P\bar{1}$, and two chloroform molecules are incorporated in the unit cell. The Fe−C distances are similar for both Cp rings, and the distances of the iron atom from the centroid of the Cp rings are also similar (1.682 and 1.667 Å). There is a slight difference in carbon−carbon distances in the two rings (average value of 1.441 Å for the pyrazole-substituted ring and 1.423 Å for the ring substituted with the phosphine oxide). The two Cp rings are in a staggered conformation and show an interplane angle of 7.9°. The bis(*tert*-butyl)phosphine oxide adopts a conformation with one *tert*-butyl group trans to the iron atom. The second *tert*-butyl group and the oxygen atom are directed toward the pyrazoles. The structure of the ferrocene core of **1** is comparable to the pentapyridyl-ferrocenyl phosphine oxide ligand we reported previously.[15] The planes of the pyrazole groups are oriented with respect to the cyclopentadienyl core by angles between 17 and 79°. The smallest inclined angle is observed for the pyrazole ring closest to the sterically demanding *tert*-butyl group. All pyrazole moieties are tilted in the same sense with the *N*-methyl groups pointing toward the second Cp ring ("up" conformation) and the lone pairs of pyrazoles directed away from the metal core of the ligand. The "all-up" conformation adopted by **1** in the solid state provides evidence for this preferred "convex" geometry of the ligand which is crucial for the formation of the desired discrete assembly with the dirhodium linker.

**Self-Assembly of the Penta(1-methylpyrazole)-ferrocene Ligand and Dirhodium(II) Tetraoctanoate.** Reaction of the ferrocenyl phosphine oxide ligand **1** with the dirhodium(II) tetraoctanoate **2** carried out in acetonitrile solution afforded a light purple precipitate **3** in 64% yield. Formation of the precipitate was instantaneous, and the yield for **3** was independent of the reaction time and concentration of the reactants. The product showed no solubility in common organic solvents with the exception of polar solvents such as THF, dimethylformamide (DMF), and dimethylsulfoxide (DMSO). Such solubility can arise from the coordinating properties of the solvents which can compete with the ligand **1** for axial binding to the linker **2** and leads to dissociation of any complex formed between the ligand and the linker. Similar solubility effects have been observed with coordination polymeric chains composed of dimetallic tetracarboxylates in coordinating solvents.[20,26] The solutions of **3** in THF were blue-green, typical of dirhodium(II) tetracarboxylates coordinated by oxygen donors,[27]giving strong evidence for dissociative dissolution, and this is consistent with the $^1$H NMR spectrum (see below). The DMSO solution was orange as expected for the DMSO adduct.[28]

The experimentally determined percentage of carbon, hydrogen, and nitrogen of **3** (52.56, 7.32 and 5.55% respectively) shows good agreement with that expected for the proposed assembly $[(\mathbf{1})_{12}(\mathbf{2})_{30}]$ (52.60, 7.38, and 5.20% for carbon, hydrogen, and nitrogen, respectively), suggesting that the compound has a ligand-to-linker (**1**/**2**) ratio of 1:2.5. The iron content was 2.34% (calculated 2.07%). The same ligand-to-linker ratio was found using $^1$H NMR by comparing integrals of a recognizable type of proton from each building block: the *tert*-butyl groups of the pentapyrazole ligand **1** and the terminal methyl protons of heptyl chains of the dirhodium linker **2**. Figure 3 shows the $^1$H NMR spectra of **3** and the dirhodium tetraoctanoate linker **2** dissolved in deuterated THF. Integration of the doublet ($\delta$ = 0.99 ppm) of the *tert*-butyl protons of **1** and the triplet ($\delta$ = 0.86 ppm) of the terminal methyl protons of **2** gives a ratio of 3:5. This is consistent with the ratio expected for the assembly $[(\mathbf{1})_{12}(\mathbf{2})_{30}]$ which would possess a total of 216 *tert*-butyl protons from the ligand **1** and 360 terminal methyl protons from the linker **2**. The doublet of the *tert*-butyl protons and the triplet of the terminal methyl protons in **3** are barely shifted downfield with respect to ligand **1** and linker **2**, respectively. However, peaks corresponding to the cyclopentadienyl and pyrazole protons of the pentapyrazole ligand become very broad in **3**. These are the protons most sensitive to complex formation, and this suggests that there may be partial complexation in solution, with rapid exchange between coordinated and uncoordinated pyrazole. Cooling the solution to 273 K slightly improved the resolution with the pyrazole protons appearing as very broad signals. Further cooling merely led to a general loss of resolution.

The coordination of the dirhodium(II) tetraoctanoate in solid **3** was probed by comparing its carboxylate stretching and rhodium—rhodium vibration frequencies with those of the free dirhodium(II) tetraoctanoate **2** and two model compounds, the *mono*- and *bis*-adduct of **2** with 1-methylpyrazole (**4** and **5**, Scheme 2). The effects of pyrazole binding on **2** were first investigated by IR spectroscopy (see Supporting Information). The carboxylate group in the unbound linker **2** exhibits a characteristic asymmetric stretching band at 1564 cm$^{-1}$, while the corresponding stretching in the *bis*-adduct **5** is shifted to 1587 cm$^{-1}$. The fact that an identical asymmetric stretching band is observed for the bound linker **2** in the precipitate **3** at 1587 cm$^{-1}$ strongly suggests that both axial coordination sites of the dirhodium linker in **3** are occupied by pyrazole, a condition that is necessary for the formation of the proposed spherical assembly $[(\mathbf{1})_{12}(\mathbf{2})_{30}]$. In comparison, the maximum of the stretching frequency of the solid isolated as the *mono*-adduct **4** is at 1577 cm$^{-1}$. The symmetric band for the carboxylate stretching in **3**, **4**, and **5** appears to be insensitive to the change of the coordination environment and essentially there are no changes to this frequency.

**Scheme 2**



The diaxially bound coordination environment of the dirhodium linker in **3** can also be established by Raman spectroscopy which is known to be more sensitive than single crystal X-ray analysis with regard to metal—metal interactions.[29] The rhodium—rhodium bond in the free dirhodium(II) tetraoctanoate **2** shows a Raman band at 344 cm$^{-1}$,[19] and the spectrum of the *bis*-(methylpyrazole)adduct **5** shows a drop to 328 cm$^{-1}$.

The *mono*-adduct **4** shows two bands at 326 and 343 cm$^{-1}$ (Figure 5) with perhaps a weaker band in between. This suggests that it may actually be a mixture of *mono*-adduct, *bis*-adduct, and unsubstituted **2**. It is not inconsistent with the infrared spectrum of **4** since the band at 1577 cm$^{-1}$ is rather broad and could be an overlay of three peaks. Both **3** and the *bis*-adduct **5** have one band showing almost the same frequency ($\nu$(Rh—Rh) = 331 cm$^{-1}$ and 328 cm$^{-1}$ respectively), lower than the unbound dirhodium(II) tetraoctanoate. These observations demonstrate that the coordination environment of the rhodium linker is similar in these compounds and is in line with the IR measurements.

The precipitate **3** was analyzed by synchrotron X-ray powder diffraction. Because of the poor crystallinity of the sample, only broad peaks were observed in the powder pattern (see Supporting Information, Figure S1). Attempts to improve the crystallinity of the sample by annealing did not give better quality diffraction data for more rigorous refinements. However, the broad reflections could be indexed in a cubic body centered (*I*) system to give cell parameter $a$ = 44.40(2) Å and cell volume $V$ = 87548(70) Å$^3$. For a body-centered arrangement of spheres, the diameter of the sphere $D_{\mathrm{sph}}$ and cell parameter are related by the equation $D_{\mathrm{sph}} = (a \times \sqrt{3})/2$ (where the diagonal length of the cubic cell should be approximately equal to $2 \times D_{\mathrm{sph}}$). This gives an estimated diameter of the sphere ($D_{\mathrm{sph}}$ = 38 Å) which is comparable with that obtained from molecular modeling

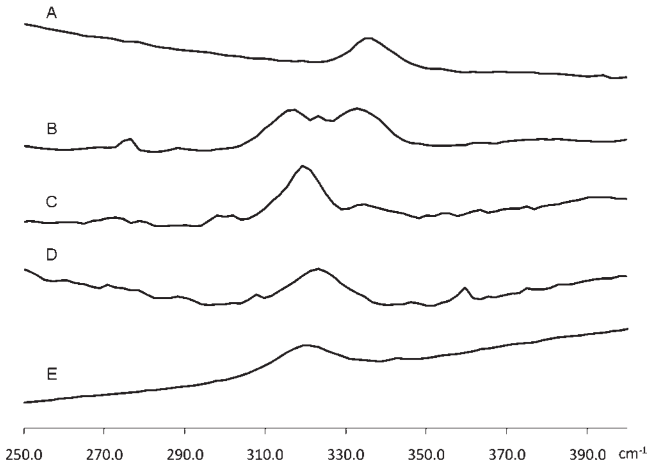


**Figure 5.** Raman spectra between 250 and 400 cm$^{-1}$. A: Dirhodium tetraoctanoate **2**. B: *Mono*-adduct **4**. C: *Bis*-adduct **5**. D: Precipitate **3**. E: Crystal **6**.

of $[(\mathbf{1})_{12}\{Rh_2(HCO_2)_4\}_{30}]$ using the Scigress program[30] (Figure 6). From the cell parameter and the molecular mass we can calculate a density of 1.22 g cm$^{-3}$. Attempts to measure the density by flotation in nitromethane-$CCl_4$ gave values around 1.33 g cm$^{-3}$. We attribute this to the large voids in between the spheres which can absorb solvent molecules, thereby inceasing the density.

**Coordination Framework of Penta(1-methylpyrazole)ferrocenyl Phosphine Oxide Ligand and Dirhodium(II) Tetraoctanoate.** Small purple crystals could be isolated when the THF solution of the precipitate **3** was layered with acetonitrile. Characterization of the polymer **6** was effected by elemental analysis, $^1$H NMR, IR, and Raman spectroscopies. Elemental analysis established a ligand-to-linker ratio of 1:2, with only small differences (ca. 0.2%) from the theoretical values. The $^1$H NMR spectrum of **6** in deuterated THF shows strong resemblance to that of **3**. This supports the hypothesis of dissociation advanced for **3**. However, the integration of the peaks of **6** corresponding to the *tert*-butyl group of the ligand and those of the terminal methyl group of the linker gives a ligand-to-linker ratio of 1:2. The asymmetric carboxylate stretching frequency in **6** and that in the *bis*-adduct model compound **5** is almost identical (1588 cm$^{-1}$ vs 1587 cm$^{-1}$), and this gives support to the diaxially bound coordination environment of the dirhodium linker in the coordination polymer. The same can be deduced from comparable rhodium−rhodium vibration frequencies observed in **6** and **5** (330 cm$^{-1}$ vs 328 cm$^{-1}$). There is negligible difference in the asymmetric stretching of carboxylates and rhodium−rhodium vibration frequencies between the two supramolecular assemblies **3** and **6**. In fact the vibrational spectroscopic data for both assemblies are virtually the same as those in the *bis*-adduct **5**.

The crystals of **6** were studied by X-ray crystallography. The resulting structure is of poor quality, since the heptyl chains of the dirhodium(II) tetraoctanoate units are highly disordered, and were modeled using the SQUEEZE routine of Spek.[25,31] One acetonitrile molecule could be observed in the electron density map. In spite of the poor quality data, the electron density map shows clearly the positions of the heavy atoms, the cyclopentadienyl and pyrazole rings, and the carboxylate functions. The structure confirms the expected ratio of ligand-to-linker with the units of **1** linked by dirhodium carboxylates. The structure of the penta(1-methylpyrazole)ferrocenyl phosphine oxide is basically the same as for free **1**, with staggered Cp rings and the conformation of the bis(*tert*-butyl)phosphine oxide as described above. The major difference concerns the orientation of the methyl pyrazole rings. Two coordinated pyrazoles have a conformation similar to **1**, a third has the N−Rh bond directed toward rather than away from the ferrocene while the fourth coordinated pyrazole, which is that closest to a *tert*-butyl group, is only slightly inclined to the Cp plane so that the N−Rh bond is almost coplanar with the Cp ring. The fifth pyrazole is uncoordinated. The molecule **1** thus acts as a four-connected node which is linked by $Rh_2$ units to give a corrugated sheet in the crystallographic *ac* plane (Figure 7). The Rh−Rh bonds are typical (2.397(3) and 2.418(3)Å), as are the Rh−N bonds (mean 2.23 Å).

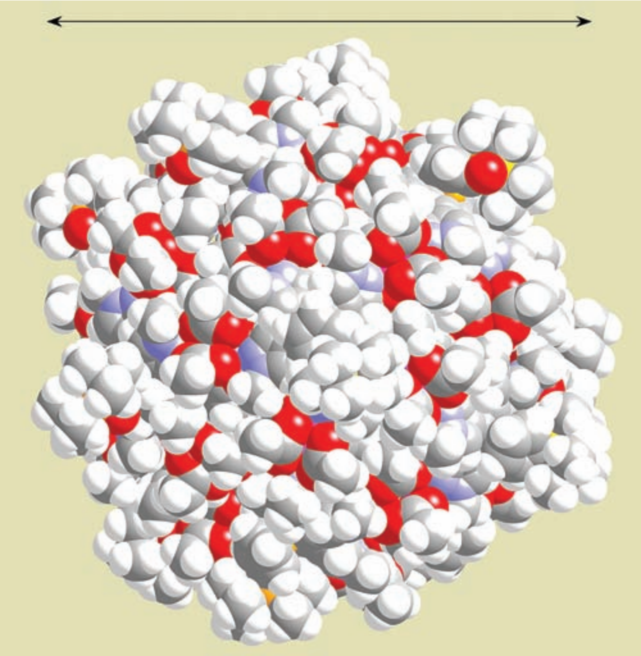


**Figure 6.** Spacefilling image of $[(\mathbf{1})_{12}(Rh_2(HCO_2)_4)_{30}]$ obtained with Scigress.[30] The arrow indicates the diameter of the sphere deduced from X-ray powder diffraction.

The structure may be described as a corrugated sheet lying in the crystallographic *ac* plane. Interestingly, our first attempts to obtain a spheroidal complex with a five-connected nodal pentacyanocyclopentadienide ligand and silver(I) also resulted in the formation of a similar 2-D polymeric structure.[32]

Examples of various ferrocene-containing coordination polymers are available in the literature, and the majority of them employed 1,1′-*bis*-functionalized ferrocene substituted with *N*-heterocycles,[33] carboxylate,[34] and borylated units.[35] The use of pentasubstituted ferrocene to construct coordination polymer has not been previously known to the best of our understanding, and the structure **6** represents the first of this kind, where the ligand behaves unexpectedly as a tetradentate instead of as a pentadentate ligand.

## DISCUSSION

The major difficulty with this type of chemistry is the characterization of the products. The sphere postulated for the structure of **3** is expected to have a molecular mass of 32319 Da. Its neutral charge and the presence of hydrophobic groups (60

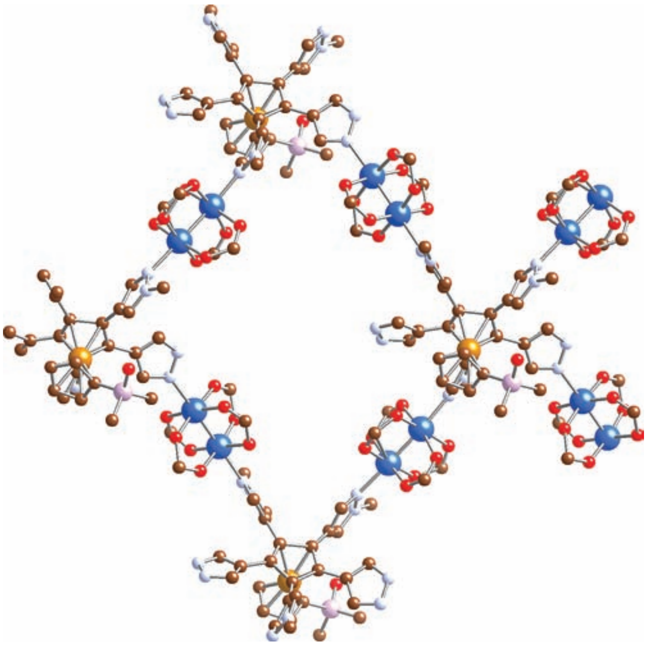


**Figure 7.** Crystal structure of $[(\mathbf{1})(\mathbf{2})_2]_\infty$ (**6**). Hydrogen atoms and heptyl chains are omitted. The heptyl chains lie in the holes in the lattice. Color code: rhodium, dark blue; iron, orange; phosphorus, violet; oxygen, red; nitrogen, light blue; carbon, brown.

*n*-heptyl groups) on the surface may encourage association and is presumably responsible for the precipitation of the product and its low solubility. For this reason the characterization of the product is of necessity less complete than for a smaller coordination complex.

If we begin with compound **6**, the chemical analysis, the $^1$H NMR spectrum of the dissociated compound in THF, the low solubility and the X-ray crystal structure show a coordination framework with dirhodium linkers between the pyrazole bearing ferrocenes. The vibrational spectra establish the coordination of two pyrazoles to each dirhodium unit.

For **3**, the chemical analysis establishes the ratio of **1** to **2** as 1:2.5 as predicted for a sphere, and this is confirmed by the $^1$H NMR spectrum of dissociated **3** in THF. The vibrational spectra show the dirhodium units are fully complexed by two pyrazoles. We can think of no structure other than the spherical $[(\mathbf{1})_{12}(\mathbf{2})_{30}]$ which would be in agreement with these observations. A structure $[(\mathbf{1})_2(\mathbf{2})_5]$ in which two units of **1** are bridged by five dirhodium units would require considerable distortion of Rh−Rh−N bonds and would involve repulsion between carboxylates. Although it is only indicative, the observation of an X-ray powder diffraction diagram which is consistent with body-centered cubic packing of spheres with a diameter very close to that estimated from modeling studies supports the formation of the sphere. It is unfortunate that we were unable to find a solvent which would dissolve **3** without dissociation of the complex, since this excludes the use of methods such as DOSY or electrochemistry to measure the diffusion coefficient, as was possible in our earlier work.[15]

One somewhat surprising observation is that the spherical $[(\mathbf{1})_{12}(\mathbf{2})_{30}]$ is formed rapidly on mixing **1** and **2** in acetonitrile but that the crystalline 2-D structure **6** grows much more slowly. The observation that the framework **6** is formed slowly from a THF solution of **3** does not necessarily imply that it is more stable, since it might simply be less soluble. Intuitively one might expect that **6** would be less stable than **3** since all the pyrazole units are not coordinated. The good analytical data and the NMR intensities confirm that **3** is not merely an impure sample of **6**.

In conclusion, we have reported the synthesis of a new pentagonal ligand, where the donor groups are oriented in a more favorable way for the formation of a fullerene-like structure. We have shown that the dirhodium unit is an efficient linker between the pyrazole groups and that reaction of the pentagonal ligand with the linear linker gives rapid formation of a compound for which analytical data suggest a spheroidal fullerene structure. This can be transformed into a coordination framework with different composition where the ligand acts as a tetravalent node. Whereas in our earlier work[15] the postulated spherical complex could only be characterized in solution, in this case we could only use solid state techniques. In both cases, however, the data are consistent with cage formation from pentasubstituted ferrocene ligands.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** X-ray crystallographic data of **1** and **6**, in CIF format, X-ray powder diffraction data for **3**, ORTEP plot of **1** and IR spectra of **2**, **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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